

GAS SEPARATION PROCESSES BY INTEGRATED ADSORPTION AND PERMEATION TECHNOLOGIES



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I would like to dedicate this thesis to my loving parents and grandparents, to whom I owe my unconditional love and friendship.

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Besides the growth of our scientific knowledge in many different areas (from chemical and mechanical engineering, instrumental methods of analysis, electricity to commercial handling and management), the main achievement reached over these years was indeed the human and personal growth, where one acquired responsibilities, expanded our mind and met different people and cultures. If I had to resume all these years in one single phrase, or advise a future PhD student, what will it be? Probability, I would write *be open to learn more, every moment of every day, believe in yourself and help your colleague and friend, and always, always be curious to pursue your PhD work. Specially have fun in the better moments to overcome the difficult ones, because when one has the thesis in hands, all that matters is what you leave behind for others to read, and the friendships you will carry onto your future life.*

Finally, and most importantly I would like to acknowledge my parents, the reason of my existence. To them I dedicate this thesis. Aos meus pais, a razão da minha existência, dedico esta tese. Por entre o longo caminho percorrido neste trabalho, muitos momentos, uns bons outros menos bons, fizeram-me sempre chegar à mesma conclusão: são o tesouro mais precioso que tenho na

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Isabel Esteves

Sumário

Esta dissertação trata do estudo de processos inovadores de separação e armazenagem de gás, usando tecnologias integradas de adsorção e permeação cíclicas. Na sua elaboração, dois objectivos principais foram assentes numa estrutura central: o fenómeno de adsorção.

Por um lado, pretendeu-se recuperar componentes economicamente viáveis ou de valor acrescentado, geralmente efluentes de refinarias, através de processos de separação inovadores, envolvendo adsorção com modulação de pressão, conhecida como *Pressure Swing Adsorption* (PSA), e permeação em membrana. A possibilidade de integrar operações membranares no seio dos processos convencionais de separação de misturas gasosas tem vindo a adquirir um interesse significativo, devido aos benefícios que daí advêm: impacto ambiental, redução de custos energéticos, minimização da unidade operativa e qualidade do produto. Assim, esta foi uma motivação para o conceito híbrido membrana/PSA criado.

Na base de qualquer processo de adsorção encontra-se a escolha do melhor adsorvente a utilizar para uma determinada separação. Neste contexto, estabeleceu-se o segundo objectivo, realizado no âmbito de um projecto europeu que englobou a criação de soluções eficientes e inovadoras para o armazenamento de Gás Natural (GN), incorporando um pré-adsorvedor para filtragem e reodorização do GN a disponibilizar ao consumidor final. Claramente presente está uma preocupação ambiental, onde o GN tem um papel decisivo pelo seu comportamento *amigo do ambiente*, constituindo uma alternativa efectiva ao uso adverso dos derivados do petróleo e potenciador da redução da emissão dos gases de estufa para a atmosfera. Assim, desenvolveu-se e estudou-se o adsorvente adequado, optimizado para a utilização no pré-adsorvedor de filtragem e reodorização de gás natural. A sua selecção visou, assim, a retenção de hidrocarbonetos pesados e compostos sulfurados presentes numa corrente típica de distribuição de GN, não tendo sido optimizado especificamente para as aplicações em PSA descritas na tese. Porém, para uma melhor gestão e maior economia dos recursos disponíveis, o mesmo adsorvente foi

utilizado em ambas as aplicações concretizadas, assentes no fenómeno cíclico de adsorção:

- separação em processos híbridos membrana/PSA, e
- armazenagem de gás usando um pré-adsorvedor para filtragem e reodorização.

Experimentalmente, realizaram-se medidas de equilíbrio de adsorção de N_2 , CO_2 , $n-C_1-C_4$ e dos compostos sulfurados mais vulgarmente utilizados na reodorização do gás natural. Aplicou-se o método gravimétrico com medição em tempo real da temperatura, pressão e massa da amostra de adsorvente. A Teoria do Potencial de Adsorção foi aplicada, de modo a caracterizar o adsorvente. Os resultados obtidos reproduzem com sucesso os dados de equilíbrio experimentais para cada componente puro.

Foram também realizados ensaios de permeação dos componentes puros CO_2 , CH_4 e N_2 numa membrana compósita de PES/PI (polietersulfona/políimida). Determinaram-se as permeâncias e selectividades dos componentes na membrana, responsáveis pela habilidade do módulo em permear ou não as referidas espécies. Os resultados obtidos confirmaram que a ordem de grandeza desses parâmetros coincide com a gama de valores usada na modelação da unidade.

Uma instalação laboratorial de PSA foi construída de raiz, com aquisição e controlo em tempo real. Ensaios de curva de ruptura foram realizados, de modo a estudar a cinética de adsorção dos componentes CO_2 e N_2 . Seguiram-se uma série de ensaios dinâmicos, os quais validaram posteriormente os modelos matemáticos desenvolvidos. Um ciclo PSA foi implementado para a separação de misturas CO_2/N_2 e compreende 5 passos: 1) Pressurização (PR) até à pressão de adsorção P_H , 2) Adsorção (HPA) a P_H , 3) Despressurização co-corrente (HBD) até uma pressão intermédia P_M , 4) Despressurização contra-corrente (LBD) até à pressão mínima de operação P_L , 5) e Purga (LPG) a P_L . Durante HPA e HBD, o produto N_2 é obtido, enquanto durante LBD e LPG, CO_2 é produzido. A validação do modelo de PSA com o ensaio dinâmico experimental permitiu analisar o processo em termos do seu desempenho, i.e., pureza e recuperação de cada um dos produtos. Os perfis de temperatura, composição das fases gasosa e adsorvida, e da velocidade no interior do leito foram estudados, bem como o historial dessas mesmas variáveis ao longo do tempo de ciclo e entre ciclos.

O trabalho computacional permitiu desenvolver o conceito de processo de separação híbrido membrana/PSA, cujo código foi construído a partir dos modelos individuais de cada uma das unidades envolvidas. A configuração integrada definida permite utilizar a gama de pressão operacional do leito PSA como gradiente de pressão necessário à permeação no módulo de membrana, que se encontra acoplado ao processo. A membrana permite obter um permeado e um resíduo, cada um dos quais enriquecido nos componentes com maior ou menor capacidade de adsorção por parte do leito de PSA. As correntes obtidas são alimentadas ao PSA em diferentes passos do ciclo, contendo o adsorvente apropriado para a consequente purificação do produto desejado. Explicitamente, a membrana assiste os passos de pressurização e de adsorção. Todo o processo integrado ocorre de um modo periódico, isto é, a permeação adquire um estado cíclico quando é acoplada aos típicos passos sequenciais de uma unidade PSA. De modo a explorar a sinergia entre ambas as unidades, o conceito híbrido membrana/PSA foi desenvolvido com capacidade para simular sob diversas condições, de carácter operacional e configuracional. Foi implementado sob duas condições estruturais principais:

- Processo MEMPSA – CASO A, onde o componente mais permeável é o menos adsorvido no leito PSA,
- Processo MEMPSA – CASO B, onde o componente mais permeável é o mais fortemente adsorvido no leito PSA.

As simulações numéricas, para separação das misturas CO_2/N_2 , CH_4/H_2 e CH_4/CO_2 , a diferentes condições de alimentação, permitiram concluir que, em estado estacionário periódico, a integração referida, de facto, tem vantagens sobre a aplicação de uma unidade isolada de PSA, para uma determinada gama de condições operacionais. Em vez da mistura binária regular de alimentação, a coluna é alimentada com uma mistura progressivamente enriquecida no componente mais adsorvido, ao longo dos passos de pressurização e adsorção do ciclo PSA. De forma a viabilizar o conceito do processo integrado membrana/PSA, foi modelado um processo híbrido para a separação de CO_2/N_2 , exactamente às mesmas condições experimentais dos ensaios e respectivas simulações do processo isolado de PSA. Os resultados obtidos permitiram confirmar a integridade do conceito híbrido, que melhora a *performance* global da separação, sob dadas condições operacionais, relativamente ao convencional sistema isolado de PSA.

Abstract

This thesis describes the study of alternative and innovative gas separation processes integrating adsorption and permeation technologies. Two main objectives were defined under a common framework: cyclic adsorption process.

One objective was to recover valuable gases, with emphasis on refinery waste-gases, through a combination of Pressure Swing Adsorption (PSA) and permeation processes. The possibility of integrating membrane operations in the gas separation industrial cycle is becoming a particular area of interest, because of several overall benefits that are arising in product quality, plant minimization, environmental impact and energetic cost reductions. Hence, this was the motivation for the hybrid concept developed. The thesis is an attempt to understand some of the concepts and principles applied in the coupling of these separation technologies, providing a guidance for improving and creating new cyclic operations, making them possible alternatives for performance enhancements compared with stand-alone units.

The selection of the best adsorbent material for a given separation is the basis for any adsorption process. In this context, the second objective of the thesis was defined and performed under an european project whose target was to provide innovative and efficient solutions for gas storage through the development of a workable pilot-scale Adsorbed Natural Gas (ANG) storage process, incorporating a guard bed system for reversibly filtering out trace contaminants from the NG feed to the process. Clearly, NG has an environmentally friendly behavior, being a truly and effective alternative to oil-derived fuels. Hence, one of the project tasks was precisely the development and study of an adequate adsorbent, to be used on a pre-adsorber to filter and reodorize the natural gas. Its selection aimed the retention of heavy hydrocarbons and sulfurated compounds present in a typical NG deliverable stream. The adsorbent was not optimized for the specific PSA applications developed in the thesis. Nonetheless, for resource economy reasons, the same adsorbent material was used in both applications performed under the same cyclic adsorption phenomena. The developed carbon formulation was the common point to both

objectives proposed for all the research performed in this thesis. One branch was concerned with the innovative hybrid membrane/PSA concept and the other was addressed to the environmentally friendly behavior of the ANG storage system.

Experimentally, adsorption equilibria measurements of N_2 , CO_2 , $n-C_1-C_4$ and the sulfurated compounds most used to odorize NG, were performed on the adsorbent selected. A gravimetric method was used with real-time acquisition of temperature, pressure and weight of the adsorbent sample. The Adsorption Potential Theory (APT) was applied in order to characterize the adsorbent. The results obtained show a very good agreement with the equilibria data experimentally measured for each pure component.

Experimental permeation runs were also performed for CO_2 , CH_4 and N_2 in a composite PES/PI(polyethersulfone/polyimide) membrane. Component permeances and selectivities were determined. These parameters are responsible for the membrane ability to permeate the species referred. The results obtained confirm that the permeances and selectivities similar to those used in the modeling work were obtained experimentally.

A laboratorial PSA unit was built and experiments were performed in order to validate the modeling work done. The real-time acquisition and control of the unit allowed the execution of breakthrough and dynamic pressure swing cyclic experiments. A PSA cycle was developed for separation of CO_2/N_2 mixtures. The periodic cycle involves five steps: 1) Pressurization (PR) up to the adsorption pressure P_H , 2) High pressure adsorption (HPA) at P_H , 3) Co-current blowdown (HBD) up to an intermediate pressure P_M , 4) Counter-current blowdown (LBD) up to the minimum operating pressure P_L , 5) and Purge (LPG) at P_L . During HPA and HBD, N_2 product is obtained, while during LBD and LPG, CO_2 is produced. The PSA model validation with the experimental dynamic runs allowed the process performance study, i.e., the product purity and recovery analysis. The temperature, component gas- and adsorbed-phases concentrations, and velocity profiles along the adsorbent bed were studied, as well as the histories of those variables during the PSA cycle and until the periodic steady-state was attained.

The hybrid membrane/PSA separation process was developed from the computational work performed. The integrated model was implemented having the stand-alone units as the starting-point of the research. The configuration schemes developed use the PSA operative pressure range as driving force

for permeation in the membrane module. The membrane produces a residue and a permeate streams, each one enriched in the components with more or less adsorption capacity towards the adsorbent bed. The obtained membrane streams are fed to the PSA at different steps of the cycle, in order to enhance the products purity and recovery. Explicitly, the membrane assists the pressurization and high-pressure adsorption steps of the PSA process. The integrated system occurs in a periodic state, where the permeation acquires a cyclic behavior when coupled with the conventional cycle step sequence of a PSA unit.

In order to explore the synergy of both units, the hybrid concept was developed to be capable of simulating under a wide range of operating and configurational conditions. Two main schemes were developed:

- MEMPSA – CASE A process, where the more permeable component is the least adsorbed one in the PSA bed,
- MEMPSA – CASE B process, where the more permeable component is the more adsorbed one in the PSA bed.

The feasibility of the integrated process was assessed through the effect of the various operating parameters on separation performance. Instead of the regular binary feed mixture, the PSA is fed with a mixture which is progressively enriched in the more adsorbed component during the pressurization and high pressure adsorption steps of a PSA cycle. An integrated mathematical model was implemented for both cases and results were obtained and compared with the conventional units involved. Dynamic simulations were performed for the binary separations of CO_2/N_2 , CH_4/H_2 and CH_4/CO_2 , at different feed conditions. The conclusion of the computational work done allows to state that, the inclusion of a membrane module into a periodic PSA process, by a truly synergistically scheme, is indeed an innovative method to improve separation performance of several gas systems when compared with the more common isolated units. In order to confirm the enhanced performance of the hybrid process, a CO_2/N_2 separation under this concept was modeled exactly at the same conditions of the experimental runs and its simulations executed for the stand-alone PSA. The results obtained confirm the integrity of the hybrid concept and the improvement of the separation performance when compared with the conventional stand-alone units.

Resumo Alargado

A elaboração de uma tese de doutoramento tem sempre por base um objectivo específico ou um conjunto deles que são delineados desde o seu início, mas que podem ser alterados consoante a envolvência e o evoluir do conhecimento científico. Deste modo, foram definidos objectivos, alguns dos quais sofreram várias alterações ao longo da dissertação. Pretende-se, pois descrever e explicar os passos concretizados para atingir esses objectivos e finalmente apresentar e analisar os resultados obtidos.

O objectivo inicial desta tese era a separação de misturas gasosas efluentes de refinarias, nomeadamente de hidrogénio e etileno, através de processos de adsorção por modulação de pressão (*Pressure Swing Adsorption*, PSA, em terminologia anglo-saxónica). Estes e outros gases efluentes (CO_2 , N_2 , $\text{C}_1\text{-C}_4$), são economicamente viáveis e, numa perspectiva ambiental, não devem ser desperdiçados como fuel ou libertados para a atmosfera. Assim, após uma pesquisa bibliográfica nesta área, verificou-se que a aplicação da tecnologia PSA se encontra largamente implementada na indústria e que as características cíclicas do processo se encontram bastante trabalhadas e afinadas para uma dada separação alvo. Artigos na literatura, referem, no entanto, um interesse crescente no desenvolvimento de processos integrados envolvendo unidades PSA com outras tecnologias já estabelecidas na indústria, de modo a que estas se possam tornar viáveis em diversas aplicações. Porém, apenas esporadicamente se encontram publicações reportando trabalho científico nesta matéria. A integração de processos membranares na operação cíclica da unidade PSA constitui, assim, um potencial processo integrado, capaz de melhorar o desempenho global da unidade híbrida de separação. Assim, um dos objectivos deste trabalho é a recuperação de componentes economicamente viáveis, geralmente efluentes de refinarias, através de processos de separação híbridos, alternativos e inovadores, envolvendo tecnologias de adsorção (PSA) e permeação em membrana. Esta vertente do trabalho foi financiada pela FCT/MCT através do projecto nacional de I&DT POCTI/EQU/45102/02.

Na base de qualquer processo de adsorção encontra-se a escolha do melhor adsorvente a utilizar para uma determinada separação. Neste contexto,

estabeleceu-se o segundo objectivo, realizado no âmbito de um projecto europeu, sob o 5º Programa Quadro – Energia, Ambiente e Desenvolvimento Sustentado. O projecto denominado ANGUARD – *Adsorbed Natural Gas System with Guard Bed Device*, envolveu a cooperação de diversas indústrias e instituições europeias [Advantica Ltd. (UK), Sutcliffe Speakman Carbons Ltd. (UK), Instituto de Soldadura e Qualidade – ISQ (Portugal), Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa – FCT/UNL (Portugal), Industrial Project Group (Itália)]. O horizonte deste projecto englobou a criação de soluções eficientes e inovadoras para o armazenamento de Gás Natural (GN), incorporando um pré-adsorvedor para filtragem e reodorização do GN a fornecer ao consumidor final. O processo à escala-piloto foi desenvolvido com sucesso para provar a operacionalidade do sistema. Este projecto compreendeu uma clara preocupação ambiental, onde o GN tem um papel decisivo pelo seu comportamento *amigo do ambiente*, constituindo uma alternativa efectiva ao uso adverso dos derivados do petróleo e à redução da emissão dos gases de estufa para a atmosfera. Portanto, umas das tarefas deste projecto europeu foi precisamente o desenvolvimento do adsorvente adequado para a retenção de hidrocarbonetos pesados e componentes sulfurados presentes numa corrente típica de distribuição de GN ao consumidor. A sua selecção visou, assim, a escolha de um adsorvente optimizado para a utilização no pré-adsorvedor de filtragem e reodorização de gás natural, não tendo sido especificamente desenvolvido para as aplicações em PSA descritas na tese. Porém, para uma melhor gestão e maior economia dos recursos disponíveis, o mesmo adsorvente foi utilizado em ambas as aplicações concretizadas, assentes numa mesma estrutura central, o fenómeno cíclico de adsorção:

- separação em processos híbridos membrana/PSA, e
- armazenagem de gás usando um pré-adsorvedor para filtragem e reodorização.

Desta forma, ambos os objectivos desta tese foram definidos, sendo os passos concretizados para os atingir, e os seus resultados, apresentados e analisados seguidamente, de modo sucinto. Esta descrição é feita cronologicamente, para realçar o evoluir do trabalho realizado.

Inicialmente, uma intensiva pesquisa bibliográfica permitiu seleccionar os potenciais processos cíclicos PSA para recuperação dos componentes alvo a estudar. Simultaneamente, a pesquisa na área das membranas para separação de misturas gasosas revelou uma panóplia de artigos, sob o mais variado tipo

de materiais e condições de operação. Como ponto de partida para a modelação destes sistemas, foram seleccionados primariamente, de entre muitos trabalhos, os ciclos PSA de [Yang and Doong \(1985\)](#), [Yang and Doong \(1986\)](#) e [Malek and Farooq \(1997a\)](#), [Malek and Farooq \(1997b\)](#), [Malek and Farooq \(1996\)](#), [Malek and Farooq \(1998\)](#), e as publicações de [Drioli and Romano \(2001\)](#), [Baker \(2002\)](#) e [D. T. Coker and Fleming \(1998\)](#) na área das membranas. Os modelos matemáticos individuais para o PSA e para a membrana foram desenvolvidos em gPROMS (general PROcess Modeling System), um *software* para modelação e simulação computacionais de processos dinâmicos [[PSE \(2004\)](#), [Nilchan \(1997\)](#), [Barton and Pantelides \(1994\)](#), [Barton \(1992\)](#), [Oh \(1995\)](#)].

Os modelos desenvolvidos quer para o PSA, quer para a membrana foram então validados com os trabalhos de [Yang and Doong \(1985\)](#), [Yang and Doong \(1986\)](#) e [D. T. Coker and Fleming \(1998\)](#). Apesar de serem conhecidos alguns trabalhos científicos que procuram abordar o conceito de integração entre as tecnologias PSA e de permeação [[Baker \(1998, 2002\)](#); [Baker and Kaaeid \(2000\)](#); [Drioli and Romano \(2001\)](#); [Ho and Sircar \(1992\)](#); [Marcea and Hwang \(1994\)](#); [R. W. Baker and Pinnau \(2001\)](#)], do conhecimento do autor, apenas o trabalho de [X. Feng and Ghosh \(1998\)](#) aborda verdadeiramente a sinergia entre estas duas unidades, reportando uma melhoria no desempenho global da separação. Ao contrário dos processos membranares convencionais, onde a pressão em ambos os lados da membrana é mantida constante, a pressão no sistema integrado varia ao longo do tempo de permeação. [X. Feng and Ghosh \(1998\)](#) analisaram parametricamente a permeação com variação de pressão, de modo a estudar a sua aplicabilidade prática ao integrar esta unidade num processo cíclico de PSA. A conclusão importante é que a permeação por membrana constitui uma ajuda efectiva no passo de pressurização de um processo típico de PSA. A incorporação de permeação no passo de despressurização do ciclo PSA também é analisado, onde os autores chegam à conclusão que a diferença de pressão no PSA pode ser usada para a operação de permeação.

A partir dos modelos desenvolvidos para cada uma das unidades, foi construído o código para o processo integrado, com capacidade de simular em diversas condições, de carácter operacional e configuracional, com relativa flexibilidade. A configuração integrada definida permite utilizar a gama de pressão operacional do leito PSA como gradiente de pressão necessário à permeação no módulo de membrana, que se encontra acoplado à unidade PSA. A membrana permite obter um permeado e um resíduo, cada um dos quais enriquecido nos

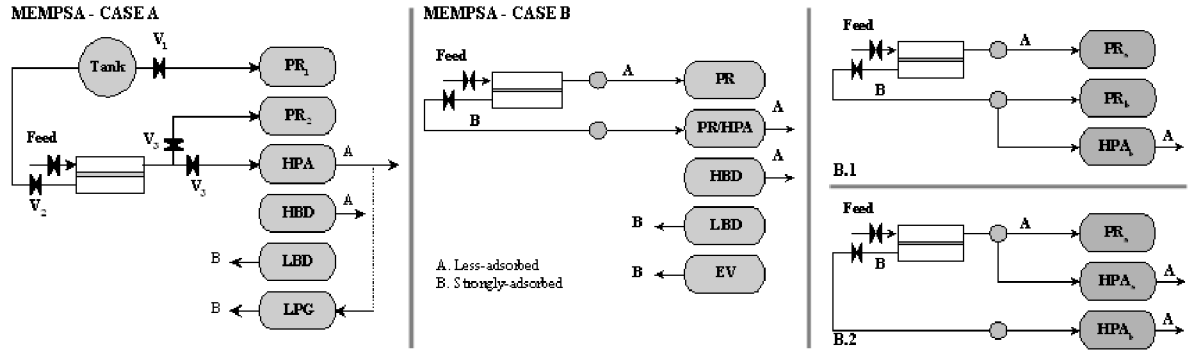


Figure 1: Processo integrado membrana/PSA – MEMPSA. CASO A: o componente que mais permeia é o que menos adsorve no leito PSA; CASO B: o componente que menos permeia a membrana é também o que menos é adsorvido no leito PSA.

componentes com maior ou menor capacidade de adsorção no leito de PSA. As correntes obtidas são alimentadas ao PSA em diferentes passos do ciclo, contendo o adsorvente apropriado para a consequente purificação do produto desejado. Explicitamente, a membrana assiste os passos de pressurização e de adsorção. Todo o processo integrado ocorre de um modo periódico, isto é, a permeação varia cíclicamente quando é acoplada aos típicos passos sequenciais de uma unidade PSA.

De modo a explorar a sinergia entre ambas as unidades, o conceito híbrido membrana/PSA foi desenvolvido e implementado sob duas condições estruturais principais [Figura (1)]:

- Processo MEMPSA – CASO A, onde o componente mais permeável é o menos adsorvido no leito PSA,
- Processo MEMPSA – CASO B, onde o componente mais permeável é o mais fortemente adsorvido no leito PSA.

Em vez da mistura binária regular A/B a separar, a coluna PSA é alimentada com uma corrente progressivamente enriquecida no adsorbato mais fortemente retido pelo adsorvente, durante os passos de pressurização e adsorção. Considere-se que A e B correspondem às espécies menos e mais adsorvidas no leito, respectivamente.

No processo MEMPSA - CASO A, aplicado à separação de $H_2(A)/CH_4(B)$, o resíduo é alimentado directamente à coluna, enquanto o permeado é armazenado num tanque antes de ser enviado para o leito. O ciclo híbrido inicia-se com uma pressurização incompleta (PR_1) do leito com a corrente

de permeado, enriquecida em A e previamente obtida do passo de adsorção (HPA) de outra coluna. Em PR_1 , a válvula V_1 é mantida aberta e V_2 e V_3 estão fechadas até que a equalização de pressão entre o tanque e o leito ocorra. A válvula V_1 é depois fechada e a coluna é pressurizada com alimentação regular (menos enriquecida em A que o permeado usado em PR_1), por abertura da válvula V_3 , até à pressão de adsorção, P_H . Neste passo, a membrana comporta-se como um tubo, uma vez que a pressão em ambos os lados é igual a P_H . O passo de adsorção é então iniciado por abertura de V_2 e simultânea alimentação do leito com resíduo da membrana, a um caudal prescrito. O resíduo é enriquecido em B, enquanto o permeado é armazenado no tanque para ser usado no próximo ciclo. Neste passo, a pressão no lado de alimentação da membrana é mantida igual a P_H , e ao contrário do convencional em membranas, a pressão no permeado vai progressivamente aumentando por acção da acumulação no tanque intermédio. De seguida, a operação periódica do processo prossegue com a despressurização co-corrente (HBD) até à pressão intermédia P_M , para recuperar o componente A residual, ainda presente na coluna. Finalmente, ocorrem a despressurização contra-corrente (LBD) até P_L e a purga (LPG), para recuperar a espécie B e regenerar o leito para o próximo ciclo.

No processo MEMPSA - CASO B, aplicado às separações de $CH_4(A)/CO_2(B)$ e $N_2(A)/CO_2(B)$, ambas as pressões na membrana são mantidas constantes ao longo da permeação. Embora o resíduo seja directamente enviado para o PSA, o permeado pode ser usado na pressurização ou enviado para o passo de HPA. A integração varia com a quantidade total alimentada por ciclo. Neste caso, o ciclo começa com permeação a pressões constantes, $P_1 = P_H$ e $P_2 = P_L$, sendo P_1 e P_2 as pressões no lado do resíduo e do permeado da membrana, respectivamente. Simultaneamente, uma primeira pressurização ocorre com a corrente de resíduo effluente da membrana (enriquecida em A). Esta fase permanece até se verificar equalização de pressões entre a membrana e a coluna. Duas situações podem ocorrer:

- Se a pressão no leito é inferior a P_H , o resíduo não é suficiente, pelo que a pressurização é terminada com permeado, agora enriquecido no componente mais adsorvido, B. Neste CASO B.1, após PR_a , a membrana deixa de estar operacional para este leito. O passo HPA_b , realizado a P_H , é iniciado com o resto de permeado existente, a um caudal prescrito.

-
- Se a pressão no leito atinge P_H e ainda existe resíduo efluente da membrana, o ciclo prossegue com um primeiro passo HPA_a , sendo o PSA alimentado por esta corrente rica em A. Após HPA_a , a membrana deixa de estar operacional para este leito. O passo de adsorção a P_H , HPA_b , termina com a corrente de permeado enriquecida na espécie B.

Finalmente, o ciclo prossegue da mesma forma que no processo MEMPSA – CASO A. A análise pormenorizada deste conceito permite concluir que a integração referida, de facto, tem vantagens sobre a aplicação de uma unidade isolada de PSA, para uma determinada gama de condições operacionais, as quais, por motivos de espaço, se omitem aqui, mas que se encontram descritas na tese.

Após o desenvolvimento e a análise paramétrica dos processos híbridos referidos, o trabalho de simulação deu lugar ao trabalho experimental. Um conjunto extensivo de medidas de equilíbrio de adsorção foram executadas em primeiro lugar, complementando quer as tarefas do projecto europeu, quer a progressão da tese proposta. Do consórcio europeu foi seleccionado o melhor adsorvente: um carvão activado hidrofóbico, extrudido em pastilhas de 2 mm de diâmetro. De entre os carvões estudados, o escolhido exhibe as melhores condições estruturais, de capacidade, de cinética de adsorção, de retenção e resistência mecânica. As características estruturais do adsorvente seleccionado (ANGUARD 5) estão listadas na Tabela 1.

Através do método gravimétrico, utilizando uma balança magnética de alta pressão (Rubotherm, GB), foi medido o equilíbrio de adsorção de n -alcanos C_1 – C_4 , CO_2 , N_2 , *tert-butyl mercaptan* (TBM) e *tetra-hydrothiophene* (THT). Estes últimos são os dois odorantes que usualmente são utilizados para odorizar

Table 1: Características principais do adsorvente usado no trabalho experimental (volumes expressos em cm^3/g).

N ₂ adsorption at 77 K		Mercury porosimetry	
BET surface area (m^2/g)	1342	Total pore volume ($20\text{-}10^5 \text{ \AA}$)	0.881
Total pore volume ($< 200 \text{ \AA}$)	0.850	Mesopore volume ($20\text{-}500 \text{ \AA}$)	0.413
Micropore volume ($< 20 \text{ \AA}$)	0.777	Macropore volume ($500\text{-}10^5 \text{ \AA}$)	0.468
Narrow micropore volume ($< 6 \text{ \AA}$)	0.367		
Broad micropore volume ($6\text{-}20 \text{ \AA}$)	0.410		

o GN de fornecimento ao consumidor final. A instalação experimental foi construída com aquisição em tempo real da massa da amostra, temperatura e pressão. A pressão pode ser medida numa gama bastante significativa (0 - 200 bar). A Teoria do Potencial de Adsorção foi aplicada aos dados de equilíbrio, de modo a caracterizar o adsorvente [C. E. Holland and Ritter (2001a,b); Dubinin (1975); F. Rouquerol and Sing (1999); Yang (1987)]. Esta teoria supõe que para um dado sistema gás-sólido, o volume específico de fase adsorvida, W , é função do potencial de adsorção, $\tilde{\phi}$,

$$W \equiv qV_m = W(\tilde{\phi}), \quad (1)$$

onde q é a quantidade de gás adsorvido no equilíbrio, e $V_m(T)$ é o volume molar da fase adsorvida, dependente da temperatura. Para uma dada temperatura e pressão parcial de equilíbrio de adsorbato, $\tilde{\phi}$ é definido por

$$\tilde{\phi} = RT \ln(P_s/P), \quad (2)$$

onde P é a pressão de equilíbrio à temperatura T , $P_s(T)$ é a pressão de vapor saturado de adsorbato e R é a constante dos gases ideais. A relação funcional entre $\tilde{\phi}$ e W é característica de cada sistema gás-sólido, sendo geralmente referida como curva característica. Esta teoria é particularmente útil na previsão do equilíbrio de adsorção do componente puro, a partir de um conjunto limitado de medidas experimentais. A curva característica é independente da temperatura. Assim, são apenas necessárias medidas de equilíbrio a uma temperatura para obter a referida curva, sendo isto suficiente para descrever a adsorção a todas as temperaturas para o mesmo sistema gás-sólido [Agarwal and Schwarz (1988), Yang (1987)]. Esta teoria pode ser generalizada se se usar o coeficiente de afinidade β , que considera as interacções adsorvente/adsorbato [Wood (2001)]. Constitui um factor de escala que faz sobrepôr as curvas características de todos os gases no mesmo adsorvente, numa curva única. A Eq. (1) é substituída por

$$W \equiv qV_m = W(\phi), \quad \phi \equiv \tilde{\phi}/\beta, \quad (3)$$

que é característica de cada adsorvente e igualmente aplicável a todos os adsorbatos. A curva característica foi ajustada à equação modificada de Dubinin-Astakhov [Dubinin and Radushkevich (1947), Dubinin and Astakhov (1970), Dubinin (1975), S. Ozawa and Ogino (1976)] que diz que, para o componente puro, o modelo de adsorção é dado por

$$W = W_s \exp(-\gamma\phi^n), \quad (4)$$

sendo W_s o volume microporoso do carvão disponível ao adsorbato, γ e n parâmetros da equação. Foram obtidos os seguintes resultados para o adsorvente seleccionado: $W_s = 0.8599 \text{ cm}^3/\text{g}$, $\gamma = 4.6657 \times 10^{-5} (\text{J/mol})^{-n}$ e $n = 1.0861$ para n -alcanos, CO_2 e N_2 , $\gamma = 1.1863 \times 10^{-4} (\text{J/mol})^{-n}$ e $n = 0.9994$ para TBM, $\gamma = 3.9092 \times 10^{-6} (\text{J/mol})^{-n}$ e $n = 1.3377$ para THT. O valor obtido de W_s está em excelente acordo com os valores determinados através da adsorção de N_2 a 77K ($0.850 \text{ cm}^3/\text{g}$) e da porosimetria de Hg ($0.881 \text{ cm}^3/\text{g}$). A Figura (2) apresenta a comparação entre os ajustes obtidos pela teoria descrita e os dados de equilíbrio experimentais para cada componente puro.

Experimentalmente, foram realizados também ensaios de permeação dos componentes puros CO_2 , CH_4 e N_2 numa membrana compósita de PES/PI (polietersulfona/poliimida). O objectivo foi a obtenção de permeâncias e selectividades destes componentes nessa membrana, parâmetros esses responsáveis pela habilidade do módulo em permear ou não as referidas espécies. Os resultados obtidos confirmaram que a ordem de grandeza desses parâmetros coincide com a gama de valores usada na modelação da unidade. De referir que, dada a dispersão de resultados na literatura, desde o início se procurou utilizar valores de permeâncias e selectividades realistas ao nível de aplicações industriais factíveis.

A Figura (3) apresenta a instalação laboratorial de PSA construída de raiz. Ensaio de curva de ruptura foram realizados, de modo a estudar a cinética de adsorção para os componentes CO_2 e N_2 . Seguiram-se uma série de ensaios dinâmicos, os quais validaram posteriormente os modelos matemáticos desenvolvidos. A célula PSA contém 130-193 g do adsorvente, num volume que varia de $322\text{-}483 \text{ cm}^3$. Uma série de sondas registam a temperatura no interior do leito. Um conjunto de equipamentos auxiliares permitem a aquisição de pressão, temperatura, composição e caudal, cujo controlo é efectuado em tempo real com um software desenvolvido internamente pelo grupo. Este programa permite operar ciclicamente a sequência dos passos do PSA.

O ciclo PSA, de ≈ 12 min, implementado para a separação de misturas CO_2/N_2 , compreende 5 passos: 1) Pressurização (PR) até à pressão de adsorção $P_H = 6 \text{ bar}$, 2) Adsorção (HPA) a P_H , 3) Despressurização co-corrente (HBD) até uma pressão intermédia $P_M = 3.2 \text{ bar}$, 4) Despressurização contra-corrente (LBD) até à pressão mínima de operação $P_L = 0.3 \text{ bar}$, 5) e Purga (LPG) a P_L . Durante HPA e HBD, o produto N_2 é obtido, enquanto durante LBD e LPG, CO_2 é produzido. Obviamente, pretende-se obter produtos de elevada pureza e à maior recuperação possível.

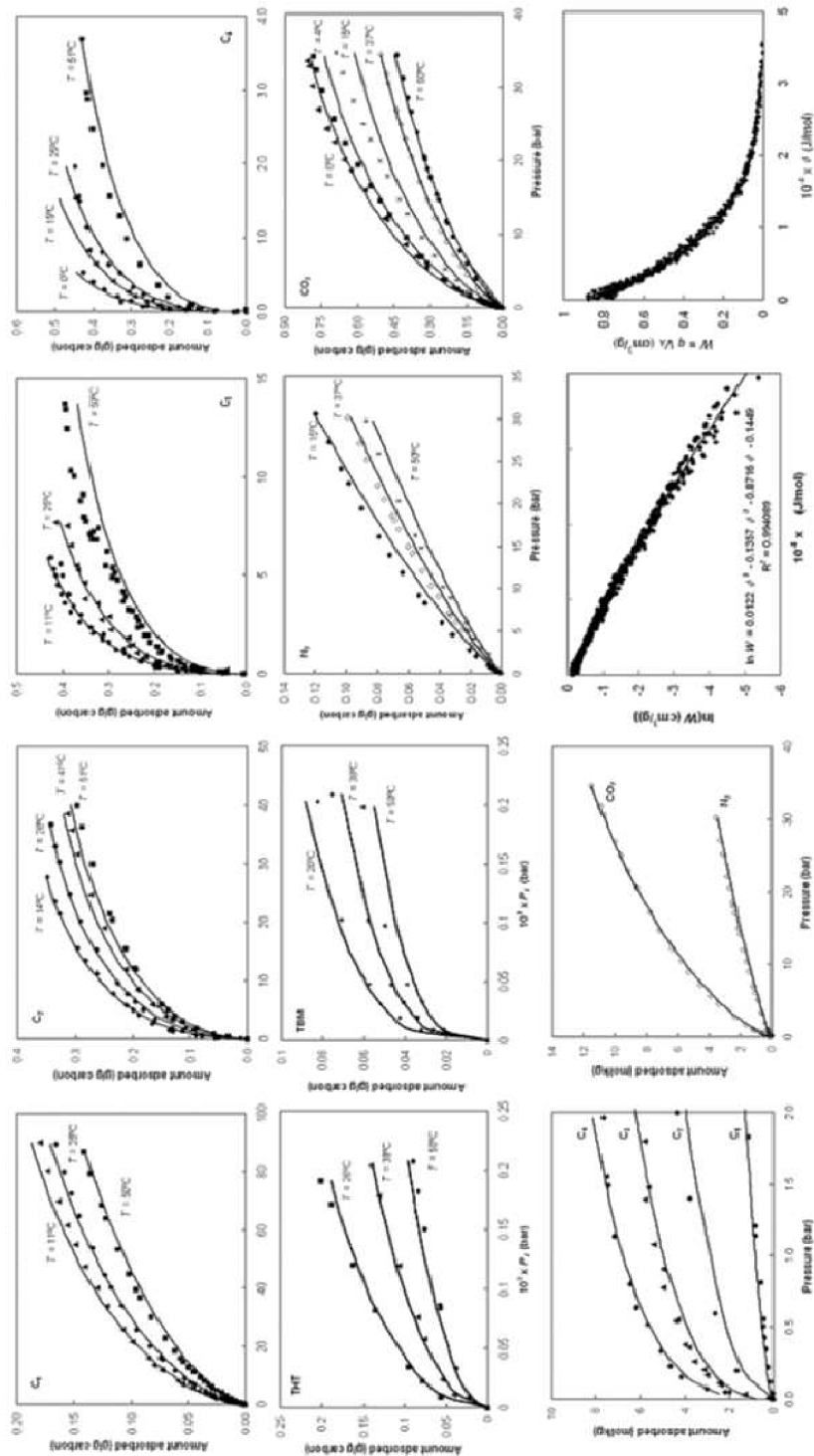


Figure 2: Comparação entre os ajustes obtidos pela teoria descrita e os dados de equilíbrio experimentais para cada componente puro. Símbolos representam dados experimentais e linhas denotam as previsões do modelo de Dubinin-Astakhov.

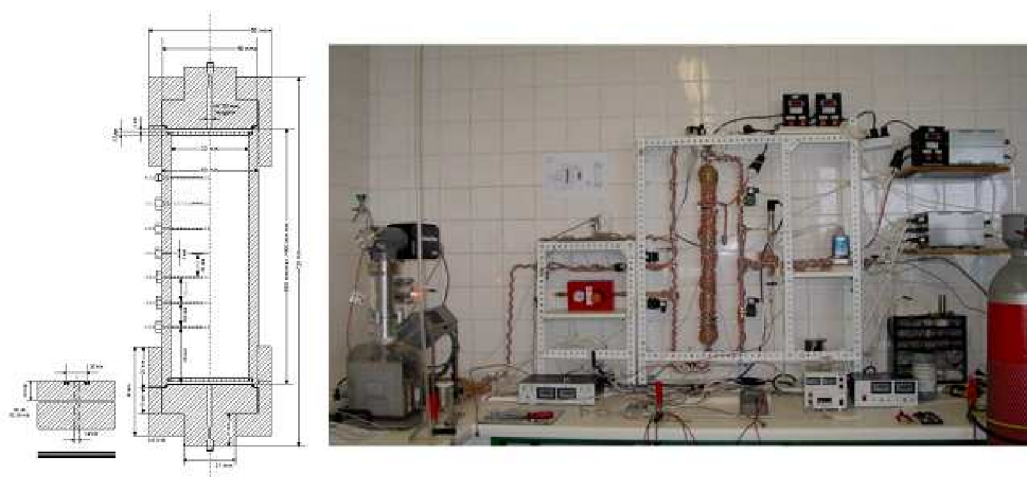


Figure 3: Esquema da célula laboratorial de PSA e fotografia da instalação laboratorial construída.

Em simultâneo, foram realizadas simulações dinâmicas computacionais, de modo a prever o número de ciclos necessários para se atingir o estado estacionário cíclico (CSS). As condições finais de um ciclo são as condições iniciais para o ciclo seguinte, até que o sistema atinge um estado estacionário periódico.

A validação do modelo de PSA com o ensaio dinâmico experimental permitiu depois analisar o processo em termos do seu desempenho, i.e., pureza e recuperação de cada um dos produtos. Os perfis de temperatura, composição das fases gasosa e adsorvida, e da velocidade no interior do leito podem assim ser estudados, bem como o historial dessas mesmas variáveis ao longo do tempo de ciclo e entre ciclos.

Finalmente, de forma a estudar a viabilidade do conceito do processo integrado membrana/PSA anteriormente desenvolvido, foi modelado um processo híbrido dessas unidades para a separação de CO_2/N_2 , exactamente às mesmas condições experimentais (temperatura, caudal, tempos dos passos) dos ensaios e respectivas simulações do processo isolado de PSA. Os resultados obtidos permitiram confirmar a integridade do conceito híbrido, que melhora o desempenho global da separação sob dadas condições operacionais, relativamente ao convencional sistema isolado de PSA.

Em geral, para o processo isolado e dependendo da composição da mistura disponível, obtêm-se purezas e recuperações de CO_2 na gama de 54–92% e 83–99%, respectivamente. Para o N_2 obtêm-se purezas e recuperações na ordem de 51–99% e 66–69%, respectivamente. Consoante a área de membrana disponível

à permeação, e a quantidade total alimentada ao sistema estudado, o processo integrado com a membrana melhora em geral a pureza e a recuperação do CO₂ até 16% e 50%, respectivamente. Para o N₂, a pureza e recuperação melhoram até cerca de 14% e 5%, respectivamente. Naturalmente, estas melhorias devem ser contrabalançadas com a necessidade de comprimir a corrente de permeado antes de a alimentar ao respectivo passo de PSA. As Figuras (4, 5) ilustram o efeito do conceito híbrido relativamente ao convencional PSA. Em vez de uma composição de entrada 30/70% (v/v), o leito adsorvente é progressivamente enriquecido no componente mais adsorvido (CO₂). Tal permite que a dispersão dos perfis de composição no interior do leito seja diminuída, o que melhora significativamente o desempenho global da separação.

Finalmente, a Figura (6) apresenta os passos do processo ANGWARD desenvolvido pelo consórcio europeu, no âmbito da armazenagem de GN. A carga do tanque de armazenagem é precedida por um leito contendo o adsorvente de trabalho, onde ficam retidos os componentes C₅₊ e os odorantes. A descarga é controlada, de modo a reodorizar a corrente de abastecimento de GN nos padrões de concentração exigidos por lei para distribuição ao consumidor final. A estratégia implementada pelo nosso grupo de investigação foi comprovada com sucesso no sistema piloto ANGWARD implementado pelo consórcio.

Em conclusão, o conjunto do trabalho realizado reúne uma série de tarefas inovadoras, nas quais se destacam as medições experimentais de equilíbrio dos odorantes do GN, pela sua dificuldade, provada pela escassez de literatura publicada nesta matéria; e o conceito híbrido dos processos membrana/PSA desenvolvidos, que podem ser alternativos aos convencionais sistemas isolados de PSA. A modelação matemática deste tipo de integração é particularmente escassa na literatura, pelo que os resultados obtidos podem de alguma forma ajudar a melhorar a *performance* de processos de separação mais convencionais e já existentes. Além do referido, a participação no projecto europeu, na temática do gás natural, foi um desafio concretizado na prática e por todos os que nele estiveram envolvidos.

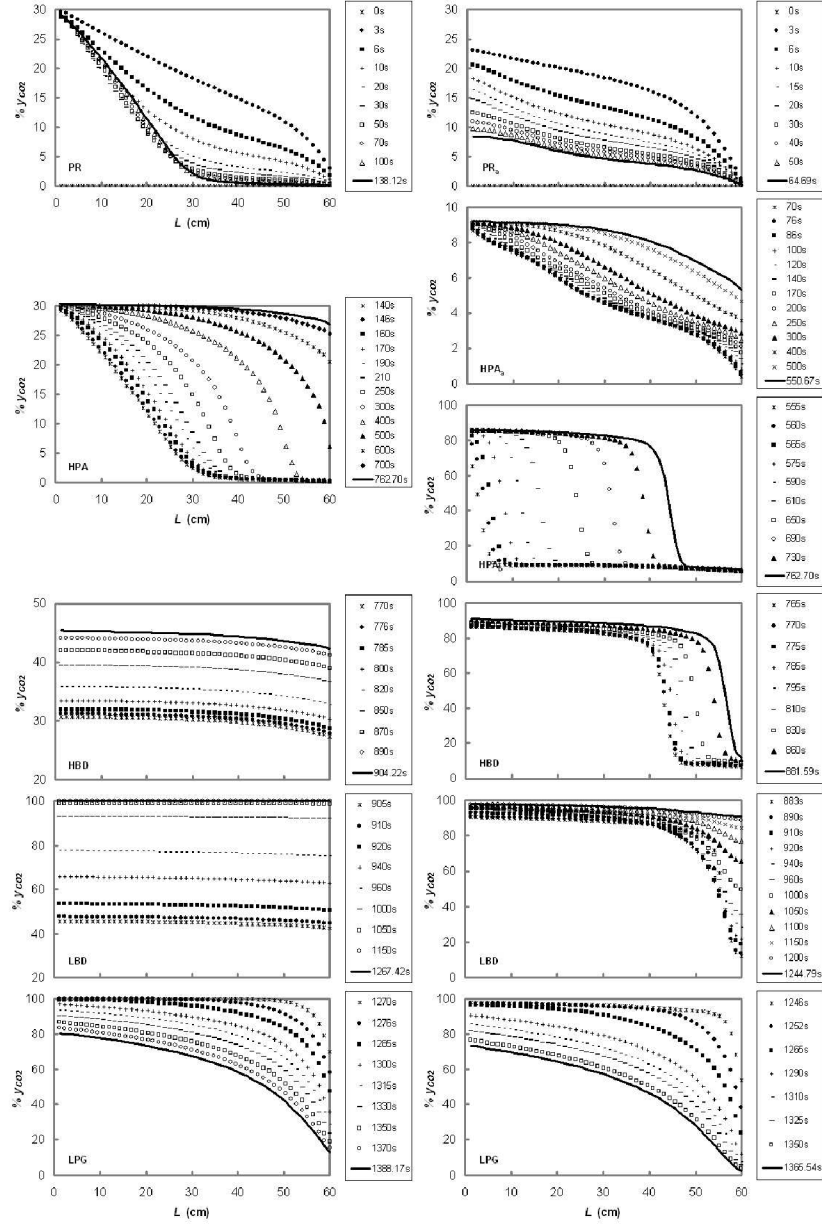


Figure 4: Perfis de composição de CO_2 na fase gasosa, no interior do leito, em estado estacionário, relativos à mistura CO_2/N_2 30/70 % (v/v), alimentada à temperatura de $35.85^\circ C$, a $P_H = 6$ bar e ao caudal volumétrico total de 3.0 slpm (STP: $0^\circ C$, 1 atm). Do topo para a base: PR_a / HPA_a / HPA_b / HBD / LBD / LPG . Da esquerda para a direita: PSA convencional/Processo híbrido.

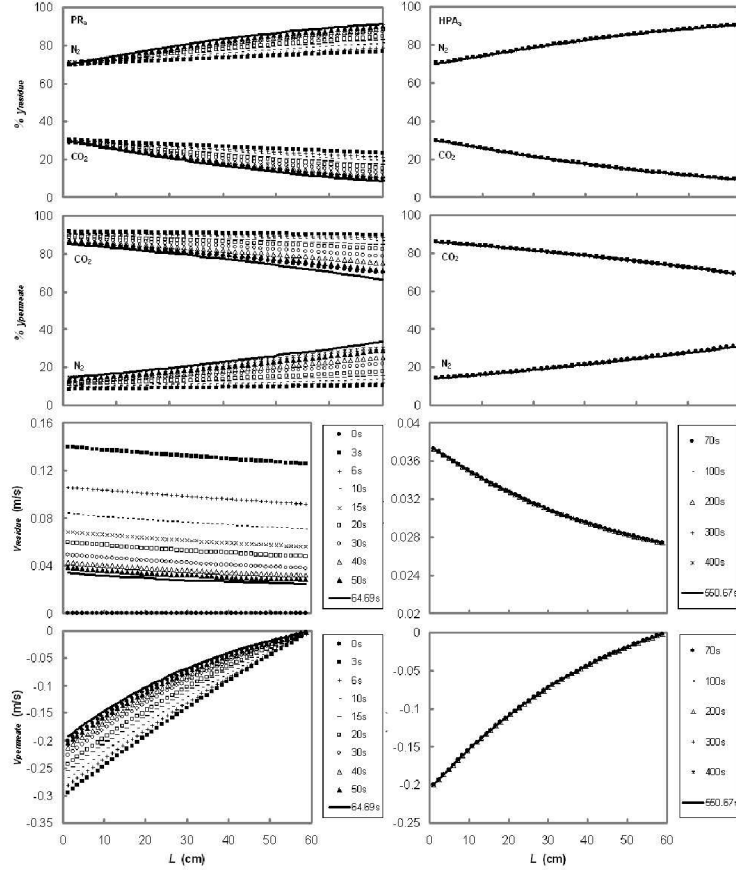


Figure 5: Evolução da composição dos gases CO_2 e N_2 , e da velocidade, no estado estacionário cíclico, em cada um dos lados da membrana, durante os passos cíclicos em que esta intervém (PR_a e HPA_a) *versus* a distância axial z .

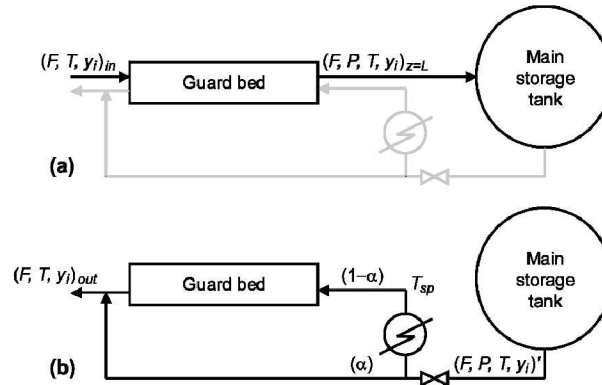


Figure 6: Passos do processo ANGWARD. (a) Carga e (b) Descarga. α é uma fracção do caudal F e T_{sp} é a temperatura do gás aquecido. Ambas as variáveis podem ser manipuladas durante a descarga.

List of Symbols

A	area, m^2
A_{bed}	PSA bed area, m^2
A_f	surface area of the membrane active layer per unit of fiber length, m
A_k	membrane cross-section area, m^2
A_p	BET surface area, m^2
A_{mem}	surface membrane area or membrane permeation area, m^2
b, b_0, b_∞	parameters of Sips and Toth isotherms, bar^{-1}
$c_{\mu s}, c_{\mu s0}$	parameters of Sips and Toth isotherms, mol kg^{-1}
C_i	concentration of component i, mol m^{-3}
C_{ip}	partial concentration of component i inside the sorbent pores, mol m^{-3}
C_{ps}	solid heat capacity, $\text{J kg}^{-1} \text{K}^{-1}$
C_{pa}	adsorbed-phase heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
C_{pm}	membrane heat capacity per unit fiber length, $\text{J mol}^{-1} \text{m}^{-1} \text{K}^{-1}$
C_{pg}	gas heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
CSS	cyclic steady state
D_i	diffusivity of component i, $\text{m}^2 \text{s}^{-1}$
D_e	effective diffusivity, $\text{m}^2 \text{s}^{-1}$
D_p	particle diameter, m
D_{im}	molecular diffusivity of component i, $\text{m}^2 \text{s}^{-1}$
D_{iL}	dispersion coefficient of component i, $\text{m}^2 \text{s}^{-1}$
D_k	Knudsen diffusivity, $\text{m}^2 \text{s}^{-1}$
D_s	surface diffusivity, $\text{m}^2 \text{s}^{-1}$
D_h	effective heat dispersion coefficient, $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$
F_f	reference total molar flow per cycle admitted in HPA step, mol s^{-1}
F_m	dimensionless permeation flow parameter
g_1	constant ($\gamma_1 D_{im}$)

g_2	constant ($\gamma_2 D_p$)
H_g	gas enthalpy, J mol ⁻¹
H_a	adsorbed-phase enthalpy, J mol ⁻¹
h_w	wall heat-transfer coefficient, W m ⁻² K ⁻¹
J_i	flux, mol s ⁻¹
k_i	LDF coefficient, s ⁻¹
k_g	gas thermal conductivity, J m ⁻¹ s ⁻¹ K ⁻¹
k_w	wall thermal conductivity, W m ⁻¹ K ⁻¹
L_p	particle length, m
L_f	membrane length, m
M	weight, g
M_w	molecular weight, g mol ⁻¹
N	total molar amount, mol
N_i	amount of transported component i, mol m ⁻² s ⁻¹
N_{ir}	intraparticle flux, mol m ⁻² s ⁻¹
NoC	number of components
NoP	number of control-volume elements
n, n_0	parameters of D-A equation and Sips isotherm
n_f	number of fibers
P	pressure, bar
P_i	partial pressure of component i, bar
P_i^o	partial pressure of pure component i, bar
P/F	purge-to-feed ratio
Pr	Prandtl number ($C_{pg}\mu/k_g$)
P_{c1}	constant for bed pressure dynamics
P_v	pressure in the intermediate tank, bar
q, c_μ	equilibrium solid loading, mol kg ⁻¹
q^σ, q_t	surface excess amount, mol, and total amount adsorbed, mol kg ⁻¹
q_i^o	amount adsorbed of pure component i, mol kg ⁻¹
Q_i	heat of adsorption of component i, J mol ⁻¹
$Q_s, \Delta H_i$	isosteric heat of adsorption of component i, J mol ⁻¹

R	universal gas constant, J mol ⁻¹ K ⁻¹
R_p	particle radius, m
r_H	hydraulic particle radius, m
r_μ, r_p	mean pore radius, m
Re	Reynolds number ($\rho_g v D_p \varepsilon_b / \mu$)
S_i	solubility of component i, mol m ⁻³ bar ⁻¹
STP	standard conditions (0°C, 1 atm)
Sc	Schmit number ($\mu / \rho_g D_{im}$)
t	time, s or min
t, t_0	parameters of Toth isotherm
T	temperature, K or °C
T_b	temperature of the liquid adsorbate at the normal boiling point, K or °C
T_g	polymer glass transition temperature, K or °C
T_m	membrane temperature, K or °C
T_v, T_w	temperature in the intermediate tank and bed wall temperature, K or °C
V	volume, m ³ or L(STP)
V_b	molar volume of the liquid adsorbate at the normal boiling point, m ³ mol ⁻¹
V_c	closed calibrated volume; volume of intermediate tank, m ³
V_m	adsorbed-phase molar volume, m ³ mol ⁻¹
V_{PSA}	PSA bed volume, m ³
v	interstitial fluid velocity, m s ⁻¹
u	superficial fluid velocity, m s ⁻¹
W	balance display, g; volume of the adsorbed phase, cm ³
W_s	micropore volume, cm ³ g ⁻¹
x_i	mole fraction of component i in the adsorbed-phase
y_i, y_{iv}	mole fraction of component i and mole fraction of component i in the intermediate tank
y_m	mole fraction of permeate
z	distance, m

Greek Symbols

μ	chemical potential, bar m ³ mol ⁻¹
δ	effective membrane thickness, m
π_i	permeability of species i, mol m ⁻¹ s ⁻¹ bar ⁻¹ or Barrer [10 ⁻¹⁰ cm ³ (STP) cm (cm ² s cm Hg) ⁻¹]
Π	spreading pressure, mol kg ⁻¹
$\wp_i$	permeance of species i, GPU [10 ⁻⁶ cm ³ (STP) (cm ² s cm Hg) ⁻¹ = 3.346E-5 mol m ⁻² s ⁻¹ bar ⁻¹]
ϕ	pressure ratio (P_H/P_L); adsorption potential, bar m ² mol ⁻¹
θ	membrane stage-cut; fractional loading (q/q_s)
β	affinity coefficient
γ	parameters of D-A equation
Γ	surface excess concentration, mol kg ⁻¹
Ω	thermal expansion coefficient, K ⁻¹
ρ_p	particle density, kg m ⁻³
ρ_b	bulk density, kg m ⁻³
ρ_s	carbon matrix density, kg m ⁻³
ρ_g	gas density, kg m ⁻³
ρ_{sLm}	effective density of the measuring system, kg m ⁻³
ε_b	interparticle porosity or (external) void fraction of packing
ε_p	intraparticle porosity
ε	total voidage
τ	tortuosity factor
μ	fluid viscosity, cP
η_i	lateral interaction parameters of component i
$\gamma_1, \gamma_2, \alpha, \beta$	constants for bed pressure dynamics
Λ_p	constant [$\varepsilon_p(1 - \varepsilon_b)/\varepsilon_b$]
Ω_p	constant [$\Lambda_p \rho_p R/\varepsilon_p$]
χ, α	parameters of Sips and Toth isotherms

Subscripts

a	adsorbed-phase
b	normal boiling point
c	carbon, critical conditions
ex	excess adsorption
f, r	feed, membrane residue
H	high-pressure conditions
HPA	high-pressure adsorption
HBD, CD	high-pressure blowdown
i	component i
k	membrane zones (1, residue or feed; 2, permeate)
l	load
L	low-pressure conditions
LBD, BD	low-pressure blowdown
LPG, PG	low-pressure purge
m	magnet
MS	mass spectrometry
o	referential condition
p	permeate
PR	pressurization
s	sample, saturated conditions

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Chapter 1

Introduction

The possibility of integrating membrane operations into the gas separation industrial cycle is becoming a particular area of interest, because of several overall benefits that are arising in product quality, plant minimization, environmental impact and energetic cost reductions. The overall properties make membrane operations ideal for the design of innovative processes, and integrated eventually with other traditional unit operations to optimize their positive synergic effects [[Drioli and Romano \(2001\)](#)].

Periodic adsorption processes, such as single or multiple bed pressure swing adsorption process, have been gaining increasing acceptance as energy efficient alternatives to other separation techniques such as cryogenic distillation. Much progress has already been achieved in improving their performance with respect to both the process economics and the attainable purity of the products [[D. M. Ruthven and Kneabel \(1994\)](#), [Yang \(1987\)](#)].

It is widely known that membrane permeation and pressure swing adsorption processes offer economically competitive alternatives for many small- and medium-scale gas separations. The possibility of integrating various of these operations within the same industrial cycle, with overall important benefits in product quality, plant compactness, environmental impact, and/or energetic aspects, offers interesting opportunities of research.

This thesis is an attempt to understand some of the concepts and principles applied in the coupling of these separation technologies, providing a guidance for improving and creating new cyclic operations, making them possible alternatives for performance enhancements compared with stand-alone units.

Taking advantage of the separating abilities of a membrane module and of the intrinsically dynamic operation in a periodic mode of a pressure swing adsorption unit, one

of the main objectives of this work is to study gas separation through hybrid adsorptive processes and characterize the system using state-of-the-art modeling tools supported by experimental characterization and validation.

The research is concerned with a novel approach for gas separation processes, where membrane and pressure swing adsorption are combined into a truly synergistically and innovative schemes, in order to enhance the separative performance when compared to the stand-alone units. From the modeling and mathematical point of view, the analysis of a variety of pressure swing adsorption cycles can be complex. It is comprehensible then, that coupling other separative technologies, such as membrane permeation, will increase even more the modeling work necessary to synchronize both systems and to operate the cyclic hybrid unit for the desired separation.

Although each one of these technologies seemed like a giant step concerning the fully understand of the stand-alone science involved, the attempt to approach a compromise between these processes was performed and the results are presented along the following chapters of this thesis.

Part of this thesis also reports on research and development work performed as part of the european project named ANGWARD - Adsorbed Natural Gas System with Guard Bed Device, which included several european industrial and scientific institutions. The target is to provide innovative and efficient solutions for gas storage through the development of a workable pilot-scale Adsorbed Natural Gas (ANG) storage process, incorporating a guard bed system for reversibly filtering out trace contaminants from the natural gas feed to the process. Modeling activities and unique experimental determinations of adsorption equilibria were performed in FCT/UNL, on a newly developed carbon formulation provided by the consortium.

The adsorbent was used both in the PSA unit and on the guard-bed system. Thus, the adsorbent and the use of a cyclic adsorption process, to fully or partially accomplish the separation task, is the framework for all the research performed in this thesis. For one part, research was focused on innovative hybrid membrane/pressure swing adsorption separation processes, and the other addressed the environmental friendly behavior of the ANG storage system, having as central starting-point the same developed carbon formulation.

1.1 Thesis Structure

This thesis is divided into seven chapters as follows:

- Chapter 1: Introduction

- Chapter 2: Background and Literature Review - A Vision of the State of the Art

This chapter examines the theory underlying membrane and pressure swing adsorption processes, and reviews the latest developments introduced in both fields of research. The final part of this chapter is concerned with the background of the european project ANGUARD, which was part of this thesis. To frame the innovative solution developed for gas storage and delivery applications, a brief introduction is given concerning the benefits that could overcome from this technology.

- Chapters 3 and 4: Permeation and Adsorption Experimental Work

The chapters present all the experimental work. The adsorption measurements section reports the adsorbent selection and equilibria experimental procedures, the methods used, the results and their analysis (Chapter 4). The experimental data was analyzed using the Adsorption Potential theory, to be incorporated into the dynamic model of the guard-bed, but for modeling of the PSA unit a more detailed study of the adsorption isotherms was done through the Sips and Toth approaches.

The permeation measurements performed are also described (Chapter 3). Permeances and selectivities similar to those used in the modeling work were obtained experimentally.

Finally, a pressure swing adsorption unit was built and experiments are reported in order to validate the modeling work, specially some of the most important steps of the integrated cycle, the pressurization and adsorption steps (Chapter 4). Experimentally, the linking between the two units may be performed by varying the inlet concentration fed to the PSA bed, which simulates the composition profile of the effluent streams from the membrane during the pressurization and high-pressure adsorption steps of the cycle.

- Chapter 5: Membrane/PSA Processes for Separation of Gas Mixtures - Insights and Modeling

The chapter examines the dynamic simulation of a hybrid membrane/pressure swing adsorption (PSA) system used for binary bulk gas separations. Single membrane and PSA models were firstly developed in order to validate and study each unit individually, and finally the integrated process was implemented and analyzed. Simulations were performed to investigate the effects of the most important operating parameters on the performance of the system.

The performance of the dynamic PSA cycle experimentally executed, was compared with the enhanced performance of an hybrid process, where a membrane unit was added to the conventional cyclic operation of the PSA process.

- Chapter 6: Adsorbed Natural Gas (ANG) Processes for Gas Storage Applications

The chapter describes with detailed attention the ANG process developed for gas storage applications and performed under the european project ANGUARD ENK6 CT-2000-00053. This project started in 2000, with the duration of 38th months, and was funded by the European Community under the Fifth Framework Programme - Energy, Environment and Sustainable Development. The project was a cooperation of several european industrial and scientific institutions (Advantica Ltd and Sutcliffe Speakman Carbons Ltd (SSCL), from UK; Instituto de Soldadura e Qualidade (ISQ), Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa (FCT/UNL), from PT; and Industrial Project Group from IT).

The ANGUARD target was to provide innovative and efficient solutions for gas storage through the development of a workable pilot-scale Adsorbed Natural Gas (ANG) storage process, incorporating a guard bed system for reversibly filtering out trace contaminants from the Natural Gas (NG) feed to the process. To develop an adsorptive gas storage system having enhanced capacity at lower pressures and increased safety relative to alternative technologies. The overall results and analysis are presented.

- Chapter 7: Conclusions

The final chapter outlines the conclusions of the research with a brief economical feasibility analysis and suggests some possible future work and research directions.

Chapter 2

Background and Literature Review - A Vision of the State of the Art

This chapter examines the theory underlying membrane and pressure swing adsorption processes, the practical application of adsorption in the context of periodic adsorption processes, and summarily reports the research and development performed as part of the ANGWARD project. It seems appropriate to include a brief introduction to membrane technology and pressure swing adsorption to provide the basic background needed to assess the comparative merits of each unit.

2.1 Membranes for Gas Separation

The background research in this section covers gas separation applied to *n*-alkanes C₁-C₄, N₂, CO₂ and H₂. From the state-of-the-art literature on permeation, a search was made in order to obtain membrane characteristics feasible for realistic industrial applications.

Membranes have a unique profile of strengths and weaknesses. The magnitude of the benefit expected from gas separation membranes is highly dependent on the exact nature of the separation problem. In some cases they provide unusual sharpness of separation, but in most cases they perform a separation at lower cost, provide more valuable products, and do so with fewer undesirable side effects than older separations methods. It is generally reported that membrane separations are not favored when a product of very high purity is required. Membrane gas separation is thus generally considered suitable for bulk separation. Unless permeate is recycled, usually high product purity is accompanied by lower product recovery. Often, membranes serve these needs by providing a moderate

purity product which may be inexpensively upgraded by a subsequent process [X. Feng and Ghosh (1998)].

The common feed gas pressure can vary from atmospheric to 63–77 bar, although there are applications performed at higher pressures. The operating temperature varies from ambient to 60–70°C. Gas mixtures separated in large scale industry are mostly CO₂/CH₄, H₂/CH₄, He/CH₄, O₂/N₂, H₂/CO and H₂S/CH₄ [P. P. Radecki and Bullock (1999)]. Very large units are in operation throughout the world. For instance, the gas separation business was evaluated in 1996 at \$85 million in the U.S., with growth of about 8% per year [Drioli and Romano (2001); Strathmann (2001)]. Baker (2002) reports that, during the past 20 years, sales of membrane gas separation equipment have grown to become a \$150 million/year in the U.S. gas separation business, with growth of about 15% per year. More than 90% of this business involves the separation of noncondensable gases, such as N₂ from air, CO₂ from CH₄, and H₂ from N₂, Ar or CH₄. However, a much larger potential market lies in condensable gases separation, like C₃₊ from H₂ or CH₄, and C₃H₆ from C₃H₈. The development of the membrane market is determined by energy costs, required product quality, environmental protection needs and the availability of new and better membranes and membrane processes.

Composite polymeric membranes developed in the 1970s made the separation of components from gas streams commercially feasible. The first large-scale gas separation modules were developed by DuPont in early 70's, but the first successful commercial membrane gas separation processes (PRISM) were announced by Monsanto in late 70's. Polymeric membranes for gas separation became economically viable around 1980, introducing the modern era of gas-separation membranes. Many more have appeared since then. Billions of cubic meters of pure gases are now produced via selective permeation in polymeric membranes. Table (2.1) shows the principal characteristics of gas commercialized membrane separation processes [Baker (2002); Ho and Sircar (1992); Koros and Fleming (1993); Spillman (1989)].

Hydrogen recovery was the first large commercial membrane gas separation. Polysulfone fiber membranes became available in 1980 at a time when H₂ needs were rising, and these novel membranes quickly came to dominate the market. Applications include recovery of H₂ from ammonia purge gas, and extraction of H₂ from petroleum cracking streams. Hydrogen, the more permeable gas, once diverted to low quality fuel use is now recovered to become ammonia, or is used to desulphurize fuel, etc.

Much of the natural gas (NG) produced in the world is co-produced with an acid gas, most commonly CO₂ and/or H₂S. While there are many successful processes for separating these gases, membrane separation is a commercially successful competitor, especially for small installations. It has been reported that the economics work best for feeds with

Table 2.1: Principal Characteristics of Gas Commercialized Membrane Separation Processes.

Characteristics	Gas Permeation
Separation goal	Stream/streams enriched or depleted in a certain species
Nature of species retained (Size)	Larger species retained unless highly soluble
Nature of species transported through the membrane	Gaseous. Smaller species/more soluble species
Minor/Major species transported	Either
Driving force	Concentration gradient (partial pressure difference)
Mechanism for transport/selectivity	Solution-diffusion
Phase of feed and permeate streams	Gaseous

very high or very low CH_4 content. In this case, methane is the slower gas permeating the membrane and CO_2 , H_2S , and H_2O are the faster gases [Perry and Green (1999)].

The membrane interposes a new phase between feed and product. It controls the mass transfer between feed and product. It is a kinetic or a rate process, not an equilibrium process. In a separation, a membrane will be selective because it transfers some components at a much higher rate than others. Either species may be the desired product.

Hence, the membrane permeation concept is quite straightforward, since the separation occurs with the difference in permeation rates through a perm-selective membrane. The efficiency of the separation is largely dependent on the selectivity and permeability of the membrane material. Gas membranes generally work because individual gases differ in their solubility and diffusivity through nonporous polymers. Other membranes operate by other mechanisms like sieving, selective adsorption or chemical complexation. Here, the focus will be mainly on polymeric type of membranes.

The ideal membrane would have both high permeability and selectivity for the target component. Unfortunately, there is often a high compensation between these two parameters and usually a high selective membrane has a low permeability and vice-versa. There are, in general, practical limitations to achieve very high levels of purification. Thus, the most important part of gas permeation is the membrane itself, since depending on the gas mixture, a proper membrane selection has to be made. This passes through the development of membranes with sufficient productivity and separating ability to make them economically attractive in industrial applications.

The basic characteristics of membrane operations make them ideal for industrial pro-

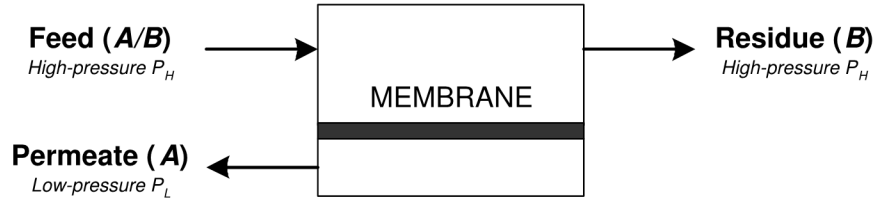


Figure 2.1: Schematic of the membrane separation process.

duction. Membranes have as advantages the low capital investment compared to other processes at lower processing volumes, the generally easy operation mode, the low energy consumption, the cost effectiveness even at low gas volumes and the good weight and space efficiency, resulting in cheaper, sustainable technical solutions. Besides the membrane limitation concerning the non-bulk separations, the disadvantages of membrane processes include fouling and possible durability and robustness of membrane material. Figure (2.1) presents a general membrane separation process.

The flux of any species across the membrane is caused by a driving force, arisen from a gradient of chemical potential, which may be due to a concentration or pressure gradient. The transmembrane flux of any species per unit driving force is proportional to the permeability of the species [D. M. Ruthven and Kneabel (1994); Ho and Sircar (1992)].

Gas separation generally occurs via pressure-driven diffusion. It is a process governed by the diffusion of the penetrant molecules in the nonporous polymer membrane matrix. Solution equilibrium is assumed to be established between the gas in contact with the membrane interfaces and the gas dissolved in the membrane at these interfaces [Stern (1994)]. The components that dissolve and then diffuse more rapidly through the membrane become enriched in the low pressure permeate stream, while the slower ones are concentrated in the residue stream. The diffusion process takes place when the change in chemical potential of the diffusing species is negative. For an ideal gas mixture the change in chemical potential, μ , across the membrane from the feed f to the permeate p is

$$\mu_{ip} - \mu_{if} = RT \ln(P_{ip}/P_{if}) \quad (2.1)$$

with T the temperature, P_i the partial pressure of component i and R the ideal gas law constant. Since this difference must be negative for spontaneous diffusion to occur, $\ln(P_{ip}/P_{if}) < 0$, i.e, $P_{ip} < P_{if}$, where P_{ip} and P_{if} are the permeate and feed partial pressures, respectively. Hence, the pressure difference is the driving force for transport across the membrane. It impacts both the membrane area required, and the volume and the

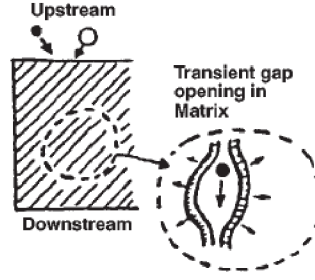


Figure 2.2: Schematic of the solution-diffusion mechanism used in the gas separations [Perry and Green (1999)].

composition of the residue and permeate streams. Figure (2.2) shows a schematic of the solution-diffusion mechanism, where the molecules dissolve in the membrane and diffuse through it.

For all membranes, Fickian diffusion is of some importance, and it is of dominant importance in gas permeation. The diffusion of the penetrant gas in the membrane is the rate-determining step in the permeation process. Gas transport through a nonporous membrane is generally governed by Fick's and Henry's laws. Fick's law gives the permeation flux

$$N_i = -D_i C \frac{dy_i}{dz}, \quad (2.2)$$

where N_i is the flux of component i , D_i is the diffusivity of component i , $C_i = C y_i$ is its concentration, and z is the distance.

Assuming D_i constant and independent of C_i , and that the concentrations in the two phases are in equilibrium with the membrane, Fick's law may be written as

$$N_i = D_i \frac{\Delta C_i}{\delta} \quad (2.3)$$

where δ is the effective membrane thickness and ΔC is the concentration difference across the membrane. If Henry's law governs concentration of the gas in the membrane,

$$C_i = S P_i \quad (2.4)$$

where S is a proportionality factor named solubility of the gas in the membrane, specific for a membrane and a penetrant and P_i is the partial pressure of component i . The diffusion coefficient is a measure of the species mobility in the polymer and S is a measure of the permeant's solubility into the polymer. If the membrane and its immediate surroundings are isothermal and if S is a function only of temperature, then

$$N_i = \frac{S \bar{D}_i}{\delta} (P_i^r - P_i^p), \quad \bar{D} = \int_{C_L}^{C_H} D(C) \frac{dC}{C_H - C_L}, \quad S = \frac{C_H - C_L}{P_H - P_L}. \quad (2.5)$$

Table 2.2: Kinetic diameters for important gases.

Penetrant	He	H ₂	CO ₂	Ar	O ₂	N ₂	CO	CH ₄	C ₂ H ₄	C ₃ H ₈
Kinetic diam. (nm)	0.26	0.289	0.33	0.34	0.346	0.364	0.376	0.38	0.39	0.43

where C_H and C_L are the equilibrium concentrations (solubilities) of the penetrant dissolved at the membrane interfaces at the pressure P_H and P_L , respectively. $\overline{SD}_i$ is defined as the permeability of species i , π_i . P_i^r is the partial pressure of component i in the residue, feed or high-pressure side of the membrane and P_i^p is the partial pressure of component i in the permeate or low-pressure side of the permeation unit.

The permeability provides a quantitative measure of the easiness with which a certain component penetrates the membrane. It depends on the nature of the gas and the polymeric matrix, on the temperature and on both P_H and P_L , which for a permeating mixture are partial pressures, function of the penetrant concentration. For simple gases the solubility increases as the gas diameter increases because the gas becomes easier to condense. The diffusivity of a gas in a membrane is inversely proportional to its molecular size, because large molecules interact more with the polymer chains (Table 2.2).

When the solubility of the penetrant gas in the matrix is sufficiently low, the solubility and diffusivity coefficients are constants. This also happens when $P_H \gg P_L$, and thus $C_H \gg C_L$, which is often the case in membrane processes. In terms of process design it is sufficient to determine the permeability for the given penetrant/polymer membrane system as a function of gas composition, pressure and temperature [Stern (1994)].

Hence, the rate of passage of material through a membrane, J_i , is then referred to as flux,

$$J_i = \pi_i \frac{A_{mem}}{\delta} (P_i^r - P_i^p) \quad (2.6)$$

where A_{mem} is the membrane area and $(P_i^r - P_i^p)$ represents the component pressure difference across the membrane. The ratio of the permeability of species, equal to π_i/δ , is generally called the permeance, $\wp_i$. It is rare that δ is known for a commercial membrane, so J_i is normally stated without regard to δ .

Pressure ratio, ϕ , is also important and is defined as the ratio between the feed pressure and the permeate pressure. The highest the pressure ratio, the higher the extent of separation. The stage cut, θ , is given by the ratio between the permeate flow rate and the feed flow rate. It is the fraction of the feed gas appearing as the permeate in the separator. For the case of a vacuum permeate, $\phi = \infty$, and since the membrane area will be an inverse function of P , ϕ influences separation and area, that is, the transmembrane pressure influences area. The larger the membrane area for a given feed gas flow rate, the higher the

cut value and the poorer the quality of the separation. In a binary separation, the highest purity of the permeate occurs when θ tends to zero. Purity decreases monotonically until it reaches the feed purity at $\theta = 1$. In a ternary system, the residue concentration of the gas with the intermediate permeability will reach a maximum at some intermediate stage cut.

One can also define the separation factor, i.e., the real selectivity of a mixture, by the ratio of the mole fractions in the permeate divided by the feed mole fractions ratio. The convention in membrane separations is to define the separation so that $\alpha > 1$, where α is given by

$$\alpha_{A/B} = \frac{y_A^p/y_B^p}{y_A^r/y_B^r} \quad (2.7)$$

with A and B the permeating components. The separation factor is equal to the ratio of the permeabilities of the two species under conditions in which the downstream (permeate) pressure or concentration is negligible in comparison to the upstream (residue) pressure or concentration. For $\alpha = 1$, or for $\phi = 1$ there is no separation at all. Selectivity values should be greater than 20 or preferably 40 (Baker (2002); Perry and Green (1999)). The permeate concentration increases as the membrane selectivity increases, the pressure ratio increases, or the stage cut decreases [Wankat (1990)].

From the relationship of Eq.(2.5), the ideal selectivity is given by the equation

$$\alpha_{A/B} = \frac{D_A S_A}{D_B S_B}, \quad (2.8)$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity, two contributions for the overall selectivity due to the differences in the diffusivities and solubilities of the penetrants A and B in the polymer. Several authors commonly refer to permeability as a measure of the membrane's intrinsic productivity, while selectivity is a measure of the separation efficiency [J. D. Wind and Koros (2002)].

Gas separation membranes are generally polymeric with an asymmetric structure. The dense selective layer is nonporous for polymeric materials, sustained on a microporous inert support. The technique to make such a membrane was first developed by Loeb and Sourirajan (1963). Melt spinning or solution casting and phase inversion methods were employed. Based on this concept, several researchers have developed methods of making efficient gas separation membranes [A. Bos and Strathmann (1999); Ekiner (1992); G. C. Kapantaidakis and Wessling (2002a,b, 2003); G. C. Kapantaidakis and Sakellaropoulos (1996); J. J. Krol and Koops (2001); K. C. Khulbe and Koops (2003); Kesting (1989); Kesting and Fritzsche (1993); Koros and Fleming (1993); Puri (1988, 1996)]. These methods are being used commercially by Ube and Air Liquide to make gas

2.1 Membranes for Gas Separation

Table 2.3: Permeability and selectivity data (at 35°C unless otherwise specified) of some polymers used in the manufacture of commercial membranes for gas separation. $P_i \times 10^{10}$: cm^3 (STP) $\text{cm/s cm}^2 \text{ cmHg}$. Ideal overall selectivity: $\alpha(\text{A/B}) \equiv P(\text{A})/P(\text{B})$.

	Permeability coefficient, P (Barrer)				Ideal Selectivity, α		
	CO ₂	O ₂	N ₂	CH ₄	CO ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄
poly[1-(trimethylsilyl)-1-propyne]	20 000	7 730	4 970	13 000	4.0	1.6	1.5
poly(dimethylsiloxane)	4 550	781	351	1 430	13.0	2.2	3.2
poly(dimethylsilomethylene)	520	91	35.9	150	14.5	2.5	3.5
poly(cis-isoprene)	191	37.5	14.5	47.4	13.2	2.6	4.0
poly(butadiene-styrene)	171	32.9	10.3	34.2	16.6	3.2	5.0
natural rubber (at 25 °C)	153	—	9.43	—	16.2	—	—
ethyl cellulose	5	12.4	3.4	6.8	1.5	3.6	0.7
polystyrene	12.4	2.9	0.52	0.78	23.8	5.6	15.9
butyl rubber	5.18	—	0.324	—	16.0	—	—
poly(ethyl methacrylate)	7.01	1.9	0.33	0.35	21.2	5.8	20.0
poly(phenylene oxide) (at 25 °C)	75.7	—	3.81	—	19.9	—	—
bisphenol A polycarbonate	6.8	1.6	0.38	0.36	17.9	4.2	18.9
cellulose acetate	4.75	0.82	0.15	0.15	31.7	5.5	31.7
bisphenol A polysulfone	4.6	1.2	0.19	0.18	24.2	6.3	25.6
PMDA-4,4'-ODA polyimide	2.7	0.61	0.1	0.059	27.0	6.1	45.8
poly(methyl methacrylate)	0.62	0.14	0.02	0.0052	31.0	7.0	119.2
poly(vinyl chloride) (at 25 °C)	0.157	—	0.0118	—	13.3	—	—
PEEK-WC (at 25 °C)	2.75	0.5	0.1	—	27.5	—	—
polyphosphazeny (at 25 °C)	5.76-10.2	0.955-1.72	—	—	—	—	—

permeation units. Other membrane manufacturers are Praxair, Cynara (Natco), Permea (Air Products), Separex (UOP) and Membrane Technology and Research (MTR) [Baker (2002)]. The ultimate goal is to provide maximum membrane area per unit of volume of the module, maintaining a high separation efficiency for the desired transmembrane pressures and temperature, and to provide a cost effective and mechanically robust separation unit. In Table (2.3), some permeability and selectivity data for the various polymers used in the manufacture of the most commercial membranes are reported [Stern (1994)].

When dealing with polymeric membranes, high permeability and high selectivity are essential to minimize the capital and operating costs, respectively. Moreover, the development of plasticization-resistant membrane materials is required for many new profitable applications such as high-pressure CO₂/CH₄ separations in NG processing, several potential CO₂ separations and propylene/propane separations, among others. The high CO₂ content in NG sources of several countries, such as U.S. and Brazil, induce the development of membrane materials in order to overcome the plasticization phenomena. The growing usage of NG as a clean fuel, makes it a very profitable product in the gas processing market. In U.S., for instance, for a NG price of \$3.0/MMBTU, CO₂ worth about \$1.3 trillion [J. D. Wind and Koros (2002)].

The plasticization effect can occur in some cases. Gas solubility in the membrane is

one of the factors governing its permeation, but the other factor, diffusivity, is not always independent of solubility. If the solubility of a gas in a polymer is too high, plasticization and swelling result, and the critical structure that controls diffusion selectivity is disrupted. These effects are particularly troublesome with condensable gases, and are most often noticed when the partial pressure of CO₂ is high [Perry and Green (1999)]. This problem is well known, but its manifestation is not always immediate and a lot of research is being published in this subject [Koros (1999), J. D. Wind and Koros (2002), M. Wessling and Strathmann (2001), etc.]. This phenomena is defined as an increase in the segmental motion of polymer chains, due to the presence of one or more sorbates, such that the permeability of the components increases and the selectivity decreases. This loss in selectivity can be mainly induced by the reduction in the diffusivity selectivity due to excessive motion of the polymeric chains.

For example, in a CO₂/CH₄ mixture, as the glassy polymer becomes plasticized with CO₂, the diffusion coefficients of both components increase with reduction of the diffusivity selectivity, since the polymer is less able to discriminate between molecules on the basis of size and shape differences because CO₂ enhanced the segmental mobility of the polymer. The polymer swells upon sorption of CO₂ accelerating the permeation of CH₄ and hence its selectivity is lost. The sorption of CO₂ on the polymer affects the main chains relaxation such as the glass transition. Sanders (1988) suggests that this motion allows easy passage of small penetrant molecules and the increase in segmental mobility due to the presence of condensable components like CO₂ result in a reduction of the diffusivity selectivity. M. Wessling and Strathmann (2001) reported that the plasticization effect also depends on the thickness of the active membrane layer. Thin films plasticize at lower CO₂ pressures than thick films. Asymmetric hollow fibers with a skin thickness around 0.1 μm are more susceptible to plasticization than the thick films greater than 25 μm . A. M. Shishatskii and Peinemann (1996) studies on dense polymeric films having different thicknesses in the range of 5-150 μm , drew to the conclusion that for all the analyzed light gases, diffusion coefficients decrease when film thickness decreases and film density increases. On the other hand, the decrease in film thickness enhances the solubility coefficients of different gases. As the diffusion and solubility coefficient are changed in an opposite way as functions of film thickness, permeability coefficients and separation factors are nearly independent of the thickness and density.

Hence, since the flux varies inversely with membrane thickness, the desirable membrane should have an active separating layer as thin as possible. Also high fluxes are usually very desirable, because the transfer area required will be lessened. Likewise, a high pressure drop across the membrane should be desired. Of course the limitation is

the membrane physical strength, which has to be enough to resist to the applied pressure. Since the membrane area is directly proportional to the feed throughput, it should be maximized. Generally, the membrane active layer is a thin polymeric film (0.1 to 1.0 μm), supported in a porous inert support that does not influence the separation and only provide the robustness needed, that is, an asymmetric or anisotropic membrane [D. M. Ruthven and Kneabel (1994); Ho and Sircar (1992); Wankat (1990)].

Polymeric membranes dominate the membrane gas separation field, because they are well developed and quite competitive in separation performance and economics. The most common commercial type of membranes are spiral wound and hollow fiber units, exhibiting a typical 1000-5000 m^2 area per cubic meter volume of the module. There is no agreement concerning the best flow direction, through the shell- or the bore-side of the membrane. It is reported that if the high-pressure flow goes through the tubes rather than through the shell, it is easier to maintain an approximation to the plug flow on the high-pressure side. However, in the practical point of view it is more difficult to apply a uniform active film free from defects to the interior surface of the hollow fibers. For this reason, the flow through the shell side is widely used in commercial systems and the deviation from ideal plug flow is minimized by a good design.

Gas separation membranes have outer diameter as small as 135 μm and inner diameter of 95 μm . For low-pressure applications such as air, they may run with tube-side feed. Gas membranes operating at high pressure (above 1.5 MPa) are almost always run with shell-side feed. The outer diameter for industrial gas membranes may be as high as 500 μm in a 15 cm shell and 300 cm long [Perry and Green (1999)]. The major advantage of the hollow fibers systems is that a huge number of fibers can be packed inside a cartridge, and thus the area/volume ratio is very high and costs are kept down. The major disadvantage is solid particles that can clog the fibers when one are dealing with dirty fluids. The spiral wound configuration has the advantages of a lower pressure drop in the flow direction, and the technology to build the system is less complex. However, the area/volume ratio is much lower than in hollow fiber membranes. In a hollow-fiber spinning plant production costs are in the range \$2-5/ m^2 . This is much less than the production costs of equivalent spiral-wound modules, which are in the \$10-100/ m^2 range. The module selling price will be 2-3 times higher than the production cost, depending on the market [Baker (2002); Wankat (1990)].

Attention should also be taken to the flow pattern, which has impact on the performance of a membrane system. As in any mass transfer process, the countercurrent flow maximizes the average driving force providing the most efficient arrangement.

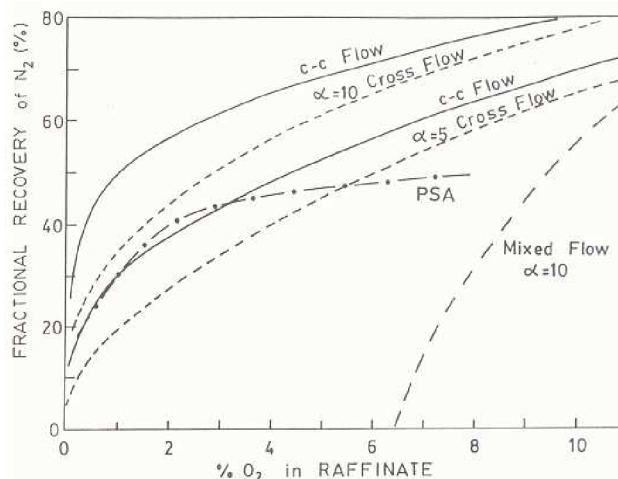


Figure 2.3: Recovery-purity profile for production of nitrogen from air by membrane and PSA processes [D. M. Ruthven and Kneabel (1994)]. Raffinate refers to the residue or high-pressure membrane stream.

Figure (2.3) clearly presents the difference in flow patterns for a typical membrane process for recovery of nitrogen from air and its comparison with a PSA process. The nitrogen is the less permeable component, the pressure ratio is 5 and the permeability ratios are 5 and 10, typical values of membrane processes for recovery of nitrogen from air. It is visible the effect of permeability and flow pattern on system performance.

Concerning the temperature effects in a polymer membrane, one can say that a temperature increase permits larger segmental motions in the polymer, producing a drastic increase in diffusivity, in opposition to a decrease in solubility. It increases the size of the gaps in the polymer matrix, decreasing diffusivity selectivity. For a glassy polymer, the net result is that permeability rises while selectivity declines. For organic permeants in rubbery polymers, this trend is often reversed.

The polymers used commercially for membrane systems can be classified into three categories: rubbery polymers like polydimethylsiloxane (PDMS), glassy polymers amorphous [cellulose acetate (CA), polysulfone (PSF), polystyrene (PS), polypropylene (PP), polyimide (PI)] or semicrystalline [polyamides (PA), polyethylene (PE), polytetrafluoroethylene (PTFE), polycarbonate (PC), polyvinylidene fluoride (PVDF)], and ion exchange membranes. The rubbery ones like silicone operate above the glass transition temperature, T_g , of the polymer. These materials have high fluxes for organics and low flux for water. Glassy polymers operate below T_g , are amorphous or partially crystalline and are selective for water. The ion exchange membranes are essentially ion exchange

Table 2.4: Permeability, diffusion and solubility coefficients for N₂, O₂, CO₂ and CH₄ in PTMSP and PDMS. P [cm³ (STP) cm/s cm² cmHg], D (cm²/s), S [cm³ (STP)/cm³ (polym.) cmHg] [Stern (1994)].

Penetrant gas	$P \times 10^8$	$D \times 10^5$ ^a	$S \times 10^2$
Glassy PTMSP; temperature: 30°C			
N ₂	49.7	3.5	1.42
O ₂	77.3	4.66	1.66
CH ₄	130	2.64	4.92
CO ₂	280	2.64	10.59
Rubbery PDMS; temperature: 35°C			
N ₂	4.7	4.0	0.118
O ₂	9.6	3.97	0.242
CH ₄	14.3	2.45	0.591
CO ₂	45.5	2.63	1.74

^a From relation $D = P/S$

resins made in membrane form and are very selective for water. Almost all the important membrane separation processes of industrial interest utilize membranes made from glassy polymers, because of their high gas selectivity and good mechanical properties. Contrary to the rubbery polymers, like silicone ones, the glassy polymers exhibit a low intrasegmental mobility and long relaxation times. The solubility, diffusion and permeability coefficients of the glassy polymers are strong functions of the penetrant gas pressure and concentration in the polymer [Stern (1994)]. The rubbery ones have higher permeability coefficients but selectivities are usually quite low [Ho and Sircar (1992), Stern (1994), Wankat (1990), P. P. Radecki and Bullock (1999)].

A glassy polymer such as poly[1-(trimethyl)-1-propyne], PTMSP, exhibits approximately ten-fold higher permeability for light gases than rubbery poly(dimethylsiloxane), PDMS, due to both high gas solubility and diffusivity if compared to PDMS and to other glassy polymers. The diffusion coefficients and the diffusivity selectivity are quite similar to both polymers. This comparison is shown in Table (2.4).

The search for an ideal membrane produced copious data on many polymers, neatly summarized by Robeson (1991). Figures (2.4) and (2.5) show an upper bound in the relationship between selectivity and permeability for various rubbery and glassy polymers. This is an attempt to indicate the limits to the separation performance of polymeric membranes. He also has determined upper-bound lines for many permeant pairs in hundreds of polymers. In Figure (2.4), the lower line shows the upper bound in 1980. Several polymers

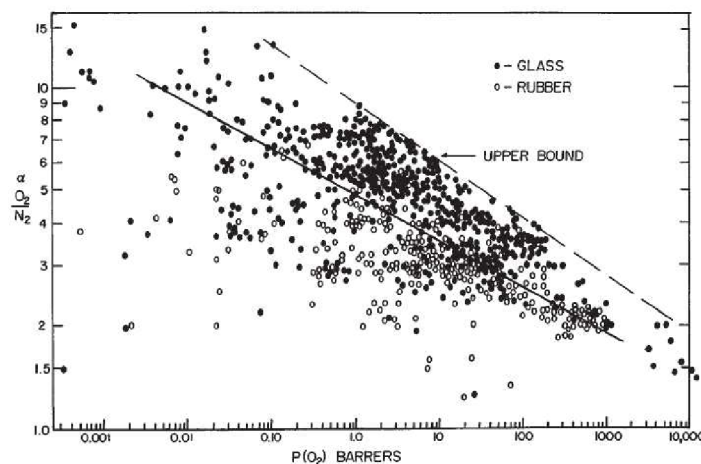


Figure 2.4: Plot of selectivity α_{O_2/N_2} versus fast gas (O_2) permeability in Barrers for several polymers, O_2/N_2 . Temperature: 25 - 30°C [Perry and Green (1999)].

exist near the bound for separations of interest. Whether these are available as commercial membranes is a different matter. As seen in both Figures (2.4) and (2.5), glassy polymers are significantly overrepresented in the high-selectivity region near the upper bound, and rubbery polymers are overrepresented at the high-permeability end, although the highest permeability polymer discovered, poly(trimethylsilylpropyne), PTMSP, is glassy. A brief characterization of the polymers that were considered in the thesis for both experimental and simulation work is presented as follows.

Figure (2.6) presents the relationship between the CO_2/CH_4 selectivity and the permeability to CO_2 of several silicone polymers at 35°C and at an applied pressure of 7 bar. It is visible the so-called usual *inverse* relation between overall selectivity and permeability. Several studies performed during the last decade make it possible to windrow the main permeating characteristics of silicone polymers:

- The decreasing trend in the permeability of these polymers, resulting from the substitution of bulkier and/or stiffer functional groups, is due mainly to a decrease in the gas diffusivity, because of the decrease in the intrasegmental mobility.
- The permeability to a penetrant gas increases with the increasing of the penetrant solubility.
- The overall selectivity of a given silicone polymer depends mainly on the solubility selectivity, being the diffusivity selectivity close to unity. The latter become more significant to the selectivity as the permeability of the polymers decrease, where the material acquires a *molecular sieving* ability. When the disparity in penetrants

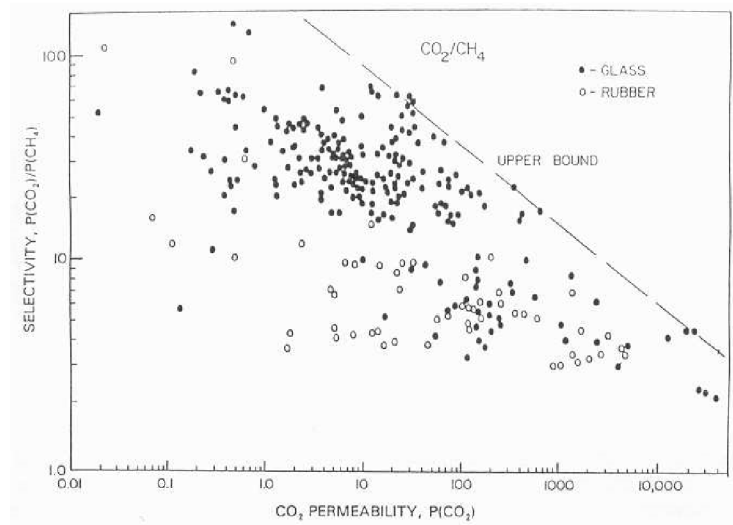


Figure 2.5: Plot of selectivity α_{CO_2/CH_4} versus fast gas (CO_2) permeability for several polymers. $P(CO_2) \times 10^{10}$: cm^3 (STP) cm/s cm^2 $cmHg$. Temperature: 20 - 40°C [Stern (1994)].

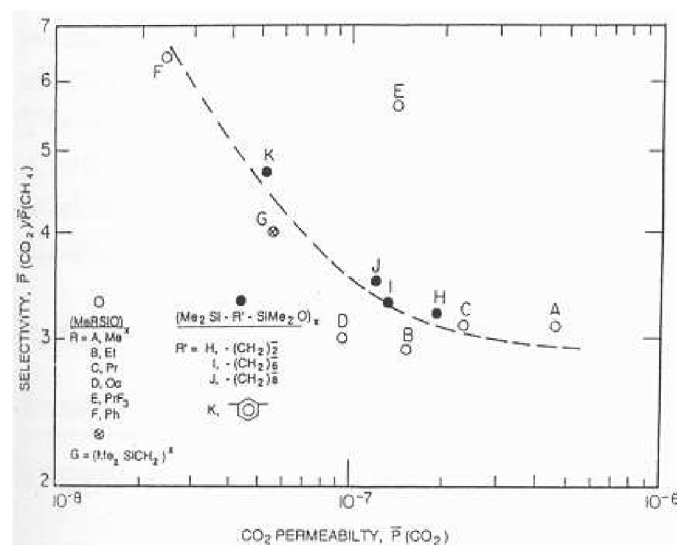


Figure 2.6: Relationship between the CO_2/CH_4 selectivity and the permeability to CO_2 of several silicone polymers at 35°C and at an applied pressure of 7 bar. $P(CH_4)$: cm^3 (STP) cm/s cm^2 $cmHg$ [Stern (1994)].

molecular size is not too large, the more permeable silicone polymers are unable to discriminate between gas molecules of different sizes and shapes.

- The functional groups substitution on the silicone polymeric structure that induce specific interactions with the desired penetrant gas is a method of increasing its selectivity in the matrix, although this procedure is a trial and error analysis concerning the selection of those functional groups.

Cellulose acetate membranes are one of the most commonly used in commercial gas separations, specially in CO_2/CH_4 mixtures and CO_2 , and H_2S removal from NG. Although these glassy polymers exhibit good stability in the presence of aggressive feed streams, their intrinsic properties are inferior to those of polyimide membranes [J. D. Wind and Koros (2002)]. Cellulose acetate membranes are strongly plasticized by CO_2 , which is shown by an increase in CO_2 permeability of the polymer for pressures above 10 atm. The extent of this effect is more pronounced the higher the CO_2 concentration in the mixture. It is reported that, for a 40/60 mol% CO_2/CH_4 mixture at 35°C , the selectivity in the polymer matrix drops around one order of magnitude, from $\approx 33 \pm 3$ at 1 atm to ≈ 22 at 14 atm [A. Bos and Strathmann (1999); Stern (1994)]. The plasticization in these polymers is explained by the high solubility of CO_2 , which at pressures above 10 atm is greater than polysulfone or polycarbonate. It has been proposed that there are interactions between the CO_2 molecules and the cellulose acetate structure and, thus, CO_2 dilates the polymer and disrupts (inhibit) interchain interactions. This increases the intrasegmental (rotational) mobility and also the diffusion and permeation rates of CO_2 in cellulose acetate.

Figure (2.7) shows the permeation of four polymers. Knowing that the permeability is the product of solubility by diffusivity [Eq. (2.5)], one can see that selectivity for rubbery membranes comes from solubility differences, since diffusivities of most gases are approximately the same. In glassy polymers both diffusivity and solubility differences are important in determining selectivity [Wankat (1990)]. The high H_2 diffusivity and CO_2 solubility give greater permeabilities to these components than the gases they are separated from. This explains the major industrial successes in these specific separation. Current membrane-materials research is strongly focused on glassy materials and on attempts to improve diffusivity, as it seems more promising than attempts to increase solubility [Koros (1994)].

Organic polymer membranes are the basis for almost all commercial gas-separation activity. Early membranes were cellulose esters and polysulfone. These membranes have a large installed base in industrial applications. New installations are dominated by

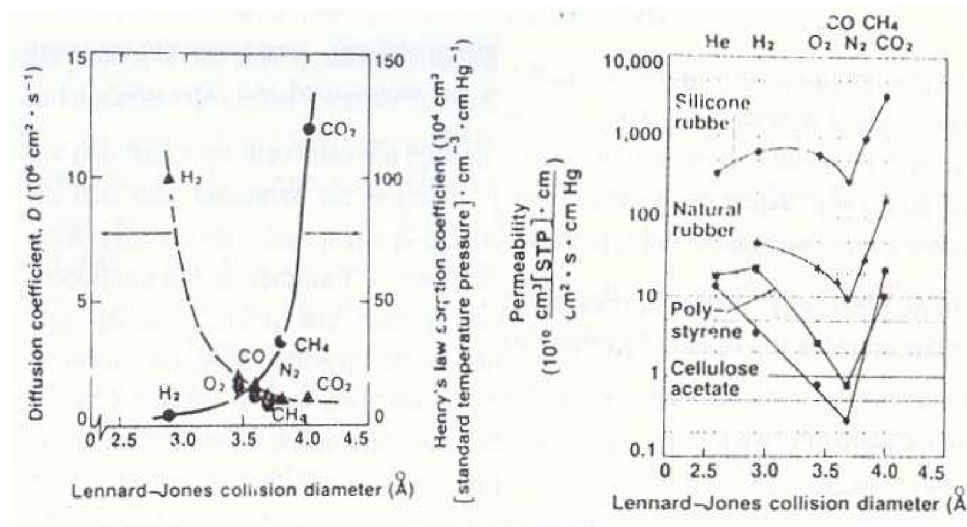


Figure 2.7: Permeation of gases in polymer membranes. Left figure reports diffusivity and solubility in natural rubber. Right figure refers to permeabilities in four polymers [Wankat (1990)].

specialty polymers designed and tailored for the purpose, including some polyimides and halogenated polycarbonates.

A variety of studies in the membrane field have shown that polyimides (PI) exhibit a higher permeability than many other glassy polymers [J. D. Wind and Koros (2002)]. The structural modification of these polymers allowed the enhancement of both selectivity and permeability, either due to stiffness of their backbone chains (intrasegmental or rotational mobility inhibition), inhibition of intersegmental packing of their chains, or weakening of interchain interactions. It has been reported that some fluorinated aromatic polyimides (6FDA-based polyimides) are considerably more gas selective, specially towards CO_2/CH_4 or CH_4/He , than other polyimides with similar permeabilities. This enhancement is justified by the chain stiffness of the polymer that enables a better discrimination between penetrant molecules of different sizes and shapes, increasing its selectivity; and reduction of the chain packing due to the size of the $-\text{C}(\text{CF}_3)_2-$ groups, increasing the permeability [Figure (2.8)]. Table (2.5) presents the permeation properties of some of the aromatic polyimides most used in light gas separations and Figure (2.9) shows the relationship between overall CO_2/CH_4 ideal selectivity and CO_2 permeability for the fluorinated polyimides [Stern (1994)]. The data shows that the permeation properties can be increased simultaneously by suitable structural modifications, namely increasing the $-\text{C}(\text{CF}_3)_2-$ incorporation.

The polyimides exhibit a dependence of the permeability on the diffusivity which is ev-

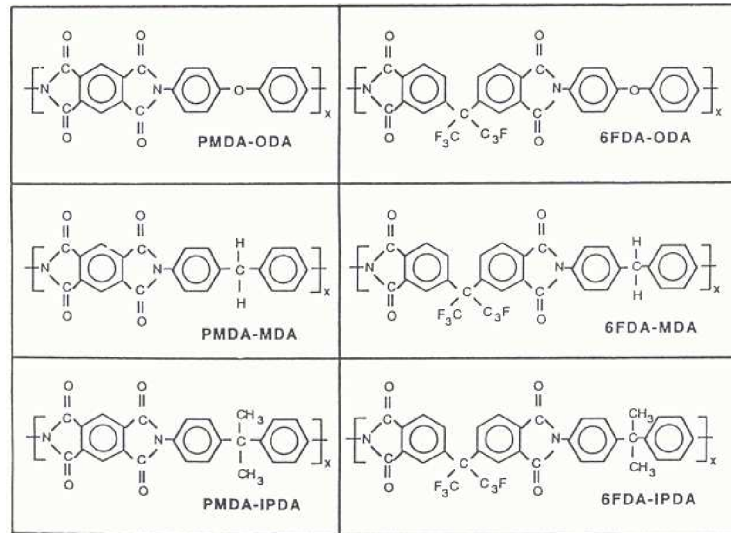


Figure 2.8: Structures of PMDA- and 6FDA-based polyimides.

Table 2.5: Permeability coefficients and overall ideal selectivities for several light gases in six aromatic polyimides at 35°C. $P \times 10^{10}$: cm^3 (STP) $\text{cm/s cm}^2 \text{ cmHg}$. Applied pressure: 10 atm for He, CO_2 , N_2 and CH_4 ; 2 atm for O_2 .

Polymer	P (He)	P (N_2)	P (O_2)	P (CO_2)	P (CH_4)	α (CO_2/CH_4)	α (He/ CH_4)	α (O_2/N_2)	α (CO_2/N_2)
PMDA-ODA	8.0	0.1	0.61	2.71	0.059	45.9	135.6	6.1	27.1
PMDA-MDA	9.4	0.2	0.98	4.03	0.1	40.3	94.0	4.9	20.2
PMDA-IPDA	37.1	1.5	7.10	26.80	0.9	29.8	41.2	4.7	17.7
6FDA-ODA	51.5	0.83	4.34	23.0	0.38	60.5	135.5	5.2	27.6
6FDA-MDA	50.0	0.81	4.60	24.2	0.43	56.3	116.3	5.7	30.0
6FDA-IPDA	71.2	1.34	7.53	30.0	0.70	42.9	101.7	5.6	22.3

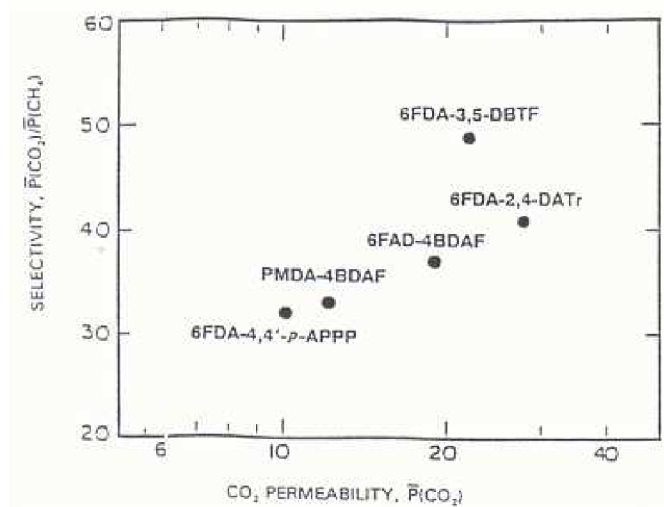


Figure 2.9: Relationship between CO_2/CH_4 ideal selectivity and CO_2 permeability of several fluorinated polyimides. $P(\text{CO}_2)$: cm^3 (STP) $\text{cm/s cm}^2 \text{ cmHg}$. Temperature: 35°C ; applied pressure: 7 atm).

identified indirectly from the fact that the permeability coefficients for different light gases decrease in the penetrant gas order $\text{He} > \text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{CH}_4$. This is also the order of increasing kinetic diameters of these molecules [See Table (2.2)]. The respective diffusion coefficients also decrease with increasing kinetic diameters. By contrast, solubility coefficients depend mainly on the intermolecular forces between penetrants and polymers, and decrease with decreasing critical temperature of the penetrant gases. Hence, polyimides and other glassy polymers have some *molecular sieving* ability. This accounts for the observation that the greater the difference in the sizes and shapes of the penetrants the higher the overall and diffusivity selectivity of these polymers. However, it is important not to forget that the global selectivity also depends on the solubility selectivity.

The polyimides exhibit very good separation characteristics at low pressures, but because of plasticization cannot maintain the same performance at high pressures in the presence of significant adsorbable components. The high pressure operation requirements and the higher average CO_2 concentrations, which make the membrane economics more favorable, assuming that the membrane remains stable, are the two considerations underscore the importance of the research in plasticization resistant materials needed for membrane gas separations. Hence, crosslinking and blending of polymeric gas separation membranes are two useful techniques to improve the separation characteristics by decreasing the plasticization effect at high pressures, and simultaneously promoting resistance to chemicals attack and reducing aging.

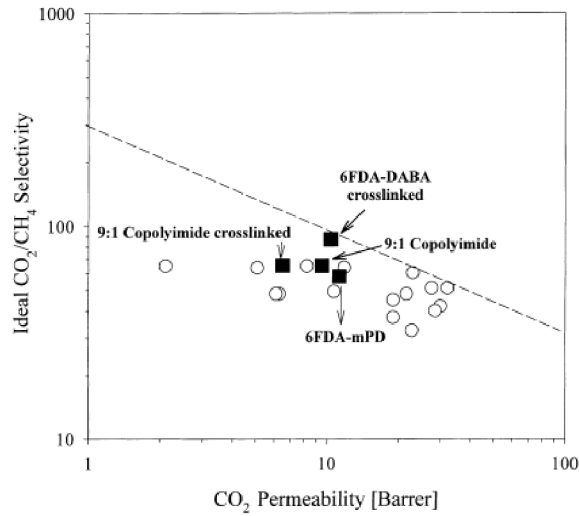


Figure 2.10: Trade-off for the CO₂/CH₄ separation, (○) 6FDA-based polyimides, (■) polyimides synthesized by Koros (1999). The dashed line represents the so-called upper bond of performance trade off reported in Figure (2.5).

Most of the crosslinking methods involve procedures that are difficult to apply in commercial membrane manufacturing systems, either due to the high temperatures needed or because the lack of reproducibility in the process. Moreover, the CO₂ permeability is often reduced after the treatment. Nevertheless, some authors recently reported new approaches for the crosslinking method at moderate temperatures, after the film or fiber formation, under a post-treatment, that can be added to the existing membrane production with small incremental costs and without significant losses in permeabilities [J. D. Wind and Koros (2002); Koros (1999); P. S. Tin and Pramoda (2003)]. For example, the incorporation of carboxylic groups (–COOH) in PI structures and its chemical crosslinking with ethylene glycol PI or co-PI, has been demonstrated to be effective in the suppression of the plasticization effect without degradation of CO₂ permeability. In fact, CO₂/CH₄ selectivity was even increased when compared to the uncrosslinked reference polyimide. Figure (2.10) shows the CO₂/CH₄ trade-off as presented in Figure (2.5), with the treated polyimides. For the crosslinked and the uncrosslinked 6FDA-based copolyimide separation properties nearby the upper bond are obtained. On the other hand, the CO₂/CH₄ separation properties of the strong crosslinked 6FDA-based polyimide are much better with an ideal selectivity of 87 and a CO₂ permeability of 10.4 Barrer. The crosslinking agent provides stability at elevated pressures over extended time periods. According to J. D. Wind and Koros (2002) covalent crosslinking of the polymer chains leads to a more significant increase in the plasticization resistance than simple thermal treatments

or crosslinking with aluminum ions. It leads to a decrease in the sorption levels of the components maintaining the diffusivity selectivity at high pressures. Since it is assumed that the chains loose at high pressure, which feeds the mobility to configure themselves to accommodate excessive amounts of CO_2 , this procedure contraries the plasticization phenomena.

The blending procedure was the technique applied to produce the membrane that was used during this thesis, in the experimental permeation measurements performed for membrane separative characterization analysis and computational model validation.

The blends contain the distinct polymers separated as an individual domains or phases, without mixing on a molecular level [RAYCHEM (1991)]. Usually the matrix of one polymer contains the other polymer as a dispersed phase. The PI which form the membrane to be used in this thesis (Matrimid 5218) can be blended with polycarbonate (PC), polysulfone (PSF) or polyethersulfone (PES). This latter polymer, polyethersulfone Sumikaexcel, is the one used in the blending of the experimental membrane module applied in the work. Blending of a polymer that is highly susceptible to plasticization (PI) with a polymer that hardly plasticizes (PES) will result in a material that shows a suppressed plasticization tendency. The expensive polyimide blended with the cheaper PES also has a financial benefit.

PES/PI hollow fibers at a given blend composition were prepared by a known dry/wet phase inversion method using a specified solvent. A suitably formulated polymer solution and a bore liquid mixture are simultaneously pumped to a tube-in-orifice spinneret. The extruded fibers pass through an air-gap of specific length and enter a nonsolvent bath, where coagulation takes place. After formation, hollow fibers are washed with ethanol to remove residual solvent. Is a complex process since it involves many process variables that influence both the geometrical characteristics and the permeation properties of the hollow fibers. The blending procedure applied is fully described in literature [Bos (1996); G. C. Kapantaidakis and Wessling (2002a,b); Strathmann (2001); T. S. Chung and Hu (1997)].

It is important to note that, specially for CO_2 separations at high pressures, the polyimides advantages will further increase the polymeric utilization in membrane technology. Higher CO_2/CH_4 selectivities and permeabilities to CO_2 than the most industrialized membrane material, cellulose acetate, are already reported [Figure (2.11)].

Nonetheless, the limitations to the large-scale industrial applicability of some membrane operations can be attributed not only to inadequate intrinsic membrane properties (low permeability and selectivity, low thermal and chemical resistance, etc.), but also to inadequate module design, hydrodynamic studies, and, in general, engineering analysis. Module design must deal with five major issues, plus a host of minor ones. First is econ-

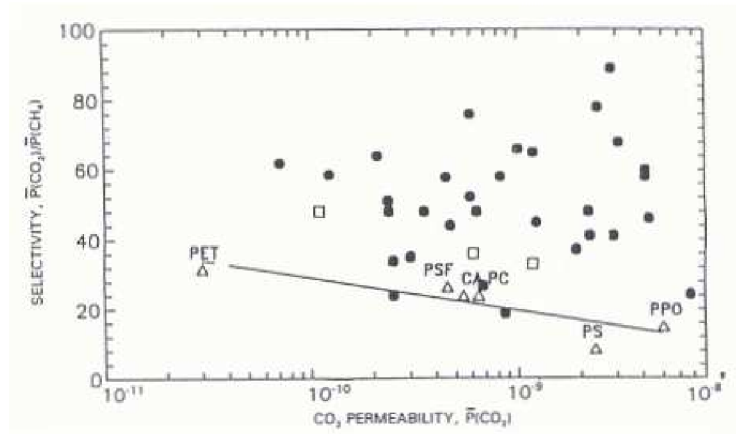


Figure 2.11: Relation between CO_2/CH_4 selectivity and CO_2 permeability for various polymers: (●) 6FDA-based polyimides; (□) PMDA-based polyimides; (Δ) common polymers; PET, poly(ethylene terephthalate); PS, polystyrene; CA, cellulose acetate, PC, polycarbonate; PSF, polysulfone; PPO, poly(phenylene oxide). $P(\text{CO}_2)$: cm^3 (STP) $\text{cm/s cm}^2 \text{ cmHg}$; Temperature: 30°C ; Applied pressure for polyimides: 7 atm.

omy of manufacture. The module should present high selectivity and fluxes. Second, a module must provide support and seals to maintain membrane integrity against damage and leaks. Must have good mechanical, chemical and thermal stability under operating conditions, and be cost-effective and defect-free. Third, it must deploy the feed stream so as to make intimate contact with the membrane, with a minimum waste of energy. Fourth, the module must permit easy egress of permeate. Fifth, the module must have low fouling tendency, good compatibility with the operation environment, and must permit the membrane to be cleaned when necessary [Perry and Green (1999)]. It is, then, realistic to state that new wide perspectives of membrane technologies and integrated membrane solutions for sustainable industrial growth are possible.

Concerning this thesis, the experimental permeation work performed was done with a bench scale asymmetric hollow fiber membrane module supplied with an active film of a polymeric PI/PES blending at the outer side of the fibers. It is a nonporous membrane where permeation takes place from the shell to the bore side of the hollow fibers. Additional characterization of the permeation setup will be given in section 3.1. In the simulation work, the membrane unit was developed in counter-current flow mode, almost like a black box, because only the separating ability and the membrane area available for permeation were taken into account.

2.2 Pressure Swing Adsorption

Adsorption separation is a phenomenon in which one or more components of a fluid (adsorbate) are extracted via selective bonding to a solid (adsorbent) medium [Yang (1987), Ruthven (1984), D. M. Ruthven and Kneabel (1994)]. This is the basis for every adsorption separation process.

The essential feature of a pressure swing adsorption (PSA) process is that, operating in cycles, an adsorbent bed passes through an adsorption step, where one component is withdrawn and is followed by a regeneration step, where the preferentially adsorbed species are removed by reducing the total pressure. One can also define the process as a gas mixture that is fed to the adsorbent bed and the most strongly adsorbed component is trapped, while the fast component is allowed to flow through. When the bed becomes full of the most strongly adsorbed component, blowdown takes place with raffinate withdraw and desorption of the slower component. Finally purge occurs to regenerate the bed for the next cycle.

From the point of view of designing practical adsorption processes, it is important to note that a given adsorbent has a finite capacity for a given adsorbate, and the adsorption is terminated when the solid is saturated with the adsorbate. At that particular point, the solid must be cleaned or regenerated so that it can be re-used economically. It is therefore important for the adsorption process to be reversible, which can be accomplished either by increasing the temperature in the solid bed, through the so called temperature swing adsorption (TSA), or by reducing the partial pressure through PSA.

Depending on the PSA cycle, it is possible to obtain useful products either from the adsorption or desorption stages or from both. The raffinate with the less strongly adsorbed species is obtained during adsorption and the desorbate or extract is the product recovered from the bed regeneration. Figure (2.12) taken from literature is illustrative of the general concept of this process [D. M. Ruthven and Kneabel (1994)].

Temperature swing is accomplished by purging the bed with a preheated gas. Pressure swing is accomplished by reducing the total pressure in the adsorbent bed at essentially constant temperature. The process operates under approximately isothermal conditions so that the capacity is given by the difference in loading between the feed and the regeneration pressures, usually the higher and lower system pressures, on the same isotherm [Figure (2.12.a)]. The inert gas purge option removes the adsorbate without changing the temperature or pressure. The void in the bed is filled with the inert gas upon regeneration. The light product becomes slightly contaminated with the inert during the next adsorption step, unless the raffinate is used as the inert purge gas. A combined P/T swing can occur by displacement of a hot gas purge that adsorbs as strongly as the adsorbate. The regeneration is thus facilitated both by adsorbate partial pressure reduction and by

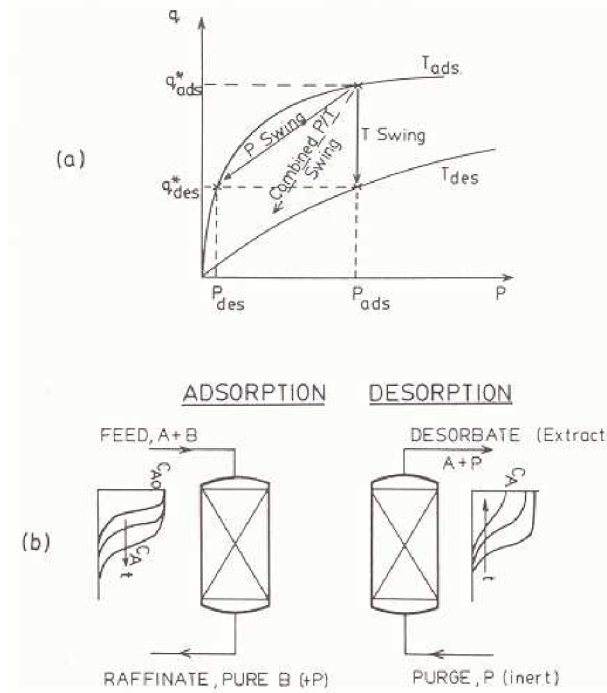


Figure 2.12: The concept of a PSA process. a) Equilibrium loading variation with pressure. b) Schematic of movement of the adsorbed phase concentration profile for the more strongly adsorbed species in a simple two-bed PSA process.

competitive adsorption of the displacement gas. However, this option results in additional separation steps due to raffinate product contamination.

In Figure (2.12.b) the movement of the concentration profiles along the bed is shown during the high-pressure adsorption and low-pressure regeneration. Generally, the feed step is terminated before the breakthrough of the strongly adsorbed species, while the regeneration is stopped before the bed is fully desorbed. Although the operation of each bed is batchwise, the system, as a whole, is a continuous one that is operated in a cyclic steady state (CSS), in which the conditions at the end of each cycle are identical to those at its start. At CSS, the profile varies in a mean position in the bed.

Based on the mechanical arrangement and the method of sorbent regeneration, a number of process cycles and combinations of cycles have been developed, but for gas separation the more widely used ones are still temperature-swing adsorption (TSA) and PSA [Yang (1987)]. In a TSA cycle, the bed is regenerated by temperature raising through the purging of the bed with a preheated gas. This gas can be a fraction of the light product of the process. Because heating is a slow and often rate-limiting step, the length of each cycle can range from hours to over a day. The cycle is used only for purification purposes, in order to make the time length of the adsorption step comparable to that of regeneration. In contrast, in a PSA cycle the bed regeneration is accomplished by

reducing the total pressure, and this makes the cycle time shorter, usually in minutes or even seconds, due to the possibility of rapid pressure reduction. Thus, this process is the most flexible one in terms of cycle steps modification, although is also the most difficult and complex to model. The main disadvantage of PSA is that it cannot be applied to too strongly adsorbed species, unless high vacuum is employed in desorption step, making the process economically unfeasible.

The PSA concept have been in the public domain since the earlier 1930s. The first patents about PSA appeared at that time [Finlayson and Sharp (1930); Hasche and Dargan (1931); Kahle (1953, 1954); Perley (1933)] but PSA processes are commonly attributed to Skarstrom [Skarstrom (1958)] and Guerin de Montgareuil and Domine [de Montgareuil and Domine (1957, 1964)] in late 1950s. They introduced the basic principles of the PSA steps that are known today.

The Skarstrom process suggested that two steps, adsorption and depressurization/purge, be carried out in two adsorbent beds operated in phase, thus enabling the processing of a continuous feed. The rapid pressure changes result in short cycles and, hence, high feed throughputs, but also make the dynamics of the gas/solid system more difficult to understand.

Nitrogen, hydrogen, oxygen, carbon monoxide and methane were then candidates for purification by PSA. Hydrogen purification by PSA become into a scale commercial practice in late 1960s. Basmadjian and Pogorski (1966) introduced the rinse step in an early PSA cycle. Similarly, separation like pure oxygen and nitrogen from air did not become commercially viable until the late 1970s. During the 1970s interest in alternative separation processes was stimulated by the huge energy costs associated with the rising price of crude oil. Several other patents were filled by Sircar and co-workers in 1977-1988, where two or more sets of parallel beds, with different adsorbents, were connected sequentially, in order to isolate different components with as little power input as possible [Sircar and et al. (1978, 1979, 1979, 1981, 1981, 1988)].

Splitting carbon monoxide and methane from contaminants only become moderately successful in the late 1980s. R. Kumar and Greskovitch (1984) approached the problem of purifying argon containing trace amounts of nitrogen and oxygen. At that time, the most obvious modes of PSA operation had been discovered and it seemed to mark the passage from drastic innovations, in which significant improvements over prior art were claimed, to a series of minor, but not less important, refinements over of existing cycles. Although energy costs fell during the 1980s, search for alternative processes matching the technology to the product specifications has continued. So, PSA gained widespread commercial acceptance in opposition to the long installed interests in the cryogenic gas

industry. Despite the achievements of modern technology, improvements in all of the applications are still being sought.

A fully understandable synopsis of PSA patent literature is presented in [D. M. Ruthven and Kneabel \(1994\)](#) and [Tondeur and Wankat \(1985\)](#). Many process improvements have consequently been developed based on the Skarstrom cycle, which enabled the rapid growing commercial use of PSA for hydrogen purification and production, *n*-paraffin separation, air separation and an increasing number of other applications [[Yang \(1987\)](#)].

In recent PSA processes, three or more beds are used to synchronize and accommodate two additional steps to those in the Skarstrom cycle: cocurrent depressurization or blow-down and pressure equalization. From all the public literature available, there are significant distinctions in the ways in which even the simplest PSA steps can be accomplished. For instance, pressurization with light product is generally superior to pressurization with feed. This is partially done by pressure equalization, when the purified product from one column is partially used to pressurize a parallel column by interconnecting the product ends. Also, simultaneous depressurization with product withdraw always improves over isobaric production or simultaneous pressurization with production. The cocurrent blow-down step has, likewise, appeared in several forms. The rinse step has advantages in terms of recovery.

Starting from these concepts and by coupling with membrane technology, the work developed in this thesis attempts to improve the separating performance of a stand-alone PSA unit for a given mixture.

A PSA cycle usually consist of four or more steps, sometimes as many as twelve, of a few seconds to several minutes duration. Figure (2.13) shows a simple four-step PSA cycle. Through the synchronized cycling process of the composition profiles and flow directions, the heavy component is preferentially adsorbed and separated from the light or less adsorbable component. The most common steps on a PSA unit are:

- Pressurization (PR) with feed or purified light product from an adsorption step.
- High-pressure adsorption step (HPA), where the contaminants are adsorbed and the purified product is produced and withdrawn.
- Blowdown (BD) co/counter-current to the feed step.
- Purge (PG) countercurrent to the feed step and with purified light product at low pressure, where the desorbed effluent is discharged.

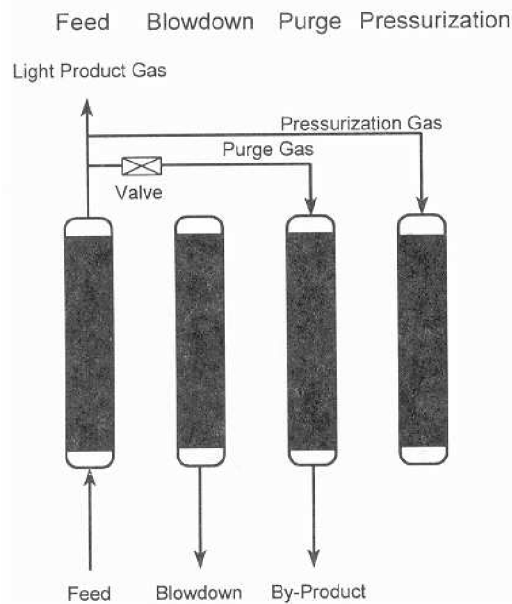


Figure 2.13: Simple four step pressure swing adsorption system [P. P. Radecki and Bullock (1999)].

In HPA step, the more strongly adsorbed component moves slowly towards to the product-end of the bed at the maximum operating pressure [as seen in Figure (2.12)]. Flow stops when breakthrough is almost starting which yields the light product. The bed regeneration is accomplished through depressurization (BD step), where an heavy product is obtained. The PG step prepares the bed for the next PSA cycle and a less pure heavy byproduct is collected.

An additional purge step at high pressure, called rinse step (RS), can be included after the HPA, as shown in Figure (2.14). Part of the heavy product is used to selectively adsorb this component, allowing the recovery of the residual feed. The rest of the cycle follows the BD, PG and PR steps.

In large-scale applications, it is typical to include equalization steps (EQ), where a high pressure bed exhausts into another bed at a lower pressure. This procedure conserves the energy and the material of the cyclic process.

One can identify six general features of a typical PSA cycle that explain both the advantages and limitations of this process and determine its suitability for a given application:

1. Product purity. Usually the light component is recovered in very pure form, whereas the heavier one is discharged as an impurity. Nevertheless, several configuration modifications can be performed to allow recovery of preferentially adsorbed species. Of course this introduces complexity to the cycle and its modeling. The purity is

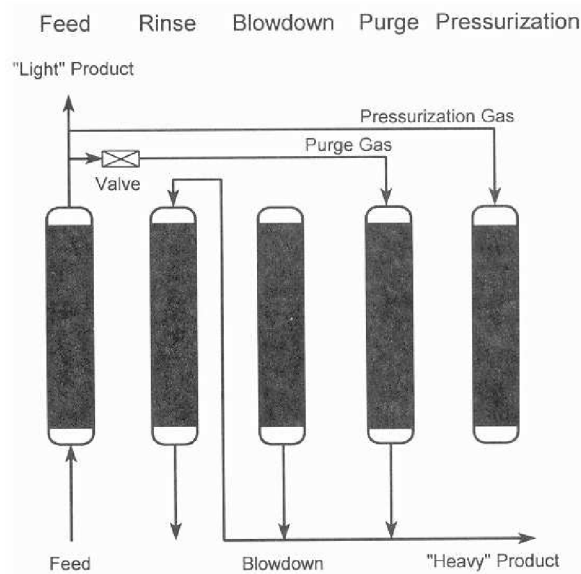


Figure 2.14: Simple five-step pressure swing adsorption system [P. P. Radecki and Bullock (1999)].

- a volume-averaged quantity, since the composition and effluent flowrate from the PSA bed vary with time.
2. **Product recovery.** The fraction of feed recovered as pure product is generally lower than the one obtained by distillation. To contrary this, increasing the number of beds or additional steps can be introduced in the PSA cycle, which will increase the capital cost. Hence, the coupling of a PSA with other separative technologies could be advantageous on both economics and yield.
 3. **Adsorbent productivity.** It is measured by the amount of product or feed mixture processed per unit amount of sorbent per unit of time. For a given separation, the product purity is usually predetermined, the energy requirement is proportional to the recovery and the size of the adsorbent bed is inversely proportional to the adsorbent productivity.
 4. **Energy requirements.** The separation work of a PSA process compared to its energy consumed is similar to that of processes like distillation. However, PSA uses mechanical energy, which is more expensive than heat. Because of this, the major component of the PSA operation cost is the power cost, as seen in Figure (2.15). This situation is greatly minimized if the feed is already available at high pressure, since capital costs, energy requirements and feed recompression costs are reduced. Even recompressing the product for later cycle usage generate lower costs than feed recompression.

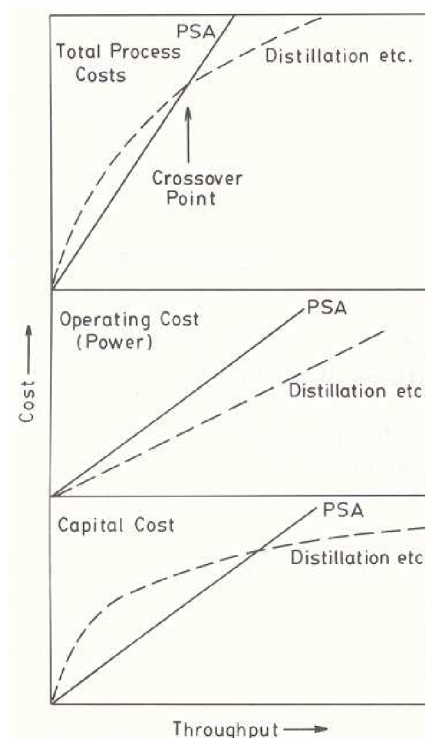


Figure 2.15: Variation of cost with throughput for PSA and other processes [D. M. Ruthven and Kneabel (1994)].

The work developed in the thesis also tries to use this advantageous concept in order to improve both separation performance and overall costs.

5. Process scaling. The overall costs increase approximately linearly with feed throughput. The capital costs of a PSA process increase linearly with throughput, in contrast with most other processes. As seen in Figure (2.15), the economics tend to favor PSA at low to moderate throughputs and to favor other systems for very large operations, considering the crossover point, varying for each given separation or specific process configuration.
6. Pressure range. The performance of the process is often enhanced for a PSA cycle with desorption at subatmospheric pressures (VPSA).

When highly pure products are desired, from a hydrocarbon mixture, for example, and/or a high-energy effort is required for recompression of feed gas streams, the stand-alone PSA process may be coupled with other separation technologies in order to enhance the performance of the cyclic process.

Like in membranes, adsorbent materials research (zeolites, for example), is crucial for PSA technology. Some coupled membrane/PSA processes have been proposed in the literature for various applications, such as He recovery, H₂ purification, N₂ production and

acid gas removal. Nevertheless, most of these schemes are essentially a simple combination of the two units and not a truly synergistically integrated process: either the membrane is followed by a PSA and is mainly used for bulk separation, or the reverse case, used for residual recovery, where the concentrated membrane product is fed to PSA for higher purity and the waste gas from the membrane is used as purge gas to PSA, for adsorbent regeneration.

X. Feng and Ghosh (1998) have reported a novel process truly synergistic, that incorporates membrane permeation into a PSA cyclic process to improve gas separation performance. Unlike in the traditional membrane processes, where pressures are kept constant, the pressure in the integrated permeation/adsorption system changes as the permeation proceeds with time. The authors analyzed parametrically permeation processes with varying pressure to study the feasibility of integrating permeation with cyclic PSA processes.

Although several published literature data concerning these hybrid systems [Baker (1998, 2002); Baker and Kaaeid (2000); Drioli and Romano (2001); Ho and Sircar (1992); R. W. Baker and Pinnau (2001)] are available, a truly synergistically concept was only found in X. Feng and Ghosh (1998) work. Zolandz and Fleming reports one example of the combined technologies in the O₂ production from air for aircraft on-board application, where bulk separation by a membrane is followed by adsorption for further purification [Ho and Sircar (1992)]. Marcea and Hwang (1994) studied O₂ separation from air on a PSA bed with a zeolite followed by O₂ enrichment using a membrane. It was shown that a higher separation degree could be obtained than by either of the two processes alone. R. W. Baker and Pinnau (2001) reports the recovery of H₂ and LPG from PSA tail gas, through a combined PSA/membrane process for treating a feed gas containing 90% H₂ and 10% light hydrocarbons [Figure (2.16)]. More than half of the H₂ formerly lost with the tail gas is recovered and recycled to the feed gas, increasing the overall H₂ recovery of the process from 87 to 95%. The off-gas from the condenser is passed through a silicone-rubber membrane unit that selectively permeates the remaining hydrocarbons.

The invention of Baker and Kaaeid (2000) relates to using a gas separation membrane to condition gas streams containing H₂ and hydrocarbons, destined for PSA separation. The difficulty that arises from this type of refinery and petrochemical streams is the presence of water vapor, heavier hydrocarbons and hydrogen sulfide. These components cause a variety of problems: in the PSA they may adsorb preferentially onto the bed and reduce its capacity to sorb the light hydrocarbons, giving rise the regeneration problems; in the membranes they may induce to the collapse of the unit, with flux decreasing and irreversible damages. For both systems, pre-treatment of H₂/hydrocarbon mixtures must

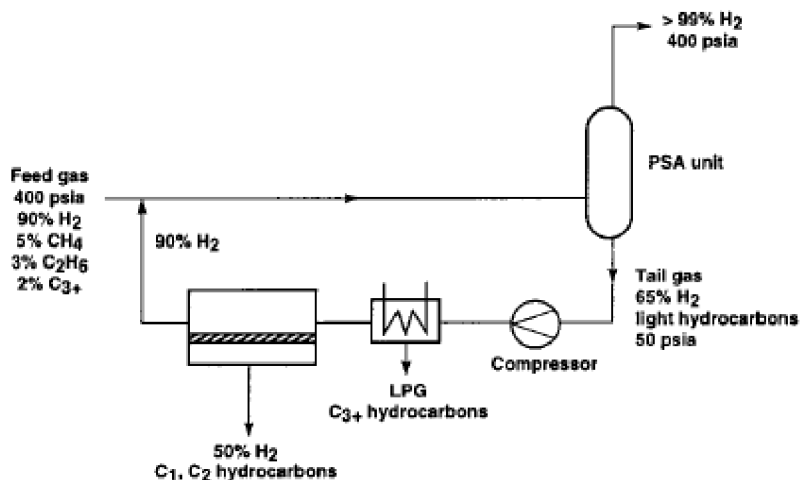


Figure 2.16: Combination of a hydrocarbon-permeable membrane with a PSA unit to increase the recovery of hydrogen from a refinery gas stream from 87 to 95%.

almost always be carried out to feed only a clean stream to the process. The patent reports a process with selective removal of water vapor, H₂S and C₅-C₈ hydrocarbons using a rubbery membrane (silicone rubber), which preferentially permeates the heavier components, and an adsorption unit capable of selectively remove CH₄ from H₂. Using this scheme, the H₂-enriched stream remains at high pressure on the feed side of the membrane, which means that this stream may be passed directly to the adsorption step of the PSA unit without the recompression that would be needed if the H₂ was in the permeate stream. This latter situation is mostly common in industrial separations, through the usage of glassy cellulose acetate membranes. The invention is specially developed for mean streams that contain no more than about 80% H₂ and 10% C₅-C₈. Such streams are typical used as fuel gas [Figure (2.17)]. A C₅-C₈ hydrocarbon removal of 86% from the feed mixture was observed in the membrane unit. The H₂ loss into the permeate in this case was about 20%. Nearly 80% H₂ recovered from the feed, at 85% purity, was obtained as residue. Thus, the residue stream obtained was suitable for passing into a PSA process.

X. Feng and Ghosh (1998) developed two configurations of the integration: membrane-assisted feed gas pressurization, and membrane-assisted co-current depressurization. The permeation occurs in a cyclic fashion and is coupled with the sequential steps of PSA. An asymmetric cellulose acetate hollow fiber module (20 fibers, 15 cm long, with 165 μm OD and feed from shell side) for permeability experiments, a membrane module containing 341 fibers (1/4" OD, area of 778 cm², packing density of 10000 m²/m³) and a pair of 5 g 5A molecular sieve packed bed adsorbers (particle sizes range of 350-500 μm), immobilized

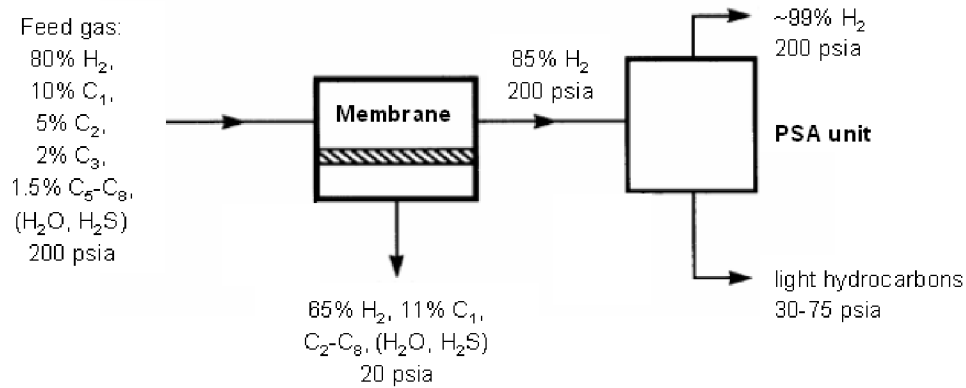


Figure 2.17: Combination of a hydrocarbon-permeable membrane with a PSA unit to decrease the gas sent to fuel line by 50% or more.

in a 3.6 mm ID tubing, were employed and tested for H₂ purification, from a H₂/N₂ 90/10 wt% mixture at 2.17 MPa. A set of controlled multi-port switching valves performed the synchronized cyclic operation. Results show that as compared to the stand-alone PSA unit, both product purity and recovery could be improved by using the integrated process, especially for the cases where the feed gas mixture contained impurities that were difficult to remove by adsorption.

Firstly, a permeation with varying permeate pressure was investigated. Figure (2.18) presents the schematic diagram of the permeator and receiver system. Two cases were considered: one refers to a permeator with constant feed pressure and varying permeate pressure, and another one refers to a permeator with varying feed and permeate pressures.

A high-pressure feed is supplied to the module, permeate gas stream is directed to a reception vessel, which would be an adsorber in the integrated membrane/PSA system. It was assumed that membrane permeability is independent of gas concentration and

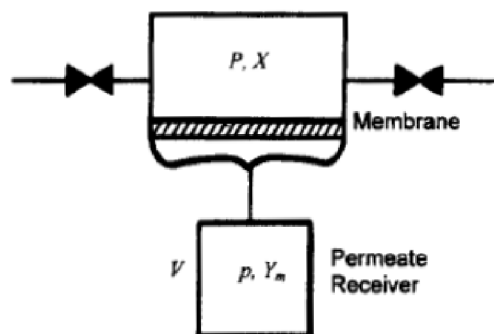


Figure 2.18: Schematic diagram of the permeator and its permeate vessel receiver.

pressure; the permeate is received at the downstream side of the membrane, as soon as the high-pressure feed is supplied to the membrane, i.e., the time lag due to passage of gas molecules through the membrane is negligible; and the dynamic permeability is the same as that at steady state.

For the case of a permeator with constant feed pressure and varying permeate pressure, Figures (2.19.a) and (2.19.b) show the results obtained for a binary 50/50 gas mixture fed at pressure 5 MPa and 20 m³/min to a membrane with 50 m² and a permeability ratio, J_1/J_2 , of 60, with $J_1 = 10^{-4}$ cm³ (STP)/cm² s cmHg. The pressure in the permeate receiver increases as permeation proceeds with time. The permeation rates determine the rate of pressure built up in the receiver, which in turn affects permeation rate. Pressure built up faster in the initial time and gradually slows down. Since PSA commonly operate under fast cycles, this fast permeate pressure built up is particularly desired for incorporating a membrane into a PSA process.

As permeate pressure builds up, the permeate rate decreases, resulting in a stage cut decrease. And because the permeation rate on the fast gas is retarded more significantly than the slow gas, the permeate concentration decreases with time. Simultaneously, the residue concentration increases with time and approach the limit of the regular feed concentration when the permeation time is sufficiently long. The effect of the permeate receiver volume is also reported. The smaller the volume, the larger the permeate pressure and the lower the permeate concentration.

Tests with a H₂/N₂ 50/50 mixture at 2.17 MPa in a permeator at about the same size of the permeate receiver result in a 90 wt% H₂ permeate at 0.72 MPa and a residue gas that contains 33 wt% H₂. The important conclusion from this is that the membrane permeation can be an effective aid to the adsorber pressurization step in a typical PSA process.

Figure (2.20) illustrates the results obtained in the case of a permeator with varying feed and permeate pressures, for a binary 50/50 gas mixture fed at pressure 5 MPa, assuming $V = V_f = 20$ L and the membrane properties to be the same as those in the prior case. For instance, after 20s permeation time, one can obtain, from a 0.5 mol fraction gas at 5 MPa and for a membrane area of 50 m², a 3.4 MPa residue at 31 wt% and a 1.6 MPa permeate at 91 wt%. The effect of varying the membrane area is also presented. The larger the membrane area, the faster the permeation is and the sooner the pressure reaches the desired value.

These results indicate the feasibility of incorporating membrane permeation into a blowdown step of a typical PSA cycle, so that the PSA pressure difference available can be used for permeation operation.

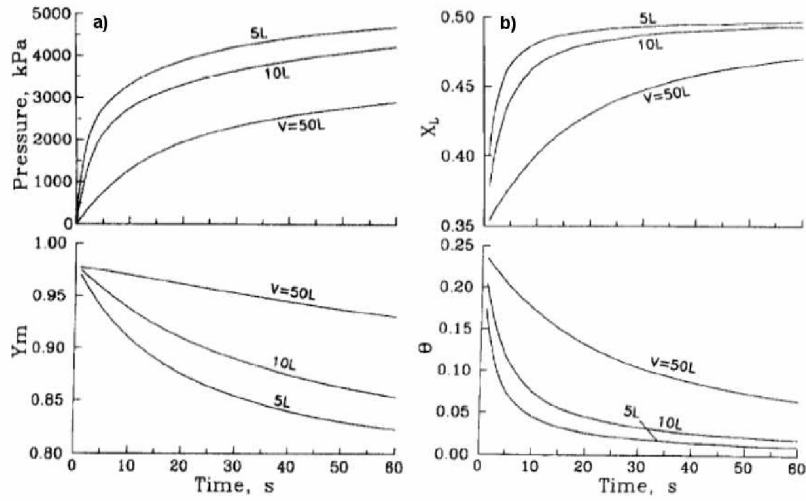


Figure 2.19: Permeator with constant feed pressure and varying permeate pressure. a) Pressure and concentration (Y_m) of permeate in the receiver volume (V) as a function of permeation time; b) Concentration of residue gas leaving the permeator (X_L) and the fraction of feed gas permeating through the membrane (stage-cut, θ) as a function of permeation time.

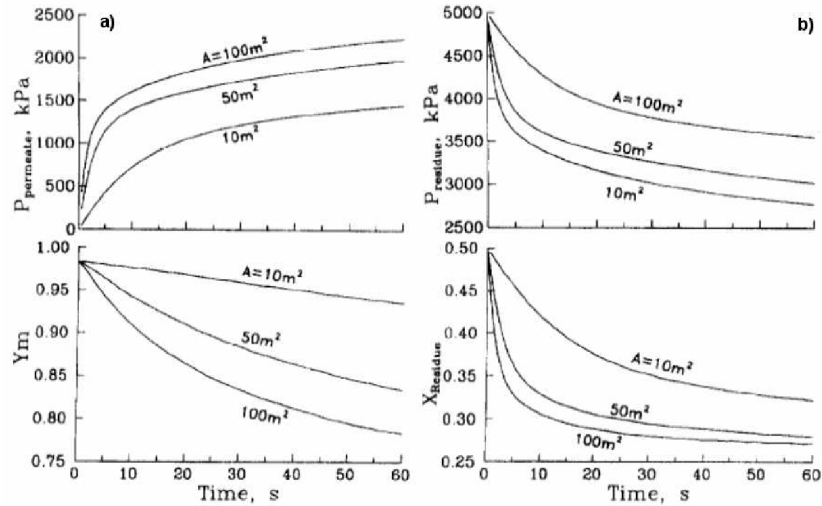
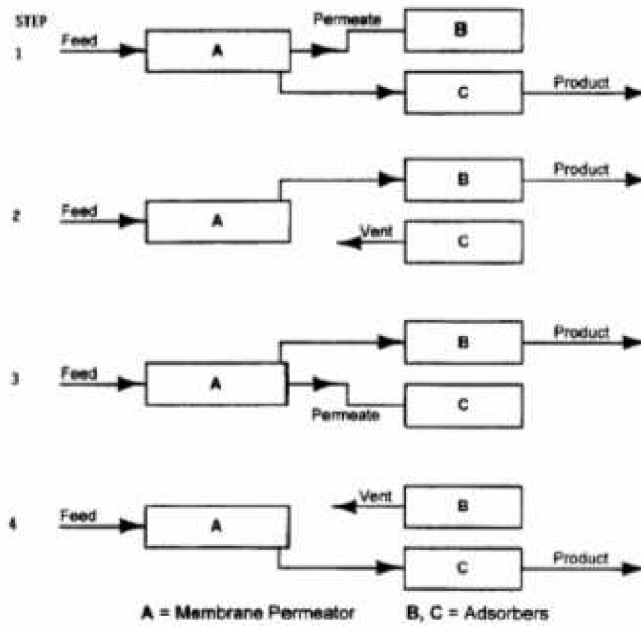


Figure 2.20: Permeator with varying feed and permeate pressures. a) Pressure and concentration (Y_m) of permeate in the receiver vessel as a function of permeation time; b) Pressure and concentration (X_{Residue}) of residue gas as a function of permeation time. A refers to the membrane area and V_f is the volume of feed gas vessel in static permeator.

Configuration I



Configuration II

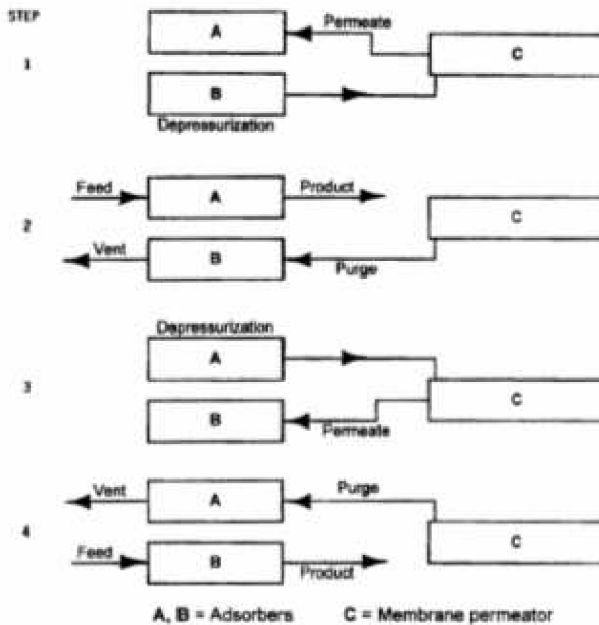


Figure 2.21: Configurations of the integrated membrane/PSA system investigated by X. Feng and Ghosh (1998). A two-bed PSA system is chosen for simplicity of the principle. I. Operating sequence of a PSA system with membrane-assisted feed gas pressurization. II. Operating sequence of a PSA system with membrane-assisted co-current depressurization.

The hybrid processes developed in the thesis used, as starting point, the approach of [X. Feng and Ghosh \(1998\)](#). The two configurations of the integration developed by those authors [Figure (2.21)] are briefly characterized as follows:

- Configuration I - membrane-assisted feed gas pressurization:

The membrane behavior is similar to the first aforementioned case of permeation with varying permeate pressure. It is installed in the feed line of the PSA unit and splits the feed mixture into two streams: the permeate, enriched in the fast permeating species that are the less adsorbed one in PSA, is fed to the column to pressurize it; and the residue enriched in the slow permeating components, which is fed to the on-stream adsorber for adsorption (step 1). The partial pressure increase in the bed, leads to an increase in the sorption capacity of the adsorber to this species.

If the permeate line is closed (step 2) to restrain permeation, the operation is similar to a typical two-bed process. The purified product is obtained from adsorbed B and the strong adsorptive impurities, retained in C, are released by vent, regenerating the adsorbent for the next adsorption step. The two beds are then reversed. Besides these two columns undergo cyclic operation, the membrane is also operated in a cyclic fashion.

The configuration does not involve co-current blowdown from the PSA bed to pressurize the other during the cycle. This step is of great importance since it can increase the concentration of the strong adsorbate in the column, thereby increasing the product purity of the strong adsorptive and the product recovery of the weak adsorbate.

- Configuration II - membrane-assisted co-current depressurization:

The membrane behavior is similar to the second aforementioned case of permeation with varying feed and permeate pressures. During the blowdown step of PSA, the membrane feed inlet is connected to the column and the permeate outlet is connected to the adsorber that is being pressurized (step 1). Hence, the PSA pressure difference is used as the driving force for permeation. The gas used for pressurization is more purified than that produced by the co-current depressurization step. The residue left on the high-pressure side of the membrane, is used for countercurrent purging of the depressurized bed (step 2).

Configuration II was also tested with a simulated ammonia synthesis purge gas containing $\text{H}_2/\text{N}_2/\text{CH}_4/\text{Ar}$ 60/20/10/10 wt%. An empty vessel with the same internal void volume of the membrane simulated the stand-alone PSA system, for comparison purposes. For a 18s cycle time and a feed pressure of 2.17 MPa, [X. Feng and Ghosh \(1998\)](#) reported

Table 2.6: Separation performance of PSA with and without membrane-assisted co-current blowdown [X. Feng and Ghosh (1998)].

Feed throughput ml/min g	Integrated Membrane/PSA		Stand-alone PSA	
	H ₂ Purity Impurity %	H ₂ Recovery %	H ₂ Purity Impurity %	H ₂ Recovery %
Feed: H ₂ /N ₂ 90/10 wt%				
300	0.12	64.9	0.28	65.2
400	0.57	73.4	1.2	75.7
500	1.40	78.5	2.65	80.1
560	2.15	80.6		
Feed: H ₂ /N ₂ /CH ₄ /Ar 60/20/10/10 wt%				
200	1.13	36.4	2.92	42.1
300	2.96	66.0	11.1	70.7
400	9.94	75.2		

the results shown in Table (2.6). The configuration II has advantages over the stand-alone PSA unit, since at a given feed throughput, the product purity is enhanced with a marginal reduction in the product recovery. In addition, for the H₂/N₂/CH₄/Ar mixture it is visible, for a given product purity, enhancements in both product recovery and feed throughput.

The concept is straightforward: the two processes complement each other by removing different components from the mixture. While adsorption removes impurities from the H₂ product, the membrane takes H₂ from the impurities that are retained as residue.

Either because the operational complexity of these type of integrations, either due to mathematical framework involved in these design procedures at cyclic steady state conditions, it seems that its still necessary a considerable amount of research concerning the study of feasible hybrid systems.

2.3 ANG Processes

This section is a summary of the research and development performed as part of the european project ENK6 CT-2000-00053 started at 2000, with the duration of 38th months, and funded by the European Community under the Fifth Framework Programme - Energy, Environment and Sustainable Development. The project was named **ANGUARD - Adsorbed Natural Gas System with Guard Bed Device** and was a cooperation of several european industrial and scientific institutions [Advantica Ltd and Sutcliffe Speakman Carbons Ltd (SSCL), from UK; Instituto de Soldadura e Qualidade (ISQ), Faculdade

de Ciências e Tecnologia da Universidade Nova de Lisboa (FCT/UNL), from PT; and Industrial Project Group from IT].

The ANGWARD target was to provide innovative and efficient solutions for gas storage through the development of a workable pilot-scale Adsorbed Natural Gas (ANG) storage process, incorporating a guard bed system for reversibly filtering out trace contaminants from the Natural Gas (NG) feed to the process. To develop an adsorptive gas storage system having enhanced capacity at lower pressures and increased safety relative to alternative technologies.

Natural gas has a clearly environmental friendly behavior and, because of this, it is a truly and effective alternative to oil-derived fuels. It provides a clean and efficient combustion, practically free of sulphur and lead oxides, benzene, and solid particles. The CO₂ emission level is 23% less than that of conventional vehicles and the CO emission level can be reduced by 85%. NG is less dense than air, which makes it spread in the case of a leak. Price of NG is also half of the equivalence price of gasoline. Another economic factor is the maintenance costs in vehicular applications which are lower due to the cleaner combustion [da Rocha (2001)]. However, as is well known, its great disadvantage is its lower heat of combustion per unit of volume, when compared with conventional fuels.

Natural gas is a gaseous fuel mainly composed by methane. The average composition of a typical NG is presented in Appendix D. In USA and Canada, natural gas normally contains 85-95 wt% methane, the remainder being carbon dioxide, nitrogen and small amounts of ethane, propane and butane. Some North Sea gases can contain up to 20% carbon dioxide, although carbon dioxide is usually reduced to below 5% when delivered by pipeline. The NG supplied to Finland, from Russia, is very rich in methane, over 98% by volume [Nylund and Lawson (2000)].

Greenhouse gases have the ability to intercept and re-emit heat which is emitted from the Earth's surface, and thus lead to increases in global temperature. Without natural (pre-industrial) greenhouse gases, global average temperature would be 34°C lower than it is now, too cold to support human life. Nevertheless, the tremendous increase of the release of these gases in the industrial era will affect natural and societal systems to a degree that could be hard for human society to adapt to.

Carbon dioxide is the most important greenhouse gas and international agreements to reduce carbon dioxide emissions have been signed. In 1998, the parties to the Kyoto Protocol to the U.N. Climate Change Convention recommended measures aimed at decreasing the global level of greenhouse gases to a target for industrial countries as a whole

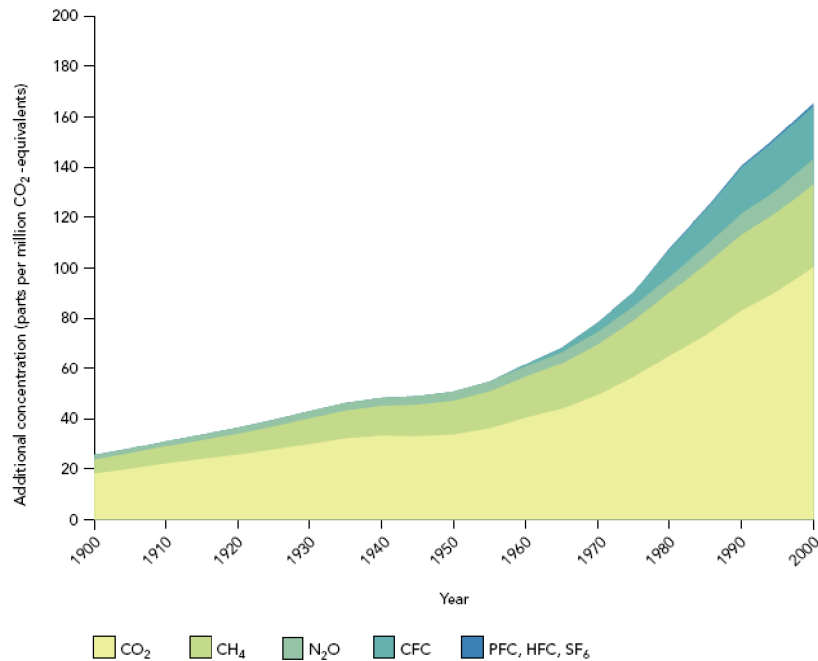


Figure 2.22: Rise of greenhouse gases concentration compared with the year 1750 [EEA (2004)].

of 5% by the 2008-2012 commitment period, compared with the base year (1990). Implementation of the Kyoto Protocol, or its recommendations as working parts of an accepted global effort, remained uncertain until February 16th of the current year. Nevertheless, some industrialized countries, including the US and Australia, have made clear that they will not ratify the Kyoto Protocol.

Atmospheric indicators show that due to human activities, the concentration of carbon dioxide, the main greenhouse gas, has increased by 34% compared with pre-industrial levels, with an accelerated rise since 1950. Other greenhouse gas concentrations have also risen as a result of human activities. The total rise in all greenhouse gases since the pre-industrial era amounts to 170 ppm CO₂-equivalent, with contributions of 61% from CO₂, 19% from methane, 13% from industrial halogenated gases (CFCs, HCFCs), and 6% from nitrous oxide [Figure (2.22)]. If no climate-driven policy measures are implemented, a further increase to 650-1215 ppm CO₂-equivalent is projected to occur by 2100. The global average surface warming by 2100 will be between 1.4-5.8°C above 1990 levels, using a broad range of scenarios of possible socio-economic developments and related greenhouse gas emissions [EEA (2004)].

Figure (2.23) presents the increase of greenhouse gases concentration in Portugal and in UK, compared with the reference year of 1990.

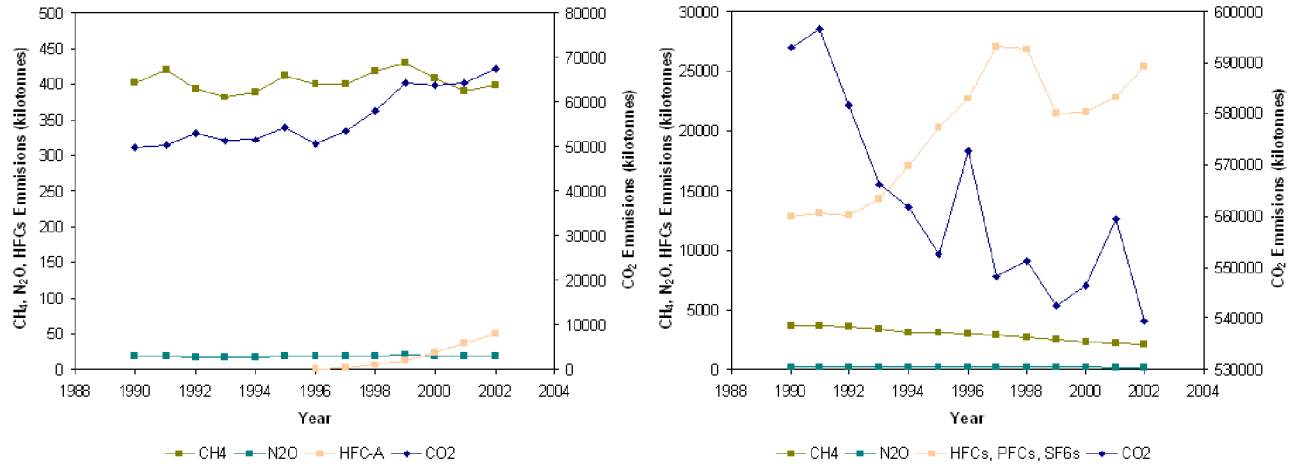


Figure 2.23: Rise of greenhouse gases concentration in Portugal (left) and UK (right) compared with the reference year of 1990 [EEA (2004)].

To achieve large global reductions in greenhouse gas emissions, both the global share of renewable energy needs to be increased and energy efficiency substantially improved. Technological developments as well as increased research, market penetration strategies and provision of price incentives are necessary. These measures have to be accomplished by a transfer of capital and technology to developing countries. A transformation of global energy systems is essential to provide access to sustainable energy for people in developing countries, which is a U.N. millennium development goal.

Hence, it seems certain that NG will be a key factor in efforts to improve overall global environmental conditions. From 1990 through 1998, NG consumption in the US increased by 14%, although in 1997, 85.3% of the domestic energy was still produced by fossil fuels. The NG greater use, as an industrial and electricity generating fuel, can be attributed, in part, to its relatively clean-burning qualities in comparison with other fossil fuels. Lower costs resulting from greater competition and deregulation in the gas industry and an expanding transmission and distribution network have also helped expand its acceptance and use. NG use by electric utilities and NG usage to generate electricity is projected to reach in US, by 2020, a little more than three times the 1998 level. By 2020, fossil fuel usage is expected to account for 89.7% of domestic energy production with 28% attributable to NG. A principal factor in this is that nearly all future electric utility capacity additions in the US are expected to be fueled by NG [eia (1999a), eia (1999b)].

Burning NG gives less carbon dioxide and more water vapor per energy unit than

burning gasoline or diesel fuel. Hence, one argument presented in promoting NG as an automotive fuel is that NG reduces carbon dioxide emissions compared to conventional hydrocarbon fuels. This is in most cases true when substituting gasoline with natural gas [Nylund and Lawson (2000)].

Small scale or bulk storage of NG gas is problematic; most of the storage methods employed, such as liquefied natural gas (LNG) plants, depleted gas fields, underground aquifers, low pressure volumetric gasholders and pressure vessels, have high associated costs as well as operational restrictions on size, location, safety criteria and delivery rates.

NG is usually stored compactly under compressed form at pressures in the range 180-240 atm. The use of compressed natural gas (CNG) has its disadvantages. The equipment employed in high-pressure compression storage systems is costly, heavy and complex, compared to that of storage and distribution of liquid fuels from oil. The CNG storage tanks must be pressure vessels and are thus constrained in their geometry (typically cylindrical), and are also rather heavy (1 kg/L for steel tanks).

Hence, there is the need for a more efficient, lower cost and potentially safer means of NG storage. This was the motivation of the work developed under the ANGWARD project. Adsorbed Natural Gas (ANG) is an innovative solution to this need. The need to substantially reduce the maximum storage pressure to 35-40 atm, for safety reasons and the high-pressure compression cost, has led to the search for competitive storage alternatives for NG at pressures well below that employed in traditional compression [Burchell and Rogers (2000)].

The most promising method to store NG at low pressure is adsorption storage, which consists of retaining the gas inside a porous adsorbent [Cook (1999), Talu (1992)]. Thus, the evaluation of single- and multi-component models in the ANGWARD project was limited to activated carbon. The storage capacity is increased since the distance between gas molecules inside the pores of the adsorbent is much shorter than that of the molecules of the compressed gas at the same pressure. For this reason, the density of the gas contained inside the pores of the adsorbent is higher than the density of the compressed gas.

Activated carbons, due to their large microporous volume, their ability to be efficiently compacted and their low production cost, are the adsorbents with the most favorable characteristics for NG storage. The enhanced storage results from the adsorption of gas molecules in the extremely small pores (micropores) present in an activated carbon. The activation procedure creates a very high surface area formed from an extensive network of small pores, in which gas molecules adsorb at ambient temperature, to give higher gas density than is possible by compression alone. The storage density enhancement factors range from 2 to 10, depending on the operating pressure. Together with the simplicity

of the process and the moderate operating conditions, these result in significant cost reduction compared to compressed or liquefied gas storage [ANGUARD (March 2004)].

These adsorbents are usually produced under the form of small particles by the carbonization of several precursors, such as coal, organic matter (wood, fruit shell, resin) and polymeric matter. There are currently several commercial activated carbons that can store, at a pressure of 35 atm, the same amount of gas that is stored by compression at a pressure 2.5 times larger.

It is stated that the activated carbon must be compressed to a bulk density of 0.6 - 0.7 g/cm³, in order to enhance its volumetric storage capacity [Tan and Gubbins (1990)]. However, the surface area and the amount adsorbed per gram of activated carbon decreased remarkably after compression. NG storage capacity of a suitable adsorbent is currently expressed in terms of the stored volume of natural gas per unit of adsorbent volume, measured at normal conditions ($P = 0.1$ MPa, $T = 273$ K). To be a commercially viable system, a delivered 150 v/v is necessary. The volumetric capacity for CNG is 200 v/v at 20 MPa [Parkyns and Quinn (1995), T. K. Bose and St-Arnold (1991)]. Thus, these aspects are a challenge to overcome with ANG technology and were part of the project motivation.

In a NG storage reservoir by adsorption there are four distinct zones where the gas density is substantially different [Figure (2.24)]:

- The void volume between adsorbent particles, where the gas is compressed at the pressure of the reservoir;
- The adsorbent macroporous and mesoporous volumes, where the gas density is not significantly higher than that of the compressed gas in the void volume;
- The volume taken by the solid matrix of the adsorbent, which does not contribute for storage;
- and the adsorbent microporous volume, where most of the stored gas is located. The density of the adsorbed gas in the micropores must compensate the volume taken by the adsorbent and the lower density of the gas in the void volume between particles and in the adsorbent macropores and mesopores.

The main technical objectives of the ANGUARD project were to:

- Develop a process scheme of the guard bed and storage vessel;

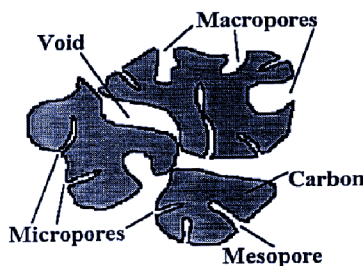


Figure 2.24: Characteristic dimension of the various existing volumes in an adsorptive storage reservoir.

- Develop a multi-component thermodynamic model of the adsorption of NG on activated carbon and provide fundamental design data for the integrated guard bed system;
- Design and build a pilot prototype guard bed system that filters out trace components during filling and releases them in a controlled manner during discharge;
- Carry out market studies and formulate routes for future applications of the technology to exploit the anticipated efficiency and improved safety of ANG storage systems;
- Undertake a safety assessment of ANG storage by modeling hazard scenarios, and provide a design for the operation of the guard bed with the main storage vessel.

In particular, the options developed in ANGUARD will allow controlled and progressive desorption of the NG components from the guard bed in order to achieve the desired and uniform gas composition at the outlet of the storage system. In fact, the results show highly efficient filtering of C_{5+} and odorants, and a process completely reversible on discharge with high degree of control.

A strategic decision was made to concentrate efforts on developing an ANG system suitable for diurnal storage of NG. Analysis had shown that this was by far the most demanding application; by developing a proof of concept solution for diurnal storage, barriers to ANG for other applications such as power plant, small commercial and vehicle storage have also been removed. The results could form part of a future full-scale demonstration of ANG technology [ANGUARD (March 2004)].

Studying the impact of NG composition on the cyclic efficiency of adsorption / desorption storage systems, results show that the net deliverable capacity is substantially decreased by high molecular weight hydrocarbons which are present in small amounts in

NG [Mota (1998)]. Then, a major technical problem with ANG is the strong adsorption of the higher hydrocarbons and sulphur-based odorants present in significant and varying levels across the range of European pipeline natural gases. If these trace components are allowed to enter a carbon-based adsorption storage system during charge, they adsorb preferentially and decrease the amount of gas that can actually be discharged. The storage-capacity deterioration in onboard storage is driven by the unfeasibility of operating the storage reservoir under sub-atmospheric pressure, for instance in an vehicular onboard storage applications. In large-scale storage, the costs associated with the compression equipment required to swing the pressure between sub- and super-atmospheric values are prohibitive.

The significant decrease in adsorbent storage capacity is illustrated by the results obtained by several other researchers [Golovoy and Blais (1983), Pedersen and Larsen (1989), T. Kasuh and Maeda (1992), Chaudron (1989), F. Strnisa and Gauthier (1989), Atlanta Gas Light Adsorbent Research Group (1994), Talu (1992)]. The solution to the deterioration of adsorbent capacity on extended operation is to fill the storage tank with a cleaner NG, which requires filtering it.

Chaudron (1989) proposed the installation of a filter before the activated carbon tank onboard an ANG vehicle, to trap impurities during the filling of the tank. Then, by heating the filter during discharge, the impurities would be desorbed and carried to the engine. F. Strnisa and Gauthier (1989) tested this idea and obtained good results. After 50 cycles in a slow cycle bed, the deterioration in storage capacity was altered from 23% without the guard bed to 12% with the installation of the guard bed.

Golovoy and Blais (1983), while using a NG containing 2.6% impurities, observed a capacity decrease of 22% after 100 cycles of operation. These authors stated that the loss depended on the logarithm of the number of cycles and was therefore still acceptable after 1000 cycles. Parkyns and Quinn (1995) performed cyclic experiments with a number of different carbons on Canadian NG and was able to replicate the results of Golovoy and Blais (1983), although a leveling off of storage capacity was found after 40 cycles with no further deterioration detected.

Pedersen and Larsen (1989) observed a capacity decrease of more than 50% using a NG with 8.9% impurities. T. Kasuh and Maeda (1992), using a NG having as much as 11.1% higher hydrocarbons, observed the irreversible adsorption of n -C₄ and a strong adsorption of n -C₂ and n -C₃. NG adsorption tests performed on a 71 L storage tank showed that the equivalent of 2% water vapor relative to the mass of carbon adsorbent, resulted in a loss of storage capacity of up to 8% [M. Sejnoha and Bose (1995)]. In all these cases, the original capacities can be restored almost completely following thermal treatment.

[Mota \(1999\)](#) studied numerically the impact of gas composition on the cyclic behavior of ANG storage on extended operation, through the simulation of the cyclic operation of an ANG onboard storage system with a model NG mixture composed by 90% methane. The system was modeled as a series of consecutive cycles composed by charge/discharge steps. The mole fractions referred to C₂-C₅ components from the overall composition of the gas delivered by the cylinder during discharge increases with cycle number, reaches a maximum at an intermediate cycle, and then decreases until it stays constant equal to steady-state value. The net delivery capacity of the ANG system for N₂ and CH₄, the less adsorbable components, converge to that value as monotonically decreasing functions of cycle number. As the number of cycles increases, the more strongly adsorbed components progressively displace the less strongly adsorbed ones from the adsorbed phase to the gas phase where there is no competition for storage between species. Thus, the gas phase is always very rich in methane regardless of the cycle number. Nonetheless, the author observed a drastic reduction in net storage capacity, similar to that obtained by [Pedersen and Larsen \(1989\)](#).

Hence, the key issue for ANGWARD is the development of a guard bed system that will protect the main gas storage vessel by filtering these components out during the filling phase and releasing them in a controlled manner on the emptying part of the cycle. The decrease of storage capacity of the adsorbent with the number of cycles is undoubtedly an important problem. If the impurities are not prevented from entering the storage tank during filling, they tend to accumulate from cycle to cycle until adsorption/desorption equilibrium is reached. This can lead to a significant decrease in adsorbent storage capacity [[Mota \(1999\)](#)]. A key requirement for ANG systems is the need to be able to deliver NG from the storage vessel to the same composition specification as the original pipeline. The complex and variable composition of EU pipeline gases and the different adsorption behavior of the trace components, make this an important technical challenge.

ANGWARD storage technology will provide improved storage capability comparable to conventional high pressure systems but at much lower pressure, typically up to 35 bar, for a given capacity. This will reduce compression costs, lead to more compact, lighter and cheaper storage vessels, and improve safety assurance for the storage operation.

Another advantage of this research is the contribution to increase the total utilization of NG from gas distribution networks, without investing in installing additional pipelines. This means that storage provides the ability to serve a greater number of gas users without the substantial cost penalty and environmental intrusion of building new pipeline networks. The expansion of NG utilization will promote reductions in CO₂ emissions,

while providing cost effective and secure energy to EU communities.

Little work has been done regarding the desirable characteristics of active carbons for guard-bed applications, the design of the guard beds themselves, e.g., fixed or mobile, and their method of operation, i.e., heated or non-heated [Tan and Gubbins (1990), Parkyns and Quinn (1995), Talu (1992), J. Alcaniz-Monge and Linares-Solano (1997), J. A. Schwarz and Amankwah (1998), A. L. Chaffee and Verheyen (1993)]. Many researchers deal with simulations of the dynamic discharge of ANG vessel [Chang and Talu (1996), M. Lamari and Malbrunot (2000), J. P. B. Mota and Rodrigues (1995), J. P. B. Mota and Tondeur (1997a), J. P. B. Mota and Tondeur (1997b)].

Single- and multi-component adsorption data were compiled from the literature as they apply to natural gas [Valenzuela and Myers (1989), among others]. The literature on both single- and multi-component adsorption isotherms is full with isolated claims of improved accuracy, either by addressing new physics of adsorption or through empirical modification of pre-existing models. Some of these developments are also shown to give improved computational efficiency. The correlation, analysis, and prediction of adsorption equilibria have been well reviewed by Myers and Prausnitz (1965), Yang (1987) and Ruthven (1984).

The collected data, however, have several limitations with regards to this study. No experimental data was found on the adsorption of natural gas odorants on activated carbon. Multi-component data is scarce and limited to few components although some papers have been recently published [C. E. Holland and Ritter (2001b), C. E. Holland and Ritter (2001a)]. The isotherm data were also limited with regard to their temperature distribution. The largest fraction of the data is in the temperature range of 20-30°C, which is clearly outside the temperature range for thermal regeneration of the guard bed.

The uptake and release of a gas mixture by an adsorbent is strongly affected by state conditions (temperature, pressure, and adsorbate composition), system operating conditions and adsorbent properties. The range of conditions that have been defined for evaluating NG storage properties of adsorbents was defined by Tramposch (1994) and was applied to the use of ANG as a vehicle fuel. The report addresses to the mean values and limits for a number of variables which influence the performance of the ANG fuel systems (temperature, NG compositions, and minimum and maximum pressures) and variables which are dependent on the adsorbent, size of the system, and vehicle operating characteristics (temperature excursions encountered during certain refueling procedures and the effect of trace oxygen levels on the degradation of the adsorbent). The envelope of operating conditions characterizing large-scale storage applications under the ANGWARD

project was based on this data.

Several others reports can be found in literature, namely through the Gas Research Institute in US, which act as an incentive for the further growing of NG applications [A. Grint and Ragan (1995); A. L. Chaffee and Verheyen (1993); Biederman and Blazek (1990); Eberle (1994)]. It has been suggested that increased natural gas use causes a disproportionate increase in methane emissions from NG systems. Eberle (1994) reports that, in spite of its global warming potential, increased NG use is a sound approach to minimizing global climate change while satisfying increasing demand for energy. A NG system model was designed based on the US natural gas production, processing, transmission, storage, and distribution grid. System components and operating changes were then engineered to accommodate seven increased demand cases, and the resulting changes in methane emissions were estimated. The rates of increase in methane emissions from all gas system components were less than or equal to the increases in system throughput.

Concerning the single-component isotherm models, the minimum number of parameters required to fit a non-linear isotherm model is three, as in the elementary Langmuir isotherm model [Langmuir (1928)]. Table (2.7) lists the more important isotherm models that have been employed in the literature in the context of modeling gas adsorption equilibrium in activated carbon. They are all non-linear isotherm models that take into account system non-idealities and have been used extensively in adsorption process modeling. The Langmuir-Freundlich (LF), Toth, and Unilan isotherms are generally popular, because of their ability to model a wide variety of equilibrium data and possess four independent parameters, thereby providing an extra degree of freedom as compared to the simple Langmuir isotherm. The latter two have been employed by Valenzuela and Myers (1989) to analyze their compilation of experimental adsorption equilibrium data.

The Virial adsorption isotherm is a thermodynamically consistent model whose accuracy can be set to a desired level by manipulating the length of the series expansion. The last isotherm model reviewed here is the potential theory [Dubinin (1960)], either in the form of the Dubinin-Asthakov equation or of the model proposed by S. Ozawa and Ogino (1976).

Except for the Nitta, FH-VSM and Virial models, all the other models considered here can be solved explicitly for the equilibrium solid loading. The Nitta, FH-VSM and Virial models are implicit and must be solved using a non-linear equation solver. The additional computation introduces significant disadvantages in dynamic adsorption process simulations. This computational load is more significant in multi-component

Table 2.7: Single-component isotherm models studied.

Isotherm model	Model equation	No. of independent parameters	Numerical solution
Modified Langmuir (O'Brien and Myers, 1984)	$\theta = \frac{b_1 P}{1 + b_1 P} \left[1 + \frac{\sigma^2 (1 - b_1 P)}{2(1 + b_1 P)^2} \right]$ $b_1 = b_{o1} \exp\left(\frac{-\Delta H_A}{RT}\right)$	4	Explicit
Langmuir-Freundlich	$\theta = \frac{b_1 P^n}{1 + b_1 P^n}, \quad b_1 = b_{o1} \exp\left(\frac{-\Delta H_A}{RT}\right)$	4	Explicit
Toth	$\theta = \frac{b_1^{1/n} P}{(1 + b_1 P^n)^{1/n}}, \quad b_1 = b_{o1} \exp\left(\frac{-\Delta H_A}{RT}\right)$	4	Explicit
Unilan	$\theta = \frac{1}{2s} \ln\left(\frac{c + P e^{+s}}{c + P e^{-s}}\right)$		Explicit
Nitta <i>et al.</i> (1984)	$\theta = n(1 - \theta)^n \frac{b_1 P}{T}, \quad b_1 = b_{o1} \exp\left(\frac{-\Delta H_A}{RT}\right)$	4	Implicit
Virial	$\ln \frac{P}{q} = A + 2B\left(\frac{q}{a}\right) + \frac{3}{2}C\left(\frac{q}{a}\right)^2 + \dots$ $\{A, B, C, \dots\} = \sum_{i=0}^m \frac{\{A^{(i)}, B^{(i)}, C^{(i)}, \dots\}}{T^i}$	≤ 6	Implicit
FH-VSM (Cochran <i>et al.</i> , 1985; Huang and Fair, 1988)	$P = \frac{q_s}{b_1} \frac{\theta}{1 - \theta} \exp\left(\frac{\alpha_b^2 \theta}{1 + \alpha_b \theta}\right)$ $b_1 = b_{o1} \exp\left(\frac{-\Delta H_A}{RT}\right)$ $q_s = q_{so} \exp\left(\frac{-h}{T}\right), \quad \alpha_b = m_1 q_s - 1$	5	Implicit
Potential theory Dubinin-Astakov	$\theta = \exp\left[-\left(\phi / \beta E_\phi\right)^n\right], \quad \phi = RT \ln(P_s / P)$	2	Explicit
Potential theory Ozawa <i>et al.</i> (1976)	$\ln \theta = \sum_{i=1}^n k_i \phi^i, \quad \phi = RT \ln(P_s / P)$	2 or 3	Explicit
P = pressure (bar) q_s = saturated equilibrium solid loading (mmol/g) P_s = saturated vapor pressure (bar) $(-\Delta H_A)$ = Heat of adsorption (J/mol) T = Temperature (K) $\theta = q / q_s$ R = Universal gas constant All other symbols represent model parameters q = equilibrium solid loading (mmol/g)			

solutions when one of these single-component models provides the primary data input for a multi-component model.

The results indicate that the Langmuir-Freundlich, Toth, Virial and Potential theory isotherm models fit the isotherm data equally well with an average precision error of less than 2%. However, it should be pointed out that there is less certainty as to the correct temperature dependency of the parameters of the Toth isotherm than of the parameters of the other isotherm models. On the other hand, the potential theory has attractive features that make it especially useful for predicting single-component adsorption equilibrium from a limited set of experimental measurements (see section 4.2 for further information):

- The characteristic curve is temperature independent and therefore, only adsorption

equilibrium measurements at one temperature are necessary to obtain the characteristic curve, and this is sufficient to describe the adsorption at all temperatures for the same gas-solid system [Agarwal and Schwarz (1988), Yang (1987)].

- The theory can be generalized if an affinity coefficient is used as a shifting factor to bring the characteristic curves of all gases on the same adsorbent into a single curve. This formulation is perhaps the best attempt to obtain a universal isotherm by which adsorption data of one reference gas are extended to other gases.

The results reported recently by Ritter [C. E. Holland and Ritter (2001b), C. E. Holland and Ritter (2001a)] are the best way to demonstrate the ability of the Adsorption Potential theory to successfully correlate hydrocarbon adsorption equilibria on activated carbon through a single temperature-independent characteristic curve. These authors measured single-component adsorption equilibria of the *n*-alkanes series C₁-C₇ on Westvaco BAX-1100 activated carbon over very broad ranges of temperature and pressure, spanning 293-393 K and 0.06-4964 Torr, depending on the *n*-alkane [Figure (2.25)]. The 4278 data points were correlated successfully with the potential theory and collapsed essentially into one characteristic curve obtained by correlating all of the experimental adsorption equilibria with the potential theory [Figure (2.26)].

A number of multicomponent isotherm models have been presented in the literature. LF, Nitta, FH-VSM and the APT for multicomponent isotherm models were evaluated by the ANGWARD Consortium. Based on the limited set of available multi-component isotherm data, which is applicable to LF, the Ideal Adsorbed Solution model resulted in the lowest accuracy and precision error between the experimental and predicted methane loadings. However, the evaluation was limited to hydrocarbon mixtures, and no conclusions can be drawn as to the accuracy of the method when applied to dissimilar mixtures, notably those involving hydrocarbons and odorants.

The ANGWARD group conclude that the thermodynamics of multi-component adsorption of a real natural gas can be predicted using an isotherm model combining the Adsorption Potential and Ideal Adsorbed Solution theories. The main advantage of this dual-theory approach is that it reduces the number of equilibrium measurements required to predict the breakthrough profiles of the various components of NG. Furthermore, the accuracy of this multicomponent adsorption model can be improved at a later stage by taking into account adsorbed-phase non-idealities through the use of activity coefficients calculated from molecular simulations and a limited set of experiments.

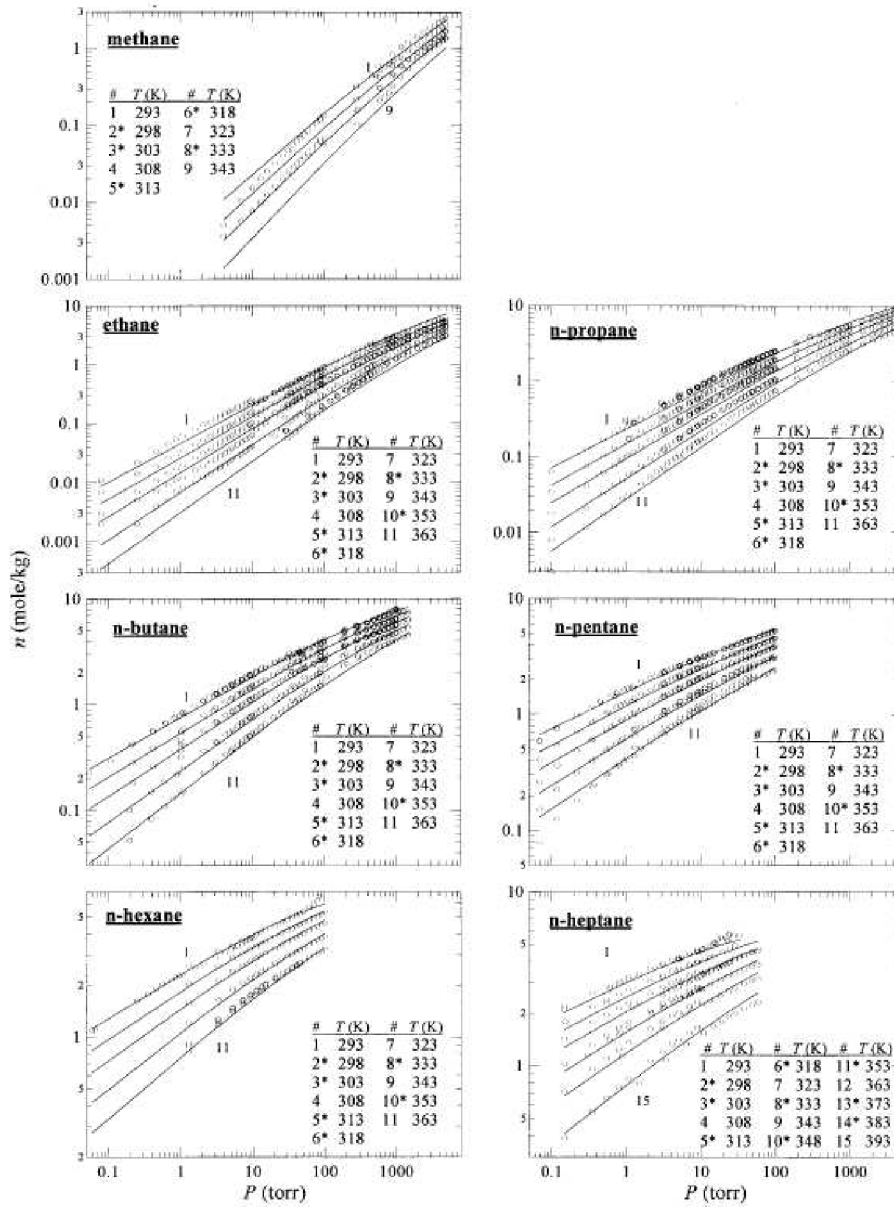


Figure 2.25: Adsorption equilibria of the n -C₁-C₇ on BAX-1100 activated carbon. Experimental adsorption isotherms for each n -alkane are displayed by symbols and lines represent predictions from the potential theory characteristic curve correlation. Asterisks denote isotherms measured but not plotted here for clarity [C. E. Holland and Ritter (2001b), C. E. Holland and Ritter (2001a)].

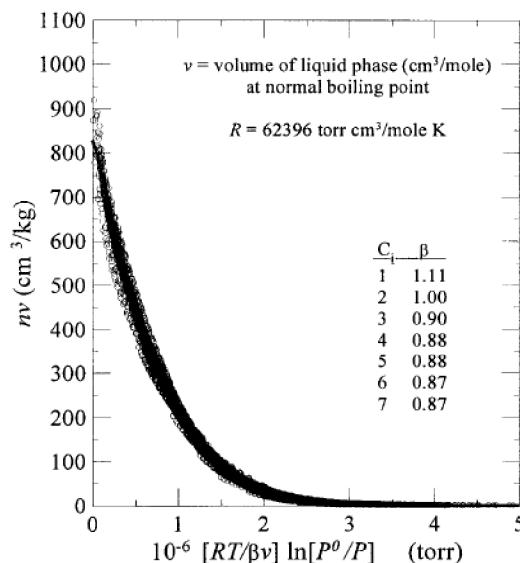


Figure 2.26: Potential theory characteristic curve obtained from the adsorption equilibria of the *n*-alkanes series C_1 - C_7 on BAX activated carbon. The average relative error in the amounts adsorbed predicted from the potential theory for the entire *n*-alkane series is 7.18%. [C. E. Holland and Ritter (2001b)].

As explained earlier, a guard bed system filters out the trace components during charging and releases them in a controlled manner during discharge, thereby preserving the capacity of the system at all times. The ANGWARD work proposed involved a set of inter-linking programme and highly integrated team-based activities such as:

1. Carry out a literature survey to identify gaps in knowledge required for ANGWARD and develop a conceptual process design incorporating the guard bed, specifying size, performance, cost targets and operational envelope.
2. Modeling of multi-component adsorption behavior to develop a prediction model in the guard bed for key higher hydrocarbon components and odorant species.
3. Carbon adsorbent development and optimization for the guard bed in terms of selective adsorption and subsequent desorption of trace hydrocarbons and sulphur odorants. The performance of these carbons also allows significant reduction of the energy requirement to regenerate pipeline quality NG on discharge from storage.
4. Produce a detailed guard bed design with associated pipework, fabrication and control strategy.
5. Laboratory testing, carrying out cyclic testing to simulate diurnal storage operation using a 0.5 m^3 main adsorbent storage bed.

6. Carry out market studies and formulate routes for future applications of the technology. Undertake safety and reliability studies for ANG storage, with experimental testing of ANG storage vessel and relief valve failure. Options for ANG vehicle refueling and associated guard bed design.

The modeling activities of the ANGUARD project were performed by our research group at FCT /UNL and further description of the work performed will be presented in Chapter 6. Unique experimental determinations of adsorption equilibria for the trace components of NG, including, *n*-ethane, *n*-propane, *n*-butane, and odorant sulphur-compounds tertbutyl mercaptan (TBM, $C_4H_{10}S$) and tetrahydrothiophene (THT, C_4H_8S) were obtained on a newly developed carbon formulation. Measurements of methane, carbon dioxide, nitrogen and helium were also carried out. The experimental adsorption data were successfully correlated using the Adsorption Potential Theory.

Using the experimental data obtained, a dynamic model of multi-component adsorption on activated carbons of the significant trace components of NG, including odorants, was developed by our group within the ANGUARD project. The adsorption equilibrium model was extended to multicomponent competitive adsorption using the Ideal Adsorbed Solution (IAS) theory. This predictive model forms the basis for the design, operation and control of the guard bed system.

The dynamic cyclic model of the guard bed was used to size the guard bed and evaluate its performance relative to the 500 L storage tank that was used in actual testing of the overall system. The computed volume of the guard bed is only 1.1% of the total volume of the main storage tank. The model was subsequently employed to demonstrate the feasibility of re-odorising the delivered NG by heating the gas. A feedback control loop using a proportional-integral controller was implemented for evaluation purposes. The results show that this simple control scheme could maintain the total odorization level of the discharged NG at acceptable values. More importantly, with a more complex predictive control scheme it is possible to odorize the outlet gas stream at a very accurate level [ANGUARD (March 2004)]. Further details will be described in Chapter 6.

The conceptual process was based on a UK large-scale diurnal storage scenario for a nominal winter demand forecast that was thought capable of maintaining the odorant in the desorbed gas within specified limits. The Consortium designed a flexible scheme and control system with the option of incorporating a by-pass loop to limit the amount of stored gas passing through the guard bed on the discharge cycle and ensure sustained gas quality throughout the discharge operation; this can potentially increase the degree of process control, as well as resulting in potential size reduction and lowering capital

costs for the overall process. Refinement and optimization of the conceptual process was central to the development.

A sophisticated software package incorporating framework, protocols and routines was developed. This was interfaced with control valves, analytical equipment, the Advantica ANG rig, and the FCT/UNL dynamic model. All the ANGUARD technical developments were integrated to produce an experimental system able to produce proof-of-concept data with real NG.

Finally, the integration of the guard bed with the main storage vessel was completed, and proof of concept testing successfully carried out. The performance of the system has been confirmed for pipeline quality UK natural gas with simulated diurnal cycles. Highly effective collaboration/synergy between the modelers, control system developers and system testers has resulted in a responsive and versatile system design that can be adapted for a range of applications and scales.

To conclude this section, very recently research work is being done concerning the enhancement effect of preadsorbed water on methane storage on activated carbon [Zhou and Sun (2002), L. Zhou and Zhou (2000), L. Zhou and Zhou (2001)]. It was reported by J. Miyawaki and Kaneko (1998) that the presence of preadsorbed water noticeably enhanced methane adsorption at 303 K, even under subatmospheric pressure. Zhou suggests that the addition of water leads to a significant enhancement on the methane-storage capacity of activated carbon that is expected to considerably improve the ANG technology.

The specific surface area of the powder carbon sample was $1800 \text{ m}^2/\text{g}$, which was estimated using the D-R plot of the CO_2 adsorption isotherm at 273 K [Gregg and Sing (1982)]. The bulk density of the carbon was $0.33 \text{ g}/\text{cm}^3$, which was measured after the sample was dried at 393 K for 24 h in a vacuum. An amount of demineralized water was added to the dry carbon sample. The water content of the wet activated carbon, i.e. the water ratio, R_w , was defined as the ratio of water weight to that of the dry activated carbon. Three wet samples were tested, with water ratios of 0.7, 1.4 and 3.0. The adsorption isotherms were performed for both dry and wet samples in a temperature range from 275 K to 283 K.

Figure (2.27) shows the reported amount of methane adsorbed expressed as the weight percent of methane on dry carbon, i.e., a gram of methane adsorbed on 100 g of activated carbon. From curve *a*, the highest CH_4 amount adsorbed per 100 g of dry carbon was 19.44 g at a pressure of 7.46 MPa. In curves *b* and *c*, the amount adsorbed is considerably less than that recorded at dry carbon before the pressure reached the inflection point, at 4.6 MPa. A sudden change in the CH_4 uptake mechanism that was indicated by the inflection point of isotherms was observed. The measured amount adsorbed always

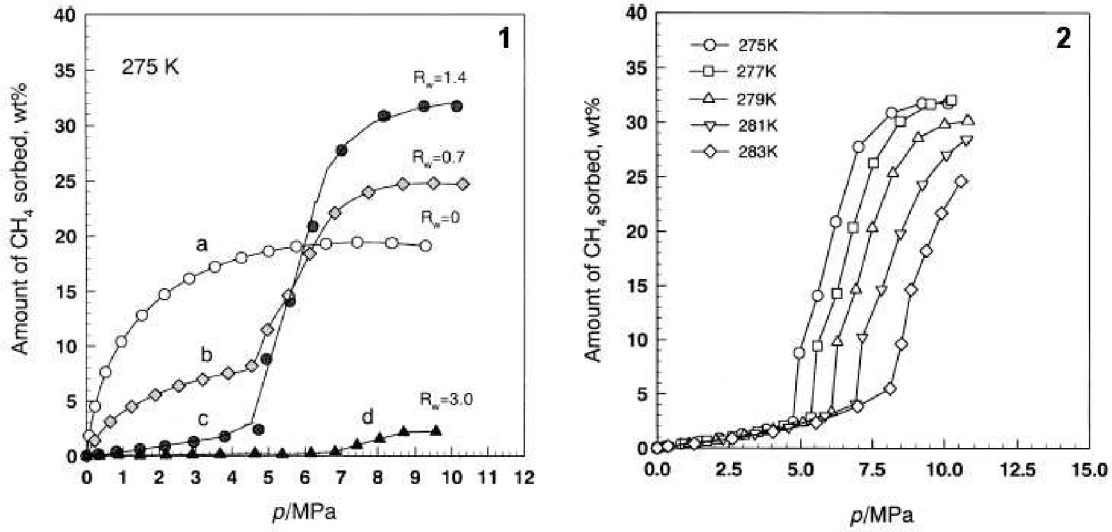


Figure 2.27: 1) Effect of water content on the storage enhancement of methane. Curve *a* is the isotherm of dry carbon (Type I, IUPAC). Isotherms *b* and *c* show a sharp increase with a water ratios of 0.7 and 1.4, respectively. 2) Effect of temperature on the storage enhancement, $R_w = 1.4$. Higher temperatures are not favorable for purposes of storage [Zhou and Sun (2002)].

decreased with the increasing water content of carbon before the inflection point. The highest amounts of methane adsorbed per 100 g of dry carbon were 24.78 g for $R_w = 0.7$ at 9.52 MPa and 31.74 g for $R_w = 1.4$ at 9.26 MPa. The net gains relative to dry carbon were 27.5% and 63.3% for a water ratios of 0.7 and 1.4, respectively. Because the inflection pressure of 4.6 MPa at 275 K is a little higher than the formation pressure of methane hydrate (3.23 MPa; Sloan and Parrish (1981)), hydrate formation is a reasonable mechanism for the sudden increase in the isotherm. The difference could be due to the inner diffusion resistance or the transport related effects in the porous space. However, larger amounts of water does not help hydrate formation as shown by curve *d*.

The charging/discharging property on wet activated carbon was also analyzed. From the desorption isotherms, although no hysteresis was observed on the dry activated carbon [L. Zhou and Zhou (2000)], a remarkable hysteresis was recorded on the wet carbons. As cited, this hysteresis was caused by the decomposition of methane hydrate. Methane hydrate decomposes as pressure becomes lower than its formation pressure. Therefore, the wet activated carbon can be applied repeatedly as a methane carrier.

Hence, Zhou states that an appropriate quantity of water preadded to activated carbon greatly enhances more than 60% the storage of CH₄ on activated carbon, as long as the pressure is no less than the value of the inflection point of the isotherm. Based on a bulk density of 0.7 g/cm³, about 200 v/v of volumetric capacity was reached on the wet

activated carbon tested. The storage pressure must be as high as 20 MPa for CNG to reach the same capacity. With this description the author conclude that if a tank with the referred sorbent is used to supply fuel for vehicles, full power could be guaranteed for a wide range of fuel pressures above 3.5 MPa at temperatures in the 2 - 8°C range.

Although Zhou reported the improvement of ANG technology, it is important to point out, in the author's opinion, that is still not clear its feasibility compared with the AN-GUARD solution proposed. The following list enumerate some of the critical points that offset the advantages stated:

- In contrast to [L. Zhou and Zhou \(2000\)](#), the use of a pelletized carbon adsorbent is not a time-consuming and inefficient process. For practical reasons and mechanical handling of the sorbent, in vehicular applications, it is in fact advantageous the usage of pellets with high activity.
- The economics of ANG applications is affected by maintaining the NG storage process in the 2 - 8°C range, and imposing a full power guarantee for pressures above 3.5 MPa. This not only affects the operating costs but also the safety of storage operations by ANG.
- Further, modeling work and experimental data is needed concerning the heavier components and the odorants present in NG streams, before ensure the suitability of NG storage by wet activated carbon.

Further characteristics on ANG operations that support the referred points are described in [section 4.2](#) and [Chapter 6](#), under the ANGUARD project development.

Chapter 3

Permeation Experiments and Modeling

3.1 Permeation Measurements

3.1.1 Introduction

In contrast to more conventional separation systems, membranes generally exhibit simplicity of operation, smaller size, effective separation and reliable performance at lower total cost [Ho and Sircar (1992); Stern (1994)]. These features has enabled membranes to penetrate into a wide and growing variety of markets and applications. Before presenting in Chapter 5 one of those applications - a novel hybrid gas separation strategy combining membrane permeation and pressure swing adsorption (PSA) technology - it is essential to study and discuss some of the insights of membrane technology.

This section reports the permeation measurements performed with a membrane module for gas separation, gratefully supplied by Dr. G.C. Kapantaidakis, from the Membrane Technology Group (Faculty of Chemical Technology, University of Twente, Netherlands). The aim was to confirm that the permeances and selectivities of CH₄, CO₂ and N₂, were in the range of values found in realistic industrial applications. This range of values was then used in the subsequent modeling work (Chapter 5).

3.1.2 Apparatus Description

Figure (3.1) shows the membrane set-up used for the permeation measurements. Each permeator consists of a bench scale asymmetric hollow fiber membrane module containing

PES/PI (polyethersulfone Sumikaexcel/ polyimide Matrimid 5218 blend) 80/20 wt% [Figures (3.2, 3.3)]. These two polymers are miscible and exhibit complementary permeation properties, plasticization behavior and cost. The commercial price of the PI is about 360 Euro/kg, while that of the PES is 12 Euro/kg (prices of 10/2001, G. C. Kapantaidakis and Wessling (2003)). Table (3.1) summarizes the geometrical characteristics and gas permeation properties of the modules supplied.

The cell has a length of 25 cm and an outer diameter of 1.5 cm. It exhibits a reported CO_2/N_2 selectivity higher than 30 and a CO_2 permeance of 30.30-31.64 GPU (35°C , 4 bar). The blending of PES and PI, used for the preparation of these membrane type modules, combines the high permeability coefficients of the PI with the high resistance to plasticization and low cost of PES. The module was prepared with the ultimate goal of producing a bundle of asymmetric hollow fibers (HF) with a ultra thin skin layer

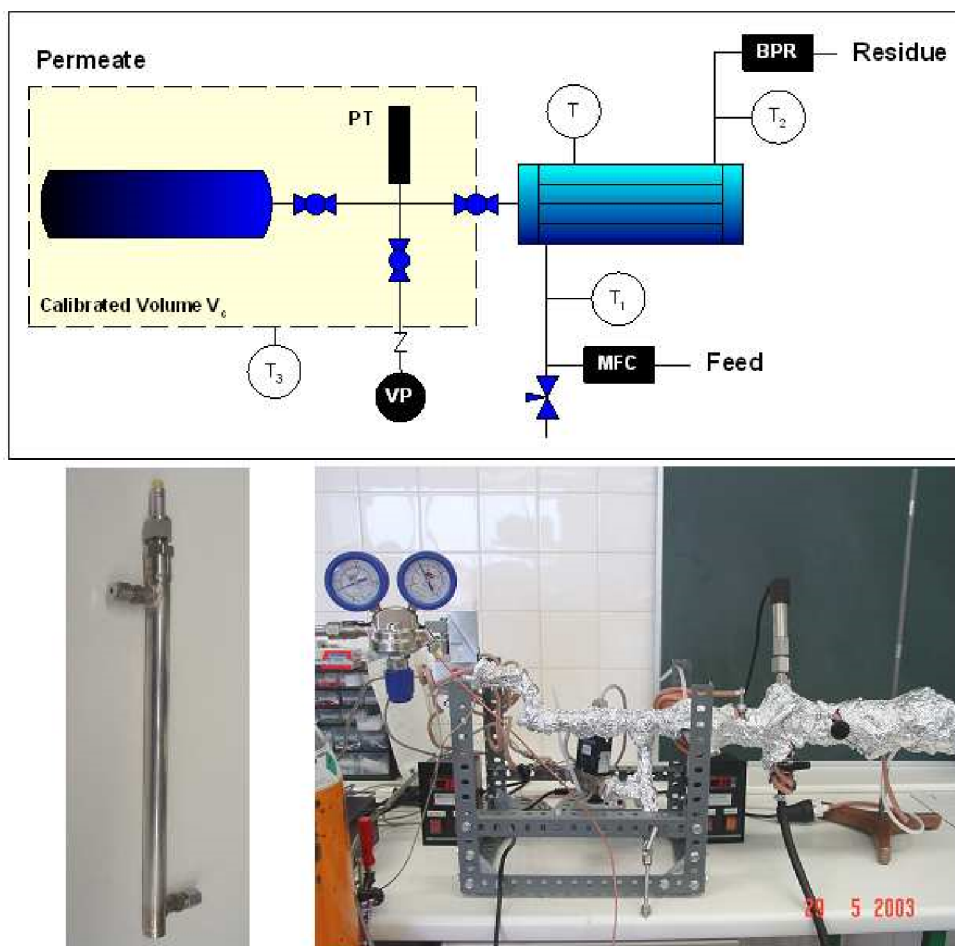


Figure 3.1: General schematic of the membrane unit set up used in the permeation measurements.

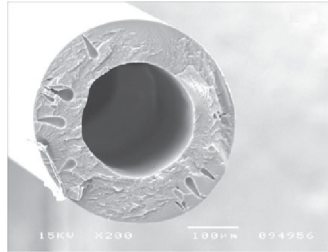


Figure 3.2: Cross section of a PES/PI 80/20 wt% hollow fiber. The ultrathin HF membrane was prepared using the dry/wet phase inversion process. The substructure layer is porous and contains few macrovoids [G. C. Kapantaidakis and Wessling (2002a,b); T. S. Chung and Hu (1997)].

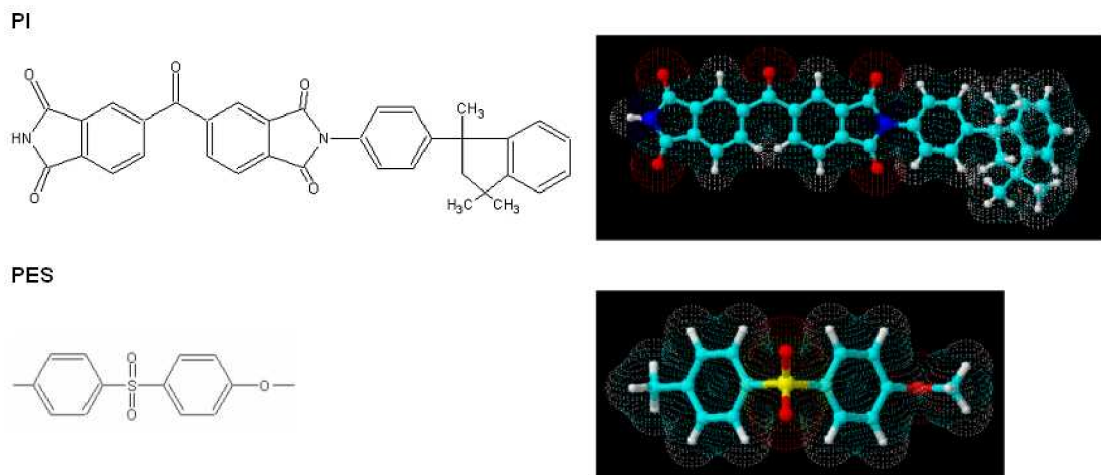


Figure 3.3: Polymers used to compose the hollow fiber experimental module.

Table 3.1: Geometrical characteristics and gas permeation properties of the membrane modules supplied.

Modules	Fiber Length, cm	No Fibers	Fiber OD, μm	Fiber ID, μm	Surface Area, cm^2
1	14	7	423	244	13.0
2	16	5	423	244	10.6

Modules	CO ₂ , GPU	N ₂ , GPU	$\alpha_{\text{CO}_2/\text{N}_2}$
1	30.30	0.88	34.4
2	31.64	0.91	34.8

(0.1-0.15 μm), minimum or no surface porosity, finely microporous substructure without macrovoids, high permeance and selectivities intrinsic to the material spun. The permeate side has 3/8" OD dimensions, while the feed side has 1/8" OD connections. The whole apparatus uses Swagelok type fittings. The skin layer is from the outer side of the fiber, so the permeation runs are performed from the shell to the bore side of the hollow fiber.

Data acquisition management works under Labview environment, using an in-house developed software, BioCTR. The acquisition channels correspond to two platinum Pt100 temperature probes coupled with an electric shielded cable rolled along the main apparatus for temperature maintenance. Each sensor measures the gas temperature in-line, and sends its signal to a digital controller that actuate on the cable. A mass flow controller is located at the inlet feed side of the membrane and a back-pressure regulator is placed at the residue exit stream, to maintain constant pressure during permeation on this side of the module. A vacuum pump is placed at the permeate side in order to evacuate when desired. The permeate is collected to a calibrated volume and pressure is acquired over time.

3.1.3 Experimental Method

3.1.3.1 Permeation Experiments with Single-Components

Single gas permeation tests of several gas components were performed using a set-up based on the variable pressure method. After increasing gradually the temperature of the unit up to the desired experimental value, the permeation rates are calculated from the pressure increase as a function of time in a calibrated volume, on the permeate side of the membrane module. For simple membrane testing, a certain feed pressure was applied

to the shell side whereas the permeate side was initialized at vacuum. For plasticization experiments at a specified temperature, the feed pressure effect was analyzed.

The pressure acquisition with time, at the known permeate volume, allows the determination of the permeation rates of each component. Knowing the driving force for permeation and the membrane physical characteristics, the component permeances can be calculated, and hence the membrane ideal selectivities. The permeance through the hollow fibers is expressed as a thickness normalized permeability value, given in Gas Permeation Units ($1\text{GPU} = 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \text{ s cm Hg}$). The ideal selectivity of a gas pair was calculated by dividing the respective permeances of the pure gases.

On the shell (feed) side of the membrane, the flow rate was regulated in order to have a stage cut (permeate to feed flow rate ratio) lower than one. This ensures that separation occurs and, when working with binary-component experiments, the feed composition does not vary along the membrane length.

Due both to the small permeate fluxes and to the residue flow necessary to meet the stage cut criterium, under the small membrane lab-module, it can be assumed that the shell side pressure drop is negligible.

Experiments were performed with the following gases: He, N₂, CH₄ and CO₂. Components C₁ - C₄ could irreversible damage the fibers by swelling effect. The gas permeation properties (permeance and CO₂/N₂ ideal selectivity) provided by the membrane manufacturer were used as initial reference values for the experiments performed.

To be sure of the certainty of the experimental data, repeatability was checked by repeating a run at least three times for the same operating conditions. Each run was executed with around 30 minutes minimum of evacuation between measurements. When switching from one gas to another, both sides of the membrane were evacuated for at least one hour, to get rid of any possibly adsorbed molecules. The maximum operational pressure in the membrane is 20 bar.

The experiments were initially performed at the reference driving force, approximately 4 bar, but other experiments were executed at other feed pressures. To study the effect of plasticization when dealing with CO₂, the feed pressure was gradually increased up to 16-18 bar, at a given temperature run. Selectivity measurements should be taken before and after exposure to higher CO₂ pressures, for example, one and five days after plasticization.

Figure (3.4) shows the CO₂ permeabilities as a function of feed pressure for the polymers that compose the blending membrane used in the experimental work. The polymers PSF and PES present high plasticization pressures compared to the polyimide material. The PES/PI blending clearly changes the plasticization behavior.

This type of membrane module should present a reversible effect after a relatively short time, as shown in Figure (3.5.a). Contrary to dense glassy membranes, where a

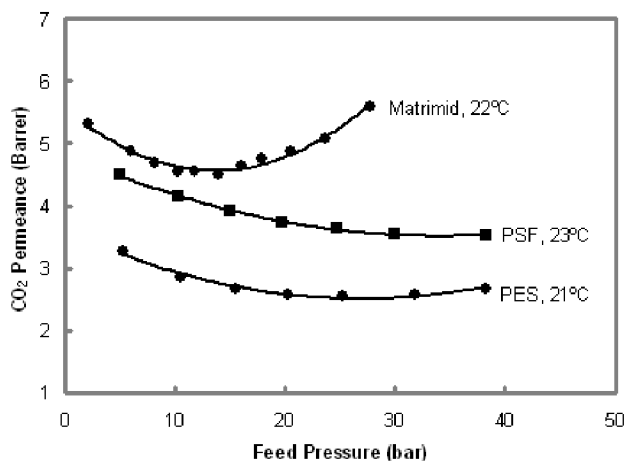


Figure 3.4: CO₂ permeabilities (Barrer) as a function of CO₂ pressure for polyethersulfone (PES), polysulfone (PSF) and polyimide (Matrimid) polymers at room temperature. Solid lines represent a second-order polynomial fit. The plasticization pressures for PES, PSF and Matrimid are 27, 34 and 12 bar, respectively [A. Bos and Strathmann (1999)].

minimum CO₂ permeance is visible at reasonable high pressures (PES, PSF: >25 bar), in the blended fibers the CO₂ permeance increases almost immediately with pressure. The selectivity reduction should be reversible since the hollow fibers recover the initial permeance values of virgin fibers in less than 5 days. Figure (3.5.b) shows the comparison of PES/PI blends with commercial gas separation membranes, where one can see that the PES/PI blend exhibits higher CO₂/N₂ selectivities and competitive CO₂ permeances compared with UBE A, UBE B-H and Monsanto Prism membranes.

After performing the single-component measurements to calculate the permeation rates and the permeances of the components, the ideal selectivity or permselectivity provides a fundamental measure of the membrane performance and is determined as the pure gas pressure-normalized flux ratio, i.e. the ratio of the permeances of the pure gases, assuming a vacuum initial permeate pressure.

Permeation experiments were taken at 36°C (±1°C). Further experiments at different temperatures would be needed to study the temperature effect on the membrane apparatus. The temperature change should induce an effect on feed flow rate and thus, membrane area, due to the permeabilities variation. The feed pressure, selectivity, feed flow rate and feed composition should impact on permeate and residue purity and stage cut [G. C. Kapantaidakis and Wessling (2003)].

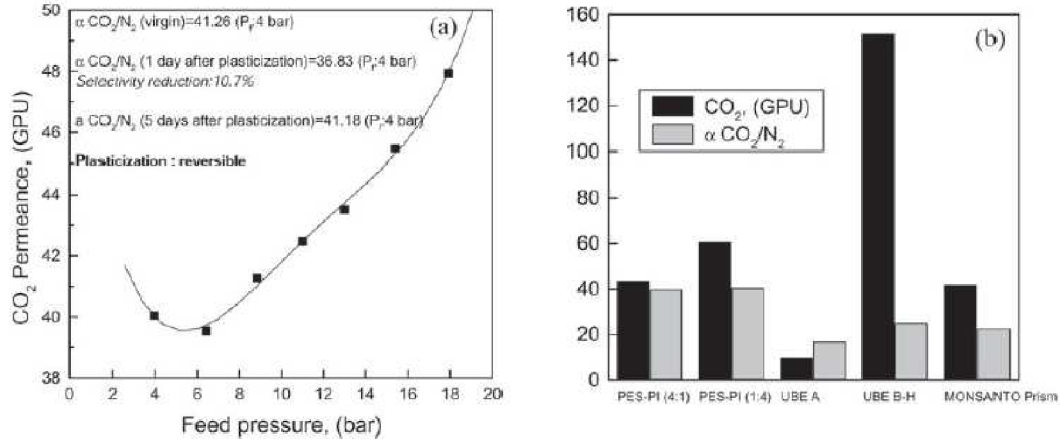


Figure 3.5: a) Feed pressure effect and plasticization behavior of PES/PI 80/20 wt% hollow fibers. b) Comparison of PES/PI hollow fibers with commercial gas separation membranes [G. C. Kapantaidakis and Wessling (2002b)].

As already referred, in a closed calibrated volume V_c , the pressure increases with time due to the permeating gas molecules. The total amount permeated through the membrane changes in time until equalization between the pressures on both sides of the membrane is achieved. The permeation stops at that time. The volume is calibrated with nitrogen, by expansion from a known externally calibrated volume ($F_e t$). Applying the ideal gas law, V_c is defined as

$$V_c = \frac{1.01325 T_c F_e t}{273.15 P_c} \quad (3.1)$$

where T_c and P_c are the experimental temperature and final pressure, respectively. F_e is given by a mass flow meter at standard conditions (0°C, 1 atm) at each instant of time t , at the feed inlet side of the membrane. Experimentally and for simplicity reasons, the calibrated volume was determined through the area, A , under the curve given by the volumetric flow fed to the system along time.

$$V_c = \frac{1.01325 T_c A}{273.15 P_c}, \quad A = \int F_e dt. \quad (3.2)$$

Seven runs were executed at 36°C, ≈ 5 bar, and at two different standard N₂ feed flows (0.25 and 0.50 slpm). An average value of the calibrated volume was obtained. Figure (3.6) presents the calibrated volume set-up.

The permeance (or pressure normalized flux) is calculated from the slope of the pressure increase $\Delta P_{\text{permeate}}/\Delta t$ in the calibrated volume with

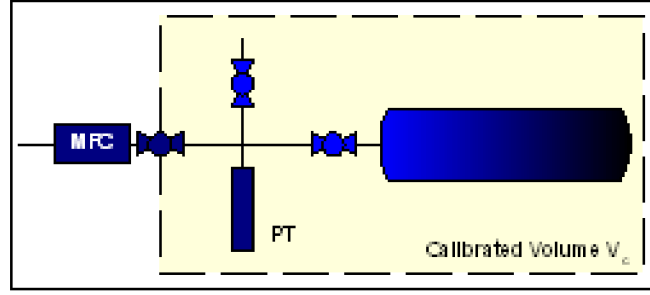


Figure 3.6: Calibrated volume set up.

$$\wp = \frac{\Delta P_{permeate}}{\Delta t(P_{feed} - P_{permeate})} \frac{V_c^* V_m}{A_{mem} RT} \quad (3.3)$$

where V_m is the molar volume at standard temperature and pressure, V_c^* the total calibrated volume including the permeate volume available, R the ideal gas law constant, T the experimental temperature and $(P_{feed} - P_{permeate})$ the driving force for permeation across the membrane. More correctly, one can define the permeation flux through the membrane as

$$\frac{dP_{permeate}}{dt} = \frac{A_{mem} \wp RT}{V_c^* V_m} (P_{feed} - P_{permeate}), \quad (3.4)$$

where by integration one can represent $\ln \frac{P_H - P_L^0}{P_H - P_L}$ versus t and obtain the permeance from the slope $A_{mem} \wp RT / (V_c^* V_m)$.

3.1.3.2 Permeation Experiments with Binary Mixtures

A binary mixture A/B can be studied at a specific temperature and in a pressure range allowed for the membrane set-up. The same experimental procedure as described in the previous section can be executed, for example, with a gas mixture of CO_2/N_2 (80/20, 50/50 or 20/80). As previously, the residue flow must be much higher than the permeate one, in order to guarantee that the feed composition does not vary during permeation and along the membrane length, i.e., that the stage-cut is maintained as small as possible.

From the permeate pressure increase with time in the calibrated volume, the total permeate flow rate and the global permeance of the mixture are determined. Analyzing the permeate composition it is possible to calculate the separation factor, i.e., the real selectivity of the mixture, by the ratio of the mole fractions in the permeate divided by the feed mole fractions ratio [Eq.(2.7)].

The real permeances of the two components are then determined from the total permeance by the equations

$$\wp_A = \frac{\wp_{total}}{y_A^p} y_A^p, \quad \wp_B = \frac{\wp_{total}}{y_B^p} y_B^p \quad (3.5)$$

where $i = A, B$, and $\wp_i$ is the permeance of the component i .

When the permeation measurements were done, it was not possible to analyze the multicomponent stream compositions from the membrane, since there was no analyzer available. Therefore, without composition analysis one can simply perform a binary mixture permeation test and determine, from the variable pressure method, the total permeance of the system, that is, an equivalent pure CO₂ and N₂ permeance value. In order to determine if the component interactions in the mixture interfere with the permeation, one can compare the total permeate pressure from the runs with the sum of the partial pressures in the permeate, given by the molar flow of each component through the membrane,

$$V_c^* \frac{dc_i}{dt} = A_{mem} \wp_i (P_i^r - P_i^p), \quad (3.6)$$

where P_i^r and P_i^p are the residue and permeate partial pressures, respectively. Considering that ideal gas law applies at the operating conditions,

$$c_i = \frac{P_i}{RT}, \quad (3.7)$$

then

$$\frac{V_c^*}{RT} \frac{dP_i^p}{dt} = A_{mem} \wp_i (P_i^r - P_i^p). \quad (3.8)$$

Integrating from the initial permeate partial pressure P_i^{po} to the permeate partial pressure P_i^p at time t , we obtain

$$\ln \frac{P_i^r - P_i^{po}}{P_i^r - P_i^p} = \frac{A_{mem} RT \wp_i}{V_c^*} t \quad (3.9)$$

$$P_i^p = P_i^r - (P_i^r - P_i^{po}) \exp \left(- \frac{A_{mem} \wp_i RT}{V_c^*} t \right), \quad (3.10)$$

where $P_i^r = y_i^r P^r$ is obtained experimentally assuming that the feed composition do not vary during permeation and along the membrane length. At time zero, $P_i^p = P_i^{po}$, and at $t \rightarrow \infty$, $P_i^p = P_i^r$.

3.1.4 Experimental Results and Data Analysis

The parametric study should be concerned with the feed operational parameters (feed pressure, feed flow rate and concentration) and the membrane material properties (permeabilities, selectivities). During experimental runs, the variables to be monitored for a

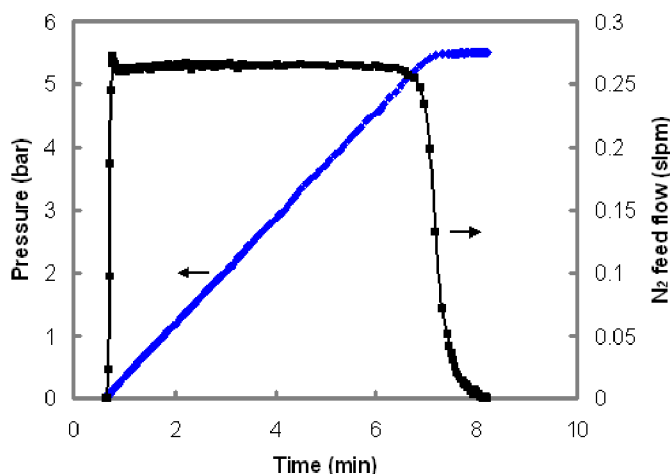


Figure 3.7: Illustrative example of the experimental tests performed for the calculation of the calibrated permeate volume used for permeation measurements. This particular run was executed during ≈ 7.5 min., at 36°C , up to 5.5 bar and with a N_2 feed flow of ≈ 0.27 slpm.

specific temperature are stage-cut (permeate to feed flow rate ratio) and permeate concentration.

The experiments to obtain the calibrated volume, V_c , reported an average value of 356.46 ml from a total of seven runs. The additional volume of permeate available, that is, the minimum permeate side of the membrane and the permeate tubing line, were considered, and hence the total calibrated volume, V_c^* , obtained was 358.06 ml, with a standard deviation of 3.84 ml from a total of seven runs. Figure (3.7) presents an illustrative example of an experimental run performed for the determination of the calibrated permeate volume.

Tables (3.2) and (3.3) summarize the permeation data measurements performed for different pure components at 36°C ($\pm 1^\circ\text{C}$) and at several transmembrane pressures. In general, for glassy polymers, no dramatic change in the absolute value of the permeability due to a small temperature difference is observed. Differences in permeability are more pronounced at temperature differences of 100°C [A. Bos and Strathmann (1999); Costello and Koros (1992, 1993)].

Figure (3.8) shows the single-pure component permeances variation with feed pressure, obtained experimentally for He, N_2 , CO_2 and CH_4 . For these components, the repeatability tests revealed an average deviations relative to permeance of 0.522, 0.011, 0.137 and 0.004, respectively. The standard deviations were 0.706, 0.015, 0.183 and 0.005, respectively. The permeances of He and N_2 are not significantly affected by feed pres-

sure change, and therefore an average value was considered for each gas. He presents an average permeance of 44.05 GPU and N₂ permeance obtained was 0.546. The overall average deviation relative to the permeances of these two gases are 0.151 and 0.007, and the standard deviation values are 0.227 and 0.01, respectively.

The average deviation returns the average of the absolute deviations of data points from their mean. Its a measure of the variability in a data set and is defined as

$$\text{AvDev} = \frac{1}{N} \sum |Y - \bar{Y}|^2, \quad (3.11)$$

where Y is the permeance variable, $\bar{Y}$ corresponds to its mean, and N is the number of data points. The standard deviation is based on a sample and is a measure of how widely values are dispersed from the average value (the mean), and is expressed as

$$\text{StDev} = \sqrt{\frac{N \sum Y^2 - (\sum Y)^2}{N(N-1)}}. \quad (3.12)$$

The values of average deviation and standard deviation obtained are quite satisfactory and therefore, this procedure is suitable over a broad range of experimental conditions for the single-pure component measurements.

The permeation results obtained for the membrane module show lower permeance values than the reference ones, provided by the membrane producer at the time of its manufacture. The reduction in the permeance values is attributed to physical membrane ageing. The first measurements were performed about 12 months after manufacture of the membrane fibers, so it would be expectable a similar decline of the gas permeance [Figure (3.9)]. Nevertheless, this membrane module is workable, since the selectivity CO₂/N₂ is still similar and quite high (32.56 against 34.43 from the membrane producer).

The selectivities obtained for several gas pairs are in the range of the realistic values for present and future industrial applications [Baker (2002); Drioli and Romano (2001); Ho and Sircar (1992); Stern (1994)]. This order of magnitude was then used in the modeling work developed for the hybrid membrane/PSA processes.

As seen in Figure (3.8), contrary to N₂, where the permeance is reduced slightly with feed pressure, the increase of feed pressure results in an increase of the CO₂ permeance, indicating immediate plasticization of the membrane. The plasticization is assumed almost reversible after a short period of time.

The data obtained by G. C. Kapantaidakis and Wessling (2003), show a selectivity reduction of 10.7%, 1 day after plasticization and a complete reversibility after 5 days. The experimental results obtained present only a 5.7% decrease, 2 days after plasticization, although the hollow fibers seems to only recover the initial permeance values after a little

Table 3.2: Summary of pure-gas permeation properties obtained from the permeation experiments and its comparison with the properties of the membrane module 1 supplied. (1. Experiments at 35°C with a $\Delta P = 4.0$ bar. 2. Experiments at 36°C with a $\Delta P \approx 4.2$ bar. Permeances are in GPU.)

	$\wp_{CO_2}$	$\wp_{N_2}$	$\wp_{He}$	$\wp_{CH_4}$	α_{CO_2/N_2}	α_{CO_2/CH_4}	α_{He/N_2}
<i>Supplier</i> ¹	30.30	0.88	-	-	34.43	-	-
<i>FCT/UNL</i> ²	17.87	0.55	44.05	0.51	32.35	34.87	80.74

Table 3.3: Summary of the pure-gas permeation properties and effect of the feed pressure in the pure-gas permeances obtained at 36°C from the permeation experiments performed with the membrane module 1.

He	ΔP (bar)	$\wp$ (GPU)
Run 1	4.48	43.45
Run 2	4.37	43.84
Run 3	4.30	44.82
average	4.38	44.03
Run 4	7.28	43.80
Run 5	11.11	44.35
Run 6	14.32	44.01

CO ₂	ΔP (bar)	$\wp$ (GPU)
Run 1	4.05	17.93
Run 2	4.05	18.02
Run 3	4.05	17.67
average	4.05	17.87
Run 4	6.92	16.83
Run 5	9.17	16.75
Run 6	11.24	17.17
Run 7	11.25	17.26
Run 8	12.68	17.22
Run 9	14.91	18.12
Run 10	18.36	18.55
Run 11	4.18	16.85
Run 12	4.18	16.75
Run 13	4.28	17.95

N ₂	ΔP (bar)	$\wp$ (GPU)
Run 1	4.28	0.549
Run 2	4.38	0.542
Run 3	4.28	0.544
Run 4	4.40	0.575
average	4.33	0.553
Run 5	7.11	0.553
Run 6	11.75	0.546
Run 7	15.21	0.531

CH ₄	ΔP (bar)	$\wp$ (GPU)
Run 1	4.14	0.517
Run 2	4.14	0.509
average	4.14	0.513
Run 3	7.57	0.499
Run 4	9.46	0.488
Run 5	10.66	0.495
Run 6	13.10	0.486
Run 7	15.36	0.481
Run 8	18.29	0.453
Run 9	5.24	0.491

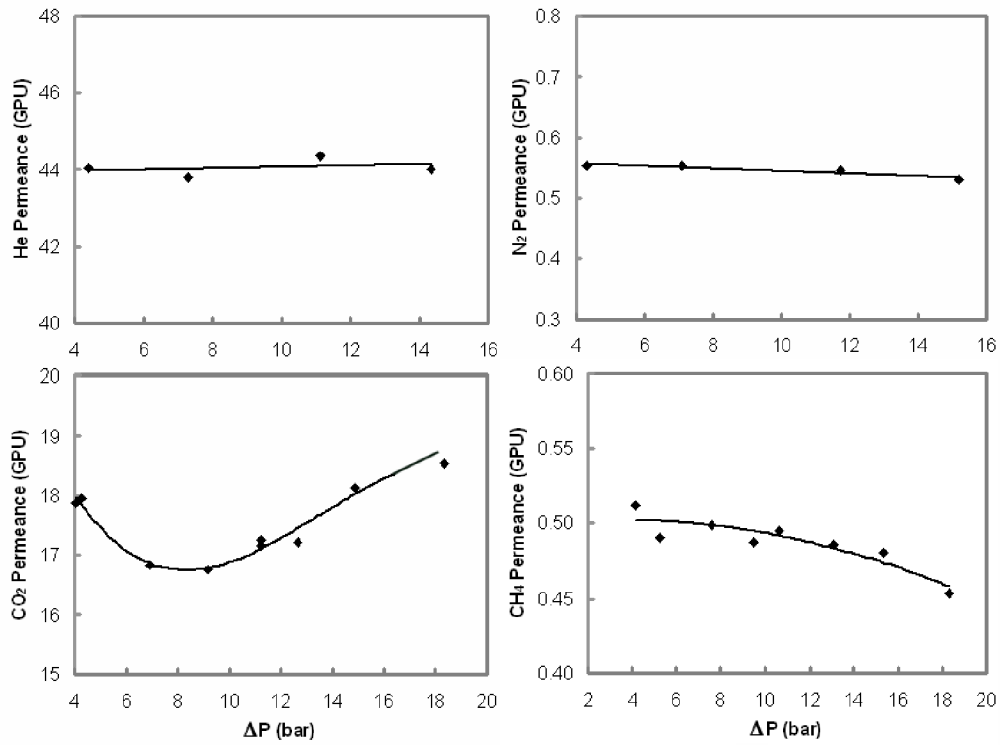


Figure 3.8: Single-pure component permeances variation with transmembrane pressure, obtained experimentally for He, N₂, CO₂ and CH₄, at 36°C ($\pm 1^\circ\text{C}$).

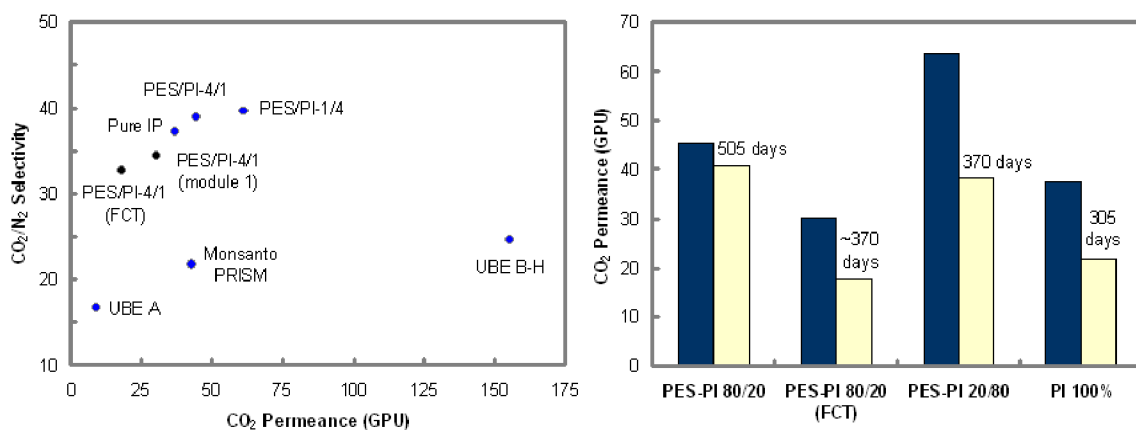


Figure 3.9: Ageing effect on CO₂ permeance and comparison with other membranes [G. C. Kapantaidakis and Wessling (2003)].

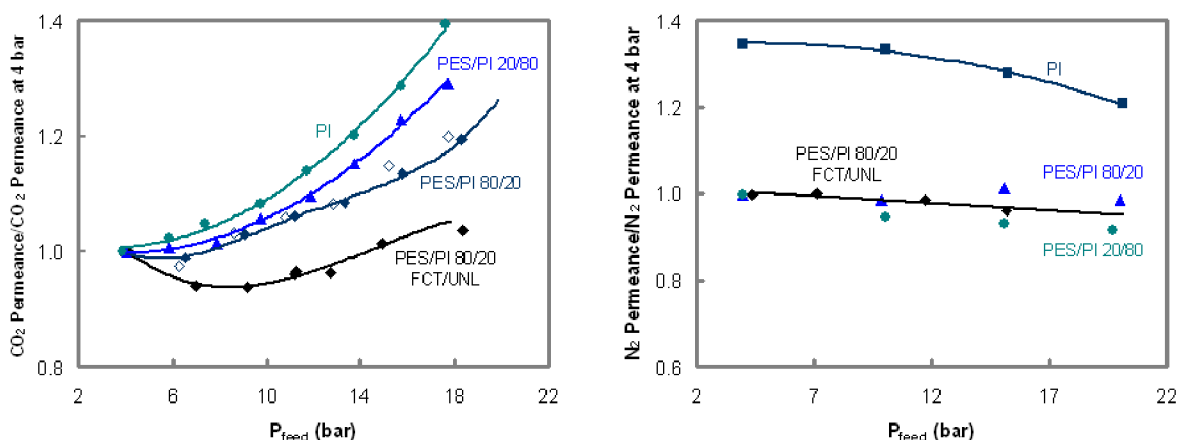


Figure 3.10: Effect of feed pressure on pure CO₂ and N₂ normalized permeances for several membrane materials [G. C. Kapantaidakis and Wessling (2003)].

longer period of time (9 days). The difference in the reversibility between the results obtained and the ones for the younger membrane [Figure (3.5.a)] are probably explained by the ageing of the polymeric blending.

Figure (3.10) presents the comparison of the experimental data obtained, with other membranes and a similar set of results from G. C. Kapantaidakis and Wessling (2003) relative to the same PES/PI 80/20 wt%. Since, from the absolute permeance values it is difficult to compare the magnitude of plasticization for the different materials, the CO₂ and N₂ permeances at 4 bar feed pressure were used to normalize the y axis. The trend of the CO₂ and N₂ permeances with feed pressure variation are quite similar to the ones obtained originally.

The plasticization pressure at 36°C ($\pm 1^\circ\text{C}$) was detected by the minimum in CO₂ permeance, 16.76 GPU, which corresponds to 8.39 bar, while the same effect was observed by Kapantaidakis et al. in a similar membrane at 6.55 bar with a CO₂ permeance of 39.55 GPU. This point correlates to the minimum CO₂ amount needed to induce plasticization. As reported by Bos (1996), J. D. Wind and Koros (2002) and Wessling (1993) the decrease in permeance at low pressures results from a decreasing solubility with increasing pressure. The permeance increases with increasing pressure, results from a high CO₂ concentration in the polymer film that disrupts the chain packing. The free volume of the polymer matrix increases, which results in an increased segmental mobility and hence permeance.

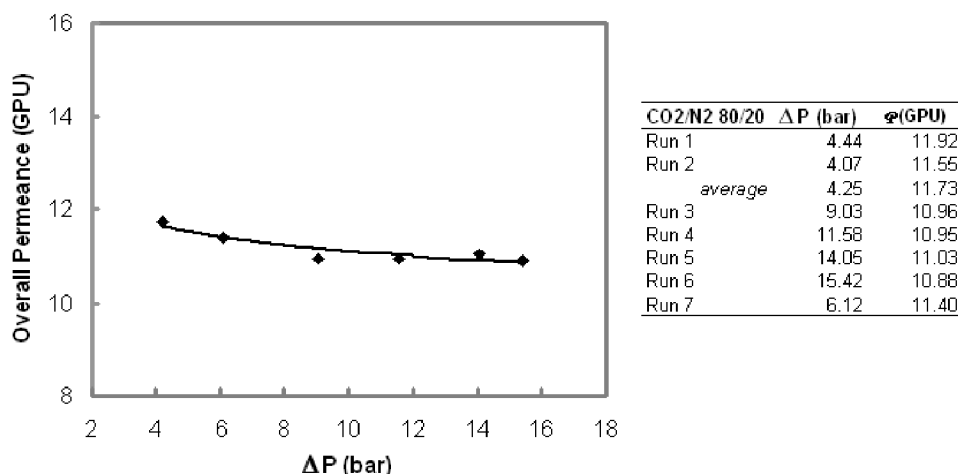


Figure 3.11: Experimental permeation data obtained at 36°C for the CO₂/N₂ 80/20 wt% mixture.

Concerning the binary mixture tests, Figure (3.11) presents the permeation data obtained at 36°C for the CO₂/N₂ 80/20 wt% mixture, and the respective overall permeance trend with feed pressure change.

From Eq. (3.10), knowing the single component permeances, one can compare the total permeate pressure from the experimental runs with the sum of the partial pressures in the permeate, given by the molar flow of each component through the membrane.

From Figure (3.12), one can conclude that the total permeate pressure from the gas mixture permeation runs have a distinct behavior from the permeate pressure obtained from the analysis initially described. It can be seen that this effect is increased for higher feed pressures, which can be due to component interactions in the mixture, their competition for permeation mechanism and CO₂ plasticization phenomena at higher feed pressures. No further conclusions can be drawn due to the impossibility of analyzing the permeate composition at the time the experiments were performed.

G. C. Kapantaidakis and Wessling (2003) report that the permeation behavior of N₂ in the mixture is similar to that reported for the pure-gas experiments. A CO₂/N₂ 45/55 wt% binary mixture was analyzed, and results show a constant or slightly lower N₂ permeance with the increase of partial feed pressure for PES/PI 80/20 wt% membrane. Taking into account that the developed ultra thin hollow-fiber membranes showed immediate and pronounced plasticization for pure CO₂, one should expect that the permeance of the slower gas N₂ would also increase with partial feed pressure. The opposite behavior is a first indication that both pure PI and PES/PI blend hollow-fiber membranes exhibit entirely different or suppressed plasticization behavior in the permeation of the binary

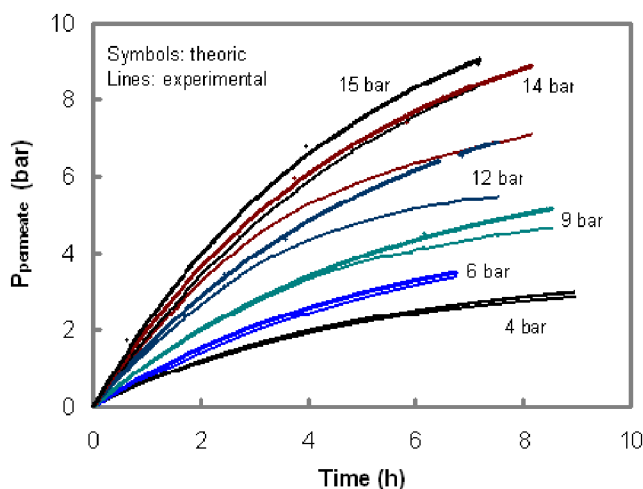


Figure 3.12: Permeate pressure behavior obtained at 36°C for the CO₂/N₂ 80/20 wt% mixture at several feed pressures. Comparison of the experimental permeate pressures obtained with the theoretical values determined from Eq. (3.10).

mixture.

Figure (3.13.a) shows the effect of CO₂ partial feed pressure on CO₂ permeance. Contrary to the permeation of pure CO₂, the equivalent CO₂ permeance, measured using a CO₂/N₂ mixture, decreases constantly with CO₂ partial feed pressure. The authors state that the distinct trend of CO₂ permeance in the binary mixture can be rationalized by considering not only the CO₂ plasticization effect, but also the competition phenomena induced by the coexistence of a second permeating gas, N₂. The gradual saturation of unrelaxed molecular-scale gaps between polymer chain segments by molecules of two different gases, can affect both solubility and diffusivity coefficients. It could be assumed that the antiplasticizing effect of a second competing gas, would be more intense when its concentration in the mixture becomes higher, point where CO₂ plasticization phenomena is completely offset by competitive sorption effects. These conclusions are also reported by S. P. Kaldis and Sakellaropoulos (1998) and Weller and Steiner (1950).

Although binary-component experiments were performed only for a CO₂/N₂ 80/20 wt% composition, the overall permeance trend with transmembrane pressure change [Figure (3.12)], clearly indicates the distinct behavior from the pure CO₂ permeance profile [Figure (3.8)], which is corroborated by the analysis of G. C. Kapantaidakis and Wessling (2003).

Figure (3.13.b) depicts the dependence of the CO₂/N₂ real selectivity on feed pressure for the three different materials. In absolute values, PES/PI 80/20 fibers exhibit the

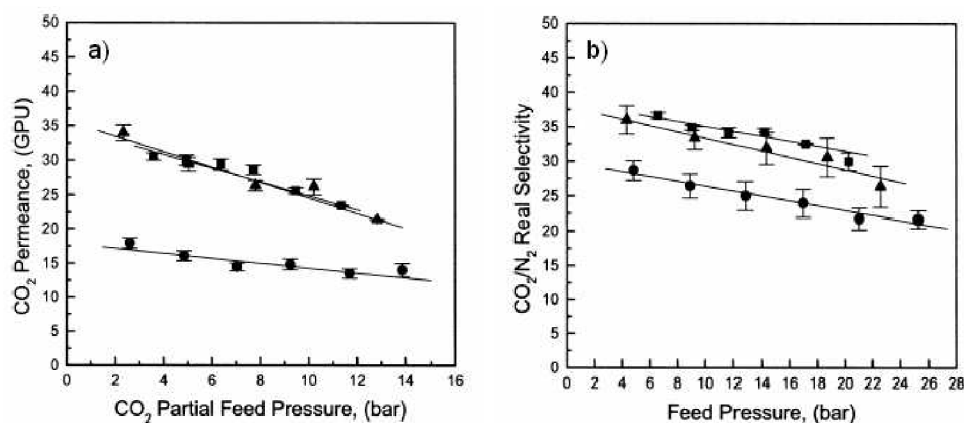


Figure 3.13: a) Effect of CO_2 feed partial pressure on the CO_2 permeance calculated from the CO_2/N_2 45/55 wt% mixed-gas experiments. b) Effect of feed pressure on the CO_2/N_2 real selectivity. ■ PES/PI 80/20, ▲ PES/PI 20/80, ● PI 100% [G. C. Kapantaidakis and Wessling (2003)].

highest real selectivity coefficients, which vary from 37 to 30. This reduction was completely reversible when the membrane modules were decompressed and tested again at low-pressure levels, such as 4 bar. This is an indication that, over the range of conditions studied, no irreversible swelling of the blend membranes has occurred. In fact, the results suggest that a decreasing selectivity is by no means a proof for plasticization.

3.1.5 Summary

From the preceding discussion, the importance of studying the performance of polymer membranes in conditions comparable to real industrial applications (ultra thin asymmetric hollow fibers, high-pressure operation, multicomponent, or at least binary mixtures) is clearly summarily depicted. These ultra thin asymmetric membranes show different CO_2 plasticization behavior. Increase of feed pressure results in an immediate increase of CO_2 permeance and subsequent reduction of the ideal CO_2/N_2 selectivity. However, this accelerated plasticization tendency is not as pronounced when a CO_2/N_2 binary mixture is fed to the PES/PI blend hollow fibers. Competition phenomena from the slower permeating gas, N_2 , reduce the sorption of CO_2 and the magnitude of membrane swelling.

It is important to note that a trade-off has to be made concerning the PES/PI blends. It is not clear if the utilization of the high-cost engineering polyimide offers any significant improvement compared with the traditional type of polyethersulfone. To the

contrary, membranes prepared from pure PI suffered from the most severe aging phenomena. Whether the higher aging resistance of PES/PI blends is due to the intrinsic endurance of pure PES or to specific chemical interactions between the two miscible components remains a speculation. For the specific separation task CO₂/N₂, the traditional glassy polymer of PES competes directly with the novel engineering PI, Matrimid 5218, in terms of stability, cost, and separation performance.

The possibility to execute a set of permeation measurements, with potential membrane materials for commercial gas separations, resulted from the opportunity given by Dr. G.C. Kapantaidakis. Taking advantage of this, one searched for the permeance and selectivity values in the order of magnitude of those applied in modeling work for several gas separations.

3.2 Membrane Modeling

3.2.1 Introduction

Modeling of membrane units provides useful guidelines to achieve desirable separations of multicomponent gas mixtures. The study of the performance of a membrane with precision has special importance in cases of high commercial interest, where the product is a valuable gas or the coupling with other separative unit makes the global process economics more attractive. The simulation can provide information for the design and optimization of the overall separation process with minimum cost and effort, reducing the experimental work that is usually extensive and time consuming. Nevertheless, the majority of the gas transport models, specially in glassy polymers, contain some adjustable parameters which must be determined experimentally [Stern (1994), Ho and Sircar (1992)].

The modeling work concerning membrane permeation was developed during the earlier period of this thesis. The stand-alone membrane model was built for separation of commercially significant multicomponent gas mixtures and validated against literature data. In the simulations performed, the membrane selection was based on [Spillman (1989)]:

- Non-porous gas separation membranes with feasibility for industrial applications (cellulosic derivatives, polysulfone, polyamides and polyimides), where gases are separated on the basis of their solubility and diffusivity through the membrane material;
- Key performance attributes that affect membrane economic utility: selectivity towards the components to be separated (directly impacts the recovery of the process

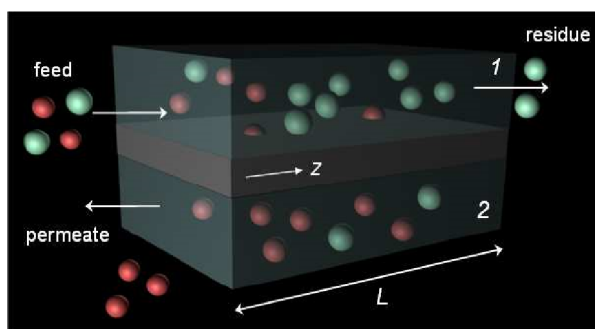


Figure 3.14: Schematic diagram of the membrane unit. L is the axial length of the membrane. The feed and permeate sides are named zones 1 and 2, respectively.

and indirectly affects membrane area and feed gas flow requirements) and membrane flux or permeability (dictates the amount of membrane required);

- Life of the membrane (maintenance and replacement costs).

It is stated in open literature that the membrane performance is mainly characterized by its penetrant transport properties, permeability and selectivity.

3.2.2 Process Description

The geometry of the membrane unit is presented in Figure (3.14). Simulations were performed for separation of commercially significant multicomponent gas mixtures using polymer permeation properties similar to those of polysulfone. The mathematical model for the membrane module was validated against [D. T. Coker and Fleming \(1998\)](#) work for H_2 separation from a multicomponent gas mixture of methane, ethane, ethylene and propane, using an hollow-fiber contactor.

Hydrotreatment is a common unit operation in refineries. In this process, petroleum intermediates are contacted with hydrogen under appropriate conditions to reduce the sulfur, nitrogen, metals, asphaltene, and carbon residue content of the feedstock. This process requires substantial amounts of hydrogen gas, and much of the excess hydrogen is available for recycle. Membranes are often used to purify the recycled hydrogen. The major impurities are light hydrocarbons. The composition of a typical feedstream to a membrane hydrogen purification from a hydrotreater is given in Table (3.4). The simulation parameters used for this separation are provided in Table (3.5).

The H_2 product is obtained at lower pressure than the feed in the permeate stream. The permeate pressure is an important process variable since the utility of the H_2 produced by the membrane process depends, in part, on the pressure at which this component is

Table 3.4: Permeance and feed composition for H₂ separation simulations. The membrane permeance values are roughly those expected for a polysulfone membrane with an 0.1 μm thick effective separating layer.

Hydrogen Separation		
Component	Feed mole fraction	Permeance GPU
H ₂	0.650	100.00
C ₂ H ₄	0.025	3.03
CH ₄	0.210	2.86
C ₂ H ₆	0.080	2.00
C ₃ H ₈	0.035	1.89

produced. Generally, the H₂ produced in the permeate stream is more valuable or useful if it is produced at higher permeate pressure to minimize or avoid recompression costs.

3.2.3 Theoretical Model

Component material balance, overall material balance, momentum balance, and energy balance equations are written for each membrane zone. The molar flux of component i due to permeation and the energy balance in the membrane are also included. The representative hollow fiber is divided into 50 NoP elements in the axial direction.

To simplify the computational model, the following assumptions are considered:

Table 3.5: Module and process simulation parameters.

Hydrogen Separation	
Feed	shell
Feed pressure (bar)	76.9/42.4
Permeate pressure (bar)	42.4/7.9
Feed temperature (°C)	50
Fiber OD/ID (μm)	300/150
Fiber length (m)	1
Fiber pot length (m)	0.1
No. of fibers	500000
Membrane area (m ²)*	377

* Active area is calculated as $\pi(\text{Fiber OD})(\text{Fiber length} - 2(\text{Fiber pot length}))(\text{No. of fibers})$

- Ideal gas law applies.
- Shell side pressure change is negligible and bore side pressure change is given the Hagen-Poiseuille equation.
- An hollow fiber polysulfone membrane is considered and all fibers have uniform inner and outer radius as well as a uniform thickness (0.1 μm) separation layer.
- The deformation of the hollow fiber under pressure is negligible.
- Shell side feed and countercurrent contacting are assumed.
- The normal assumption of steady state operation is not considered here, because the model will be subsequently linked to that of the pressure swing adsorption unit.
- The gas on the shell side of the hollow fibers and in the lumen is in plug flow.
- Negligible time lag due to passage of gas molecules through the membrane, i.e., a permeate stream is obtained instantaneously as the high pressure feed is supplied to the membrane.
- Axial dispersion is considered negligible and constant permeances are assumed.

It is reported that, when the gas permeance values are considered constant and pressure independent, the membrane separation performance is clearly overestimated [G. C. Kapantaidakis and Wessling \(2003\)](#). Nonetheless, some modeling results from [S. P. Kaldis and Sakellaropoulos \(1998\)](#); [Weller and Steiner \(1950\)](#) suggest that the separation performance is insensitive to the applied flow conditions inside the specific PES/PI modules, which correspond to the membrane type applied in the experimental work. Simulation predictions from [G. C. Kapantaidakis and Wessling \(2003\)](#) report a relative deviation varying between 0.3 and 1.4%. Hence, for simplicity reasons, constant permeances were always assumed in the modeling work.

The molar flow of component i due to permeation is given by

$$N_{i,1 \rightarrow 2} = \wp_i (P_1 y_{i1} - P_2 y_{i2}), \quad (3.13)$$

where $\wp_i$ is the permeance of species i (i.e., the permeability divided by active layer membrane thickness), and P_1 and P_2 are the feed and permeate pressures on both sides of the membrane, respectively. For both membrane zones 1 and 2, i.e., for the shell and bore sides of the module, the following equations were considered:

1. Material balance equations

- **Global material balance**

The global material balance equations in both residue ($k = 1$) and permeate ($k = 2$) sides of the membrane are

$$\frac{\partial c_k}{\partial t} + \frac{\partial(v_k c_k)}{\partial z} = (2k - 3) \frac{A_f n_f}{A_k} N_{1 \rightarrow 2}, \quad (3.14)$$

where c_i is the molar concentration of component i in the gas mixture, $c = \sum_i^n c_i$ is the total molar concentration of the gas mixture, A_k is the cross-section area of each membrane zone, v is the gas velocity, t is time and z is bed length position. Since

$$c = \frac{P}{RT}, \quad c_i = \frac{P_i}{RT}, \quad (3.15)$$

the global balance can be rewritten as

$$\frac{\partial}{\partial t} \left(\frac{P_k}{T_k} \right) + \frac{\partial}{\partial z} \left(\frac{v_k P_k}{T_k} \right) = (2k - 3) \frac{A_f n_k R}{A_k} N_{1 \rightarrow 2} \quad (3.16)$$

$$\Leftrightarrow \frac{1}{T_k} \left(\frac{\partial P_k}{\partial t} - \frac{P_k}{T_k} \frac{\partial T_k}{\partial t} \right) + \frac{\partial}{\partial z} \left(\frac{v_k P_k}{T_k} \right) = (2k - 3) \frac{A_f n_k R}{A_k} N_{1 \rightarrow 2}. \quad (3.17)$$

The pressure drop on the shell side of the fibers is generally neglected [[A. S. Kowali and Khan \(1992\)](#)]. In the permeate side, pressure change is calculated using the Hagen-Poiseuille relation for laminar flow [[R. B. Bird and Lightfoot \(1960\)](#)]. Hence, when the pressure drop in one of the zones (say zone k) is negligible, then

$$\frac{\partial P_k}{\partial z} \approx 0, \quad 0 < z < L, \quad t \geq 0. \quad (3.18)$$

When the pressure drop is modeled using the Hagen-Poiseuille-type relation, as in the permeate side, then one have

$$-\frac{\partial P_k}{\partial z} = \alpha_k \mu v_k, \quad (3.19)$$

where μ is the gas mixture viscosity and α_k is a constant dependent on the geometry of the cross section. In the bore-side of the membrane, $\alpha = 8/r_i^2$, with r_i the inner radius of the hollow fiber.

- **Individual material balance**

The differential material balance equations to component i in both zones of the membrane are given by

$$\frac{\partial c_{ik}}{\partial t} + \frac{\partial(v_k c_{ik})}{\partial z} - \frac{\partial}{\partial z} \left(k_k c \frac{\partial y_{ik}}{\partial z} \right) = (2k - 3) \frac{A_f n_f}{A_k} N_{i,1 \rightarrow 2}, \quad (3.20)$$

which can be rewritten as

$$\frac{\partial}{\partial t} \left(\frac{P_{ik}}{T_k} \right) + \frac{\partial}{\partial z} \left(\frac{v_k P_{ik}}{T_k} \right) - \frac{\partial}{\partial z} \left(\frac{k_k P}{T_k} \frac{\partial y_{ik}}{\partial z} \right) = (2k - 3) \frac{A_f n_f R}{A_k} N_{i,1 \rightarrow 2}, \quad (3.21)$$

$$\begin{aligned} \Leftrightarrow \frac{1}{T_k} \left(\frac{\partial P_{ik}}{\partial t} - \frac{P_{ik}}{T_k} \frac{\partial T_k}{\partial z} \right) + \frac{\partial}{\partial z} \left(\frac{v_k P_{ik}}{T_k} \right) - \frac{\partial}{\partial z} \left(\frac{k_k P}{T_k} \frac{\partial y_{ik}}{\partial z} \right) \\ = (2k - 3) \frac{A_f n_f R}{A_k} N_{i,1 \rightarrow 2}, \end{aligned} \quad (3.22)$$

with $i = 1, \dots, \text{NoC}$, and k_{ik} the axial dispersion coefficient of species i , which accounts for molecular diffusion and hydrodynamic dispersion.

2. Energy balance equation

For completeness, one derives a nonisothermal model of the membrane module. Note, however, that in the hybrid systems developed the membrane operates isothermally. Nonisothermal modeling work of gas permeation is rare in the open literature [A. S. Kowali and Khan (1992); D. T. Coker and Fleming (1998, 1999); K. R. Krovvidi and Khan (1992); S. W. Smith and Rautenbach (1996)]. The energy balance in zone 1 of the membrane is expressed as

$$\frac{\partial(v_1 c_1 H_1)}{\partial z} - k_{g1} \frac{\partial^2 T_1}{\partial z^2} + \frac{\partial(c_1 H_1)}{\partial t} - \frac{\partial P_1}{\partial t} = -\frac{A_f n_f H_1}{A_1} N_{1 \rightarrow 2} + \frac{A_f n_f h_{1m}}{A_1} (T_m - T_1), \quad (3.23)$$

where k_{g1} is the thermal dispersion coefficient of the gas in the shell side, $H_{1,2}$ is the molar enthalpy of the gas mixture on each side of the membrane, and h_{1m} is the shell-side wall heat transfer coefficient. Taking into account the global material balance, the preceding equation can be written as

$$C_{pg} c_1 \frac{\partial T_1}{\partial t} - \frac{\partial P_1}{\partial t} + v_1 c_1 C_{pg} \frac{\partial T_1}{\partial t} - k_{1g} \frac{\partial^2 T_1}{\partial z^2} = \frac{A_f n_f h_{1m}}{A_1} (T_m - T_1). \quad (3.24)$$

In a similarly way as in zone 1, the energy balance equation for the permeate side of the membrane ($k = 2$) is

$$C_{pg} c_2 \frac{\partial T_2}{\partial t} - \frac{\partial P_2}{\partial t} + v_2 c_2 C_{pg} \frac{\partial T_2}{\partial t} - k_{2g} \frac{\partial^2 T_2}{\partial z^2} = \frac{A_f n_f C_{pg}}{A_2} (T_m - T_2) N_{1 \rightarrow 2} + \frac{A_f n_f h_{2m}}{A_2} (T_m - T_2), \quad (3.25)$$

where h_{2m} is the bore-side wall heat transfer coefficient. The energy balance in the membrane is expressed as

$$C_{pm} \frac{\partial T_m}{\partial t} - k_m \frac{\partial^2 T_m}{\partial z^2} = \frac{A_f}{A_m} [C_{pg} (T_1 - T_m) N_{1 \rightarrow 2} + h_{1m} (T_1 - T_m) + h_{2m} (T_2 - T_m)], \quad (3.26)$$

with $N_{1 \rightarrow 2} = \sum_i N_{i,1 \rightarrow 2}$, T_m the membrane temperature, A_f the surface area of active layer per unit of fiber length, A_m is the cross-sectional area of a fiber, k_m is the thermal conductivity of the membrane material, C_{pg} the gas heat capacity, and C_{pm} the heat capacity of membrane per unit fiber length.

3. Auxiliary variables

Several auxiliary variables were defined in order to analyze the performance of the unit. The inlet ($z = 0$) and exit ($z = L$) molar flows at both zones of the membrane were defined as

$$N_{ok} = (3 - 2k) \frac{A_k v_{ok} P_k}{RT_{ok}}, \quad N_{Lk} = (3 - 2k) \frac{A_k v_{Lk} P_k}{RT_{Lk}}, \quad (3.27)$$

where $k = 1$ and $k = 2$ for residue and permeate sides of the unit, respectively. The percentage recovery of product i is given by

$$P_{i,rec} = \frac{y_{i,o2} N_{o2}}{y_{i,o1} N_{o1}} 100. \quad (3.28)$$

4. Boundary conditions

The modeling of the membrane unit accounts for the following inlet ($z = 0$)/outlet ($z = L$) boundary conditions in zone 1:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0 & \text{for pressure dynamics,} \\ P_{1io} = y_{in} P_1, \quad v_{o1} = v_{in}, \quad T_{1o} = T_{in} & \text{for } z = 0, \\ \frac{\partial^2 P_{1i}}{\partial z^2} = 0, \quad \frac{\partial^2 T_1}{\partial z^2} = 0 & \text{for } z = L. \end{array} \right. \quad (3.29)$$

For the zone 2 the boundary conditions are

$$\left\{ \begin{array}{ll} P_{o2} = P_L & \text{for } z = 0, \\ \frac{\partial^2 P_{2i}}{\partial z^2} = 0, \quad \frac{\partial^2 T_2}{\partial z^2} = 0 & \text{for } z = 0, \\ v_{L2} = 0, \quad \frac{\partial P_{2i}}{\partial z} = 0, \quad \frac{\partial T_2}{\partial z} = 0 & \text{for } z = L, \end{array} \right. \quad (3.30)$$

5. Initial conditions

The initial conditions defined at $t = 0, \forall z$ are

$$P_1 = P_H, \quad T_1 = T_{in}, \quad P_1 = y_{in} P_H, \quad (3.31)$$

$$T_m = T_{in}, \quad P_{2,j} = P_L, \quad (3.32)$$

$$P_2 = y_{in} P_L, \quad T_{2j} = T_{in}, \quad (3.33)$$

with P_H the feed pressure, P_L the lower permeate pressure, (1, 2) subscripts the shell and bore-sides of the membrane, respectively, and *in* subscript denoting the feed conditions.

The membrane model was implemented and solved in gPROMS. Further details are given in Chapter 5.

3.2.4 Model Validation, Results and Analysis

The model was validated using the conditions presented in Table (3.5) for a feed flow rate of 0.079 m³ (STP)/s (STP: 0°C, 1 atm). The following relation was assumed for the cross-section areas of each side of the membrane

$$\frac{A_1}{A_2} = \frac{n_f \pi R_o^2 / 2}{n_f \pi R_i^2 / 2} = \left(\frac{R_o}{R_i} \right)^2 = 4 \quad (3.34)$$

Figure (3.15) shows the steady-state permeate and residue composition profiles for H₂ and CH₄, as a function of the axial position in the module, for a case that exhibits high permeate recovery. For a feed-to-purge pressure ratio (P_H/P_L) of 5.37 and a feed flow rate of 0.079 m³ (STP)/s, the total permeate recovery was 94.6% against 94.4% obtained from D. T. Coker and Fleming (1998). At these conditions, the H₂ product purity is 68.7%. z/L is the normalized axial coordinate in the module, and L is the active fiber length, which is the total fiber length (1 m) less than the length of the potted ends of the fibers (0.2 m). The residue end of the module is at $z = 0$, and $z = L$ corresponds to the feed and permeate ends of the module.

As one can see, there is a very good agreement between the results obtained and the ones reported by D. T. Coker and Fleming (1998) work. The H₂ concentration decreases rapidly from the feed end of the module ($z/L = 1$) where it permeates through the membrane. The H₂ partial pressure on both permeate and residue sides are equal between $0 < z/L < 0.76$, where the composition profiles becomes extremely small near the residue end of the membrane. As stated by D. T. Coker and Fleming (1998), to get the referred high H₂ recovery value, only 20% of the membrane area is efficiently used for H₂ purification. This example serves to illustrate that, the CH₄ composition, a component with an intermediate permeance value in the mixture, shows a maximum with axial position ($z/L = 0.74$), which is typically observed in multicomponent permeation.

The performance curve for the simulated system is shown in Figure (3.16). Changing the feed flow rate and using the simulation parameters described in Tables (3.4, 3.5), it is possible to obtain the H₂ purity/recovery profile. In both cases, the pressure difference between the feed and permeate streams is maintained constant at 34.7 bar. However, as one can see, the ratio of feed to permeate pressure is quite different for the two cases. When the pressure ratio is higher, H₂ recovery is higher at each H₂ purity or, alternatively, H₂ purity in the permeate is higher at any recovery even though absolute feed pressure is lower. Nevertheless, this enhancement in the separation performance comes

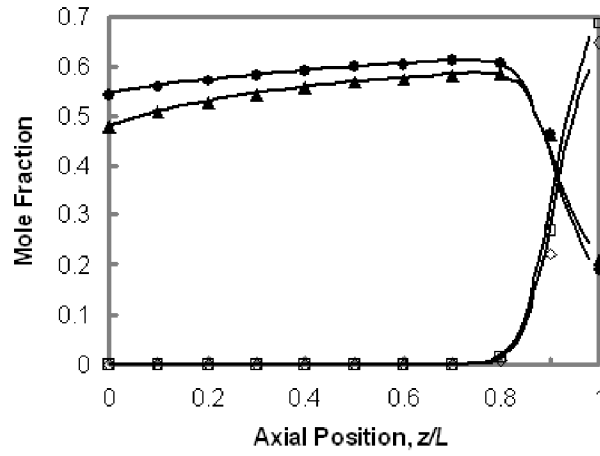


Figure 3.15: Steady-state H_2 and CH_4 composition profiles in permeate and residue sides of the membrane as a function of axial position in the module ($P_H = 42.4$ bar, $P_L = 7.9$ bar). The symbols denote the data from [D. T. Coker and Fleming \(1998\)](#) for CH_4 permeate $\bullet$, CH_4 residue $\blacktriangle$, H_2 residue $\diamond$ and H_2 permeate $\square$. The solid lines represent the simulated results.

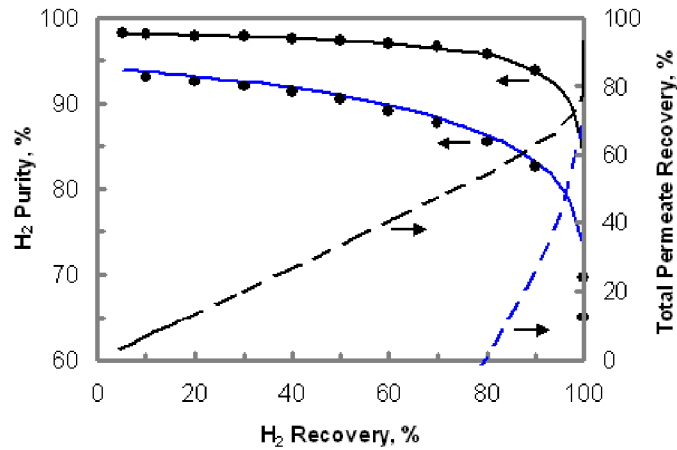


Figure 3.16: H_2 performance characteristic curve for $P_H/P_L = 5.37$. The symbols $\bullet$ denote the data from [D. T. Coker and Fleming \(1998\)](#) and the solid lines represent the simulated results. The black color corresponds to $P_H/P_L = 5.37$ ($P_H = 42.4$ bar, $P_L = 7.9$ bar) and the blue one is relative to $P_H/P_L = 1.81$ ($P_H = 76.9$ bar, $P_L = 42.4$ bar).

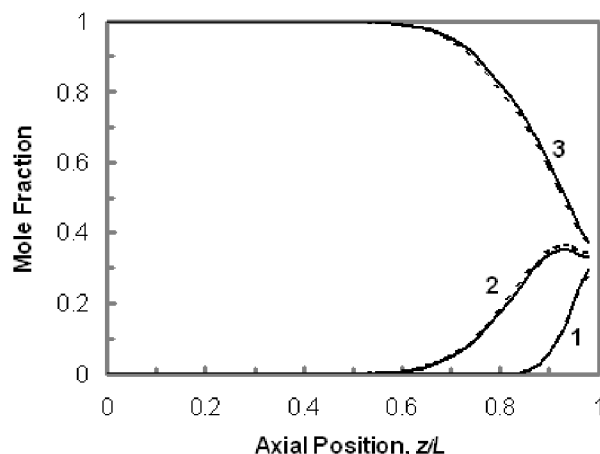


Figure 3.17: Residue and permeate concentration profiles in an equimolar ternary case for a feed flow rate of $0.079 \text{ m}^3 \text{ (STP)/s}$, and a pressure ratio, $P_H/P_L = 1.35$ ($P_H = 57.4 \text{ bar}$, $P_L = 42.4 \text{ bar}$). The continuous lines correspond to the permeate streams and the dashed ones represent the residue streams.

with a penalty, since the permeate pressure is lower in the higher-pressure ratio case and would, therefore, result in more recompression costs if the H_2 needed to be supplied to a downstream process or recycled at, for example, the feed pressure. These results suggest an economic trade-off between compression costs, and show the typical relation between component purity and recovery.

Figure (3.17) shows further simulation results in accordance with [D. T. Coker and Fleming \(1998\)](#) conclusions. A ternary case was selected for studies of the maxima in composition profiles because this is the simplest case which, with constant permeability coefficients, can exhibit the maxima in compositions seen in the five component refinery case. One used an equimolar feed mixture of three components (1, 2, 3) with the permeances 500, 100 and 10 GPU, respectively. Typical composition profiles are presented for the same feed flow rate of $0.079 \text{ m}^3 \text{ (STP)/s}$, and a pressure ratio, $P_H/P_L = 1.35$ ($P_H = 57.4 \text{ bar}$, $P_L = 42.4 \text{ bar}$). The residue and permeate composition of the most permeable component (that is, component 1) decreases as z/L (that is, distance from the residue end of the module) decreases since this component is most efficiently stripped from the feed. The residue and permeate compositions of component 3, the least permeable component, increase monotonically as z/L decreases, which reflects the enrichment of the residue stream in this component (due to selective removal of the other more permeable species) as distance from the feed end of the membrane increases. The residue and permeate compositions of component 2, whose permeability is intermediate between that of

the other components, exhibit a maximum.

In a mixture of two components, the composition of the more permeable component always increases in both the permeate and residue as the distance from the closed (that is, residue) end of the fibers is increased and vice-versa for the less permeable component. In a three-component mixture, a very permeable component will be largely removed from the feed in a relatively short distance from the feed end of the fibers, which will increase the composition of the remaining two components in the residue. Then, the composition of the second most permeable component must begin to decrease as this component is selectively removed from the residue, and the composition of the least permeable component will continue to increase over the entire length of the fibers. In this way, in mixtures with at least three components, maxima in the compositions of components of intermediate composition may be observed. The staging of membrane modules in series could be used to harvest components of intermediate permeability at maximum concentration.

Spillman (1989) used as an example a binary natural gas feed stream (CH_4/CO_2 90/10 wt%), where the product gas is 97% CH_4 delivered as residue. The following generalizations can be made for single-stage membrane processes:

- Increasing the membrane area results in a purer residue, and decreasing the membrane area results in a purer permeate. Recovery drops as the purity requirements is increased.
- Increasing the transmembrane pressure will minimize the membrane requirements and improve the recovery of the residue product.
- For a constant transmembrane pressure, an increase in the permeate pressure induces a decrease of the residue recovery and an increase in membrane requirements.
- There is an opposite trade-off between purity and recovery. The purer the product, the lower the recovery, with increasing of the membrane requirements.
- Feed flow rate impacts the membrane requirements. An increase in feed flow reduces residue purity, but increases recovery.
- An economical compromise of membrane capital and operating costs, compression costs and product losses has to be considered in the membrane process design.
- For very high purity requirements the membrane became less efficient and thus, it serves as good applications for bulk separations prior to a second purification system, such as PSA or cryogenic treatment.

3.2.5 Summary

The modeling work concerning membrane permeation was developed for separation of commercially significant multicomponent gas mixtures using polymer permeation properties similar to those of polysulfone. The mathematical model for the membrane module was successfully validated against [D. T. Coker and Fleming \(1998\)](#) work for H₂ separation from a multicomponent gas mixture of methane, ethane, ethylene and propane, using an hollow-fiber contactor.

Chapter 4

Adsorption Experiments and Modeling

4.1 Adsorbent Selection and Characterization

The literature review showing detailed information, which relates directly to the design, effectiveness and operation of carbon guard beds in ANG, is somewhat scarce. The desirable characteristics of active carbons for guard-bed applications, the design of the guard beds themselves, e.g., fixed or mobile, and their method of operation, i.e., heated or non-heated, have not yet been studied or evaluated in real depth.

The selection and the optimization of a carbon adsorbent for guard-bed applications are based on the following issues:

- The high relative pressures of the trace components suggest the need for a carbon with a high adsorption capacity, i.e., one containing a high microporous volume.
- However, the micropores cannot be too small to slow down or even suppress the adsorption kinetics of the larger hydrocarbons; this issue cannot be neglected, since the characteristic residence time of the gas in the guard bed is considerably shorter than that in the main storage system.
- The adsorbent must also provide easy desorption to prevent retention of the higher hydrocarbons on the guard bed, which would increase the heat requirements for its regeneration and shorten its operating life.
- Lastly, the adsorbent should possess high thermal conductivity, a property that favors high-density carbons, in order to dissipate and subsequently recover the heats

of adsorption and desorption, which would allow an effective restoring of its original capacity using heat management techniques.

Enhanced thermal conductivity is advantageous during rapid charge and discharge situations. Since physical adsorption is an exothermic process, the adsorbent heats during adsorption. Similarly, desorption is an endothermic process and, therefore, the adsorbent temperature drops as the gas is desorbed. These temperature changes have design implications and, therefore, minimizing the temperature changes is particularly important. The amount of gas adsorbed decreases as the temperature increases. Therefore, during charge the adsorbent capacity is diminished by the rise in its temperature. When the adsorbent cools during discharge the gas pressure drops and the adsorbed gas is not released. Enhanced thermal conductivity will tend to reduce the significance of the two phenomena.

Therefore, the desired guard-bed adsorbent is one that combines high adsorptive capacity, no sieving effects for the larger impurities, fast adsorption kinetics, low retentivity, and which also has good thermal conductivity.

At the beginning of the ANGWARD project the technical approach for the optimal guard bed carbon was to focus on commercially manufactured activated carbon, as opposed to a specialized or novel carbon product. Generally, commercial grades of activated carbon have the advantages of larger scale availability, lower cost, extended options of particle size and adsorption activity. Available commercial carbon grades include those derived from coconut shell, coal, or wood precursors, each generally obtainable in either powder, granular or pelletized (extruded) forms. So, an initial selection of twelve potential carbon formulations was tested for uptake and desorption performance, using butane as a model adsorbate, according to the protocol outlined below. This allowed an iterative development process so that promising carbons could be further modified to improve performance. Carbon selections included those manufactured from high temperature steam activation of carbonized coconut shell, bituminous coal and pre-treated lignite (brown coal).

The objective was to develop advanced carbon adsorbents for the guard bed that show efficient trapping of the higher hydrocarbons and odorant species on the charge cycle, allied to the easiness of desorption and regeneration on the discharge cycle. This work package was carried out in close collaboration with SSCL and Advantica.

The initial screening process at SSCL involved the analytical testing of potential carbons for the selection of the appropriate adsorbent. Carbon testing included:

- physicochemical properties (Particle size range - Sieve analysis; Bulk Density - Packing Density (weight per unit volume determination); Activation level - Carbon tetrachloride (CTC)% adsorption - Vapor phase adsorption of carbon; Tetrachloride solvent at 298 K to saturation; BET Surface Area and Micropore Distribution Analysis - 77 K Nitrogen isotherm determination using Coulter Omnisorb 610 instrumentation; Mesopore and Macropore determination using Carlo Erber Porosimeter 4000 - Mercury intrusion)
- *n*-butane adsorption/desorption testing at 298 K and at atmospheric pressure. Adsorption/Desorption testing at SSCL used *n*-butane as a surrogate for the higher hydrocarbons found in NG. The test involves flowing 100 cm³/min flow of *n*-butane gas through a 10 cm³ bed of pre-weighed activated carbon until the carbon is saturated, i.e., until no further increase in weight can be measured. Calculation of weight increase gives Butane Saturation Capacity usually quoted in g butane/100 g carbon, or more usefully as g/100 cm³. The subsequent desorption test involves directing a 100 cm³/minute flow of dried air through the 10 cm³ saturated carbon sample at 298 K for a total of 20 minutes (200 bed volumes of desorption air flow). In practice, periodic weighing of the desorbing carbon is also made at 5, 10 and 15 min. air flow throughput. Calculation of weight loss determines the Working Capacity of the carbon at 200 bed volumes desorption at 298 K.

A series of carbon adsorbents was developed by SSCL, in UK, and identified showing promising performance in terms of adsorption and desorption of NG components. The adsorbent selection covered five hydrophobic (nonpolar surface) carbons as prospective candidates for guard bed applications. Samples of these carbons were provided to FCT/UNL for further testing to acquire data for model development. The pre-selected carbons were designated as project test samples **ANGUARD 1** to **5** respectively as follows:

- **ANGUARD 1** - Granular, higher density carbon, coconut shell based medium activation.
- **ANGUARD 2** - Granular coal based carbon, slightly higher activity than 1.
- **ANGUARD 3** - Smaller particle size granular carbon, lignite-coal based, low density, decolourising carbon, wider pore structure, lower retention capacity.
- **ANGUARD 4** - Granular, coconut shell carbon, appreciable activity level (119% CTC).
- **ANGUARD 5** - Extruded carbon (2 mm diameter pellets) coal based, high activity (109% CTC).

Table 4.1: Characteristics of ANGWARD carbons 1 to 5.

	ANGUARD 1	ANGUARD 2	ANGUARD 3	ANGUARD 4	ANGUARD 5
Carbon size mm	2.36 x 1.18	2.36 x 1.00	1.70 x 0.425	2.00 x 0.6	2mm pellets
ASTM Mesh Size	8 x 16	8 x 18	12 x 40	10 x 30	
B. Density g cm⁻³	0.49	0.43	0.28	0.40	0.40
CTC Sorption	65%	77%	110%	119%	109%
NITROGEN POROSIMETRY 77K					
BET Surface Area m² g⁻¹	746	1068	1227	1669	1342
Total Pore Volume cm³ g⁻¹	0.318	0.541	1.063	0.819	0.850
Micropore Volume cm³ g⁻¹	0.308	0.499	0.719	0.771	0.777
Narrow Micropore Vol. cm³ g⁻¹	0.261	0.322	0.320	0.516	0.367
Broad Micropore Vol. cm³ g⁻¹	0.047	0.177	0.399	0.258	0.410
MERCURY POROSIMETRY					
Total Pore Volume cm³ g⁻¹	0.225	-	1.137	0.673	0.881
Mesopore Volume "	0.114	-	0.392	0.416	0.413
Macropore Volume "	0.111	-	0.745	0.257	0.468

Note:	Nitrogen	Total Pore Volume	0 - 200 $\text{\AA}$ width	Mercury	Total Pore Volume	20 - 10 ³ $\text{\AA}$ width
		Micropore Volume	0 - 20 $\text{\AA}$ width		Mesopore "	20 - 500 $\text{\AA}$ width
		Narrow Micro. Vol.	0 - 6 $\text{\AA}$ width		Macropore "	500 - 10 ³ $\text{\AA}$ width
		Broad Micro. Vol.	6 - 20 $\text{\AA}$ width			

Table (4.1) presents the characteristics of ANGWARD carbons 1 to 5 selected. Since the guard bed is a fixed volume, comparison of performances on an uptake per unit volume basis (g/cm³) is the more relevant parameter for comparing performance.

ANGUARD 1 carbon is significantly retentive, with a butane working capacity (BWC) of 3.05 g/100 cm³, some 24.3% of the Saturation Capacity.

ANGUARD 2 carbon, is less retentive. BWC is 5.17 g/100 cm³, being 44.5% of its Saturation value.

ANGUARD 3 carbon takes up an appreciable amount of butane per unit weight (36.17 g/100 g). However, uptake on a volume basis is comparatively low (10.02 g/100 ml) due to the lower packing density of the carbon (0.28 g/cm³). Nevertheless, the carbon is less retentive, with a Working Capacity of 5.56 g/100 cm³, or 55.4% of the Saturation Uptake.

ANGUARD 4 carbon, a small granular coconut shell carbon with the highest CTC activity of the five carbons, also gives the highest Butane Saturation value (16.34 g/100 cm³).

Table 4.2: Main characteristics of the ANGWARD 5 carbon sample used in this work (volumes are expressed in cm³/g).

N ₂ adsorption at 77 K		Mercury porosimetry	
BET surface area (m ² /g)	1342	Total pore volume (20-10 ⁵ Å)	0.881
Total pore volume (< 200 Å)	0.850	Mesopore volume (20-500 Å)	0.413
Micropore volume (< 20 Å)	0.777	Macropore volume (500-10 ⁵ Å)	0.468
Narrow micropore volume (< 6 Å)	0.367		
Broad micropore volume (6-20 Å)	0.410		

However, the coconut shell precursor does influence butane retention. Working Capacity (5.58 g/100 cm³) represents only 34.1% of Saturation value. Thus, ANGWARD 4 carbon has a high Saturation Uptake and a high retention property. In ANG guard-bed applications, this carbon would desorb components more slowly with reverse gas throughput (which might be an advantageous characteristic) and would require heat input to fully regenerate.

ANGWARD 5 carbon is a high activity (109% CTC) pelletized carbon (2 mm extruded diameter) with a relatively good packing density value. Butane Saturation capacity is high (16.01 g/100 cm³). Butane retention is advantageously low, which results in the highest Butane Working Capacity of the five carbons (8.89 g/100 cm³), or 55.5% of the saturation value. This carbon was found to be very promising for ANG guard bed applications.

From a diversity of commercially available activated carbons tested at SSCL, two carbon grades have been identified as candidate adsorbents for ANG guard-bed applications: ANGWARD 4 and 5. Each of the two candidate carbons has a high sorption capacity for hydrocarbons, although they were proven to have disparate retention properties. ANGWARD 4, a coconut shell carbon, have greater retention property than the coal based product ANGWARD 5. Nevertheless, ANGWARD 5 carbon is an extruded form, giving higher density, better mechanical strength and less dusting which is a practical product for use in guard-bed applications.

Thus, the carbon selected for further research is ANGWARD 5. The carbon was also characterized at FCT/UNL, using N₂ adsorption at 77 K and mercury porosimetry. A surface chemistry analysis using the PZC method and Bohem titration revealed that the carbon surface is mostly clean of acidic groups (see Appendix C). The structural characteristics of the ANGWARD carbon sample selected for study are listed in Table 4.2.

4.2 Adsorption Equilibrium Measurements

4.2.1 Introduction

The extensive adsorption equilibrium data measured experimentally during the thesis was performed under the ANGWARD project and, since the components to be separated through the hybrid PSA/membrane process developed are common to natural gas components, the work described in this section served for both researches on the adsorbent selected.

4.2.2 Experimental Description

The adsorption equilibria of the *n*-alkanes C₁–C₄ and of the odorants TBM and THT on SSCL carbon were measured gravimetrically using a high-pressure magnetic suspension balance (MSB) ISOSORP 2000 from Rubotherm (GmbH), driven with in-house-developed Labview software. TBM and THT are currently two of the more widely used odorants for natural gas supply streams. All gases employed were obtained from Praxair Portugal Gases and Air Liquide Portugal. Figure (4.1) shows the MSB and its components. The operating principles of this high-precision balance and the corrections due to buoyancy forces are described in Appendix B.

4.2.2.1 Adsorbent Sample Pre-Treatment

Before the adsorption runs, some preliminary experiments were carried out to study the best way to prepare the adsorbent sample. Since the samples have a relatively high BET surface area and were previously subjected to high temperature pre-treatments, they can be exposed to higher degassing temperatures without decomposition or degradation. The temperature limitation of the balance (100°C) could be a limiting problem for the degassing procedure of the sample if high temperatures were needed. Experiments in the MSB at 90°C and vacuum, with and without inert passage, were carried out, starting either with a sample exposed at ambient conditions or saturated in high humidity conditions for several hours. In the first case, values lower than 7% in weight were obtained, whereas in the second case, the humidity weight loss was nearly 33%. The regular carbon sample was also subjected to high vacuum at 300°C during 24 h, and revealed a loss about 9%. Nevertheless, the important issue is that after a certain period of time the sample weight, on-line monitored with the in-house Labview software (BioCTR), stabilized, indicating that, at the in-site possible conditions, the sample was ready for the adsorption experiments. Hence, the degassing procedure was defined as a period of 4 - 5 hours at

4.2 Adsorption Equilibrium Measurements



Figure 4.1: Magnetic suspension balance components.

80 - 90°C, in vacuum, of the regular carbon sample, usually 2.5 - 3.0 g for *n*-alkanes and 0.025 - 0.04 g for the odorants, prior to each run.

4.2.2.2 Experimental Apparatus

The measurements were carried out with the apparatus shown in Figures (4.2) and (4.3). Gas enters into the sealed chamber of the MSB and pressure is registered at the exit line of the apparatus, by several high accurate pressure sensors, each one for a given pressure range. Temperature is acquired inside the MSB chamber and along the apparatus using temperature sensors. Silicone oil baths, a vacuum pump and a set of valves are also coupled to the system. A complete description of the equipment used is given in Appendix A.

The apparatus was built for temperatures up to 160°C and pressures from high vacuum to 200 bar, although the MSB is limited to 150 bar and 100°C. All fittings, stainless steel

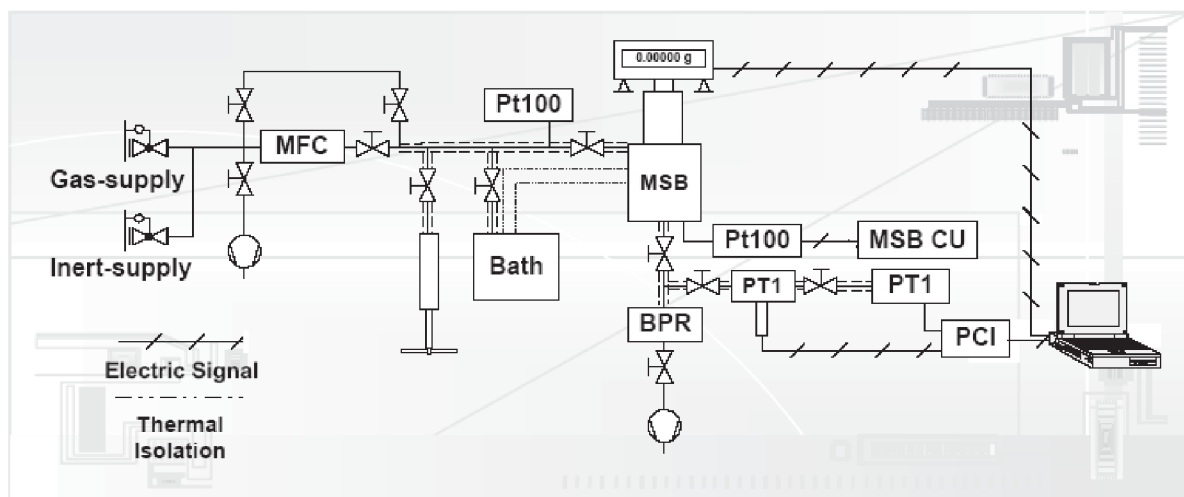


Figure 4.2: Schematic diagram of the experimental apparatus used in the equilibrium measurements.



Figure 4.3: Pictures of the experimental apparatus used in the equilibrium measurements.

(SS) tubing, valves and instrumentation are 1/4" OD Swagelok type. The all apparatus is thermostabilized with flexible thermal insulation. The adsorption chamber was kept at the desired temperature by means of a double-jacket connected to a thermostatic bath Selecta Ultratherm with a circulating fluid, silicone oil (5 and 10 CST of viscosity, i.e. $<10 \text{ mm}^2/\text{s}$) at all operating temperatures. The controlled variable was the signal of a high-pressure thermocouple (4-wire Pt100 probe) inserted directly into the adsorption chamber. This control system coupled with the temperature measuring and control unit, effectively maintains the temperature of the adsorption chamber within $\pm 0.1 \text{ K}$ of the target value.

All the instruments were voltage supplied using typical power suppliers Velleman with variable voltage that cover the range of supply needed for the equipment operation. A couple of Paralab power supplies were also used for instruments like mass-flow controllers and a back-pressure regulator.

The adsorption laboratory apparatus is composed by four main units:

- Feed system unit
- Gravimetric unit with data acquisition
- Pressure measuring and control system
- Temperature measuring and control unit.

Feed Unit:

The feed unit is composed by a 1/4" OD SS tubing system prepared with a secondary vacuum line and two feed lines, one for an inert, and another for the studied component. The vacuum line is connected to a vacuum pump Boc Edwards protected by a glass trap. Mass flow meter/controllers (MFC) Teledyne Hastings HFC-202 (flux range 0.01-30 slpm) are coupled to the feed line. There is also a HiP pressure generator to be applied whenever the desired pressure is higher than the available feed pressure.

Gravimetric Unit:

The gravimetric unit is composed by the MSB, with acquisition of the weight values from the microbalance directly to the PC, and simultaneous pressure data acquisition with a National Instruments PCI-6023E Board. Acquisition is made using Labview construction, where the measurements are monitorized in order to see when equilibrium conditions have been reached. This is done by means of equilibrium criteria (mass, pressure and temperature changes).

Temperature Measuring and Control Unit:

The temperature control unit is composed by:

- a refrigerator Selecta,
- two silicone oil circulating baths Selecta Ultratherm, one for thermostabilize the suspension coupling of the MSB in the double tube thermostat and the measuring cell in the SS double walled jacket, and another for temperature control of the gas,
- a Pt100 temperature probe, connected to the control unit of the MSB and supplied by Rubotherm (GmbH), for temperature measurement on the measuring cell,
- and two Pt100 temperature probes, from RS Amidata, to measure and control gas temperature using an heating cable rolled along the main entrance of the feed gas supply line to the MSB and at the exit end of the installation. These Pt100 probes measure gas temperature and send each signal to a digital controller Ero Electronic which actuates in the cable.

Pressure Measuring and Control Unit:

A back-pressure regulator (BPR) Bronkhrost High-tech P-702C-FAC-020R was used at the exit of the apparatus to control the system pressure whenever needed. Depending on the system pressure range to be measured, several transducers (PT) were used (see Appendix A). The pressure measurements were performed with the following absolute sensors:

1. PT P9071-0003 from Lukas Polaron Schaevitz Sensors, used in the pressure range of 0-5 bar,
2. PT 4090B02A1 piezoresistive pressure sensor from Kistler Instrumente AG, used for pressure measurements up to 200 bar,
3. PT PAA-215/80549.3 from Keller AG, used in the pressure range of 0-1 bar,
4. PT BTE 6035A4 from Technics, used in the pressure range of 0-35 bar,
5. PT P9071-0003 from Lukas Polaron Schaevitz Sensors, used in the pressure range of 0-35 bar,
6. PT PX03D1-3KA5T from Omegadyne Inc., used in the range of 0-3000 psia (207 bar).

4.2.2.3 Experimental procedure

The adsorption data of the *n*-alkanes C₁-C₄, CO₂, He and N₂ were measured according to standard procedures:

- Isothermal pressurization of the adsorption chamber of the MSB containing the carbon sample with the pure gas up to the desired pressure, after previously preparation of the system ($\simeq$ 3-4 g previously weighed several times using an analytical balance and an average of these measurements was used to determine an initial mass of the sample; this mass was confirmed at the initial start-up condition of the MSB).
- Online measurement of pressure, temperature, and weight change of the sample until thermodynamic equilibrium is attained. Adsorption equilibrium is assumed to occur when the change in mass of the sample with respect to time approaches zero (i.e., no mass change is observed over a period of one hour). The gain in sample mass is recorded, and the adsorbed material is determined. At this time, pressure and temperature are acquired. The gas pressure in the adsorption chamber is then increased, and the sample is allowed to reach equilibrium with this new condition. These measurements are repeated until an entire adsorption isotherm is obtained for the sample. Duplicate measurements were made for several adsorbate-adsorbent combinations and the average standard deviation agreed within about 0.38%.

On the other hand, obtaining reliable adsorption equilibrium data for the odorants, TBM and THT, at the very low concentrations usually found in NG (0-25 mg/Nm³; see Appendix D) was a more challenging task. No experimental data was found in literature on the adsorption of NG odorants on activated carbon. The following procedure for the odorant adsorption equilibrium data measurements was performed:

- Measurement of the weight change of the sample upon saturation with various feed concentrations of the odorant diluted in an inert gaseous carrier. For this purpose, calibrated mixtures of TBM in He (6.74 ppmv) and THT in He (6.80 ppmv) were continuously circulated through the adsorption chamber at different pressures. This was possible in practice because, in the adsorption apparatus, the pressure can be spanned and accurately measured over a wide range. This procedure is more convenient than the alternative method of fixing the operating pressure and changing the odorant mole fraction in the feed gas. Preliminary adsorption tests with pure He showed that its adsorption was negligible compared with those of the odorants, even at the low partial pressures considered in the work. It was concluded that helium can be safely used as the inert carrier, without the need for correction of the results. The partial pressure of the odorant is changed by increasing the total

pressure of the mixture up to ≈ 35 bar. This procedure allows us to accurately measure the adsorption equilibrium of the odorants in the concentration range of practical interest.

- A MFC located at the inlet and a BPR placed at the outlet of the system maintained constant both feed flow rate and pressure inside the adsorption chamber. Although the MFC is not strictly necessary, it is useful to maintain constant hydrodynamic conditions in the sample chamber, thereby suppressing fluctuations in the recorded sample weight due to changes in the drag force exerted by the circulating gas.
- When the change in weight attained a steady value, the inlet port was slowly closed while maintaining a constant pressure in the chamber by means of the back-pressure regulator. The final weight was then recorded, keeping in mind that the gas flow must be suppressed before recording the final weight value, to eliminate the drag force exerted by the circulating gas.

These experiments took considerably more time than those for the other gases which employed the conventional gravimetric procedure. During each continuous-flow experiment, the feed stream to the adsorption chamber was routed through a coil immersed in a second temperature-controlled thermostatic bath to maintain consistent isothermal conditions at the inlet of the adsorption chamber. The first temperature-controlled thermostatic bath was used to control the temperature in the MSB jacket. As an example, Figure (4.4) shows a plot of the sample weight and pressure readings during a continuous-flow experiment to obtain a single TBM adsorption isotherm data point measurement on the carbon sample.

4.2.3 Experimental Results and Data Analysis

4.2.3.1 Adsorption Potential Theory

The evaluation of single- and multi-component adsorption models, as applied to ANG storage, suggests that the thermodynamics of multi-component adsorption of a real natural gas (NG) can be predicted using an isotherm model combining the Adsorption Potential [Brunauer (1945)] and Ideal Adsorbed Solution [Myers and Prausnitz (1965), Myers (1989)] theories. The former is useful for correlating single-component isotherm data, whereas the latter predicts multicomponent adsorption equilibrium from single-component adsorption data. Mota and Rodrigo (2000) report a detailed description of the coupling of the two theories. The main advantage of this dual-theory approach is that it reduces the number of equilibrium measurements required to predict the breakthrough profiles of

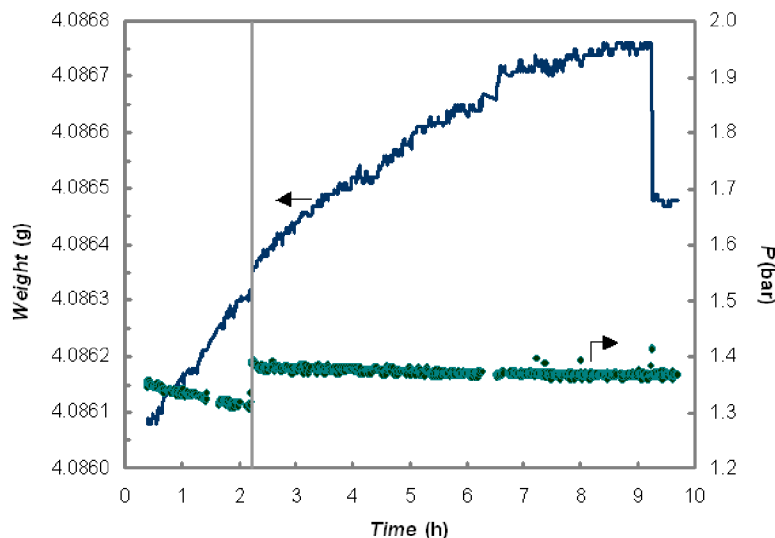


Figure 4.4: Experimental adsorption equilibrium and pressure profiles for a TBM data point measurement on SSCL activated carbon (ANGUARD 5), at 51°C, 1.37 bar of final pressure and a mean flow rate of 5.26 cm³/s. It was necessary to acquire 1019 data points until a steadily TBM data point was reached at this conditions of temperature, pressure and mean flow rate. Vertical gray line represents one night run stop.

the various components of NG. The accuracy of this multi-component adsorption model can be further improved by relaxing the assumption of an ideal adsorbed solution and taking into account adsorbed-phase non-idealities through the use of activity coefficients calculated from molecular simulations and a limited set of experiments.

The Adsorption Potential theory (APT) from Polanyi was then applied to the experimental data performed. The APT has been used extensively for correlating adsorption equilibria on porous adsorbents [C. E. Holland and Ritter (2001a,b); F. Rouquerol and Sing (1999); Yang (1987)]. One of the most widely used theories to describe physical adsorption of gases and vapors onto microporous adsorbents was developed by M. M. Dubinin and co-workers and is generally referred to as the theory of volume filling of micropores [Dubinin (1975)]. It assumes that the very fine pores, micropores, are responsible for adsorption. A strong adsorptive potential exists at the pore surface. The adsorbed species within the micropores are considered to behave as a liquid, although due to the effect of the force field of the adsorbent, the properties of this liquid phase may differ from the properties of the bulk liquid phase at the same temperature. Because of the strength of the potential at the micropore level, the adsorbate condenses during adsorption. The adsorbate fills the volume within the micropores and only the unoccupied volume remains available for adsorption. This is the micropore filling concept.

Once the characteristics of the adsorbent are known, the predicted volume for a different adsorbate can be determined. The physisorption isotherm data can be expressed in the form of a temperature-invariant characteristic curve. The difference in free energy between the adsorbed phase and the saturated liquid sorbate, determined from the ratio of the equilibrium pressure and the saturated vapor pressure of the adsorbate, is referred to as the adsorption potential.

The APT states that for a given gas-solid system the volume of the adsorbed phase, W , is a function of the adsorption potential, $\tilde{\phi}$,

$$W \equiv qV_m = W(\tilde{\phi}), \quad (4.1)$$

where q is the amount of gas adsorbed at equilibrium and $V_m(T)$ is the adsorbed-phase molar volume, which is temperature dependent. At a given temperature, T , and an equilibrium partial pressure of the adsorbate, P , the adsorption potential, that is, the maximum differential molar work, $-\Delta G$, needed to transport one mole of the adsorbate from the liquid or gas phase to a surface of an infinitely large amount of adsorbent is defined as

$$\tilde{\phi} = RT \ln(P_s/P), \quad (4.2)$$

where P is the equilibrium pressure at temperature T , $P_s(T)$ is the saturated vapor pressure of the adsorbate, R is the ideal gas law constant and $-\Delta G$ is the Gibbs free energy. At high pressure, however, P and P_s should be replaced by the corresponding fugacities, f and f_s , to correct non-ideal gas behavior. The functional relationship between $\tilde{\phi}$ and W is characteristic of the particular gas-solid system and is usually referred to as the characteristic curve.

The APT is especially useful for predicting single-component adsorption equilibria from a limited set of experimental measurements. Firstly, the characteristic curve is temperature independent according to the theory. Therefore, only adsorption equilibrium measurements at one temperature are necessary to obtain the characteristic curve, and this is sufficient to describe the adsorption at all temperatures for the same gas-solid system [Agarwal and Schwarz (1988), Yang (1987)]. Secondly, in many cases the theory can be generalized if an affinity coefficient or scaling divisor, β , the polar interactions between adsorbent/adsorbates, is used as a shifting factor to bring the characteristic curves of all gases on the same adsorbent into a single curve. Under this assumption, Eq. (4.1) can be replaced by

$$W \equiv qV_m = W(\phi), \quad \phi \equiv \tilde{\phi}/\beta, \quad (4.3)$$

which is characteristic of a given adsorbent and can be equally applicable to all adsorbates. This formulation is perhaps the best attempt to obtain an universal isotherm by which the adsorption data of one reference gas are extended to other gases [Yang (1987)].

practical applicability of this feature is limited by our ability to predict affinity coefficients, but a recent study on the affinity factors for adsorption of several adsorbates on activated carbon has been carried out by [Wood \(2001\)](#), who has published an extensive compilation of experimental β values for gases and vapors and showed that β is highly correlated to the listed molecular parachor, according to

$$\beta = 8.27 \times 10^{-3} (\text{Parachor})^{0.90}. \quad (4.4)$$

Since one have not found the parachor values of the two odorants, they were estimated using the following correlation [[Wood \(1992\)](#)] based on the critical volume, V_c ,

$$\text{Parachor} = 8.0 + 0.7068V_c. \quad (4.5)$$

Under conditions below the critical temperature, T_c , of the adsorbate, V_m is assumed equal to the molar volume of the saturated liquid at system temperature [[Ruthven \(1984\)](#)], calculated from the modified Rackett equation [[Spencer and Danner \(1972\)](#)] as

$$V_m = \frac{RT_c}{P_c} Z_{ra} [(1 - T/T_c)]^{2/7}. \quad (4.6)$$

where R is the ideal gas constant, P_c is the critical pressure, and Z_{ra} is the Rackett compressibility factor. These constants were taken from the ASPEN PLUS database. P_s was estimated using the Wagner equation with parameters taken from [R. C. Reid and Prausnitz \(1988\)](#),

$$\ln \frac{P_s(T)}{P_c} = \frac{Ax + Bx^{1.5} + Cx^3 + Dx^6}{1 - x}, \quad x = 1 - T/T_c. \quad (4.7)$$

Above T_c the adsorbed phase is ill-defined, and this has led to the proposal of different approximations for V_m . Likewise, in the supercritical region the concept of vapor pressure does not exist and P_s , in Eq. (4.2), must be replaced by a pseudo-vapor pressure. A comprehensive summary of these methods was given by [Agarwal and Schwarz \(1988\)](#). In the present work one followed the suggestions of [Agarwal and Schwarz \(1988\)](#), and estimated P_s and V_m , at temperatures above T_c , as follows

$$P_s = (T/T_c)^2 P_c, \quad V_m(T) = V_b \exp[\Omega(T - T_b)], \quad \Omega = \ln(b/V_b)/(T_c - T_b), \quad (4.8)$$

where P_c is the critical pressure of the adsorbate, T_b and V_b are the temperature and molar volume of the liquid adsorbate at the normal boiling point, and Ω is an estimate of the thermal expansion coefficient of the adsorbate in a superheated liquid state, which for light gases was assumed as $\Omega \approx 2.5 \times 10^{-3} \text{ K}^{-1}$ [[S. Ozawa and Ogino \(1976\)](#)].

Hence, the success of Wood's correlation, Eq. (4.4), led us to use it for estimating the β values for the adsorbates C_{3+} , which are clearly vapors at ambient temperature.

On the other hand, the β values for the adsorbates C_{2-} , which have critical temperatures close to or below ambient temperature, had to be obtained experimentally by superposing the corresponding adsorption data onto the characteristic curve of the higher n -alkanes. One believe that the reason for this is the difficulty in calculating densities of condensed adsorbed phases at temperatures approaching and exceeding critical temperatures.

To obtain a workable isotherm model for further process simulation, the experimental characteristic curve was successfully fitted using a modified Dubinin equation [Dubinin and Radushkevich (1947)]. The improved Dubinin-Astakhov (D-A) equation [Dubinin and Astakhov (1970), Dubinin (1975), S. Ozawa and Ogino (1976)] states that for a pure component, this isotherm model can be written as

$$W = W_s \exp(-\gamma\phi^n), \quad (4.9)$$

where W/W_s is the fractional filling of the specific micropore volume, W_s , of the carbon, accessible to the given adsorbate, and ϕ is the adsorption potential, which has been scaled by the affinity coefficient β of the adsorbate, to collapse the isotherm data of different adsorbates into a single curve. γ and n are parameters, where the former is a function of the characteristic energy for the given system and the later is related to the pore size distribution. These values are determined experimentally from the linear fitting of $\ln[\ln(W_s/W)]$ versus $\ln\phi$ (see Figure 4.14).

$$\ln(\ln W_s/W) = \ln\gamma + n\ln\phi \quad (4.10)$$

Expressing the $\ln W$ as a function of ϕ , provides good fitting of the experimental data and W_s was determined through the form

$$\ln(W_s/W) = \sum c_n \phi^n = c_1\phi + c_2\phi^2 + \dots + c_n\phi^n, \quad (4.11)$$

which is called the temperature-independent characteristic curve of adsorption on the carbon under study, where $(c_1, c_2, \dots, c_n)$ are constants characteristic of the adsorbent. A third-order polynomial iterative method was considered enough to calculate W_s for the carbon under study [see Figure (4.15)]. Several works corroborate the applicability of this theory [C. E. Holland and Ritter (2001a,b); Chang and Talu (1996); Mota and Rodrigo (2000)].

4.2.3.2 Sorption Results using the APT approach

The gravimetric measurements, as well as all other conventional adsorption methods, rather than giving the total amount adsorbed, q , give just the amount in excess, q_{ex} , with respect to that of the bulk gas occupying the same volume as the adsorbed phase [F. Rouquerol and Sing (1999), Perry and Green (1999)].

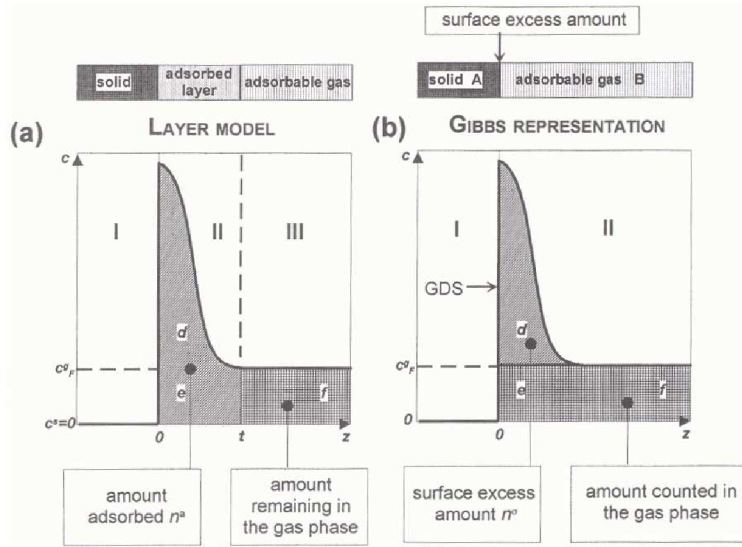


Figure 4.5: Gibbs representation of the surface excess amount. c is the local concentration dn/dV of the adsorbate [F. Rouquerol and Sing (1999)].

According to a layer model, an hypothetical variation of local concentration is presented in Figure (4.5.(a)). The local concentration of the adsorbate decreases progressively with increased distance z from the adsorbent surface. At $z = t$, this concentration reaches the constant value of the gas phase, c_g . Zone I is only occupied by the adsorbent and therefore $c_s = 0$. Zone II is the adsorbed layer confined between $z = 0$ and $z = t$, where the local concentration, dependent on z , is higher than the gas concentration in zone III. In zone III, at $z > t$, the adsorbate has a uniform concentration c_g only dependent on the equilibrium pressure and temperature.

Hence, the volume of the adsorbed layer, V_a , is given by

$$V_a = At, \quad (4.12)$$

where A is the surface area of the solid and t the thickness. The amount of adsorbed component in the layer, q^a , equivalent to the area $(d + e)$, is

$$q^a = \int_0^{V_a} c dV = A \int_0^t c dz. \quad (4.13)$$

The total amount adsorbed, q , of the adsorbable component accounts for both adsorbed phase and coexisting gas within the pore space, and is then given by the sum of q^a and the amount remaining in the gas phase

$$q = q^a + V_g \rho_g, \quad (4.14)$$

where V_g is the volume occupied by the gas at the concentration c_g and ρ_g is the density of the bulk gas phase at the equilibrium pressure and temperature.

The Gibbs representation is an alternative approach, quantifying the amount adsorbed with the surface excess amount [Figure (4.5.(b))]. A zone I with volume V_s^o , is divided from zone II of volume V_g^o , through the Gibbs dividing surface, located on the surface which is accessible to the adsorbate. The system volume is

$$V = V_s^o + V_g^o = V_s + V_a + V_g. \quad (4.15)$$

The surface excess amount, q^σ , is represented by area d in Figure (4.5.(b)). The total amount adsorbed given by area (d + e + f) is then represented by the sum of q^σ and the amount which would be present in the volume V_g^o of the system, if the final concentration c_g was constant up to the Gibbs dividing surface [area (e + f)]. This is expressed through

$$q^\sigma = q - V_g^o \rho_g. \quad (4.16)$$

Thus, from Eqs. (4.14, 4.15) one gets

$$q^\sigma = q - V_a \rho_g - V_g \rho_g \quad (4.17)$$

$$q^a = q^\sigma + V_a \rho_g, \quad (4.18)$$

Generally, for the usual experimental conditions, the term $V_a \rho_g$ is negligible and hence $q^a \approx q^\sigma$. Hence,

$$q = q^\sigma + V_g \rho_g. \quad (4.19)$$

The surface excess concentration, Γ , is given by

$$\Gamma = q^\sigma / A \quad (4.20)$$

where $A = aM_c$, with M_c the adsorbent mass and a the specific surface area. The relation

$$\Gamma a = q^\sigma / M_c = q_{ex} = f(P)_T \quad (4.21)$$

gives the specific excess amount, q_{ex} , dependent on the equilibrium pressure, P , and temperature, T , which is known as the adsorption isotherm.

To apply the APT, the required variable is q and not q_{ex} . In this work, the amount adsorbed was estimated from the measured q_{ex} value [Eq.(B.10)] by assuming, as a starting point, that the volume V_g is equal to the total pore volume of the carbon [Sircar (1999)], $W_s = 0.850 \text{ cm}^3/\text{g}$ for ANGWARD 5, determined from N_2 adsorption at 77 K. The complete sorption data was then analyzed and through iteration the values of W_s , γ and n from Eq. (4.9) were determined.

4.2 Adsorption Equilibrium Measurements

Table 4.3: Calculated and estimated β values and Ω values for the adsorbates n -C₁-C₄, the odorants, CO₂ and N₂. ^a From Eq. (4.4) and listed in Wood (2001). ^b Calculated from Eq. (4.5).

	n -C ₁	n -C ₂	n -C ₃	n -C ₄	TBM	THT	CO ₂	N ₂
Parachor ^a	73.20	112.2	151.2	190.2	-	-	91.2	71.1
Parachor ^b	77.70	-	-	-	225.0	184.0	-	-
β_{calc}^a	0.394	0.579	0.757	0.931	-	-	0.480	0.384
β_{calc}^b	0.416	-	-	-	1.083	0.903	-	-
β_{exp}	0.470	0.630	0.780	0.860	1.030	0.840	0.420	0.380
Ω (K ⁻¹)	0.0036	0.0025	-	-	-	-	0.0036	0.0025

Using Wood's correlation, Eqs. (4.4, 4.5), Table (4.3) shows both calculated and estimated β values for the adsorbates n -C₁-C₄, the odorants, CO₂ and N₂. Through the characteristic curve obtained, one found that was necessary to fine tune each individual β , starting from the calculated values. The estimated thermal expansion coefficient of each adsorbate, Ω , is also presented. All other properties needed for the calculations were obtained using Aspen Engineering Suite, from AspenTech software package.

To obtain a workable isotherm model for further process simulation, the experimental characteristic curve was successfully fitted using Eq. (4.9). The regressed values obtained experimentally for the ANGUARD 5 carbon sample are the following:

$$\left\{ \begin{array}{l} W_s = 0.8599 \text{ cm}^3/\text{g}, \\ \gamma = 4.6657 \times 10^{-5} \text{ (J/mol)}^{-n} \quad \text{and} \quad n = 1.0861 \text{ (} n\text{-alkanes, CO}_2 \text{ and N}_2\text{)}, \\ \gamma = 1.1863 \times 10^{-4} \text{ (J/mol)}^{-n} \quad \text{and} \quad n = 0.9994 \text{ (TBM)}, \\ \gamma = 3.9092 \times 10^{-6} \text{ (J/mol)}^{-n} \quad \text{and} \quad n = 1.3377 \text{ (THT)}. \end{array} \right. \quad (4.22)$$

The regressed value of W_s is in excellent agreement with the total pore volume determined from the N₂ adsorption at 77 K (0.850 cm³/g) and from the mercury porosimetry (0.881 cm³/g) on the carbon under study. It is also somewhat surprising to observe that most of the odorant measurements were in the nonlinear range of the isotherms even at the low concentrations considered in this study. Although a unique γ and n values for all the data points was obtained, the agreement between experimental and predicted values was slightly poor for THT and TBM. Hence, in order to improve the accuracy of the correlation for the particular case of odorant adsorption, Eq. (4.9) was again fitted in the narrower adsorption potential range for odorant adsorption, keeping W_s constant.

The regressed values for each odorant, γ and n , were calculated individually for better agreement between the experimental and predicted values of the amount of component adsorbed. The degree of difficulty in the measurements of the odorant adsorption isotherms, which increase the possible experimental errors, may explain this problem.

The isotherm model is compared directly to the experimental adsorption data in Figures (4.6 - 4.13) and Tables (4.4 - 4.15) which presents the experimental single-component isotherms at different temperatures for adsorption of the n -alkanes C₁-C₄, CO₂, N₂, TBM and THT, on the SSCL sample carbon under analysis. P and P_s were replaced by the corresponding fugacities, f and f_s , to correct non-ideal gas behavior. The amount of species adsorbed per carbon weight unit versus the species concentration is represented by a typical Type I isotherm characteristic of a microporous adsorbent. Since adsorption is exothermic while desorption is an endothermic process, adsorption is favored by lower temperatures than desorption, and thus the slope and curvature of the isotherms decrease with increasing temperature.

4.2 Adsorption Equilibrium Measurements

Table 4.4: Adsorption isotherm data of methane (CH_4) on carbon sample ANGWARD 5. 101 experimental data points were measured. Gray values represent points not included in the average relative error (ARE) calculation. For 284.3 K, 298.3 K and 323.3 K the % ARE is 2.73, 3.39 and 4.67, respectively. The C_1 overall ARE is 3.64%.

T = 284.3 K					T = 298.3 K					T = 323.3 K				
P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE		P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE		P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE	
0.007	0.001	0.000			0.006	0.000	0.000	0.000		0.004	0.000	0.000		
0.008	0.001	0.000			0.007	0.000	0.000			0.042	0.001	0.001		
0.173	0.006	0.003	71.06		0.123	0.003	0.002			0.112	0.002	0.001	96.09	
0.246	0.007	0.005	51.43		0.224	0.005	0.003	84.86		0.282	0.003	0.002	36.05	
0.370	0.009	0.007	37.73		0.351	0.007	0.005	43.97		0.382	0.004	0.003	42.21	
0.498	0.011	0.009	30.32		0.429	0.008	0.006	26.33		0.499	0.005	0.004	25.91	
0.569	0.012	0.011	5.61		0.509	0.009	0.007	17.23		0.574	0.006	0.005	22.92	
0.746	0.014	0.012	21.81		0.563	0.009	0.007	31.09		0.748	0.007	0.006	19.06	
1.005	0.017	0.017	3.47		0.815	0.012	0.009	22.86		1.008	0.008	0.008	8.14	
1.454	0.021	0.019	10.60		1.142	0.014	0.013	8.79		1.038	0.008	0.007	13.94	
2.120	0.027	0.027	0.71		1.207	0.015	0.013	15.66		1.349	0.010	0.009	10.30	
2.135	0.027	0.027	0.45		1.832	0.019	0.018	9.33		2.100	0.014	0.013	6.72	
2.635	0.030	0.029	3.47		2.260	0.022	0.021	6.52		2.920	0.017	0.017	0.98	
3.670	0.037	0.037	0.67		3.265	0.028	0.027	2.53		3.025	0.018	0.017	4.89	
4.520	0.042	0.042	0.57		3.760	0.030	0.031	1.00		4.060	0.022	0.021	4.51	
5.497	0.046	0.047	0.62		4.800	0.035	0.035	0.53		5.065	0.025	0.024	2.41	
6.879	0.053	0.055	4.40		6.899	0.044	0.044	1.38		5.655	0.027	0.028	3.35	
6.958	0.053	0.055	3.84		7.709	0.047	0.047	1.60		6.169	0.029	0.029	1.67	
8.084	0.058	0.059	2.45		8.973	0.051	0.053	2.83		7.195	0.032	0.033	3.15	
8.143	0.058	0.059	2.11		11.757	0.060	0.062	3.31		8.380	0.035	0.037	4.24	
11.836	0.071	0.073	2.82		15.411	0.070	0.072	3.48		9.466	0.038	0.040	5.07	
13.535	0.077	0.080	3.69		16.122	0.072	0.074	3.06		11.343	0.043	0.045	5.81	
15.865	0.083	0.085	2.08		20.032	0.081	0.083	2.53		12.942	0.046	0.049	6.28	
21.552	0.098	0.099	0.89		25.936	0.093	0.095	1.51		14.858	0.051	0.054	6.48	
25.897	0.108	0.108	0.07		33.954	0.108	0.108	0.25		16.082	0.053	0.057	6.98	
33.875	0.123	0.121	1.26		40.273	0.118	0.117	0.43		18.590	0.058	0.062	6.42	
40.036	0.133	0.130	2.32		44.756	0.124	0.123	1.07		22.895	0.066	0.071	6.10	
47.501	0.144	0.140	2.88		53.860	0.136	0.134	1.53		30.064	0.078	0.082	5.19	
55.065	0.154	0.149	3.54		64.954	0.148	0.145	2.23		36.936	0.088	0.092	4.29	
61.680	0.162	0.156	3.65		72.640	0.156	0.152	2.56		39.503	0.092	0.096	4.24	
69.974	0.170	0.164	3.97		80.125	0.163	0.158	2.79		45.072	0.099	0.102	3.29	
80.342	0.180	0.173	3.89		89.624	0.171	0.166	2.95		53.426	0.109	0.111	2.43	
90.019	0.187	0.180	3.93							64.168	0.120	0.122	1.55	
										68.651	0.124	0.126	1.34	
										79.690	0.134	0.135	0.60	
										87.056	0.141	0.141	0.33	

4.2 Adsorption Equilibrium Measurements

Table 4.5: Adsorption isotherm data of ethane (C_2H_6) on carbon sample ANGWARD 5. 63 experimental data points were measured. Gray values represent points not included in the ARE calculation. For 287.5 K, 299.2 K, 314.0 K and 324.2 K the % ARE is 3.62, 3.60, 4.40 and 3.56, respectively. The C_2 overall ARE is 3.78%.

T = 299.2 K				T = 287.5 K			
P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE	P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
0.000	0.000	0.000		0.000	0.001	0.000	
0.200	0.041	0.050	16.74	0.100	0.037	0.057	34.70
0.600	0.069	0.079	13.24	0.550	0.079	0.091	12.96
1.400	0.101	0.113	10.91	1.300	0.115	0.131	11.90
2.000	0.118	0.131	9.80	1.550	0.124	0.137	9.40
3.500	0.150	0.160	6.06	2.700	0.156	0.165	5.54
5.050	0.175	0.180	3.06	4.100	0.184	0.189	2.40
6.400	0.192	0.195	1.09	4.900	0.198	0.200	0.90
7.800	0.208	0.208	0.14	5.800	0.211	0.211	0.04
9.699	0.226	0.225	0.74	7.800	0.236	0.233	1.06
15.236	0.267	0.262	1.59	11.157	0.268	0.263	1.86
20.239	0.293	0.290	1.16	13.448	0.285	0.281	1.59
24.847	0.311	0.309	0.76	15.495	0.298	0.295	1.29
30.345	0.329	0.327	0.59	21.373	0.328	0.326	0.49
32.935	0.335	0.333	0.51	23.602	0.337	0.335	0.45
36.811	0.343	0.341	0.78	27.757	0.350	0.347	0.80

T = 314.0 K				T = 324.2 K			
P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE	P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
0.001	0.002	0.000		0.049	0.017	0.000	
0.060	0.018	0.015	18.12	0.422	0.041	0.034	21.90
0.600	0.056	0.060	7.22	0.948	0.061	0.058	5.16
1.450	0.085	0.095	10.09	1.988	0.088	0.090	1.72
2.000	0.099	0.108	8.41	3.145	0.110	0.113	2.87
3.350	0.125	0.133	5.85	4.025	0.123	0.127	2.51
3.950	0.135	0.143	6.01	5.000	0.136	0.139	1.75
5.900	0.161	0.166	2.86	6.030	0.148	0.150	0.83
8.531	0.188	0.192	1.73	11.989	0.200	0.194	3.39
11.975	0.216	0.212	1.68	12.167	0.201	0.196	2.98
19.022	0.257	0.250	3.03	15.465	0.222	0.213	4.45
24.690	0.281	0.273	3.02	20.462	0.247	0.234	5.50
31.638	0.304	0.296	2.63	21.469	0.252	0.239	5.27
35.692	0.314	0.307	2.39	30.041	0.283	0.269	5.17
38.527	0.320	0.313	2.24	36.301	0.300	0.287	4.35
				39.994	0.308	0.297	3.84

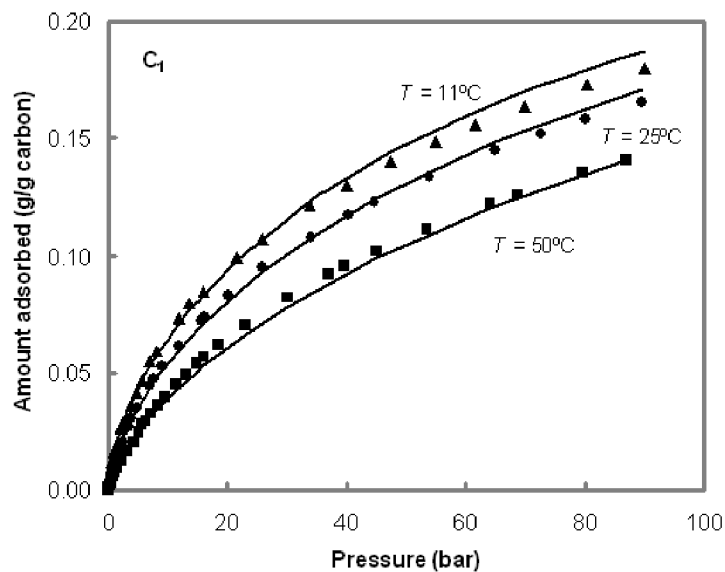


Figure 4.6: Experimental single-component isotherm for adsorption of the *n*-alkane C_1 . Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{C_1} = 0.47$.

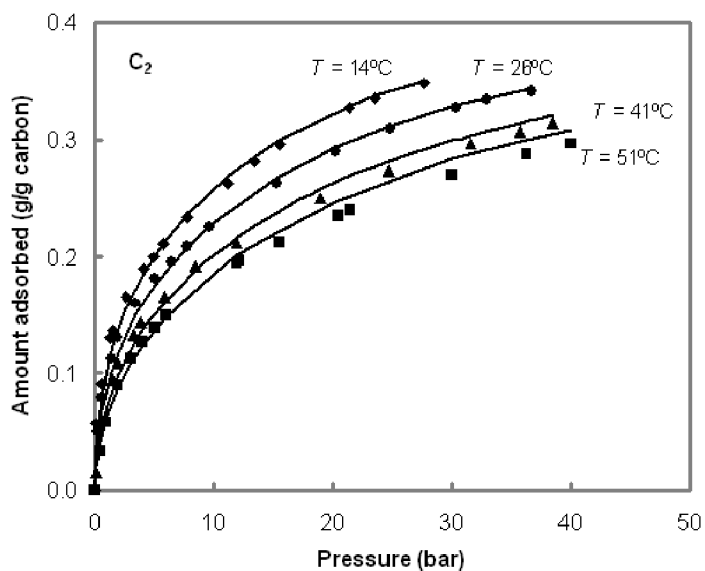


Figure 4.7: Experimental single-component isotherm for adsorption of the *n*-alkane C_2 . Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{C_2} = 0.63$.

4.2 Adsorption Equilibrium Measurements

Table 4.6: Isotherm data of propane (C_3H_8) on carbon sample ANGWARD 5. 136 experimental points were measured. Gray values represent points not included in the ARE calculation. For 283.9 K, 297.8 K and 323.4 K the % ARE is 3.15, 4.31 and 8.54, respectively. The C_3 overall ARE is 5.86%.

T = 297.8 K				T = 283.9 K			
P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE	P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
0.007	0.035	0.009		0.006	0.044	0.003	
0.007	0.036	0.009		0.006	0.044	0.003	
0.011	0.042	0.010		0.051	0.096	0.003	
0.035	0.065	0.057	14.91	0.074	0.110	0.050	
0.101	0.097	0.105	8.02	0.094	0.120	0.055	
0.114	0.101	0.108	6.27	0.097	0.120	0.099	21.13
0.163	0.115	0.045		0.136	0.136	0.149	8.76
0.170	0.117	0.133	11.94	0.182	0.150	0.150	0.18
0.206	0.126	0.139	9.61	0.251	0.167	0.118	41.76
0.262	0.137	0.157	12.69	0.319	0.181	0.190	4.64
0.348	0.152	0.119	27.25	0.344	0.186	0.197	5.50
0.361	0.154	0.168	8.51	0.385	0.192	0.200	4.00
0.380	0.156	0.176	11.43	0.522	0.213	0.194	9.74
0.549	0.178	0.196	9.60	0.607	0.224	0.228	1.69
0.557	0.179	0.191	6.43	0.617	0.224	0.231	2.80
0.776	0.200	0.219	8.38	0.766	0.241	0.225	7.46
0.908	0.211	0.218	3.14	0.891	0.253	0.255	1.05
1.077	0.224	0.239	6.39	1.068	0.268	0.265	1.26
1.392	0.244	0.256	4.95	1.241	0.280	0.283	0.90
1.479	0.249	0.250	0.31	1.272	0.283	0.267	6.06
1.798	0.265	0.257	3.18	1.602	0.304	0.298	1.84
1.801	0.265	0.256	3.53	1.730	0.310	0.314	1.10
2.215	0.283	0.296	4.09	1.975	0.324	0.311	4.08
2.740	0.303	0.316	4.05	2.070	0.327	0.333	1.77
2.750	0.303	0.316	4.07	2.380	0.342	0.338	1.03
2.905	0.309	0.299	3.11	2.650	0.352	0.362	2.87
3.550	0.328	0.326	0.79	3.030	0.366	0.358	2.17
3.785	0.334	0.351	4.91	3.155	0.369	0.382	3.24
4.410	0.349	0.369	5.35	3.430	0.379	0.376	0.80
4.615	0.354	0.351	1.01	3.605	0.383	0.395	2.99
4.775	0.357	0.379	5.57	4.030	0.395	0.386	2.43
5.265	0.368	0.366	0.37	4.030	0.395	0.403	2.08
5.525	0.373	0.369	0.83	4.035	0.396	0.387	2.13
5.855	0.378	0.398	4.89	4.535	0.407	0.410	0.69
6.465	0.388	0.406	4.32	4.985	0.417	0.399	4.51
6.525	0.389	0.383	1.68	5.015	0.417	0.415	0.58
7.535	0.404	0.391	3.31	5.340	0.423	0.419	1.07
7.700	0.405	0.415	2.32	5.585	0.429	0.404	6.03
				5.615	0.429	0.404	6.19
				5.620	0.429	0.405	6.11
				5.910	0.433	0.425	1.99

4.2 Adsorption Equilibrium Measurements

Table 4.7: (Continued) Isotherm data of propane (C_3H_8) on carbon sample ANGWARD 5. 136 experimental points were measured. Gray values represent points not included in the ARE calculation. For 283.9 K, 297.8 K and 323.4 K the % ARE is 3.15, 4.31 and 8.54, respectively. The C_3 overall ARE is 5.86%.

T = 323.4 K							
P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE	P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE
0.006	0.019	0.004		3.660	0.246	0.268	8.31
0.009	0.023	0.006		3.930	0.252	0.263	4.08
0.012	0.026	0.008		3.940	0.252	0.263	4.09
0.058	0.050	0.045	9.44	4.180	0.257	0.268	3.97
0.087	0.059	0.058	0.39	4.765	0.269	0.279	3.77
0.100	0.062	0.051	22.60	4.800	0.270	0.280	3.69
0.205	0.083	0.095	13.00	4.910	0.272	0.292	7.07
0.247	0.089	0.101	11.90	5.135	0.276	0.286	3.75
0.296	0.096	0.112	14.63	5.415	0.280	0.290	3.46
0.346	0.102	0.114	10.19	5.530	0.282	0.306	7.66
0.422	0.110	0.133	16.92	6.220	0.293	0.304	3.49
0.556	0.123	0.143	13.96	6.840	0.302	0.336	10.00
0.654	0.131	0.149	12.56	6.850	0.302	0.327	7.49
0.722	0.136	0.163	16.59	7.116	0.306	0.339	9.78
0.882	0.146	0.166	11.87	7.260	0.308	0.334	7.99
1.082	0.158	0.186	14.98	7.440	0.310	0.322	3.74
1.167	0.163	0.183	11.22	7.788	0.314	0.348	9.74
1.420	0.175	0.194	9.57	7.966	0.317	0.352	10.05
1.597	0.183	0.210	12.79	8.005	0.317	0.352	10.05
1.943	0.196	0.213	7.72	8.005	0.317	0.353	10.29
1.958	0.197	0.221	10.83	8.815	0.326	0.360	9.35
1.961	0.197	0.221	10.83	9.111	0.329	0.355	7.17
1.969	0.197	0.221	10.59	9.151	0.330	0.355	7.08
2.380	0.211	0.236	10.33	10.059	0.339	0.375	9.70
2.435	0.213	0.228	6.36	10.355	0.342	0.382	10.52
2.705	0.221	0.235	5.80	12.547	0.359	0.390	7.85
2.895	0.227	0.240	5.45	13.456	0.366	0.394	7.11
3.220	0.235	0.247	4.82	13.752	0.368	0.395	6.93
3.255	0.236	0.257	8.21				

4.2 Adsorption Equilibrium Measurements

Table 4.8: Isotherm data of butane (C_4H_{10}) on carbon sample ANGWARD 5. 64 experimental points were measured. Gray values represent points not included in the ARE calculation. For 273.2 K, 288.2 K, 297.9 K and 324.6 K the % ARE is 4.70, 4.85, 6.11 and 7.13 respectively. The C_4 overall ARE is 5.69%.

T = 273.2 K				T = 288.2 K			
P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE	P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
0.003	0.100	0.000		0.004	0.082	0.003	
0.004	0.105	0.033		0.004	0.082	0.087	5.73
0.005	0.117	0.022		0.021	0.139	0.160	13.34
0.021	0.179	0.075		0.078	0.211	0.228	7.28
0.028	0.195	0.152	28.37	0.140	0.252	0.260	3.35
0.034	0.208	0.199	4.50	0.213	0.285	0.292	2.36
0.039	0.216	0.202	6.52	0.269	0.306	0.308	0.75
0.048	0.230	0.216	6.43	0.412	0.346	0.348	0.51
0.070	0.256	0.270	4.96	0.650	0.393	0.394	0.23
0.084	0.270	0.257	5.03	0.827	0.419	0.411	1.91
0.137	0.310	0.325	4.73	0.964	0.437	0.422	3.48
0.143	0.314	0.299	4.94	1.086	0.450	0.427	5.36
0.214	0.350	0.335	4.53	1.188	0.460	0.435	5.74
0.302	0.384	0.371	3.70	1.313	0.472	0.435	8.55
0.303	0.385	0.370	4.00	1.434	0.482	0.443	8.64
0.399	0.413	0.399	3.52	1.534	0.489	0.448	9.26
0.405	0.415	0.401	3.55	1.535	0.489	0.442	10.55
0.525	0.443	0.424	4.63				
T = 297.9 K				T = 324.6 K			
P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE	P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
0.036	0.141	0.001		0.028	0.083	0.000	
0.045	0.152	0.115	31.38	0.072	0.117	0.145	19.17
0.045	0.152	0.126	20.83	0.096	0.130	0.140	7.06
0.068	0.174	0.175	0.71	0.205	0.170	0.205	17.01
0.155	0.226	0.242	6.47	0.353	0.205	0.230	10.53
0.228	0.255	0.270	5.60	0.645	0.252	0.276	8.72
0.332	0.286	0.296	3.12	0.993	0.290	0.312	7.13
0.519	0.327	0.330	0.75	1.304	0.316	0.329	3.96
0.636	0.347	0.359	3.30	1.569	0.335	0.355	5.49
0.800	0.371	0.376	1.35	1.978	0.360	0.374	3.88
1.134	0.409	0.416	1.52	2.470	0.384	0.400	4.01
1.137	0.409	0.415	1.45	2.880	0.402	0.413	2.80
1.493	0.440	0.434	1.44	2.970	0.405	0.415	2.32
1.557	0.445	0.436	1.99	3.690	0.430	0.427	0.65
1.964	0.472	0.446	5.67				

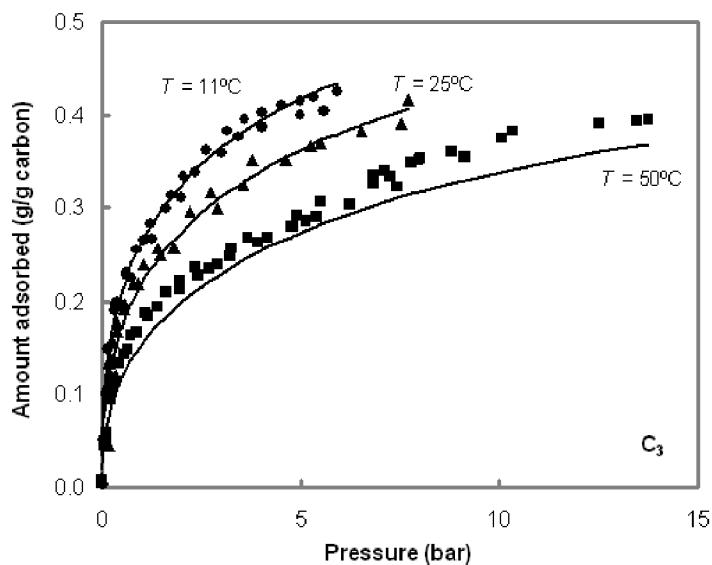


Figure 4.8: Experimental single-component isotherm for adsorption of the *n*-alkane C_3 . Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{C_3} = 0.78$.

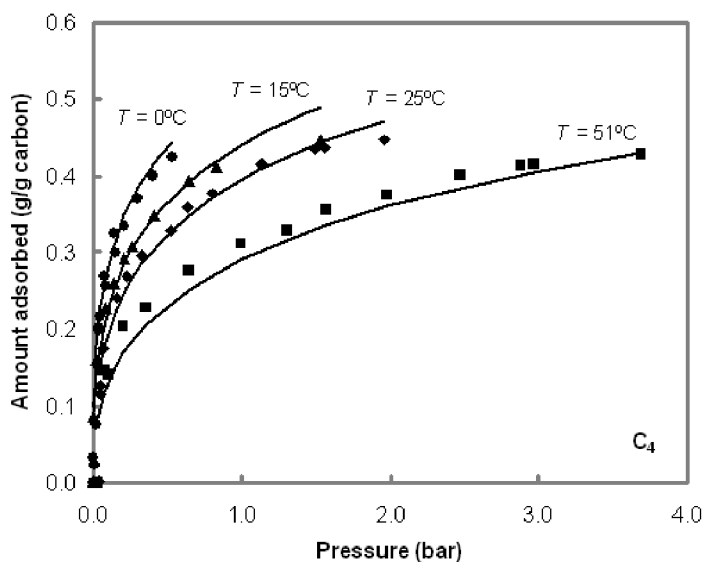


Figure 4.9: Experimental single-component isotherm for adsorption of the *n*-alkane C_4 . Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{C_4} = 0.86$.

4.2 Adsorption Equilibrium Measurements

Table 4.9: Isotherm data of carbon dioxide (CO_2) on carbon sample ANGWARD 5. 117 experimental points were measured. Gray values represent points not included in the ARE calculation. For 273.3 K, 279.4 K, 290.1 K, 310.5 and 323.3 K the % ARE is 3.67, 3.03, 7.36, 2.93 and 3.08 respectively. The CO_2 overall ARE is 4.10%.

T = 273.3 K				T = 279.4 K			
P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE	P (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
0.034	0.013	0.010	22.83	0.089	0.020	0.018	8.64
0.133	0.031	0.027	16.67	0.298	0.045	0.042	6.19
0.327	0.057	0.050	13.18	0.426	0.057	0.054	5.06
0.512	0.076	0.068	11.03	0.638	0.075	0.072	3.63
1.589	0.155	0.148	5.14	0.786	0.086	0.083	2.64
2.056	0.182	0.174	4.76	0.977	0.099	0.097	1.69
2.733	0.216	0.209	3.59	1.589	0.135	0.135	0.20
3.815	0.264	0.254	4.19	2.583	0.183	0.185	0.85
5.505	0.327	0.316	3.58	3.807	0.233	0.237	1.64
6.966	0.374	0.360	4.00	6.147	0.311	0.312	0.53
8.620	0.421	0.403	4.62	6.966	0.334	0.334	0.02
11.955	0.501	0.484	3.49	9.623	0.401	0.398	0.85
12.139	0.505	0.488	3.48	12.650	0.466	0.466	0.03
16.046	0.581	0.572	1.55	14.665	0.504	0.504	0.13
18.660	0.624	0.626	0.27	16.698	0.538	0.544	1.14
20.112	0.646	0.654	1.24	19.531	0.581	0.596	2.52
22.575	0.679	0.699	2.79	22.479	0.620	0.648	4.25
24.362	0.701	0.729	3.82	25.831	0.660	0.699	5.62
27.045	0.731	0.762	4.04	29.615	0.698	0.746	6.51
30.231	0.762	0.787	3.21	32.431	0.722	0.769	6.04
32.959	0.784	0.803	2.40	34.366	0.737	0.780	5.48
33.663	0.789	0.809	2.45				

Table 4.10: (Continued) Isotherm data of carbon dioxide (CO_2) on carbon ANGWARD 5. 117 experimental points were measured. Gray values represent points not included in the ARE calculation. For 273.3 K, 279.4.1 K, 290.1 K, 310.5 and 323.3 K the % ARE is 3.67, 3.03, 7.36, 2.93 and 3.08 respectively. The CO_2 overall ARE is 4.10%.

T = 290.1 K			
P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE
0.114	0.016	0.017	3.73
0.190	0.023	0.024	3.75
0.316	0.033	0.034	4.97
0.474	0.043	0.046	5.76
0.635	0.053	0.057	6.33
0.861	0.066	0.071	7.11
0.991	0.072	0.080	9.66
1.246	0.084	0.093	9.45
1.299	0.087	0.095	8.49
2.319	0.128	0.140	8.89
3.683	0.173	0.191	9.63
5.206	0.215	0.236	8.83
7.080	0.261	0.285	8.50
9.508	0.311	0.335	7.15
12.747	0.369	0.395	6.55
14.779	0.401	0.428	6.38
17.956	0.446	0.478	6.70
19.927	0.471	0.507	7.03
22.848	0.505	0.548	7.85
25.004	0.528	0.577	8.49
28.119	0.558	0.615	9.39
31.991	0.591	0.661	10.57
34.806	0.612	0.690	11.25

4.2 Adsorption Equilibrium Measurements

Table 4.11: (Continued) Isotherm data of carbon dioxide (CO_2) on carbon ANGWARD 5. 117 experimental points were measured. Gray values represent points not included in the ARE calculation. For 273.3 K, 279.4.1 K, 290.1 K, 310.5 and 323.3 K the % ARE is 3.67, 3.03, 7.36, 2.93 and 3.08 respectively. The CO_2 overall ARE is 4.10%.

T = 310.5 K				T = 323.3 K			
P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE	P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE
0.049	0.005	0.005	1.74	0.010	0.001	0.001	13.29
0.235	0.016	0.017	3.13	0.054	0.004	0.004	3.14
0.300	0.019	0.020	3.78	0.206	0.011	0.011	5.52
0.477	0.027	0.029	4.07	0.305	0.014	0.015	6.34
0.611	0.033	0.035	4.64	0.434	0.019	0.020	6.76
0.894	0.044	0.046	5.17	0.606	0.025	0.027	7.12
1.061	0.050	0.054	8.68	0.846	0.032	0.035	7.45
1.624	0.068	0.073	6.84	1.404	0.048	0.050	3.94
2.777	0.100	0.106	5.53	1.853	0.059	0.061	3.52
4.519	0.141	0.148	5.09	3.956	0.104	0.109	4.60
5.637	0.164	0.173	4.89	4.106	0.107	0.112	3.96
7.185	0.194	0.202	4.05	6.033	0.142	0.147	3.35
8.928	0.224	0.232	3.58	7.749	0.170	0.175	3.30
10.468	0.249	0.256	2.66	9.746	0.199	0.204	2.48
12.245	0.275	0.281	1.96	11.506	0.223	0.227	1.79
14.718	0.309	0.313	1.19	11.796	0.227	0.231	1.45
17.137	0.340	0.341	0.43	14.718	0.264	0.266	0.75
20.534	0.379	0.378	0.15	15.457	0.272	0.274	0.47
22.989	0.405	0.403	0.47	17.824	0.299	0.298	0.29
25.004	0.425	0.422	0.59	18.915	0.311	0.309	0.52
26.931	0.443	0.440	0.58	20.200	0.324	0.321	0.96
30.583	0.475	0.472	0.49	20.569	0.328	0.324	1.06
31.727	0.484	0.482	0.47	23.878	0.360	0.354	1.68
34.542	0.506	0.505	0.16	26.729	0.385	0.377	2.11
				28.559	0.401	0.392	2.33
				31.287	0.423	0.412	2.53
				34.542	0.447	0.435	2.72

4.2 Adsorption Equilibrium Measurements

Table 4.12: Isotherm data of nitrogen (N_2) on carbon sample ANGWARD 5. 64 experimental points were measured. Gray values represent points not included in the ARE calculation. For 288.2 K, 312.5 K and 323.4 K the % ARE is 9.32, 6.71 and 8.71 respectively. The N_2 overall ARE is 8.01%.

T = 288.2 K				T = 312.5 K			
P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE	P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE
0.249	0.002	0.003	11.17	0.103	0.001	0.001	16.73
0.437	0.004	0.004	11.37	0.205	0.002	0.002	1.68
0.632	0.005	0.006	13.36	0.235	0.002	0.002	5.84
0.861	0.007	0.008	13.05	0.490	0.003	0.003	3.29
0.997	0.008	0.009	12.74	0.753	0.005	0.005	3.84
2.082	0.014	0.016	14.37	1.005	0.006	0.006	4.94
2.759	0.018	0.021	14.76	1.052	0.006	0.007	4.90
4.599	0.027	0.031	14.14	1.985	0.011	0.012	7.70
6.006	0.033	0.038	12.94	3.199	0.016	0.017	8.35
8.338	0.044	0.049	11.44	3.580	0.017	0.019	8.69
9.218	0.047	0.053	11.01	5.065	0.023	0.026	9.15
11.858	0.058	0.064	9.35	6.015	0.027	0.030	9.24
14.040	0.066	0.072	8.24	6.790	0.030	0.033	9.25
16.178	0.074	0.079	6.76	7.124	0.031	0.034	9.24
19.513	0.085	0.090	5.12	9.016	0.037	0.041	8.87
22.417	0.095	0.098	3.28	10.406	0.042	0.046	8.61
24.159	0.101	0.103	2.33	12.016	0.047	0.051	8.10
27.318	0.110	0.111	0.72	14.163	0.054	0.058	7.48
30.671	0.121	0.120	0.96	14.973	0.056	0.060	7.17
				17.058	0.062	0.066	6.63
				18.017	0.065	0.069	6.10
				18.633	0.067	0.071	6.06
				20.525	0.072	0.076	5.40
				22.100	0.076	0.080	4.84
				25.189	0.084	0.088	3.81
				27.054	0.089	0.092	3.10
				30.143	0.097	0.099	2.11

Table 4.13: (Continued) Isotherm data of nitrogen (N_2) on carbon sample ANGWARD 5. 64 experimental points were measured. Gray values represent points not included in the ARE calculation. For 288.2 K, 312.5 K and 323.4 K the % ARE is 9.32, 6.71 and 8.71 respectively. The N_2 overall ARE is 8.01%.

T = 323.4 K			
P (bar)	q_{pred} (g/g)	q_{exp} (g/g)	% ARE
0.007	0.000	0.000	
0.009	0.000	0.000	58.73
0.552	0.003	0.003	0.18
1.399	0.006	0.007	9.34
1.670	0.007	0.008	8.89
2.258	0.009	0.008	15.56
3.010	0.012	0.014	11.51
4.100	0.016	0.018	12.06
4.995	0.019	0.022	12.96
5.951	0.022	0.023	5.40
8.835	0.030	0.033	7.03
10.197	0.034	0.038	9.70
14.818	0.047	0.052	9.21
16.201	0.050	0.055	9.04
20.367	0.061	0.066	8.12
25.976	0.074	0.079	6.47
29.827	0.083	0.088	5.22

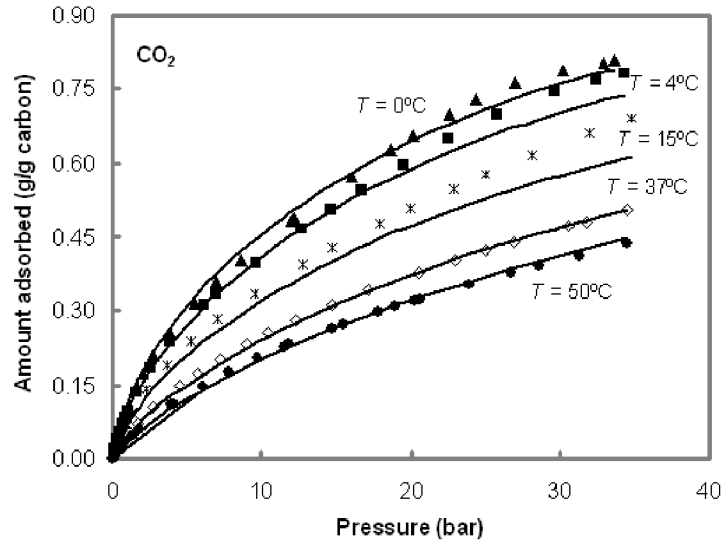


Figure 4.10: Experimental single-component isotherm for adsorption of CO_2 . Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{\text{CO}_2} = 0.42$.

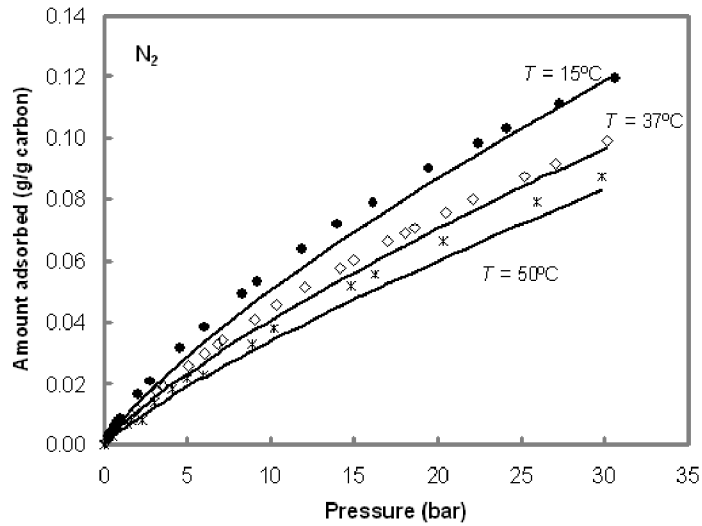


Figure 4.11: Experimental single-component isotherm for adsorption of N_2 . Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{\text{N}_2} = 0.38$.

Table 4.14: Isotherm data of TBM on carbon sample ANGWARD 5. 17 experimental points were measured. Gray values represent points not included in the ARE calculation. For 298.8 K, 310.9 K and 323.6 K the % ARE is 5.89, 3.02 and 6.53 respectively. The TBM overall ARE is 5.07%.

T = 298.8 K			
P _i (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
9.317E-06	0.037	0.032	15.68
1.919E-05	0.045	0.043	6.22
3.112E-05	0.052	0.052	0.25
4.805E-05	0.059	0.057	2.48
1.025E-04	0.073	0.070	3.39
2.029E-04	0.088	0.082	7.33

T = 310.9 K			
P _i (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
9.024E-06	0.028	0.026	6.20
1.969E-05	0.035	0.034	3.68
3.224E-05	0.041	0.040	0.65
4.798E-05	0.046	0.046	1.04
1.027E-04	0.057	0.057	0.29
2.091E-04	0.071	0.075	6.26

T = 323.6 K			
P _i (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
9.209E-06	0.021	0.022	0.98
3.288E-05	0.032	0.032	0.41
4.795E-05	0.035	0.039	9.53
9.781E-05	0.044	0.050	11.75
1.984E-04	0.055	0.061	10.00

Table 4.15: Isotherm data of THT on carbon sample ANGWARD 5. 21 experimental points were measured. Gray values represent points not included in the ARE calculation. For 298.9 K, 310.8 K and 323.6 K the % ARE is 4.10, 4.92 and 9.38 respectively. The THT overall ARE is 6.13%.

T = 298.9 K			
P _i (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
9.232E-06	0.051	0.057	10.47
2.258E-05	0.077	0.079	2.40
3.439E-05	0.092	0.095	3.10
8.225E-05	0.134	0.135	0.79
1.205E-04	0.157	0.162	2.74
1.718E-04	0.182	0.188	3.59
1.913E-04	0.190	0.201	5.60

T = 310.8 K			
P _i (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
1.054E-05	0.035	0.041	14.50
2.366E-05	0.052	0.055	6.74
7.599E-05	0.089	0.085	5.08
1.197E-04	0.110	0.107	3.07
1.782E-04	0.131	0.131	0.27
2.038E-04	0.139	0.141	1.41
5.769E-05	0.079	0.076	3.34

T = 323.6 K			
P _i (bar)	q _{pred} (g/g)	q _{exp} (g/g)	% ARE
9.232E-06	0.020	0.022	10.33
3.361E-05	0.039	0.037	6.59
8.398E-05	0.062	0.056	10.84
8.678E-05	0.063	0.057	10.79
1.507E-04	0.083	0.075	10.68
1.829E-04	0.091	0.083	9.03
2.080E-04	0.097	0.090	7.40

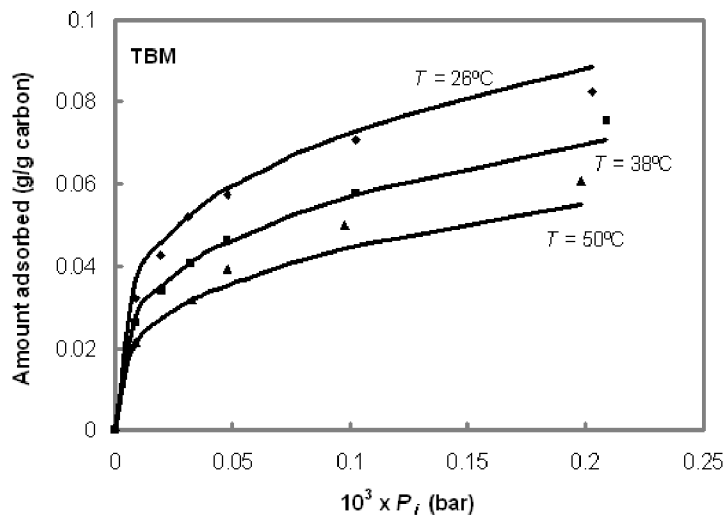


Figure 4.12: Experimental single-component isotherm for adsorption of the odorant TBM. Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{TBM} = 1.03$.

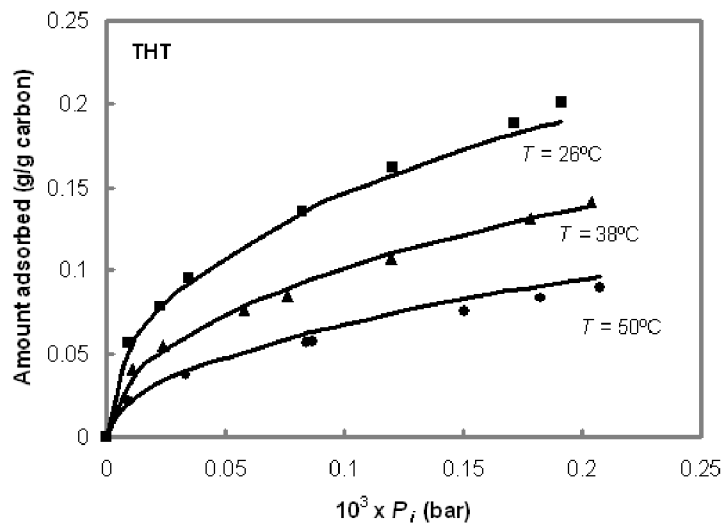


Figure 4.13: Experimental single-component isotherm for adsorption of the odorant THT. Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{THT} = 0.84$.

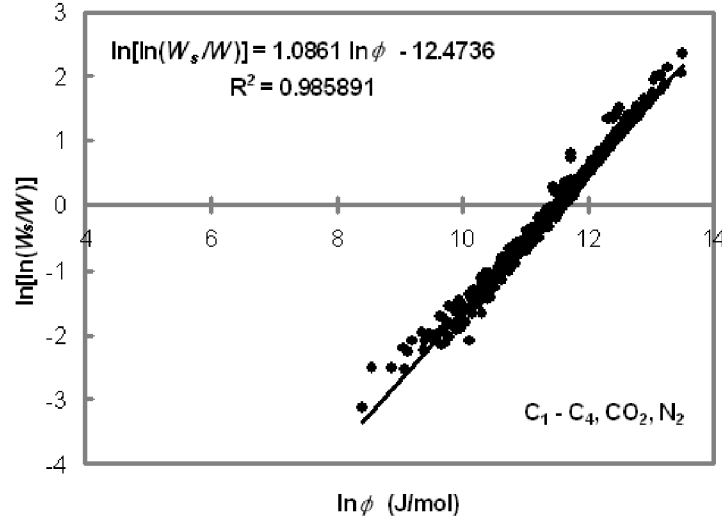


Figure 4.14: Linear fitting of $\ln[\ln(W_s/W)]$ versus $\ln\phi$ to determine γ and n parameters for experimental adsorption of the n -alkanes C_1 - C_4 , CO_2 and N_2 on activated carbon ANGWARD 5. The RSS is 6.85947 and FSE is 0.12172.

The plots show that there is good agreement between model predictions and the experimental data for all of the adsorbates. The single-component adsorption equilibrium data of the various n -alkanes were successfully correlated using the APT.

Figures (4.15) and (4.16) display the experimental characteristic curve obtained. The existence of very little scatter in the data demonstrates that the isotherms of the various adsorbates were successfully correlated as a single temperature-independent characteristic curve. This fact corroborates the applicability of the AP theory to the carbon under study.

The regression sum of squares due to error (RSS) is defined as

$$RSS = \sum (Y_{exp} - Y_{pred})^2, \quad (4.23)$$

where Y is the specific variable (W or q), subscripts exp correspond to the experimental value and $pred$ to the predicted value. The fit standard error is expressed as

$$FSE = \sqrt{\frac{RSS}{DOF}}, \quad (4.24)$$

where DOF is the degree of freedom defined as $(N - m)$, the difference between the number of data points N and the number of coefficients fitted m . The average relative error (ARE) in the amounts adsorbed for the n -alkanes series is defined as

$$ARE \% = \frac{100}{\sum N_{n,Cn}} \sum \left(\sum \frac{|q_{pred} - q_{exp}|}{q_{exp}} \right). \quad (4.25)$$

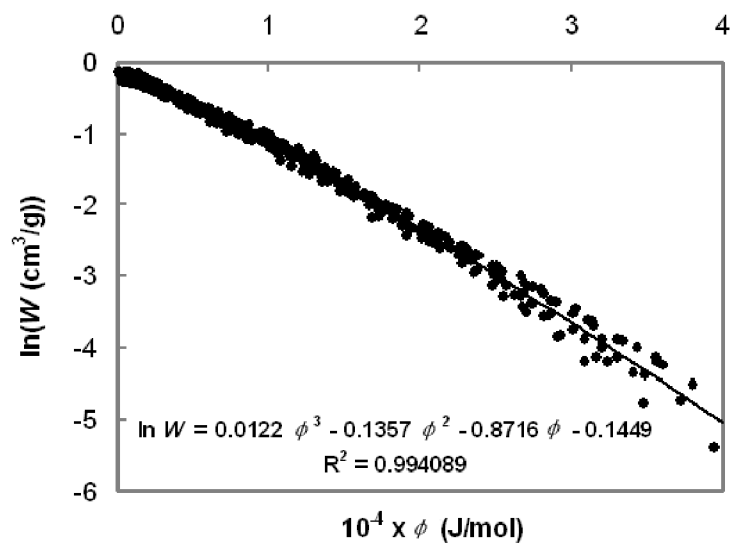


Figure 4.15: Characteristic curve for adsorption of the *n*-alkanes C₁-C₄, CO₂, N₂, TBM and THT, on activated carbon ANGWARD 5. The RSS is 0.97805 and FSE is 0.05148.

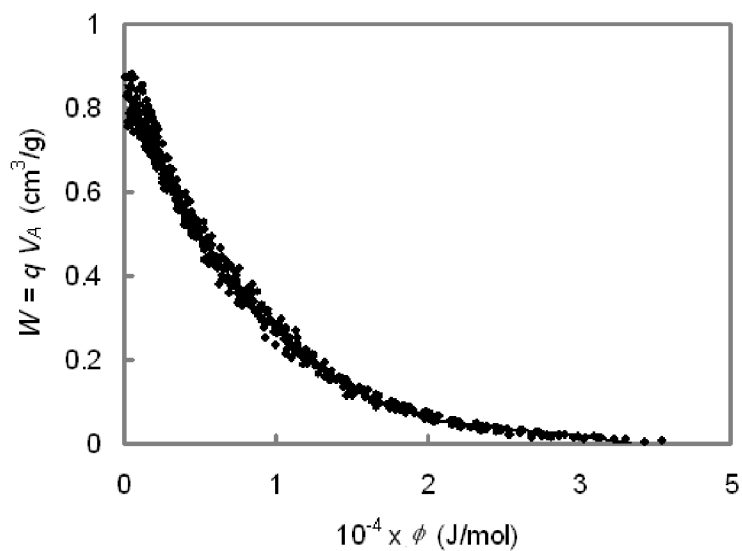


Figure 4.16: Characteristic curve for adsorption of the *n*-alkanes C₁-C₄, CO₂, N₂, TBM and THT, on activated carbon ANGWARD 5.

Except for low-pressure range, where the experimental errors are more pronounced, the low values of the single and overall ARE; the values of the determination coefficients, R^2 , and of the FSE, indicate the quality of the method. Eq.(4.25) satisfactorily represents the system error of adsorption equilibria. Therefore, this potential theory is quite accurate over a broad range of experimental conditions for the *n*-alkanes series C_1 - C_4 adsorbed on ANGWARD 5 activated carbon.

Concerning the adsorbent-capacity deterioration on extended operation due to the nature of NG composition, mainly due to the higher molecular-weight hydrocarbons more strongly adsorbed than methane, Figures (4.17) and (4.18) present this behavior in the low-pressure region, showing the single-component sorption (adsorption/desorption) isotherms at a given temperature for the first four *n*-alkanes and for CO_2 and N_2 , respectively, on the adsorbent chosen (ANGWARD 5). Experimental work revealed no hysteresis and no significant loss of carbon capacity, since, after each isotherm, the carbon conditions reached the starting point of the run, indicating no residual component adsorbed. This reinforces the suitability of the adsorbent selected for the application under work.

Other adsorbents, besides ANGWARDS 1 to 4, were also tested, namely a monolith material supplied by SSCL (rugged and durable material, carbon skeleton that offers enhanced thermal conductivity over packed beds of carbon which translates to smaller temperature gradients during tank charging/discharging and, hence, allows greater storage capacities; $W_s = 0.938 \text{ cm}^3/\text{g}$, $\beta_{C_1} = 0.416$, $\beta_{CO_2} = 0.370$, $\gamma = 3.636 \times 10^{-6}$, $n = 1.307$, $\rho_c = 2.2 \text{ g/cm}^3$) and a nanotube sample S95 ($W_s = 0.440 \text{ cm}^3/\text{g}$, $\rho_c = 1.2 \text{ g/cm}^3$, BET Surface Area = $500 \text{ m}^2/\text{g}$) analyzed in collaboration with Sandeep Agnihotri and Prof. Massoud Rostam-Abadi, from the Department of Civil and Environmental Engineering, University of Illinois, USA. Figures (4.19 - 4.21) compare adsorption isotherms for methane and carbon dioxide for these adsorbents with the ANGWARD 5 carbon sample. The results, as shown in Figure (4.21), show that ANGWARD 5 has higher adsorption capacity for the given adsorbate relative to the nanotube sample, which is illustrative of the proper selection that was made regarding the adsorbent selection for the work we proposed to do. Figures (4.19) and (4.20) present the opposite conclusion, where the monolith sample seems to have at the same operating temperature, higher adsorption capacity for both CO_2 and CH_4 .

4.2.3.3 Sorption Results using Sips and Toth approaches

Two approaches were performed concerning the sorption analysis. One is described in the previous section, where the APT was applied. This analysis was used for adsorbent characterization under the ANGWARD project and later incorporated into the dynamic model of the guard bed. All the data collapsed to a single temperature independent

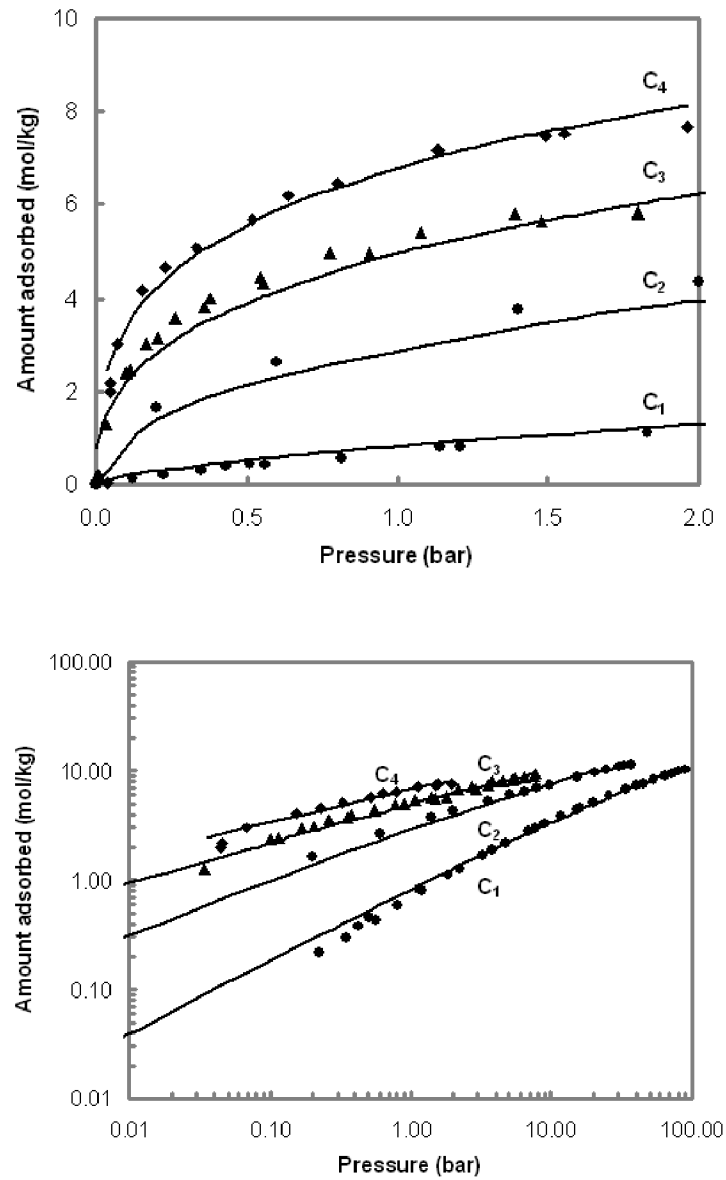


Figure 4.17: Single-component isotherms for hydrocarbons C₁-C₄ adsorption on AN-GUARD 5 at 25°C. Symbols denote experimental data and lines represent predictions from the D-A isotherm model.

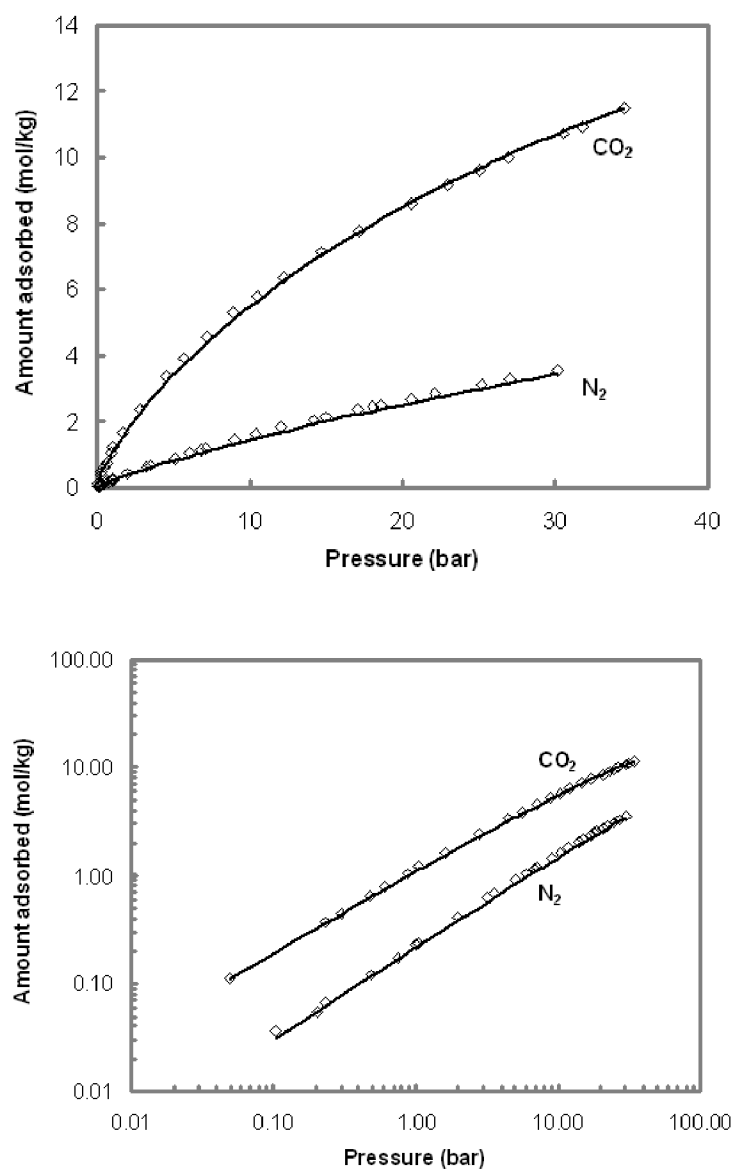


Figure 4.18: Single-component isotherms for CO₂ and N₂ adsorption on ANGWARD 5 at 37°C. Symbols denote experimental data and lines represent predictions from the D-A isotherm model.

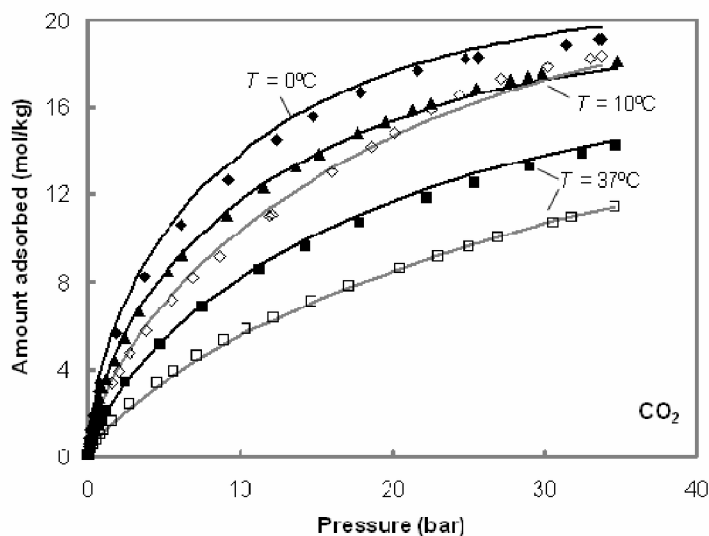


Figure 4.19: Single-component isotherms for CO_2 adsorption on ANGWARD 5 and on monolith samples. Lines represent the D-A prediction and symbols the experimental data measured. Gray lines and open symbols correspond to the ANGWARD 5 sample. Black lines and filled symbols correspond to the monolith sample.

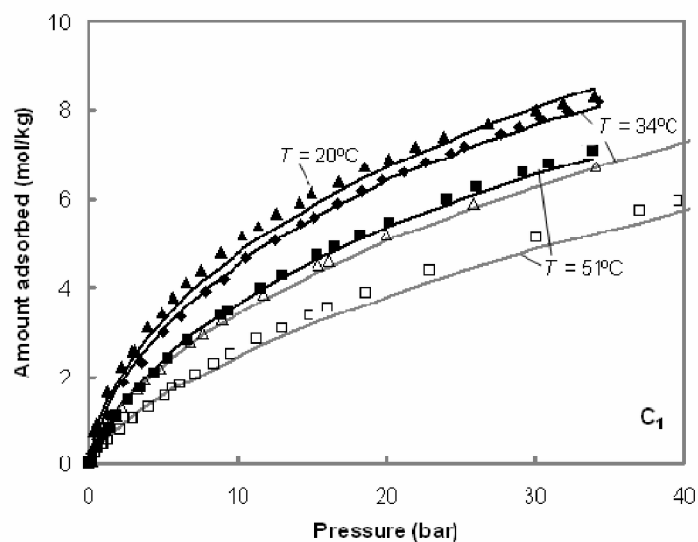


Figure 4.20: Single-component isotherms for CH_4 adsorption on ANGWARD 5 and on monolith samples. Lines represent the D-A prediction and symbols the experimental data measured. Gray lines and open symbols correspond to the ANGWARD 5 sample. Black lines and filled symbols correspond to the monolith sample.

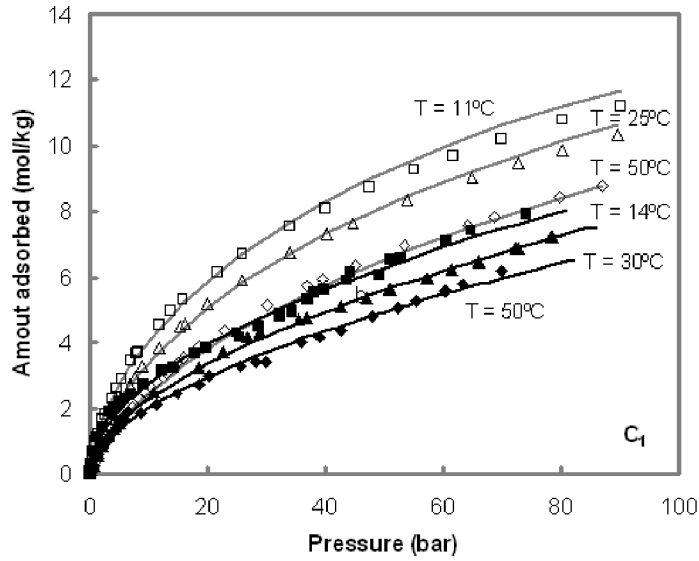


Figure 4.21: Single-component isotherms for CH_4 adsorption on ANGWARD 5 and on nanotube samples. Gray lines and open symbols represent the ANGWARD 5 sample D-A predicted and experimental data, respectively. Black lines and filled symbols represent the nanotube sample Langmuir-Freundlich predicted and experimental data, respectively.

characteristic curve. A second approach, to be applied later on the validation of the experimental PSA unit, was done using an individual fitting at different temperatures for each component [Do (1998)].

An extension of the Freundlich equation (also called Sips equation or Langmuir-Freundlich model) and the Toth model were the empirical isotherm equations applied. These isotherm models were considered, since they have been extensively used to model gas adsorption on microporous adsorbents. In order to obtain a global isotherm equation for each component, at different temperatures, the data was fitted using TableCurve 3D or the Matlab nonlinear optimization routine (ISOFIT2.M) of Do (1998). This script M-file program allows user to obtain optimal parameters for various adsorption isotherm models, by fitting them simultaneously with data of multiple temperatures.

The Sips isotherm is given by

$$c_\mu = \frac{c_{\mu s}(bP)^{1/n}}{1 + (bP)^{1/n}}, \quad (4.26)$$

$$b = b_\infty \exp\left(\frac{Q}{RT}\right) = b_0 \exp\left[\frac{Q}{RT_0} \left(\frac{T_0}{T} - 1\right)\right], \quad (4.27)$$

$$c_{\mu s} = c_{\mu s0} \exp\left[\chi \left(1 - \frac{T}{T_0}\right)\right], \quad (4.28)$$

$$1/n = 1/n_0 + \alpha \left(1 - \frac{T_0}{T}\right). \quad (4.29)$$

The parameters obtained are the maximum adsorbed amount at reference temperature T_0 , $c_{\mu s0}$, the adsorption affinity constant at infinite temperature, b_∞ , the affinity at T_0 , b_0 , the heat coefficient, $\gamma = Q/RT_0$, the coefficient n_0 , the constant for the exponent n , α , and the coefficient χ . P is the pressure, c_μ is the data of the adsorbed amount and Q is the heat of adsorption. The parameter n that characterizes the system adsorbate/adsorbent heterogeneity, is usually greater than 1 and the larger is the more heterogeneous is usually the system.

To obtain the isosteric heat of adsorption for the temperature dependence form of the Sips equation, one uses van't Hoff's equation, which relates the adsorption heat effects to the temperature dependence of the adsorption isotherm,

$$(-\Delta H) = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_\theta, \quad (4.30)$$

where θ is the fractional loading $c_\mu/c_{\mu s0}$. At constant loading $d\theta = 0$ and from Eq. (4.26), $d[(bP)^{1/n}] = 0$. Knowing that

$$d[(bP)^{1/n}] = nbP \ln(bP) d\left(\frac{1}{n}\right) + bdP + Pdb = 0, \quad (4.31)$$

$$d\left(\frac{1}{n}\right) = \frac{\alpha T_0}{T^2} dT, \quad (4.32)$$

and

$$db = -b \frac{Q}{RT^2} dT, \quad (4.33)$$

by substitution of Eqs. (4.32, 4.33) into Eq. (4.31) and then into van't Hoff equation, one obtain

$$(-\Delta H) = Q - n\alpha RT_0 \ln(bP) \quad (4.34)$$

or in terms of θ ,

$$(-\Delta H) = Q - n^2 \alpha RT_0 \ln \left(\frac{\theta}{1 - \theta} \right). \quad (4.35)$$

The isosteric heat of adsorption $(-\Delta H)$ equals the heat of adsorption Q at the fractional loading of 0.5.

The Toth isotherm is given by

$$c_\mu = \frac{c_{\mu s} b P}{[1 + (bP)^t]^{1/t}}, \quad (4.36)$$

$$t = t_0 + \alpha \left(1 - \frac{T_0}{T}\right), \quad (4.37)$$

with b and $c_{\mu s}$ defined the same way as for the Sips approach. To obtain the isosteric heat of adsorption for the temperature dependence form of the Toth equation, one rewrites the Toth equation in the form

$$\theta^t = \frac{(bP)^t}{1 + (bP)^t}, \quad (4.38)$$

to set

$$d[\theta^t] = \theta^t \ln \theta dt, \quad (4.39)$$

$$d[(bP)^t] = (bP)^t \ln(bP) dt + t(bP)^{t-1} d(bP), \quad (4.40)$$

with

$$dt = \alpha \frac{T_o}{T^2} dT. \quad (4.41)$$

Hence

$$\theta^t \ln \theta dt = \frac{(bP)^t \ln(bP) dt + t(bP)^{t-1} d(bP)}{[1 + (bP)^t]^2}. \quad (4.42)$$

Knowing the temperature dependence of t and b , substitution into the van't Hoff equation gives the final expression for the isosteric heat of adsorption

$$(-\Delta H) = Q - \frac{1}{t} \alpha R T_o \left\{ \ln \frac{\theta}{(1 - \theta^t)^{1/t}} - \frac{\ln \theta}{(1 - \theta)^t} \right\}. \quad (4.43)$$

Parameter Q equals the isosteric heat of adsorption $(-\Delta H)$ when the fractional loading is zero.

Adsorption equilibrium data and heats of adsorption are essential for the proper design and operation of adsorption processes. The main problem with Sips and D-A models is their incorrect behavior at low pressure, where the isotherms do not give the correct Henry's law limit. Moreover, heats of adsorption are usually estimated from the temperature dependence of the adsorption isotherms. Therefore, correlations that are very sensitive to temperature over relatively wide ranges are essential to the design and operation of such processes. Several models are available in the literature for describing the temperature dependence of gas adsorption equilibria. However, they have revealed to be not very promising for the estimation of properties, such as the isosteric heat of adsorption, which require determining the dependencies on temperature. They can lose much of their accuracy after some manipulation. Those models do not work well for highly non-ideal systems and give physically unrealistic values for the parameters. Instead, other alternative models to describe the temperature-dependent vapor-adsorbate equilibrium, such as the remodified, modified Antoine and virial adsorption isotherms can be eventually more usefully applied to predict the isosteric heat of adsorption [Al-Muhtaseb and Ritter (1998a,b); Friday and LeVan (1982); HacsKaylo and LeVan (1985); J. J. Mahle and Friday (1994); Siperstein and Myers (2001); Sundaram and Yang (1998); Taqvi and LeVan (1997a,b)]. The modified virial equation has the correct asymptotic behavior at high and

low pressure plus sufficient flexibility to fit all the isotherms within experimental error. The average difference between the experimental pressure and the value calculated by Siperstein and Myers (2001) is 1.1%. It is estimated that the assumption of constant heat of adsorption over a temperature interval of $\pm 30^\circ\text{C}$, from a reference temperature, generates errors less than 1% in pressure and loading [Siperstein and Myers (2001), D. Shen and Myers (2000)]. That's why commonly the assumption regarding the temperature independence of isosteric heats is considered under these conditions, simplifying the models of heat of adsorption on an heterogeneous adsorbent [Sircar and Cao (2002)].

From an engineering perspective, for the simulation of adsorption processes, the mathematical model must satisfy as much as possible all thermodynamic limits and consistency checks that can correlate the available data accurately over wide ranges of temperature and pressure irrespective of the type of adsorbent or the degree of non-ideality present in the system. Hence, in order to obtain enhanced global isotherm fits and overcome possible problems in the CO_2 breakthrough modeling, one performed refined CO_2 experimental isotherms at the low pressure zone, complementing the data reported in Tables (4.9-4.11). Table (4.16) shows the single-component isotherm data for CO_2 adsorption on ANGWARD 5 carbon sample at three different temperatures, used in the kinetic studies.

As a first approximation $c_{\mu s}$, t and n were considered independent of temperature. Both Sips and Toth fittings gave an indication of the heat of adsorption of each component. Table (4.17) presents the optimum results obtained from the two equations, in fitting the components data on the carbon sample. N_2 , CO_2 and CH_4 were the gases used in the laboratorial PSA unit and the ones considered in the modeling validation of the experimental work. Through the Sips model, the heat of adsorption of N_2 , CO_2 and CH_4 , independent of the loading and pressure, are 11.404 kJ/mol, 20.366 kJ/mol and 16.172 kJ/mol, respectively, and for the Toth isotherm are 11.133 kJ/mol, 20.257 kJ/mol and 16.143 kJ/mol, respectively. As one can see, using both models the values are quite similar and satisfactory.

The n and t dependencies of temperature were then considered and Table (4.18) presents the optimum results obtained from the two isotherm type-equations, in fitting the components data on the carbon sample. Figures (4.22-4.27) show the fitting degree between these equations and the experimental data obtained. The fit is in excellent agreement with the experimental points, describing the data of the components on the ANGWARD 5 carbon sample with good success.

Figure (4.28) illustrates the variation of the isosteric heat of the three components on the carbon sample with pressure, for both Sips and Toth approaches, at three different temperatures. As one can see, using both models the heat values are quite satisfactory when compared with literature [Al-Muhtaseb and Ritter (1998a), K. T. Chue and Yang

Table 4.16: Isotherm data of carbon dioxide (CO_2) on carbon ANGWARD 5 at the low pressure region. 76 experimental points were measured at three different temperatures.

T = 299.08 K		T = 310.23 K		T = 319.22 K	
P (bar)	q_t (mol/kg)	P (bar)	q_t (mol/kg)	P (bar)	q_t (mol/kg)
0.000	0.000	0.000	0.000	0.000	0.000
0.008	0.017	0.009	0.025	0.009	0.008
0.024	0.062	0.025	0.055	0.025	0.032
0.039	0.100	0.038	0.079	0.039	0.053
0.052	0.132	0.052	0.103	0.054	0.074
0.066	0.160	0.067	0.126	0.073	0.098
0.079	0.193	0.082	0.149	0.086	0.115
0.115	0.269	0.110	0.191	0.102	0.136
0.151	0.325	0.126	0.212	0.125	0.162
0.184	0.391	0.162	0.262	0.151	0.194
0.285	0.541	0.202	0.312	0.201	0.248
0.444	0.740	0.251	0.371	0.251	0.300
0.739	1.074	0.372	0.506	0.352	0.397
0.972	1.323	0.451	0.588	0.445	0.483
1.393	1.752	0.548	0.685	0.532	0.555
1.852	2.151	0.697	0.823	0.698	0.689
3.175	3.112	0.796	0.915	0.798	0.763
4.256	3.789	0.977	1.065	0.973	0.894
4.256	3.785	1.491	1.462	1.481	1.226
5.152	4.280	2.240	1.950	2.212	1.670
7.007	5.160	3.238	2.549	2.727	1.945
7.007	5.160	4.057	2.980	3.224	2.195
7.014	5.171	5.033	3.471	3.798	2.488
7.287	5.325	6.237	3.989	4.932	2.963
10.136	6.407	7.935	4.646	6.790	3.676
		9.482	5.178	9.762	4.655

4.2 Adsorption Equilibrium Measurements

Table 4.17: Parameters obtained from the data fitting with the Sips and Toth equations assuming $c_{\mu s}$, t and n independent of temperature. The equilibria data of N_2 and CH_4 was taken from Tables (4.12), (4.13) and (4.4) up to 10-12 bar [Do (1998)].

	Sips			Toth		
	N_2	CO_2	CH_4	N_2	CO_2	CH_4
$c_{\mu s}$ (mol/kg)	9.350	19.855	11.607	241.296	157.683	29.769
b_o (bar ⁻¹)	0.024	0.039	0.050	0.002	0.024	0.056
n, t	1.095	1.240	1.203	0.299	0.286	0.418
Q (kJ/mol)	11.404	20.366	16.172	11.133	20.257	16.143
T_o (K)	288.20	299.08	284.25	288.20	299.08	284.25
R^2	0.99960	0.99994	0.99961	0.99893	0.99992	0.99957
FSE	0.01236	0.01324	0.02526	0.02113	0.01457	0.02656
Residuals (mol/kg)	< 0.03	< 0.03	< 0.05	< 0.03	< 0.03	< 0.05

Table 4.18: Parameters obtained from the data fitting with the Sips and Toth equations assuming $c_{\mu s}$ independent of temperature. The equilibria data of N_2 and CH_4 was taken from Tables (4.12), (4.13) and (4.4) up to 10-12 bar. See also Figures (4.22-4.27) [Do (1998)].

	Sips			Toth		
	N_2	CO_2	CH_4	N_2	CO_2	CH_4
$c_{\mu s}$ (mol/kg)	11.282	20.608	12.951	94.044	73.863	46.796
b_o (bar ⁻¹)	0.018	0.036	0.039	0.005	0.042	0.046
α	0.383	0.126	0.373	0.545	0.080	0.270
n_o, t_o	1.140	1.252	1.257	0.340	0.348	0.346
Q (kJ/mol)	8.974	19.583	14.128	17.777	22.019	20.800
T_o (K)	288.20	299.08	284.25	288.20	299.08	284.25
R^2	0.99975	0.99994	0.99974	0.99986	0.99991	0.99970
FSE	0.01063	0.01286	0.02088	0.00794	0.01592	0.02247
Residuals (mol/kg)	< 0.04	< 0.04	< 0.05	< 0.03	< 0.04	< 0.05

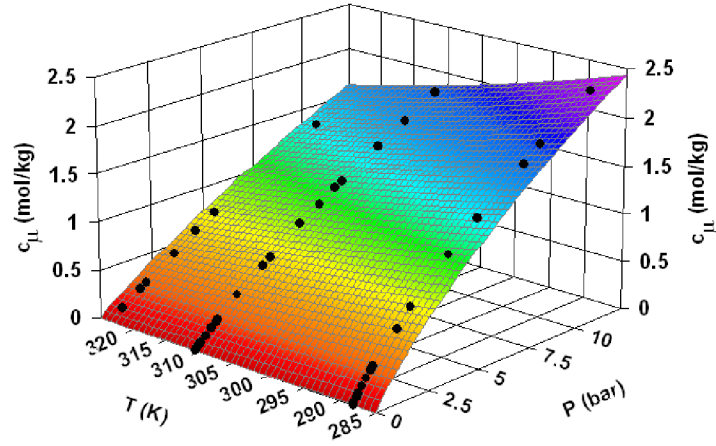


Figure 4.22: Fitting of the N_2 experimental data with the Sips equation, assuming $c_{\mu s}$ independent of temperature. Symbols denote the experimental data and surface represents the fitted equation.

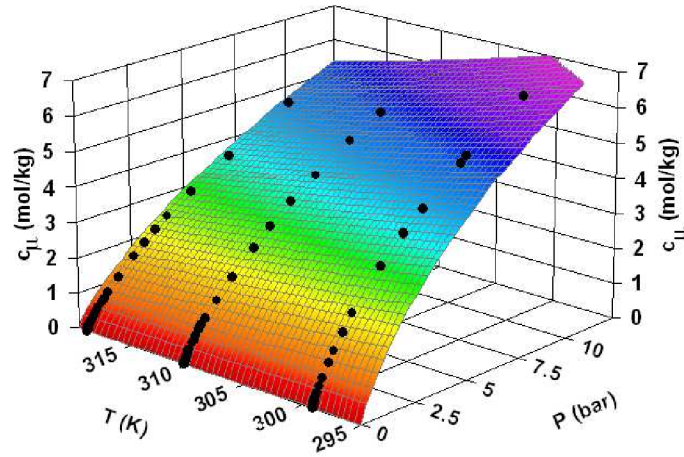


Figure 4.23: Fitting of the CO_2 experimental data with the Sips equation, assuming $c_{\mu s}$ independent of temperature. Symbols denote the experimental data and surface represents the fitted equation.

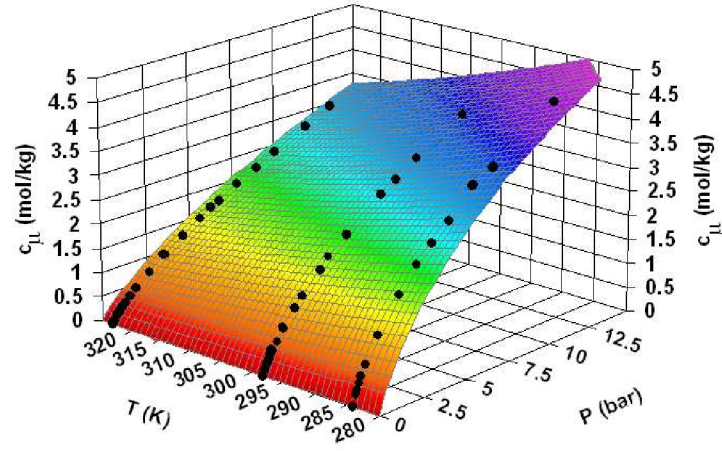


Figure 4.24: Fitting of the CH_4 experimental data with the Sips equation, assuming $c_{\mu s}$ independent of temperature. Symbols denote the experimental data and surface represents the fitted equation.

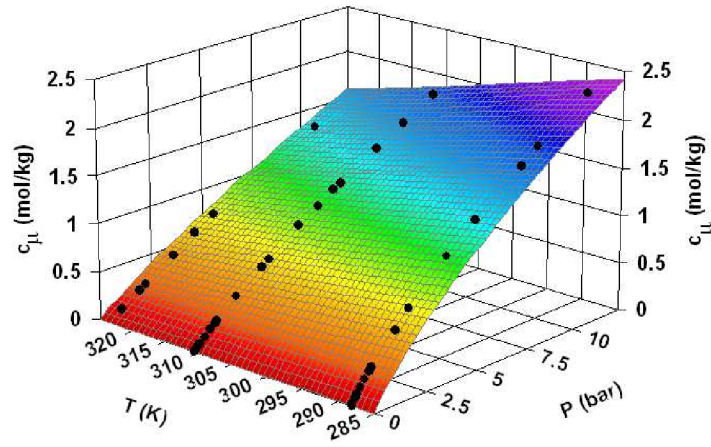


Figure 4.25: Fitting of the N_2 experimental data with the Toth equation, assuming $c_{\mu s}$ independent of temperature. Symbols denote the experimental data and surface represents the fitted equation.

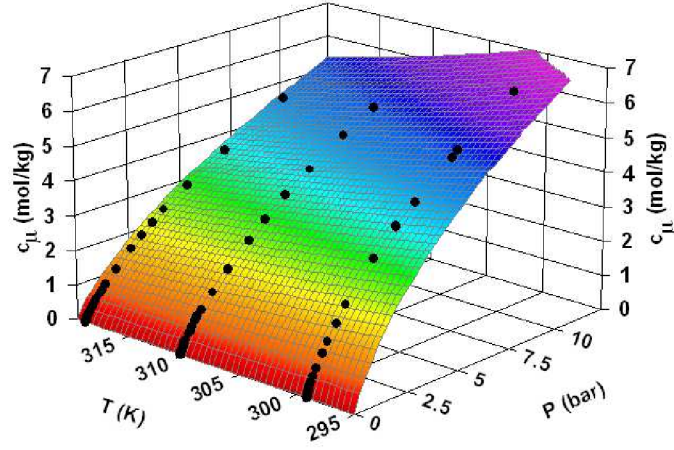


Figure 4.26: Fitting of the CO₂ experimental data with the Toth equation, assuming $c_{\mu s}$ independent of temperature. Symbols denote the experimental data and surface represents the fitted equation.

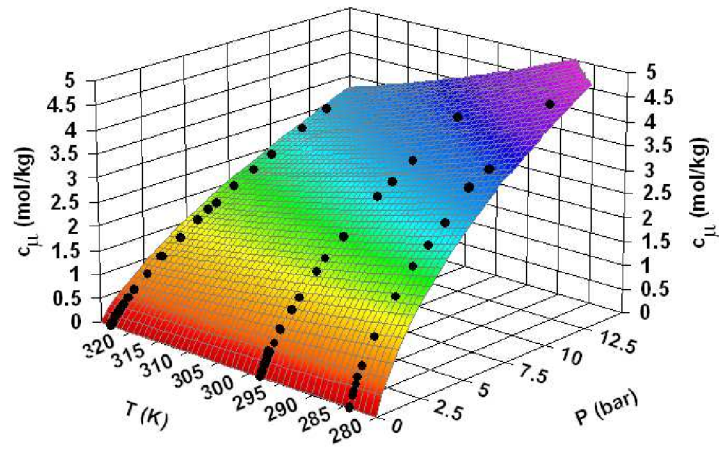


Figure 4.27: Fitting of the CH₄ experimental data with the Toth equation, assuming $c_{\mu s}$ independent of temperature. Symbols denote the experimental data and surface represents the fitted equation.

(1995)]. The isosteric heat of each pure gas decreases with increasing loading, showing that the carbon is energetically heterogeneous for adsorption of N₂, CO₂ and CH₄. Most amorphous adsorbents like activated carbons belong to this category. Heterogeneity is introduced by the presence of a distribution (network) of micro-meso pores of different sizes and shapes within the adsorbent mass, as well as by a distribution of chemically different adsorption sites within the pores. It can also be introduced by the presence of a binder material used for pelletizing an otherwise homogeneous adsorbent. Hence, this behavior is due to the preferential filling of the higher energy adsorption sites at lower pressures. At higher pressures the lower energy sites are preferentially filled. The degree of heterogeneity is intensified when the decrease in the isosteric heat with increasing coverage is present at a very low pressure, where even the Henry's law region may not be experimentally measurable [D. Shen and Myers (2000), Sircar and Cao (2001), S. Sircar and Rao (1999)].

For example, from the Toth model, the heat in the Henry's law limit is 22 kJ/mol for CO₂ and then it decreases with increased adsorbate loadings, and finally levels off at the average value of 21.5 kJ/mol, at higher pressures. As one can see, the heat dependencies on temperature over a range of 20°C for CO₂ and 65°C for N₂ and CH₄ are not greatly significant, which corroborates the commonly simplified modeling assumption already referred regarding the temperature dependence of isosteric heats [D. Shen and Myers (2000)].

The attempt to account for all the dependencies of $c_{\mu s}$, n and t on temperature in Eqs. (4.26) and (4.36) was also considered, although these models did not work well giving physically unrealistic values for parameters, namely the Q value for the N₂ data up to 12 bar, and Ω for the CH₄ data.

The D-A approach was also implemented in the calculation of the isosteric heat of adsorption of each component, in order to compare the results with the previous Sips and Toth approaches. Through the Eqs. (4.1, 4.30) one gets

$$(-\Delta H) = \beta \bar{\phi} + RT^2 \left(\frac{d \ln P_s}{dT} \right) - \beta T \left(\frac{d \ln V_m}{dT} \right) / \left(\frac{d \ln W}{d \phi} \right), \quad (4.44)$$

where $\bar{\phi}$ is such that $W(\bar{\phi}) = \bar{q} V_m$ [Mota and Rodrigo (2000)]. This is a straightforward calculation because the D-A equation can be inverted to give an expression for $\bar{\phi}$ that is explicit in $\bar{q}$. Figure (4.29) illustrates the respective variation of the isosteric heat of the three components on the carbon sample with the loading. The CO₂ line which differ from the general trend corresponds to the CO₂ data under conditions below the critical temperature, where the adsorbed-phase molar volume, V_m , and the saturated vapor pressure of the adsorbate, P_s , are calculated from the modified Rackett equation [Eq.(4.6)] and the Wagner equation [Eq.(4.7)], respectively. Above the critical temperature, the work

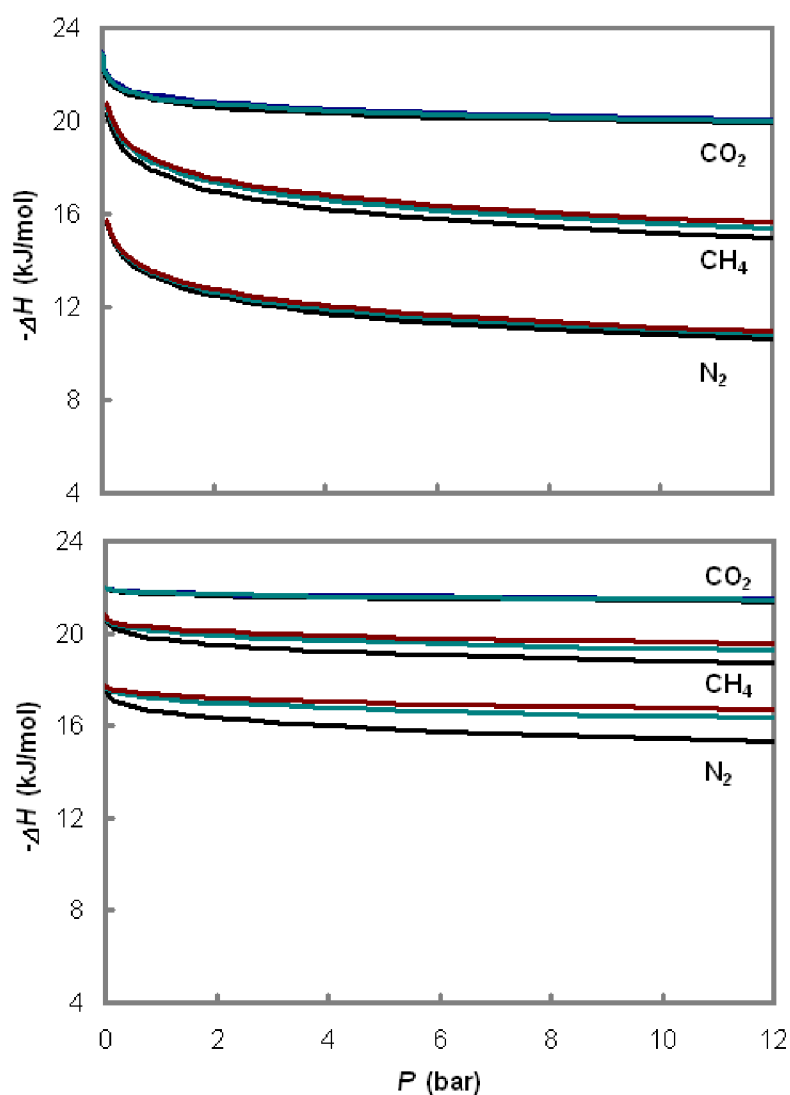


Figure 4.28: Plots of the isosteric heat of adsorption of N_2 , CO_2 and CH_4 on ANGWARD 5 carbon sample versus pressure, applying the Sips (top) and Toth (bottom) approaches. The several lines for each component correspond to the experimental temperatures at which the equilibria data were taken.

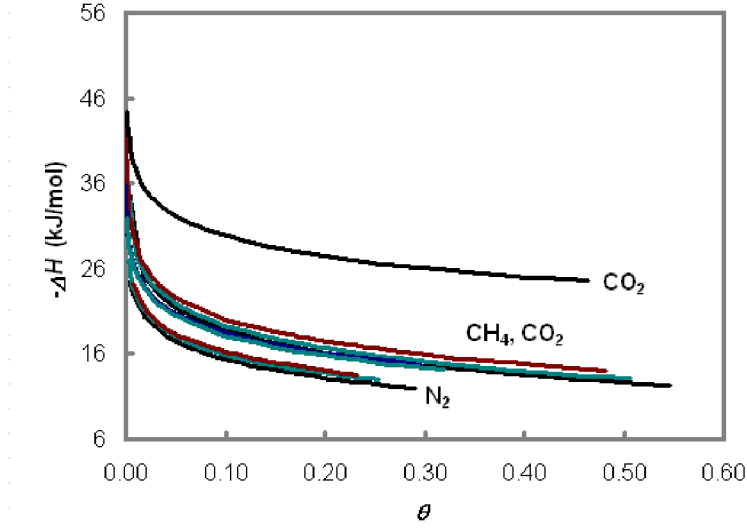


Figure 4.29: Variation of the isosteric heat of adsorption of N_2 , CO_2 and CH_4 on AN-GUARD 5 carbon sample with the loading, applying the D-A approach. The several lines for each component correspond to the experimental temperatures at which the equilibria data were taken.

followed the suggestions of [Agarwal and Schwarz \(1988\)](#), and [S. Ozawa and Ogino \(1976\)](#), and this could explain the differences observed in Figure (4.29).

The results showed that the assumptions made may cause significant discrepancies in calculated isosteric heats of adsorption, even at moderate pressures that are relevant to industrial adsorption processes. Nevertheless, the Sips model was the method selected for the equilibrium and kinetics determination, and the modeling of the adsorption based-process. The advantage of this model is its direct extension to multicomponent prediction, its mathematical simplicity and its great ability to fit experimental data. For these reasons, the Sips model is predominantly used in the modeling and design of adsorbers and cyclic gas separation processes for concentrated mixtures [[Yang \(1987\)](#)]. The multicomponent extension of the Sips model is

$$c_{\mu i} = \frac{c_{\mu si}(b_i P y_i)^{1/n_i}}{1 + \sum (b_i P y_i)^{1/n_i}}, \quad (4.45)$$

where it is assumed that $c_{\mu si}$ is independent of temperature, y_i is the molar fraction of component i in the gas phase, and b_i and n_i are given by Eqs.(4.27, 4.29) for each component i .

4.2.4 Summary

Single-component adsorption equilibria of methane, ethane, propane, butane, carbon dioxide, nitrogen, tert-butyl mercaptan (TBM) and tetrahydrothiophene (THT) were measured on an activated carbon with the desirable characteristics for a guard bed intended for ANG storage and for cyclic gas separation processes. The adsorption equilibria plots show a very good agreement between the D-A model predictions and the experimental values for all of the adsorbates. It is also somewhat surprising to observe that most of the odorant measurements were in the non-linear range of the isotherms even at the very low concentrations considered in this study.

The experimental adsorption data were successfully correlated using the Adsorption Potential Theory in the form of a characteristic curve. The existence of very little scatter in the characteristic curve data demonstrates that the isotherms of the various adsorbates were successfully correlated as a single temperature independent curve. This corroborates the applicability of the Adsorption Potential theory to the carbon under study.

To obtain a workable isotherm model for process simulation of the guard bed, the experimental characteristic curve was successfully fitted to the Dubinin-Astakhov (D-A) equation. The regressed value of W_s is in excellent agreement with the total pore volume determined from the N_2 adsorption at 77 K.

For breakthrough analysis, adsorption kinetics studies and process modeling purposes of the PSA, the experimental data was also successfully fitted to the Sips isotherm model, extended to the multicomponent form. By fitting the equilibrium data, the isosteric heat of adsorption for the components was calculated with the van't Hoff relation equation, obtaining its dependence on the loading.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

4.3.1 Introduction

This section reports the pressure swing adsorption experimental apparatus built and the studies performed to understand the process operation and to validate the modeling work developed.

4.3.2 Apparatus Description

An experimental PSA apparatus capable of operating at several process conditions was built. In an attempt to operate a more flexible and versatile bed, and use different adsorbent amounts, the bed was built in such a way that its length is variable. The vessel is prepared to adjust the axial position of the temperature sensors located at the inside, depending on the bed length considered.

Figure (4.30) shows the schematic diagram of the 316 stainless steel (SS) PSA cell developed for experimental studies. The bed length is adjusted using solid SS blocks with different volumes. The empty cell has a maximum available volume of 483 cm³, which corresponds to approximately 193 g of adsorbent ANGWARD 5, and is capable of containing 129 g of adsorbent at the minimum volume of 322 cm³ [see also Table (4.24)]. Besides the adsorbent, were placed approximately 30 to 40 mm height of SS solid spheres at both ends of the bed, separated by a 2 mm SS perforated plate and a thin cotton film as filter. This procedure ensures a suitable gas distribution through the adsorbent bed and avoids loss of adsorbent particles. The cell is sealed by teflon rings. The flow through the bed was generally assumed from the bottom to the top, and the temperature profiles during measurements were acquired at 150, 350 and 550 mm from the column base.

Figure (4.31) presents a picture of the PSA apparatus. The unit is equipped with three platinum Pt100 temperature probes coupled with digital controllers and electric shielded cables rolled along the main apparatus, for temperature control. Several power supplier, acquisition and control boards ensure the operation of all instruments. The composition analysis is performed by mass spectrometry using a Dycor ProLine spectrometer, operated with DYCOR System 2000 software (Appendix A).

The system data acquisition and control is done using an in-house developed software, BioCTR, which was developed in Labview. In this software it is possible to establish two execution modes: a manual and an automatic one. The acquisition channels correspond to:

- three RTD's for temperature recording along the bed, located inside the vessel,
- two mass flow controllers (MFCs) positioned at the inlet to feed the system, and one extra-MFC located at system exit, which is used as auxiliary for the determination of the total feed exiting the PSA unit, and is directed to the composition analyzer,
- one back pressure regulator located at the end side of the system, to control the inside pressure through an analogic output,
- a pressure transducer (PT Technics),

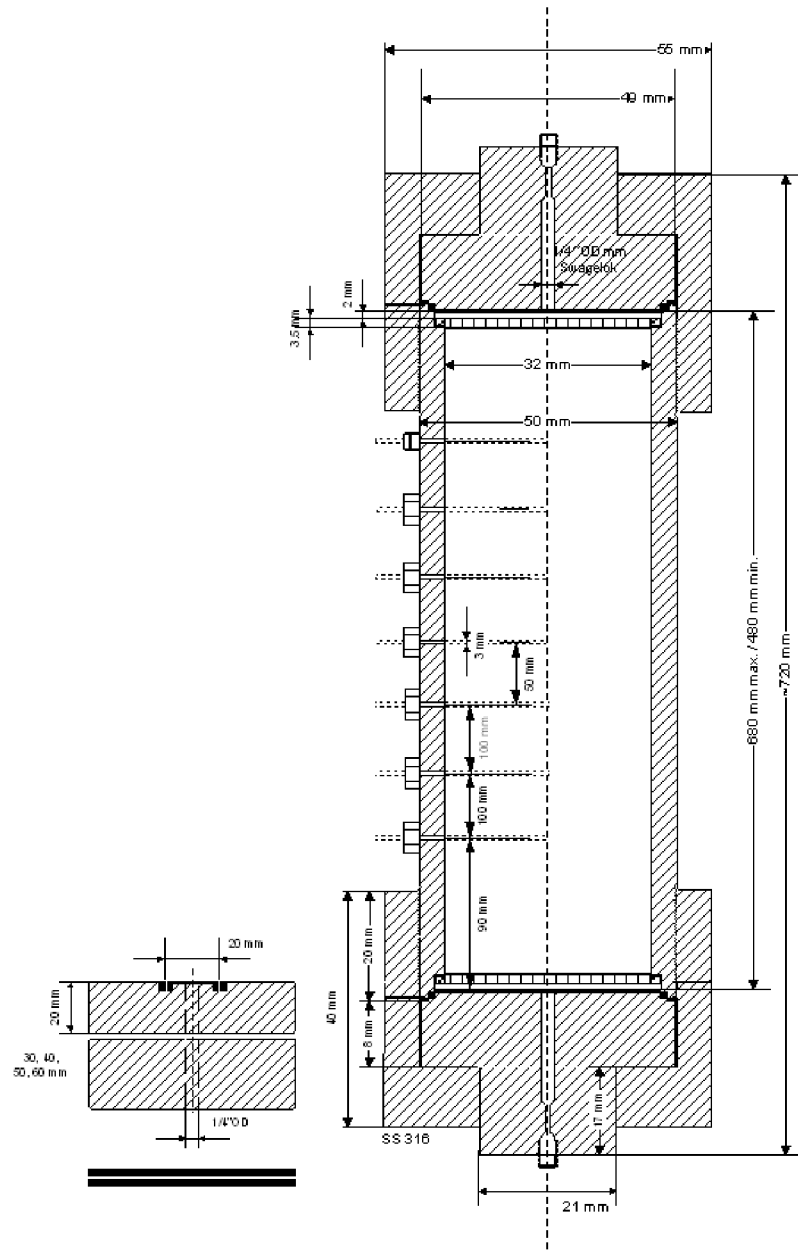


Figure 4.30: Schematic diagram of the PSA vessel built in the laboratory for experimental measurements.

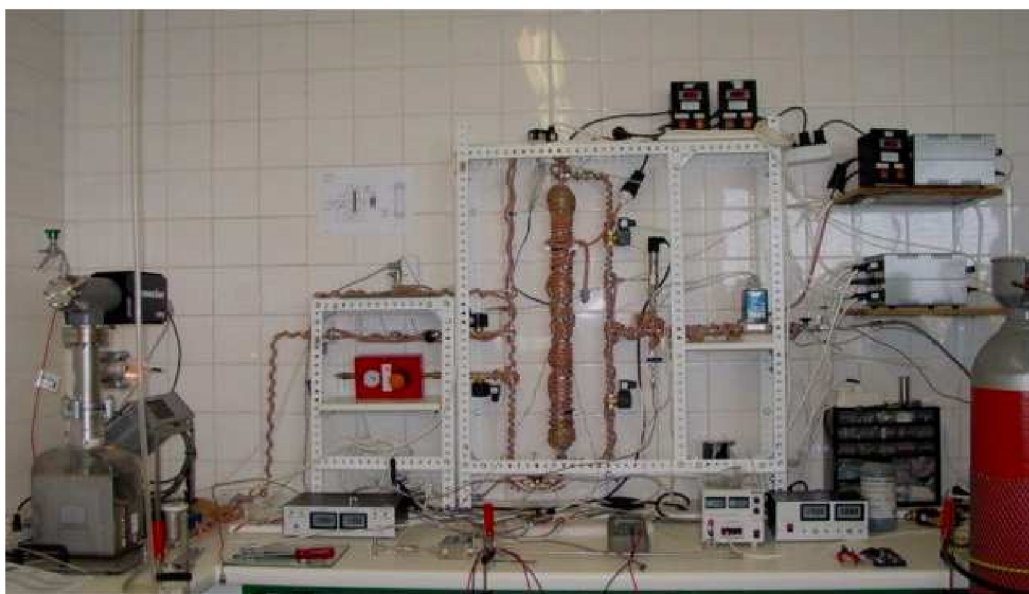


Figure 4.31: PSA apparatus built in the laboratory for experimental measurements.

- digital outputs signed for ten solenoid electric valves, normally closed.

Figures (4.32), (4.33) and (4.34) show the real-time data acquisition console, the cycle schedule console and the real-time display of measured data, respectively. During the real-time measurements, notes can be added to the acquisition file in order to help the user during experiments. The program was developed in such a way that the user is able to schedule a complete or a partial PSA cycle, and to control temperature, pressure and/or flow profile, using polynomial or exponential functions. Each PSA configuration file can be stored and reused when necessary.

4.3.2.1 Start-up

Experiments with gases such as N_2 , CH_4 , He and CO_2 , at different operating conditions, were performed in the PSA unit. To prepare the apparatus for the pressure swing experimental runs, the following procedure is executed:

- Temperature increase of the adsorbent bed progressively up to ≈ 70 - $80^\circ C$.
- Adsorbent degassing at high temperature and vacuum with or without a flow of helium (30-50 ml/min) for several hours.
- Electronic stabilization of the instruments (MFC's, BPR, power supplies) for approximately 30 minutes.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

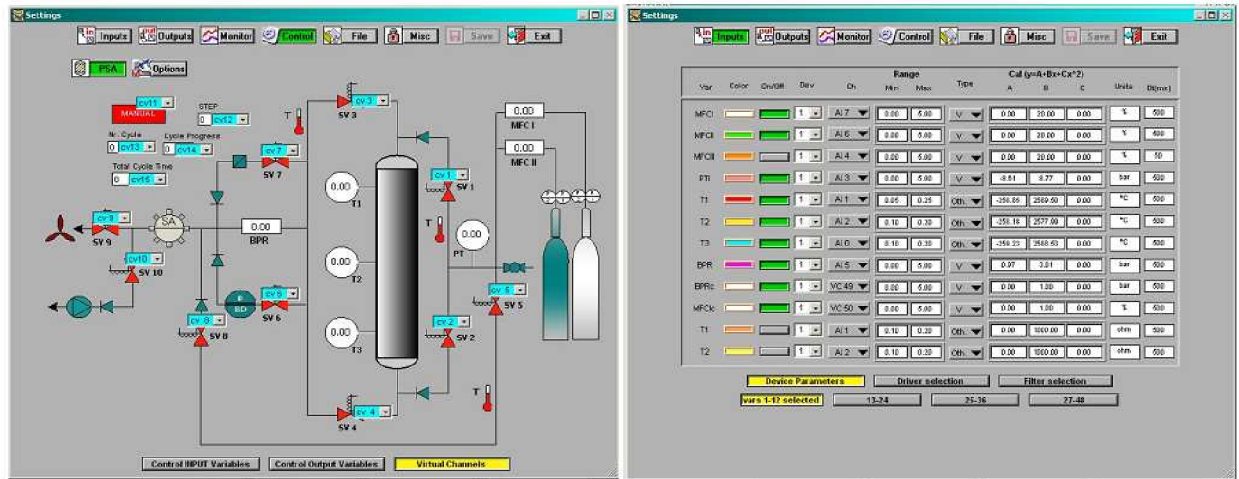


Figure 4.32: BioCTR real-time data acquisition console.

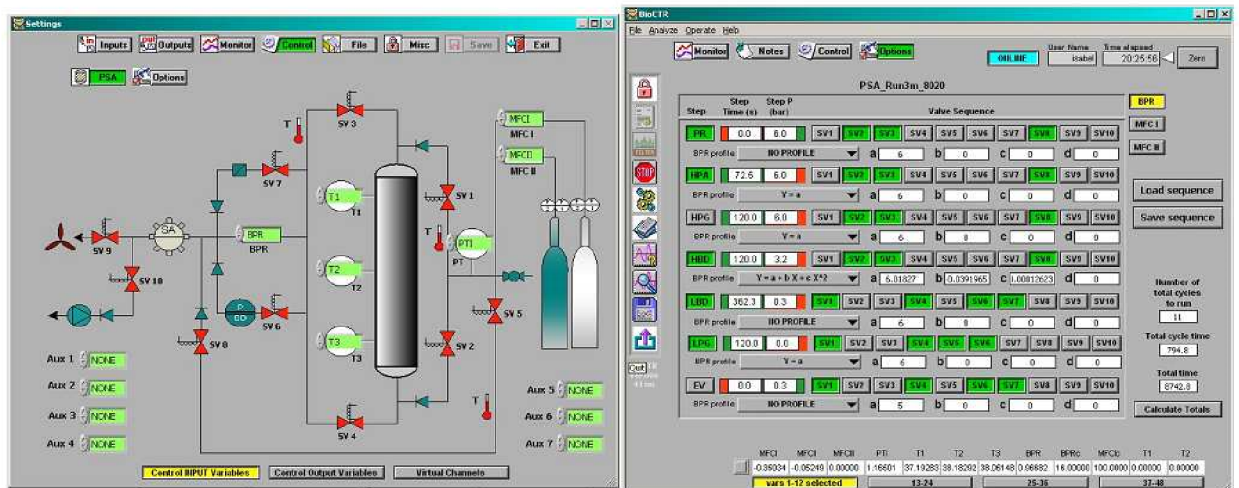


Figure 4.33: BioCTR cycle schedule console.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

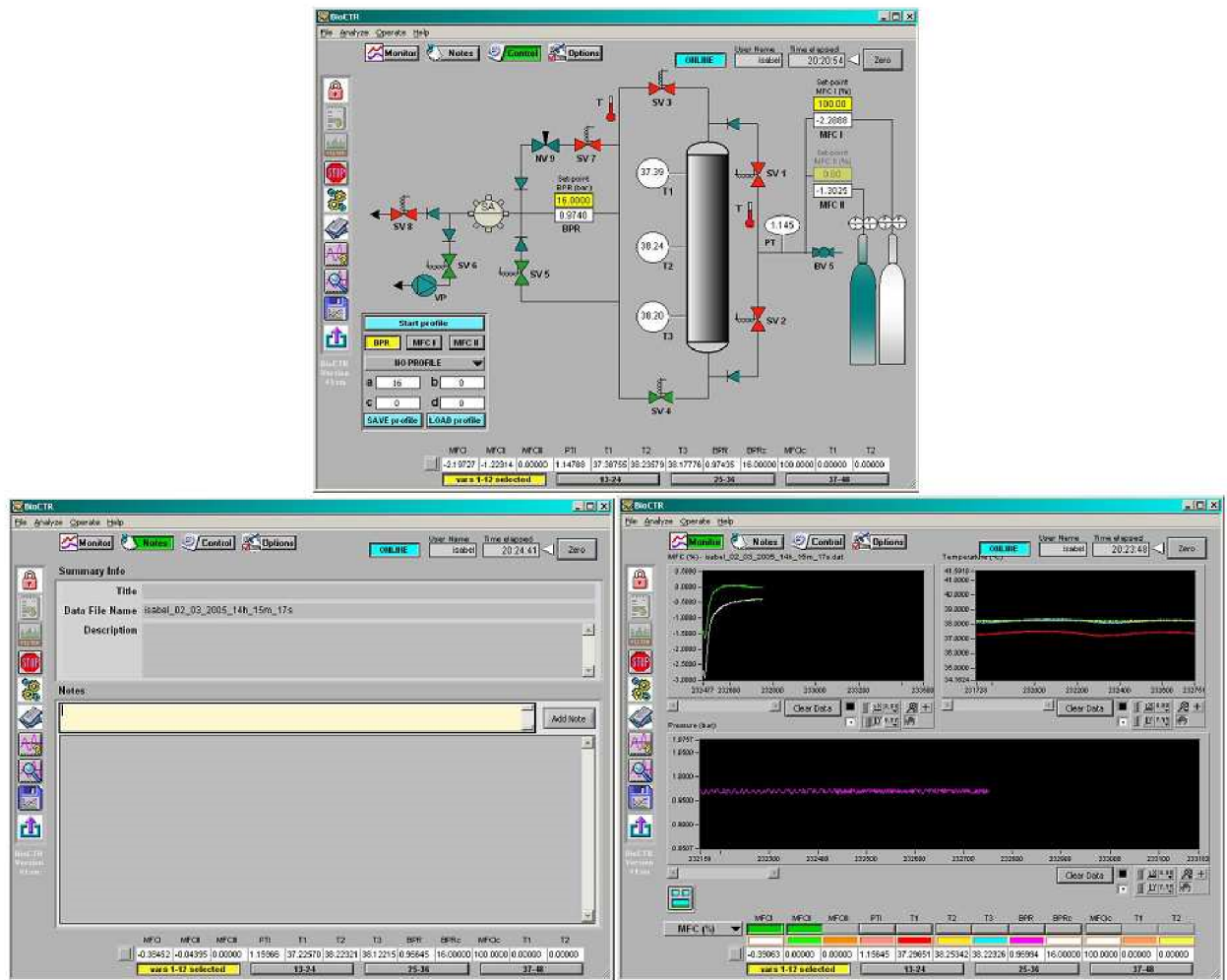


Figure 4.34: BioCTR real-time display of measured data.

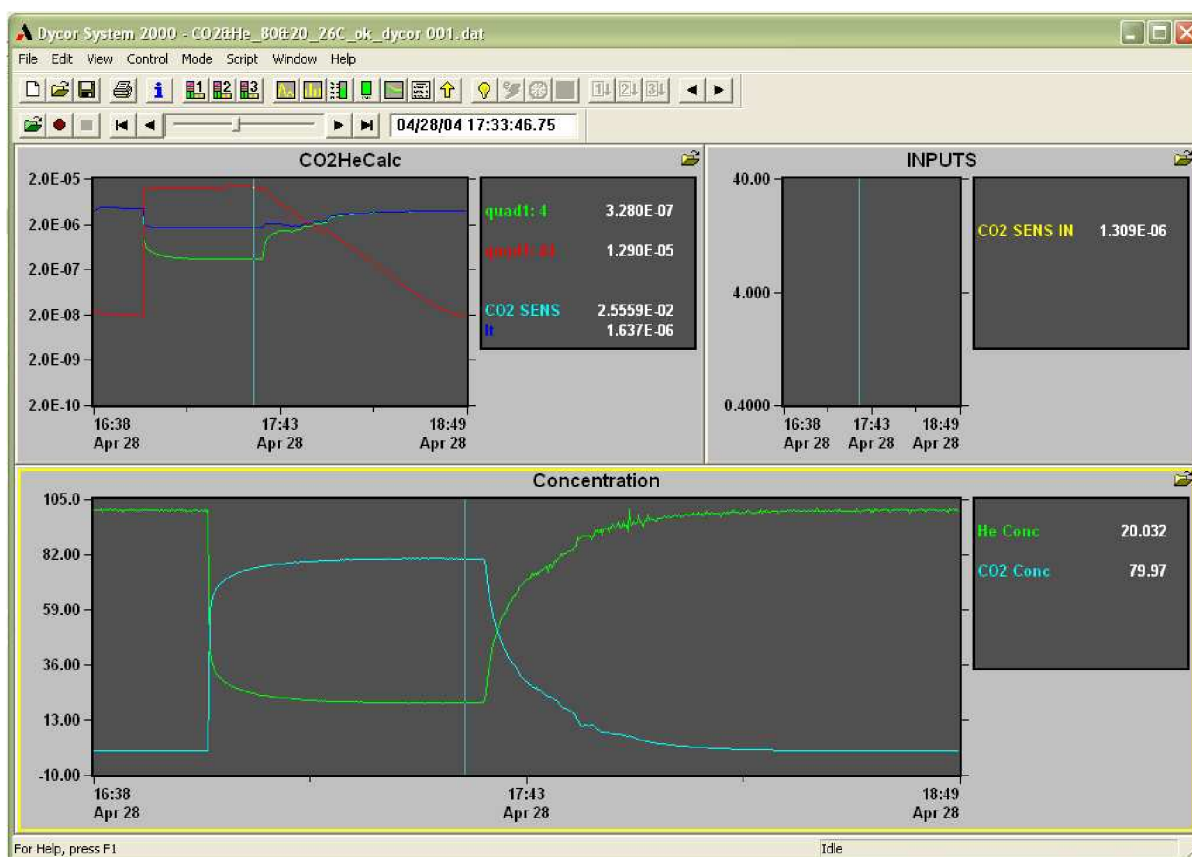


Figure 4.35: Illustrative example of the experimental method applied for composition analysis of the PSA exit stream. For the specified mixture, the mass spectrometer uses a configuration file built in the DYCOR System 2000 software. The file refers to a CO₂/He 80/20 wt% mixture at 26°C.

- MS preparation for operation. The system is warmed up for 1 hour prior to performing the auto-calibration feature in the System 2000 software. Dycor ProLine MS offers automatic calibration and output in quantitative concentration units like percent, and does all the calculations needed for composition analysis. A configuration file that works with DYCOR System 2000 software is built for each mixture to be analyzed. These files provide three trend screens for data acquisition, input, and reporting of concentrations, and allow for the calculation and reporting of normalized concentrations of the gaseous streams [Figure (4.35)]. Appendix E fully describes these calculations and the configuration files needed for the composition analysis.

4.3.2.2 Breakthrough and Blowdown Experiments

Assuming a certain temperature and feed flow, a set of breakthrough experiments followed by complete desorption was performed in order to analyze the unit and to study its kinetics. These runs have strong similarities to a typical high pressure adsorption step (HPA) at pressure P_H , and a desorption step, here called blowdown, at constant pressure P_H , by displacement with an inert or weakly adsorbed component. The method used is a chromatographic-type procedure, where a column response at the outlet end was obtained, after a step change in the feed mixture [Yang (1987)].

The experimental operating conditions are used to obtain an estimation of the intra-particle diffusion coefficients of each adsorbate, through the experimental data validation with the breakthrough and blowdown simulation model. From the experiments, the analysis of the concentration profiles exiting the bed gives the indication of the t_{HPA} and t_{BD} step times needed for filling the column in the adsorption step and emptying it in the blowdown, respectively. This also defines the maximum time values of these two steps once introduced into a cycle sequence, with the feed flow assumed at the pressure range $[P_H; P_L]$.

Hence, this section reports the experimental runs executed with CO_2/He , CO_2/N_2 , N_2/He and CH_4/He mixtures at several average interstitial gas velocities, at average flowrates from 0.84 to 5.05 slpm (STP: 0°C , 1 atm), and at average run temperatures, T_{run} , of 26, 36 and 46°C ($\pm 1^\circ\text{C}$). To be sure of the certainty of the data, repeatability was checked by repeating some runs for several systems, at least three times for the same conditions. Tables (4.19), (4.20) and (4.21) present the experimental operating conditions applied in the PSA laboratory-scale unit, for CO_2/He , CO_2/N_2 , CH_4/He and N_2/He mixtures. The experiments were taken during a total period of time of approximately 80 h. These results obtained were then used in the modeling work.

To study the effect of the pressure, P_H , in the adsorption step and its influence in blowdown, breakthrough experiments were performed at two different pressures, 10 and 5 bar. Lowering P_H should reduce the breakthrough time in the feed step, decrease the temperature peaks because of the lower loading in the feed step. These runs allow the definition of the time period between $t_{breakthrough}$ at each P_H value needed to saturate the bed at T_{run} , limiting the adsorption step time to a value lower than the breakthrough time at the higher P_H value.

A study of the feed composition effect was also performed. Runs with single breakthrough at P_H , such as CO_2 , CH_4 or N_2 in He, or runs with composition change maintaining the total volumetric flow at the same T_{run} , allow the study of the system behavior. Increasing the ratio strongly/weakly adsorbed component should make a wider breakthrough and temperature profiles. The increment in the more adsorbed component

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.19: Experimental operating conditions applied in the PSA laboratory-scale unit, for CO₂/He mixtures.

CO ₂ /He (v/v %)	50/50			80/20		30/70			
T_{run} (°C)	27.63	37.15	46.67	26.04	46.86	25.79	37.01	36.92	47.38
P_H (bar)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	4.99	10.00
y_{MS} (wt %), CO ₂	3.19E-04	1.00E-03	2.24E-04	3.47E-04	4.25E-04	1.77E-04	3.13E-04	1.00E-04	3.35E-04
y_f (wt %), CO ₂	0.4982	0.4609	0.4979	0.7992	0.7998	0.2993	0.2988	0.2998	0.2991
v_{HPA} (cm/s)	1.3804	1.2871	1.3822	1.3698	1.3805	1.3734	1.3800	1.3844	1.3862
Feed (slpm)	2.8418	2.5685	2.6761	2.8350	2.6712	2.8448	2.7549	1.3809	2.6779
t_{HPA} (min)	53.13	47.25	38.58	50.63	41.99	43.32	32.63	48.53	47.34
t_{BD} (min)	51.59	50.28	57.38	72.63	69.56	58.48	64.87	76.06	44.66
$t_{run\ with\ vacuum}$ (h)	2.75	2.63	2.60	3.05	2.86	2.70	2.63	3.08	2.53

CO ₂ /He (v/v %)	0.7/99.3	1.24/98.76	0.7/99.3	0.71/99.29
T_{run} (°C)	36.77	35.82	46.17	26.63
P_H (bar)	4.00	4.00	4.00	4.00
y_{MS} (wt %), CO ₂	2.96E-04	2.00E-04	1.00E-04	2.43E-04
y_f (wt %), CO ₂	0.0072	0.0124	0.0070	0.0071
v_{HPA} (cm/s)	1.3774	1.3804	1.3860	1.3782
Feed (slpm)	1.1008	1.1066	1.0750	1.1387
t_{HPA} (min)	50.56	64.53	39.85	67.69
t_{BD} (min)	124.90	75.97	76.31	111.17
$t_{run\ with\ vacuum}$ (h)	3.92	3.34	2.94	3.98

Table 4.20: Experimental operating conditions applied in the PSA laboratory-scale unit, for CH₄/He and N₂/He mixtures.

CH ₄ /He (v/v %)	30/70		N ₂ /He (v/v %)	50/50	30/70			
T_{run} (°C)	36.77	46.48	T_{run} (°C)	37.49	38.35	37.30	37.28	46.72
P_H (bar)	10.00	10.00	P_H (bar)	10.00	10.00	10.00	10.00	10.00
y_{MS} (wt %), CH ₄	3.49E-04	2.08E-05	y_{MS} (wt %), N ₂	4.82E-05	3.56E-05	3.98E-04	6.57E-04	1.33E-04
y_f (wt %), CH ₄	0.3012	0.3010	y_f (wt %), N ₂	0.5031	0.3025	0.2960	0.2979	0.3002
v_{HPA} (cm/s)	1.3791	1.3830	v_{HPA} (cm/s)	1.3766	1.3797	1.3777	1.3794	1.3857
Feed (slpm)	2.7554	2.6792	Feed (slpm)	2.7439	2.7426	2.7479	2.7514	2.6825
t_{HPA} (min)	48.45	42.50	t_{HPA} (min)	30.35	25.64	26.65	14.47	18.18
t_{BD} (min)	16.69	18.46	t_{BD} (min)	11.25	14.36	13.35	19.83	11.82
$t_{run\ with\ vacuum}$ (h)	2.09	2.02	$t_{run\ with\ vacuum}$ (h)	1.69	1.67	1.67	1.57	1.50

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.21: Experimental operating conditions applied in the PSA laboratory-scale unit, for CO₂/N₂ mixtures.

CO ₂ /N ₂ (v/v %)	6/94			14/86		30/70	
T_{run} (°C)	34.15	35.48	36.45	35.76	35.10	36.14	36.75
P_H (bar)	4.9870	4.9877	4.9875	4.9878	4.9872	9.9821	9.9823
y_{MS} (wt %), CO ₂	8.53E-04	1.46E-03	1.25E-03	4.94E-04	3.71E-03	1.95E-03	6.41E-04
y_f (wt %), CO ₂	0.0597	0.0624	0.0618	0.1413	0.1406	0.3015	0.3001
v_{HPA} (cm/s)	0.8371	7.9404	7.9597	2.5229	2.6371	0.8464	2.5318
Feed (slpm)	0.8412	2.5292	2.5273	2.5223	0.8409	1.6914	5.0497
t_{HPA} (min)	57.41	28.63	35.00	28.60	48.40	35.25	27.86
t_{BD} (min)	71.31	37.08	29.65	29.27	60.59	58.81	30.23
$t_{run\ with\ vacuum}$ (h)	3.15	2.10	2.08	1.96	2.82	2.57	1.97

CO ₂ /N ₂ (v/v %)	50/50		80/20		
T_{run} (°C)	36.17	36.38	35.09	36.09	37.43
P_H (bar)	9.9815	9.9818	9.9809	9.9818	9.9824
y_{MS} (wt %), CO ₂	5.13E-04	1.85E-04	5.75E-04	2.23E-03	6.31E-04
y_f (wt %), CO ₂	0.5005	0.5003	0.7998	0.7999	0.8000
v_{HPA} (cm/s)	0.8413	2.5294	0.8397	0.8431	2.5395
Feed (slpm)	1.6810	5.0508	1.6837	1.6850	5.0541
t_{HPA} (min)	40.03	24.34	38.97	46.23	23.19
t_{BD} (min)	48.28	24.55	55.58	65.71	34.62
$t_{run\ with\ vacuum}$ (h)	2.47	1.81	2.58	2.87	1.96

should have higher temperature increments in the adsorption step and higher temperature drops in the desorption stage.

The temperature effect was studied on the fixed bed apparatus through experiments at three different temperatures, as referred above. The lower the T_{run} , the slower the breakthrough and the larger the concentration tail in the HPA step, which reduces the separation performance of a PSA process. At lower temperatures, a more favorable adsorption isotherm is obtained, which corroborates the slower response at lower temperatures.

The effect of the total volumetric feed flow was also assessed through experiments at different average gas velocities. For instance, half of the total feed flow should take nearly twice the breakthrough time and temperature signal to appear.

4.3.2.3 PSA Cycle Steps Experiments

The apparatus is prepared to include the following cyclic steps that can be programmed into the BioCTR software, in manual or automatic mode. Assuming a given binary mixture, the following steps can be implemented experimentally in a PSA cycle:

- Pressurization (PR) with feed at a given mass flow rate assumed up to P_H , during

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

the step time t_{PR} ; the bed operation starts with a previous passage of an inert or of the less adsorbed component of the mixture that is being analyzed, at P_L . The gas composition of the PSA exit stream is continuously fed to the MS and real-time analyzed. N_{PR} is the average inlet volumetric flow in PR step.

- High pressure adsorption (HPA) at P_H , co-current to the feed end, during t_{HPA} ; the more strongly adsorbed component is being trapped along the adsorbent bed and an stream enriched in the less adsorbed product is produced. N_{HPA} is the average volumetric flow fed to the HPA step. $(t_{PR} + t_{HPA})$ is determined from the breakthrough time, previously obtained from the breakthrough experiments.
- High pressure purge (HPG) at P_H , in the direction of the feed, with part of the Low Pressure Purge (LPG) product, during t_{HPG} , to improve the purity of the more strongly adsorbed component at the cost of LPG product utilization. This stage is generally used when the lighter species are coadsorbed in large amount with heavier components. Experimentally, this could be done using a composition similar to the LPG product, previously pressurized up to P_H . As a first approach, this step can be ignored, since it increases energy cost.
- High pressure blowdown (HBD), co-current to the feed end of the bed, from P_H to the intermediate pressure P_{HBD} , in order to recover the less adsorbed product that is still present in the column, and enrich the gas phase with the other component of the binary mixture. This increases the heavier product purity and may also increase the lighter component recovery. The HBD pressure profile is performed through a 2nd order polynomial profile imposed by the control software.
- Low pressure blowdown (LBD), counter-current to the feed, from P_{HBD} to P_{LBD} , in order to collect the more strongly adsorbed product. This step is called Evacuation (EV) when the system pressure drops to sub-atmospheric values, inducing to high purity of both products. EV is generally performed when the adsorbed phase is very strongly held. The LBD pressure profile is imposed manually trough an accurate needle valve, which is well described by an 3rd or 4th order polynomial profile, for modeling purposes.
- Low pressure purge (LPG) at P_{LBD} , during t_{LPG} , with part of the HPA product if necessary, to recover the more strongly adsorbed product at the expense of decrease in the HPA product recovery.

At all times, the feed flow, temperature and pressure are being acquired and controlled through the BioCTR, although only the feed flow of one of the two components is being

controlled automatically. This is an experimental limitation, since one has only two analog outputs available through the acquisition board II (Appendix A). They are occupied with the back-pressure regulator (BPR) and the other feed flow device (MFCI). The second MFCII is manually actuated through a external MFC power supply. Composition analysis is performed by the MS in real-time.

A set of preliminary experimental tests were done for a CO₂/N₂ 50/50 %(v/v) separation, at temperature T , in order to define the period of time t_{LBD} , which gives a specific pressure profile for the LBD/EV step, through the aperture of the manual needle valve. Maintaining $(t_{PR} + t_{HPA})$, T and the total feed flow, preliminary runs were performed varying P_H , P_{HBD} and the total cycle time through t_{LBD} changing and inclusion of the HPG and LPG cycle steps. The lower system pressure, P_L , is defined by the suction capacity of the vacuum pump connected to the apparatus. The discharge pressures obtained are in accordance with the industrial standards [Freitas (1999)].

Simultaneously, simulations were carried out in order to predict the number of cycles needed to achieve the cyclic steady state condition (CSS) and determine the performance of the separation for various experimental operating conditions. Attention was taken regarding some variables, such as the purge amount used, t_{HPG} , t_{HBD} , t_{LBD} , t_{LPG} and P_{HBD} , in a PSA cycle composed by a pressurization step, followed by the high pressure adsorption, two blowdown steps, and a high- or low- purge stage. The operating conditions were limited by the ones experimentally available. Table (4.22) reports the preliminary PSA simulated runs, its operating conditions and separation performance at nearly CSS for a CO₂/N₂ 50/50 %(v/v) mixture, at an average temperature of 36°C, an adsorption pressure, P_H , of 6 bar, a low-pressure, P_L , of 0.3 bar, and a gas velocity of approximately 2.5 cm/s during the HPA step (i.e., 3.0 slpm of total volumetric flowrate). CSS was reached at the 11th cycle. The total feed per cycle is the throughput in STP conditions (0°C, 1 atm) admitted per cycle and the purge to feed ratio, P/F , is taken as the fraction of N₂ in the HPA feed that is consumed in the purge step.

The objective is to obtain a reasonable CO₂/N₂ separation for specific operating conditions, i.e., product purities over 90-95% and recoveries as high as possible, usually known for commercial applications [Yang (1987), D. M. Ruthven and Kneabel (1994)]. Checking the consistency of the experimental PSA apparatus, the modeling work is then validated with this experimental base separation case at CSS, comparing the simulation results with the experimental ones.

Given the data from Table (4.22), Run 3 was selected to perform the experimental CO₂/N₂ separation using the PSA laboratory unit. A schematic diagram of the implemented cycle is shown in Figure (4.36).

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.22: Preliminary analysis on the operating conditions applied in the PSA cycle to be implemented experimentally in the laboratory-scale unit for a CO₂/N₂ 50/50 %(v/v) mixture.

RUN	PSA Cycle Steps	Total Feed per cycle (L STP)	P _{HBD} bar	P/F	t _{PR+HPA} s	t _{HPG} s	t _{HBD} s	t _{LBD} s	t _{PG} s	t _{cycle} min	CO ₂ Purity %	N ₂ Purity %	CO ₂ Recovery %	N ₂ Recovery %
1	PR/HPA/HBD/LBD	11.998	4.0	-	240	-	120	240	-	10.0	69.21	88.65	92.57	58.47
2	PR/HPA/HBD/LBD	11.998	3.2	-	240	-	120	240	-	10.0	74.35	88.50	88.35	69.27
3	PR/HPA/HBD/LBD/LPG	12.254	3.2	0.12	240	-	120	240	120	12.0	74.92	96.66	97.70	67.01
4	PR/HPA/HBD/LBD/LPG	12.124	4.0	0.06	240	-	120	240	120	12.0	69.66	96.91	98.20	56.87
5	PR/HPA/HBD/LBD/LPG	12.165	4.0	0.08	240	-	120	240	120	12.0	69.57	98.00	98.86	56.39
6	PR/HPA/HBD/LBD/LPG	12.171	3.2	0.08	240	-	120	240	120	12.0	75.18	94.64	96.19	67.97
7	PR/HPA/HBD/LBD/LPG	12.184	4.0	0.08	240	-	180	240	120	13.0	69.16	93.22	95.90	56.87
8	PR/HPA/HBD/LBD/LPG	12.253	3.2	0.12	240	-	120	240	240	14.0	74.96	97.18	98.07	66.96
9	PR/HPA/HBD/LBD/LPG	11.015	3.2	0.12	216	-	120	240	120	11.6	71.36	90.73	93.71	62.07
10	PR/HPA/HBD/LBD/LPG	12.527	3.2	0.25	240	-	120	240	120	12.0	73.12	99.61	99.76	63.02
11	PR/HPA/HPG/HBD/LBD/LPG	15.290	3.2	0.12	240	60	120	262	120	13.4	87.72	85.48	58.48	84.47
12	PR/HPA/HPG/HBD/LBD/LPG	14.090	3.2	0.12	240	60	120	262	120	13.4	82.38	87.52	69.71	78.65
13	PR/HPA/HBD/HPG/LBD/LPG	14.430	3.2	0.12	240	60	120	262	120	13.4	85.46	84.15	63.32	83.04

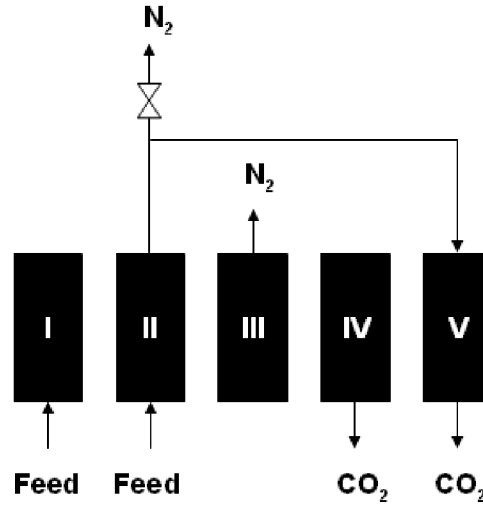


Figure 4.36: Schematic diagram of the experimental PSA cycle implemented for the CO_2/N_2 separation. (I) PR from $P_L = 0.3$ bar to $P_H = 6.0$ bar; (II) HPA at P_H with N_2 recovery; (III) HBD from P_H to $P_{HBD} = 3.2$ bar with N_2 recovery; (IV) LBD from P_{HBD} to P_L with CO_2 withdraw; (V) LPG at P_L through N_2 product and with CO_2 withdraw.

The experimental cycle includes PR, HPA, HBD, LBD up to a sub-atmospheric pressure, and LPG steps. The runs start with the bed saturated with pure nitrogen at P_L . Thereafter, the final conditions of the previous step/cycle become the initial conditions for the next step/cycle. Table (4.23) presents the experimental operating conditions applied in the PSA laboratory-scale unit, for the CO_2/N_2 mixtures.

Carbon dioxide is present at relatively high concentrations, for instance, in the flue gases from many industries such as steel production, power plants or fermentation processes. Typical flue gas consists of nitrogen, carbon dioxide, oxygen, water vapor, and minor impurities such as SO_x , and NO_x . We assume that oxygen, SO_x , and NO_x were removed in the pretreatment process, water was removed by, for example, a presorber or guard-bed containing activated alumina or silica gel desiccants, and that the feed of the CO_2 PSA process is mainly composed of carbon dioxide and nitrogen. This is the target mixture to be separated. Since CO_2 is strongly adsorbed on the adsorbent (activated carbon, CMS, zeolites, etc.), a vacuum desorption system is usually necessary when using PSA processes [Yang (1987), D. M. Ruthven and Kneabel (1994), Gomes and Yee (2002), J. H. Park and Cho (2002), K. T. Chue and Yang (1995)]. This explains the inclusion of sub-atmospheric pressures in the LBD and LPG steps of the experimental PSA cycle.

Table 4.23: Experimental operating conditions applied in the PSA cycle implemented in the laboratory-scale unit for a CO₂/N₂ 50/50, 30/70 and 80/20 %(v/v) mixtures.

		Run		
		1	2	3
CO ₂ /N ₂ Mixture	% (v/v)	50.31/49.69	30.21/69.79	80.1/19.9
T_{run}	°C	33.04	35.85	34.14
V_{HPA}	cm/s	2.474	2.485	2.478
V_{LPG}	cm/s	0.025	0.028	0.028
$y_{LPG}(N_2)$	% (v/v)	99.88	99.74	97.33
t_{PR}	s	166.40	141.52	216.48
t_{HPA}	s	72.50	72.43	73.77
t_{PR+HPA}	s	238.90	213.95	290.25
t_{HBD}	s	118.30	118.89	118.96
t_{LBD}	s	362.30	363.20	361.68
t_{LPG}	s	120.00	120.75	119.93
t_{cycle}	min	13.99	13.61	14.85

4.3.3 Experimental Method

4.3.3.1 Breakthrough and Blowdown Experiments

This set of fixed-bed experiments was performed according to the following method:

- Start-up execution to prepare the laboratory system for operation. Degassing was performed at high temperature (70-80°C) and for several hours at vacuum. After this procedure, the temperature set-point is decreased up to the temperature of the experiment. Note that both acquisitions from the BioCTR and the MS softwares have to be synchronized in real-time, in order to correctly analyze the experimental results.
- At constant temperature and starting from vacuum, a constant feed flow of the inert (in the entire range of temperature) or the less adsorbable component enters the column from its bottom. At this point, the software acquisitions are turned on. Pressurization takes place up to pressure P_H .
- The system is stabilized at a constant pressure, P_H , through the back-pressure regulator (BPR), at temperature T_{run} and at a given standard average flowrate $Feed$. The MS signal, which analyzes the PSA exit stream, is monitored at the same time.

- After stabilization, the more adsorbable component enters the column from its bottom, at a specified feed flow. The inert flowrate is rearranged in order to admit a certain gas composition of the mixture and maintain the total volumetric feed flow, *Feed*, fed to the bed. This avoids serious variations due to changes in the gas velocity conditions. At this time the adsorption stage occurs resulting in temperature and composition profiles along the adsorbent bed. The behavior of the system is very similar to a regular adsorption step of a PSA cycle.
- The system is monitored continuously until breakthrough of the more adsorbable component takes place. At this point the more adsorbable component starts exiting the column and is detected through mass spectrometry.
- The system is continuously fed over a period long enough to equilibrate the inlet and exit streams of the column, i.e., until adsorbent saturation.
- The pressure, temperature and total feed flowrate are maintained constant, but the source of the more adsorbable component is stopped. Hence, only inert is admitted again to the column, at the same prescribed total volumetric flow. The desorption stage takes place by displacement of the adsorbed component through the inert admittance. This is observed by the typical temperature and composition profiles inside the bed, during desorption time.
- The experiment is continuously monitored until the MS signal detects only a pure inert stream exiting the PSA column. The acquisition is stopped. The system pressure is decreased, temperature is increased and the unit is evacuated to prepare the apparatus for the next experiment.

Figures (4.37) and (4.38) show an example of a typical breakthrough and blowdown experiment performed with the described procedure.

4.3.3.2 PSA Cycle Steps Experiments

This set of experiments was performed according to the following method:

- Start-up execution to prepare the laboratory system for operation. Degassing was performed at high temperature (70-80°C) and for several hours at vacuum. After this procedure, the temperature set-point is decreased up to the temperature of the experiment. Note that both acquisitions from the BioCTR and the MS softwares have to be synchronized at real-time, in order to correctly analyze the experimental results.

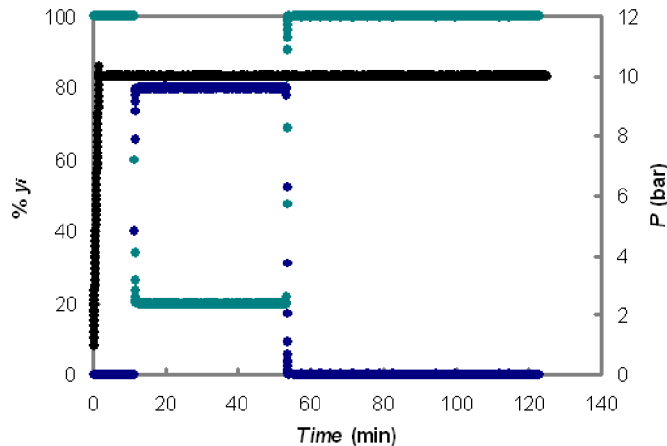


Figure 4.37: Experimental pressure and feed composition histories of a typical break-through and blowdown experiment performed in the PSA laboratory-scale unit, for a CO_2/He 80/20 wt% mixture, at an average T_{run} of 47°C , a pressure P_H of 10 bar and a total volumetric flow of 2.67 slpm (STP: 0°C , 1 atm). Black symbols denote the pressure history, blue and green symbols correspond to CO_2 and He compositions, respectively.

- At constant temperature and vacuum, a constant volumetric feed flow of the inert or the less adsorbable component enters the column from its bottom. At this point, the software acquisitions are turned on. The systems remains at P_L for a period of time enough to ensure the adsorbent saturation with the pure lighter component. These starting conditions try to reproduce the final state of the previous step/cycle, which correspond to the initial conditions of the next step/cycle. Feed and MS signals are monitored at all times.
- At time zero, the PSA cycle implemented in BioCTR cycle schedule console starts, repeating itself for a given number of cycles. Simultaneously, all devices (BPR, MFCs, SVs) respond to the control actions planned and the bed exit streams, i.e., the gas-phase compositions drawn out of the column at each cycle step, are being acquired.
- The experiment is continuously monitored until CSS is reached. The run is stopped and afterwards the system pressure is decreased, temperature is increased and the unit is evacuated to prepare the apparatus for the next experiment.

A schematic diagram of the implemented cycle is shown in Figure (4.36). Figures (4.39, 4.41) illustrate two typical PSA experiments at CSS performed with the described pro-

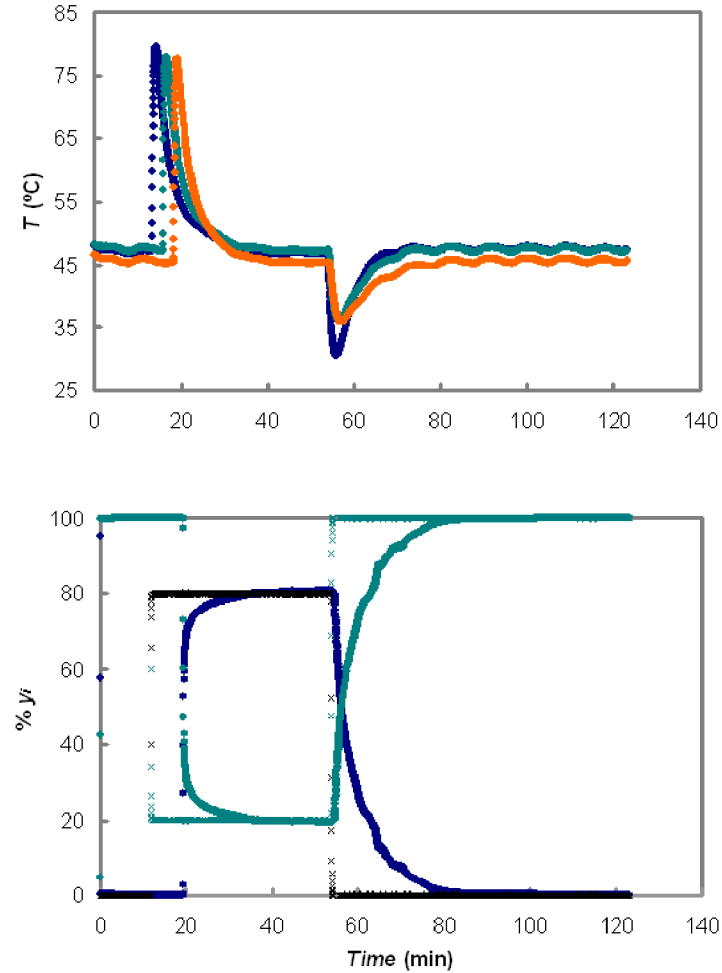


Figure 4.38: Experimental temperature (top) and composition (bottom) histories inside the adsorbent bed for a typical breakthrough and blowdown experiment performed in the PSA laboratory-scale unit. Corresponds to a CO_2/He 80/20 wt% mixture at an average T_{run} of 47°C , a pressure P_H of 10 bar and a total volumetric flow of 2.67 slpm (STP: 0°C , 1 atm). Top figure: blue, green and orange symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively. Bottom figure: Black and green crosses correspond to the PSA inlet CO_2 and He compositions, respectively. Blue and green filled symbols denote the exit CO_2 and He compositions detected by mass spectrometry, respectively.

cedure and the cycle conditions described in Table (4.23). Figures (4.40, 4.42) show the respective experimental process operation until CSS is reached.

4.3.4 Experimental Results, Modeling Validation and Data Analysis

4.3.4.1 System Properties

Excellent sources of information on the characteristics of adsorbent products for specific applications are the manufacturers themselves. Under the ANGWARD project some of the adsorbent properties were provided by SSCL and others were obtained experimentally during the thesis.

For adsorbents, usually the bulk density, ρ_b , that is the weight of clean material per unit bulk volume as packed in a column, is reported. The dry particle density, ρ_p , is related to the (external) void fraction of packing, ε_b , by

$$\rho_p = \frac{\rho_b}{(1 - \varepsilon_b)}. \quad (4.46)$$

For a given density of the carbon matrix, ρ_s , the internal or intraparticle porosity, ε_p , is defined as

$$\varepsilon_p = \rho_p \left(\frac{1}{\rho_p} - \frac{1}{\rho_s} \right). \quad (4.47)$$

The total voidage, ε , in a packed bed (outside and inside the particles) is given by

$$\varepsilon = \varepsilon_b + (1 - \varepsilon_b)\varepsilon_p. \quad (4.48)$$

Through the BET surface area, A_p , obtained from N₂ sorption isotherm at 77 K, and the total pore volume, W_s , determined from Eq. (4.22), one can calculate the adsorbent mean pore radius, r_p ,

$$r_p = 2 \frac{W_s}{A_p}. \quad (4.49)$$

The tortuosity factor, τ , was assumed to be 4.0, which is a typical value for activated carbon [Ruthven (1984), E. Costa and Domingo (1985)]. The tortuosity factor is usually defined as the ratio between the actual diffusion path length, which depends on the pore structure, and the net distance in the direction of flux, or the radial distance. The effective diffusivity for porous adsorbents is then defined as $D_e = \varepsilon_p D / \tau$, where D is the diffusivity coefficient including both Knudsen and molecular mechanisms for diffusion [Fair and Huang (1988); Ruthven (1984); Yang (1987); Yang and Doong (1985)].

Besides the gas-phase diffusion, there also exists surface diffusion. As a result of the concentration gradient in the pores, a surface gradient also exists on the pore wall.

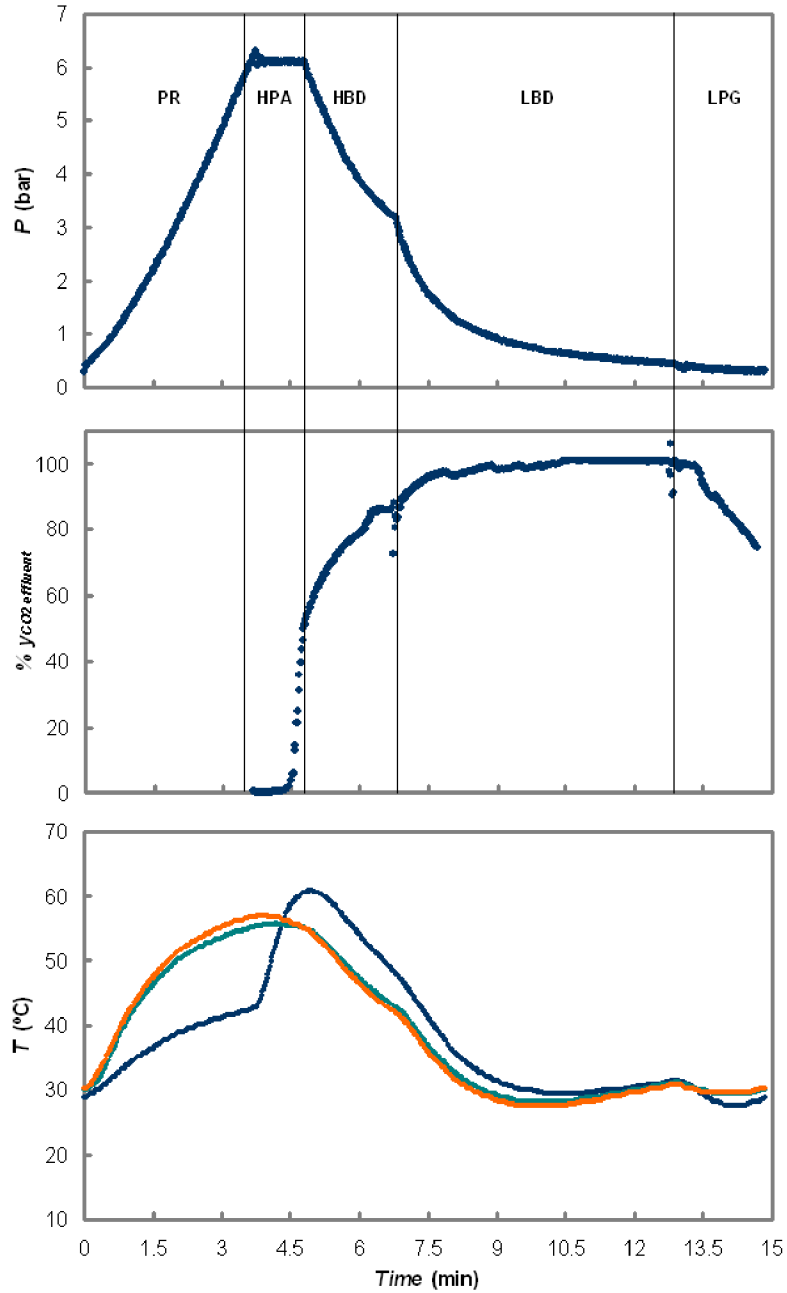


Figure 4.39: Experimental pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed, for a typical PSA experiment at CSS (NoCycle = 11), performed in the PSA laboratory-scale unit. Corresponds to a CO_2/N_2 80/20 % (v/v) mixture at an average T_{run} of $34.14^{\circ}C$, a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: $0^{\circ}C$, 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

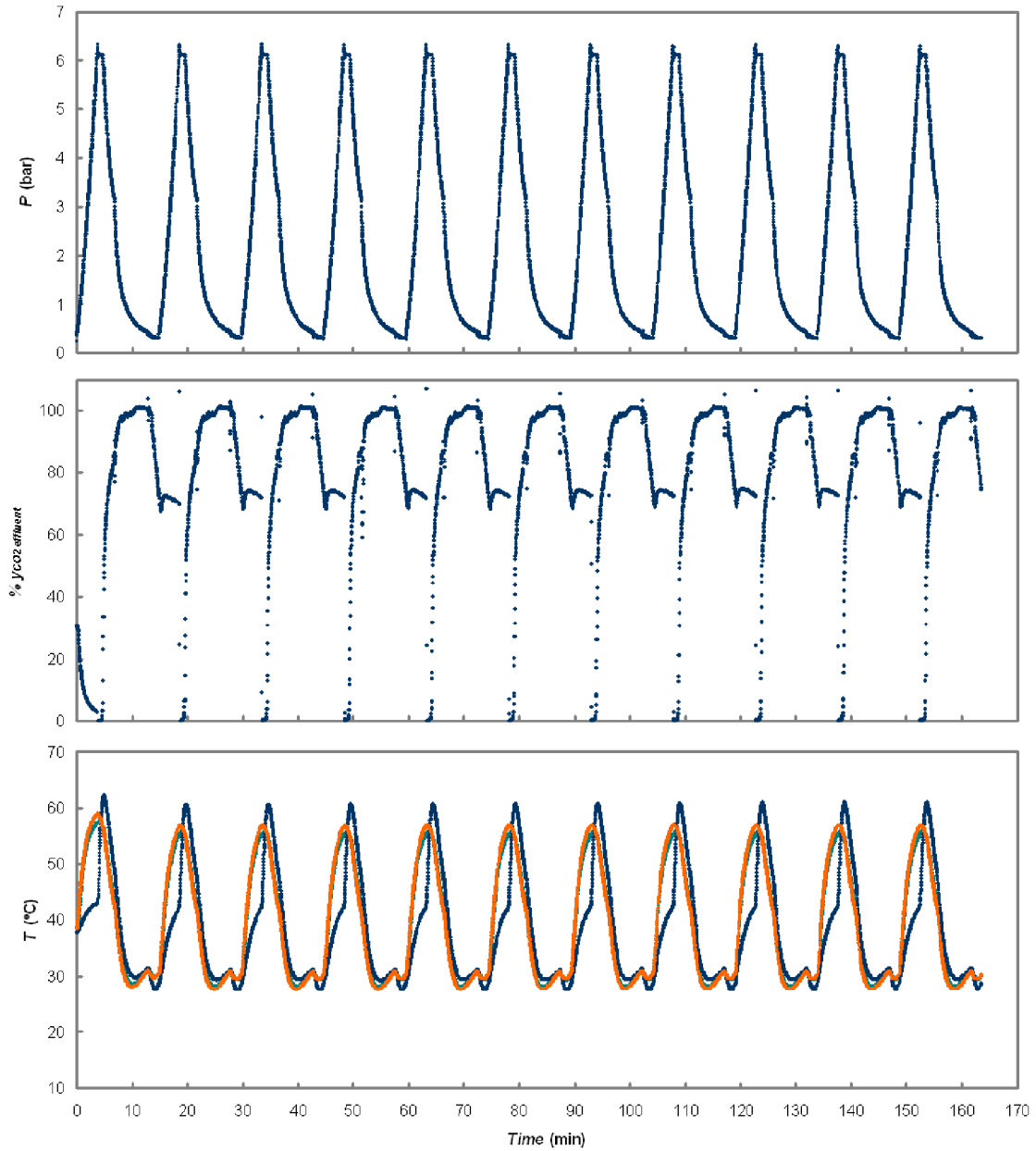


Figure 4.40: Experimental pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed, for a typical PSA experiment up to the CSS condition, performed in the PSA laboratory-scale unit. Corresponds to a CO_2/N_2 80/20 % (v/v) mixture at an average T_{run} of 34.14°C , a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: 0°C , 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

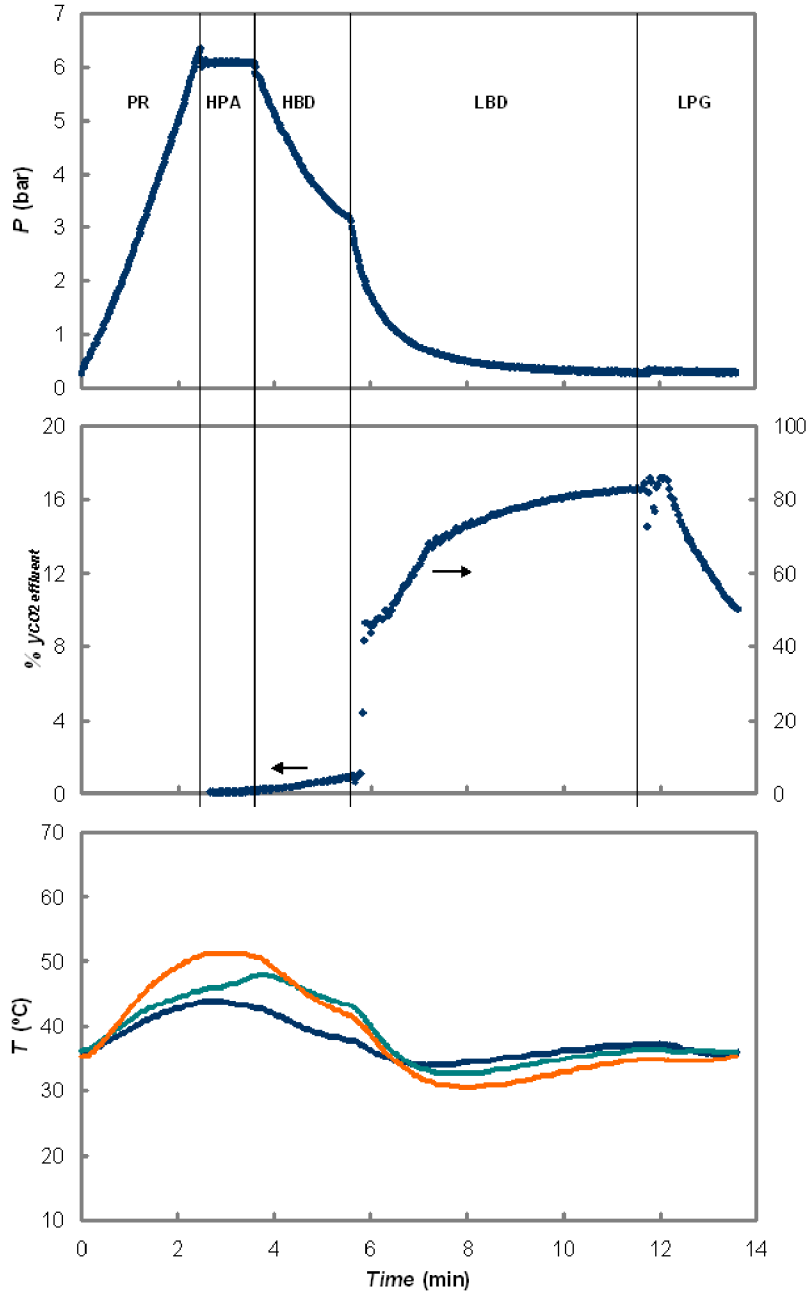


Figure 4.41: Experimental pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed, for a typical PSA experiment at CSS (NoCycle = 11), performed in the PSA laboratory-scale unit. Corresponds to a CO_2/N_2 30/70 % (v/v) mixture at an average T_{run} of $35.85^\circ C$, a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: $0^\circ C$, 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

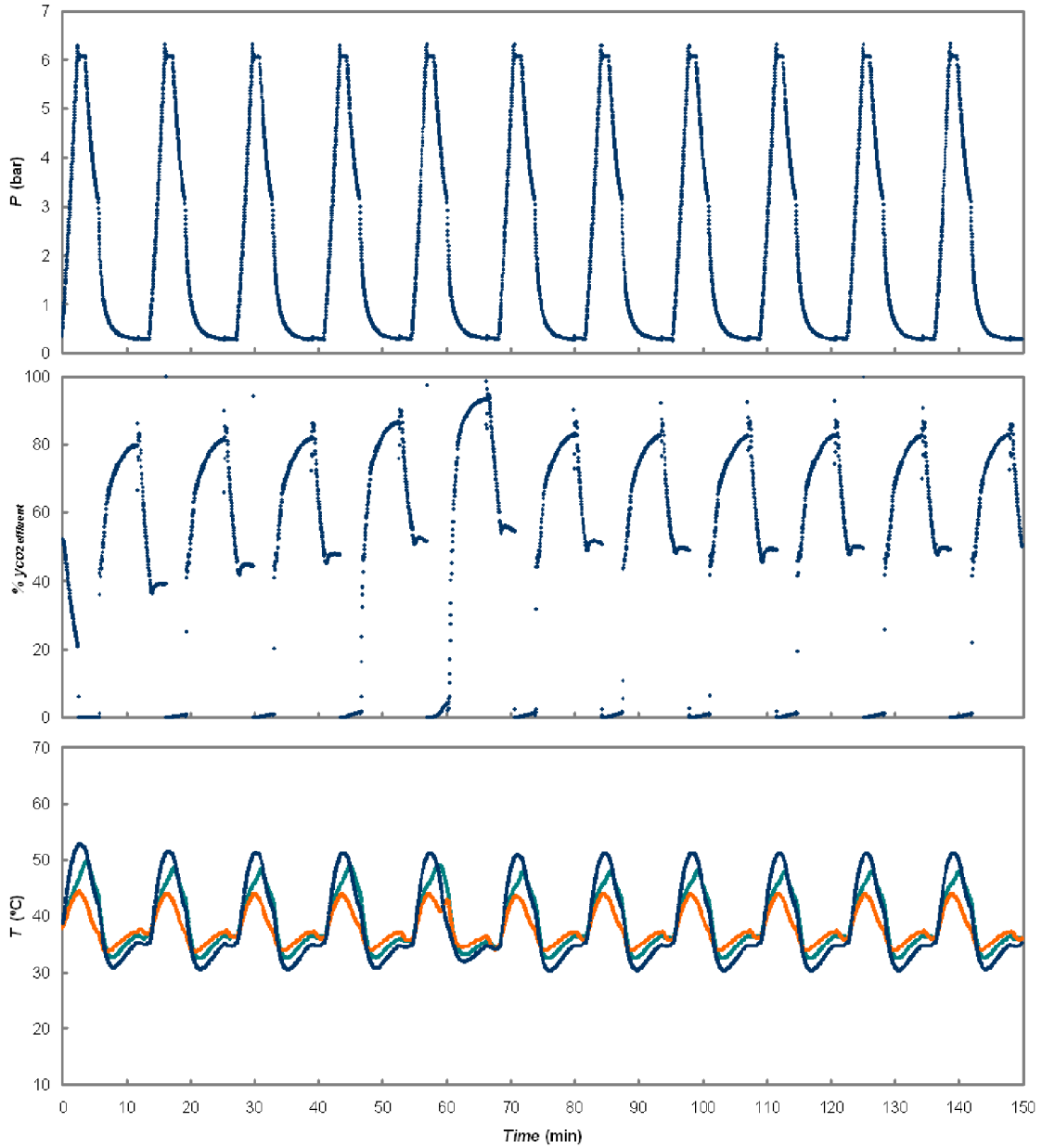


Figure 4.42: Experimental pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed, for a typical PSA experiment up to the CSS condition, performed in the PSA laboratory-scale unit. Corresponds to a CO_2/N_2 30/70 % (v/v) mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: 0°C , 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

Table 4.24: Characteristics of the experimental system built with the ANGWARD 5 carbon selected.

Physical properties	
Specific pore volume, W_s (cm³/g)	0.860
Density of the carbon matrix, ρ_s (g/cm³)	2.222
Particle density, ρ_p (g/cm³)	0.763
Bulk density, ρ_b (g/cm³)	0.400
Bed porosity, ϵ_b	0.476
Intraparticle void fraction, ϵ_p	0.656
Total Voidage, ϵ	0.820
BET surface area, A_p (m²/g)	1342.0
Mean pore radius, r_p (Å)	12.815
Tortuosity, τ	4.000
Particle hydraulic radius, r_H (mm)	1.668
Mean particle radius, R_p (mm)	1.073
Mean particle length, L_p (mm)	5.374
Bed length, L (cm)	60 - 40
Bed radius, R_b (cm)	1.600
Maximum adsorbent weight, M_c (g)	193.0

Hence, a surface diffusion coefficient, D_s , must be taken into account, specially when the adsorbent surface area and the surface concentration are high. Sometimes an effective diffusivity is considered instead of the surface one. However, the process may not be correctly simulated or predicted, since the surface diffusivity has a strong dependence on concentration, whereas the effective diffusivity is assumed constant. The surface diffusion has also an Arrhenius temperature dependence.

If the cylindrical pellet is treated as an equivalent sphere with a radius equal to the hydraulic radius of the cylinder, r_H , the shape has no effect on the breakthrough curves for a wide range of height-to-diameter ratios [Yang (1987)]. Hence, the hydraulic particle radius, defined as

$$r_H = \left(\frac{3}{4} r_p^2 L_p \right)^{1/3}, \quad (4.50)$$

was determined experimentally. R_p and L_p are the mean particle radius and length, respectively. The physical properties data for the experimental system built with the carbon sample is given in Table (4.24).

As the fluid flows through void spaces between solid particles, it incurs in energy losses which lead to a pressure loss. Hence, a pressure drop estimation of the laboratory PSA unit built was performed using the Ergun's equation

$$-\frac{\partial P}{\partial z} = \frac{u}{gD_p} \left(\frac{1 - \varepsilon_b}{\varepsilon_b^3} \right) \left[\frac{150(1 - \varepsilon_b)\mu}{D_p} + 1.75u\rho \right], \quad (4.51)$$

where P is the pressure, u the superficial fluid velocity based on empty column cross section, D_p the particle diameter, μ the absolute viscosity of fluid, ρ the density of fluid and ε_b the interparticle void fraction in the packed bed [Fogler (1992), Brodkey and Hershey (1988), Sereno and Rodrigues (1993), J. Hart and Thomas (1990)]. The first term on the right hand side (RHS) of the equation represents the viscous energy losses per unit length, while the second term represents the kinetic energy losses.

In the laminar flow regime ($Re_{pb} < 20$), only viscous energy losses are important and the pressure drop equation simplifies to Darcy's law

$$-\frac{\partial P}{\partial z} = \frac{u}{gD_p} \left(\frac{1 - \varepsilon_b}{\varepsilon_b^3} \right) \frac{150(1 - \varepsilon_b)\mu}{D_p}. \quad (4.52)$$

For the laboratory PSA bed packed with ANGWARD 5 carbon, an upper bound of pressure drop was estimated for pure component at the maximum flow through the bed. Since the maximum flow given by the mass flow controllers for each single component (He, N₂, CH₄ and CO₂) was never reached, the real pressure loss is smaller than the one obtained by this assumption. Hence, Table (4.25) presents these estimated results, where one concludes that the pressure drop across the carbon bed gives very reasonable values and should not exceed 10 mbar, for the bed geometry used ($D_b = 3.2$ cm and $L = 40$ -60 cm).

4.3.4.2 PSA Process Simulation Model

Before presenting the breakthrough and PSA process simulation results to validate the experiments, the model must be described first. The mass, momentum and energy balances that govern the adsorption phenomena in the packed bed are presented next. The dynamic behavior that requires the solution of coupled partial differential and algebraic equations (PDAEs), both in time and space domains, were developed in gPROMS simulator package.

A PSA simulation model was implemented in order to reproduce the breakthrough and blowdown experiments performed, and to obtain the component diffusivity coefficients. Material and energy are exchanged between the gas and adsorbent phases, while only energy is exchanged with the bed surface wall. Hence, for the gas phase, the component

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.25: Estimation of the maximum pressure drop, ΔP , of the PSA experimental adsorbent bed. The calculations were performed considering the ANGUARD 5 carbon sample, where D_b is the bed diameter. The modified Reynolds number for packed beds, Re_{pb} , is defined as $uD_p\rho/[\mu(1 - \varepsilon_b)]$.

Gas		He	CO ₂	CH ₄	N ₂
Mw	g/mol	4.003	44.010	16.043	28.013
ρ	kg/m ³	1.317	14.619	5.299	9.207
μ	cP	0.003	0.027	0.019	0.029
Flow	lpm	0.922	0.502	0.530	0.657
g	m/s ²	9.81	9.81	9.81	9.81
T	K	309.15	309.15	309.15	309.15
D_b	mm	32	32	32	32
L	cm	60	60	60	60
P	bar	16	16	16	16
u	m/s	0.0091	0.0049	0.0052	0.0064
Re_{pb}		18.23	10.89	5.88	8.39
ε_b		0.474	0.474	0.474	0.474
D_p	mm	2.15	2.15	2.15	2.15
ΔP	mbar	1.34	7.39	5.52	10.34

mass balance, the overall material balance and the energy balance equations were written. Concerning the solid phase, a component mass balance is included and a thermal equilibrium between the gas inside the particle and the solid is assumed, i.e., there are no temperature gradients inside the pellet. Since the column wall of the experimental PSA vessel was insulated, the respective energy balance, related to the energy exchange between the nearby gas, the adsorbent inside the column and the surrounding environment, was omitted in these set of simulations. The model uses these equations, coupled with several different boundary and initial conditions, combined with appropriate time schedule that describe the process.

Table (4.24) lists the model parameters applied in the simulations. Figure (4.43) shows the schematic diagram of the PSA bed and corresponding axi-symmetric (z, r) coordinate system. For simplicity reasons, the following assumptions were regarded:

- Ideal gas law applies, since the experimental runs were carried out with light adsorbates at pressures lower than 10 bar.
- The average particle diameter, bulk porosity and tortuosity of the packing are assumed constant in the bed.
- No radial mass, velocity and temperature gradients are considered.

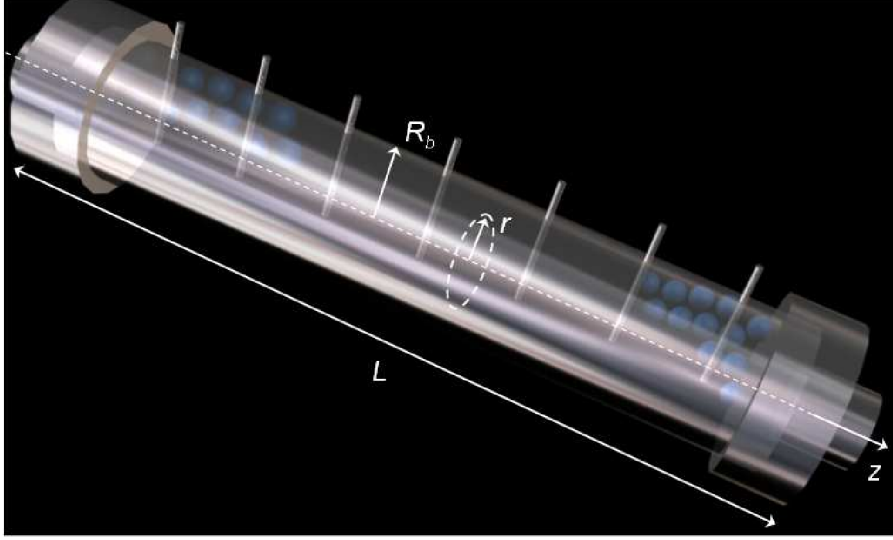


Figure 4.43: Schematic diagram of the PSA bed and corresponding axis-symmetric (z, r) coordinate system. L is the axial length of the cylinder, R_b is the inner radius and e_w is the wall thickness.

- The axial dispersed plug flow model describes the flow pattern.
- Thermal dispersion in the axial direction is considered, with negligible radial gradients.
- Physical properties are assumed constant and independent of temperature, because of the narrow temperature range of the process.
- Although the adsorption capacity is considered negligible for the carrier gas, the capacity provided by the particle void for the carrier is taken into account in the material balance.
- The mass transfer rate is described by a linear driving force model.

1. Material balance equations

- **Individual material balance**

The differential material balance to the i th component of the n -component gas mixture can be written as

$$\varepsilon_b \frac{\partial c_i}{\partial t} + (1 - \varepsilon_b) \rho_p \frac{\partial \bar{q}_i}{\partial t} + \varepsilon_b \frac{\partial}{\partial z} \left(c_i v - D_L c \frac{\partial y_i}{\partial z} \right) = 0, \quad (4.53)$$

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

where $y_i = c_i/c$ is the mole fraction of component i in the gas, $\bar{q}_i$ denotes the total average concentration of component i inside the adsorbent and D_L is the mass dispersion coefficient.

The symbol $\bar{q}_i$ denotes the total average concentration of component i inside the adsorbent, and is defined as

$$\bar{q}_i = \frac{3}{R_p^3} \int_0^{R_p} q_i r_p^2 dr_p, \quad (4.54)$$

where R_p is the particle radius. Note that q_i accounts for both adsorbed phase and coexisting gas within the pore space,

$$q_i = q_i^{ex} + \frac{\varepsilon_p}{\rho_p} c_{ip}, \quad (4.55)$$

where c_{ip} is the concentration of component i inside the pores of the adsorbent particles. The symbol q_i^{ex} denotes the well-defined thermodynamic quantity known as excess adsorption [Sircar (1999)], which is the amount adsorbed in excess of the equilibrium gas occupying the same volume.

The preceding equation can be rewritten in the form

$$\frac{\partial}{\partial t} \left(\frac{y_i P}{T} \right) + \Omega_p \frac{\partial \bar{q}_i}{\partial t} + P \frac{\partial}{\partial z} \left(\frac{y_i v}{T} - \frac{D_{iL}}{T} \frac{\partial y_i}{\partial z} \right) = 0, \quad (4.56)$$

with

$$\Lambda_p = \frac{(1 - \varepsilon_b) \varepsilon_p}{\varepsilon_b}, \quad \Omega_p = \frac{\Lambda_p \rho_p R}{\varepsilon_p}. \quad (4.57)$$

The dispersion coefficient is given by

$$D_L = \gamma_1 D_m + \frac{\gamma_2}{\varepsilon_b} D_m Re Sc, \quad (4.58)$$

where γ_1 , γ_2 are constants, D_m is the molecular diffusion coefficient, and the Reynolds and Schmit numbers are defined as $Re = \rho v D_p \varepsilon_b / \mu$ and $Sc = \mu / (\rho D_m)$, respectively. The first term on the RHS accounts for the molecular diffusion and the second one is relative to turbulent mixing arising from the splitting and recombination of flows around the adsorbent particles.

The dispersion coefficient can be rewritten as

$$D_L = \gamma_1 D_m + \gamma_2 D_p |v|, \quad (4.59)$$

with $\gamma_1 = 0.7$, $\gamma_2 = 0.5$ [Yang (1987)]. The dispersion coefficient determined in this way, through previous experiments either with nonporous particles or with

porous particles under nonadsorbing conditions, is commonly assumed and applied to an adsorption bed packed with porous adsorbent particles. Nonetheless, [Funazkri and Wakao \(1978\)](#) stated that this assumption is not necessarily valid. If adsorption within the particle is sufficiently rapid and strong, the concentration profile through the particle becomes asymmetric, which leads to an incremental contribution to the axial dispersion in the low Reynolds number regime. Hence, Wakao suggests that $\gamma_1 = 20/\varepsilon_b$ and $\gamma_2 = 0.5$, giving more importance to the axial dispersion with strongly adsorbed species under laminar flow conditions. However, for our system this assumption excessively broadens the simulated concentration profiles with respect to the experimentally measured. Therefore, the values $\gamma_1 = 0.7$, $\gamma_2 = 0.5$ were used instead. D_{im} is a function of the gas mixture considered and the system pressure, and is obtained from [R. C. Reid and Prausnitz \(1988\)](#) and [Perry and Green \(1999\)](#), through the Chapman-Enskog and Fuller *et al.* equations, whichever presents the smallest error. The molecular diffusivity for the binary mixtures is assumed concentration-independent, which is usually a good approximation for most systems [[Ruthven \(1984\)](#)].

- **Global material balance**

The global material balance is obtained

$$\varepsilon_b \frac{\partial c}{\partial t} + (1 - \varepsilon_b) \rho_p \frac{\partial \bar{q}}{\partial t} + \varepsilon_b \frac{\partial (cv)}{\partial z} = 0, \quad (4.60)$$

where $c = \sum_i^n c_i$ is the total molar concentration of the gas mixture, c_i is the molar concentration of component i in the gas, $\bar{q} = \sum_i^n \bar{q}_i$ is the total average amount of gas adsorbed, v is the interstitial velocity, t is time and z is bed axial position. Since

$$c = \frac{P}{RT}, \quad (4.61)$$

and $P = P(t)$, the global material balance can be rewritten as

$$\frac{\partial (P/T)}{\partial t} + \Omega_p \frac{\partial \bar{q}}{\partial t} + P \frac{\partial (v/T)}{\partial z} = 0. \quad (4.62)$$

- **Mass Transfer Rate**

As a first approximation, the sorption rate, $\partial \bar{q}_i / \partial t$, in the heat and mass balance equations was evaluated by solving the mass balance equation within the sorbent particle. Gas-solid equilibrium is assumed within the pores, providing the link between the equilibrium isotherms and the heat and mass balance

equations. The material balance for each component inside the pores of a spherical carbon particle can be written as

$$\rho_p \frac{\partial q_i}{\partial t} + \frac{1}{r_p^2} \frac{\partial}{\partial r_p} (r_p^2 N_{ir}) = 0, \quad \forall r_p \in (0, R_p), \quad t \geq 0, \quad (4.63)$$

where ε_p is the intraparticle void fraction, r_p denotes the radial coordinate inside the particle (assumed spherical) of radius R_p . The intraparticle flux N_{ir} of component i comprises pore and surface diffusion. The pore diffusion is dominated by Knudsen diffusion with a constant diffusivity D_{ik} .

In molecular diffusion, the resistance to flow arises from collisions between diffusing molecules. The effect of the pore is merely to reduce the flux as a result of geometric constraints which are accounted for by tortuosity factor. However, in small pores and at low pressure, the collisions of molecules with the pore walls occur more frequently than collision between diffusing molecules. In this case, the collisions between molecules and pore wall provide the main diffusional resistance. This is known as the Knudsen diffusion. Here, each species diffuses independently, so the Knudsen diffusivity does not depend on either concentration or composition. It has the usual inverse dependence on the square root of gas molecular weight.

Both Knudsen and molecular diffusion mechanisms involve flow through the gas phase within the pore. Additionally, a contribution to the flux from transport through the adsorbed layer on the surface of the macropores can exist. When the thickness of that layer is significant, one has the so-called surface diffusion. The surface flux becomes small compared with the flux through the gas phase for higher temperatures, where the thickness of the adsorbed layer decreases [Ruthven (1984)].

The surface diffusivity, D_{is} , is a function of total surface coverage, except for within the Henry's law region [Ruthven (1984), G. L. Haller and Yang (1973)]. The concentration dependence arises from the nonlinearity of the equilibrium relationship. Thus, one has

$$N_{ir} = -D_{ik} \frac{\partial c_{ip}}{\partial r_p} - \rho_p D_{is} \frac{\partial q_i^{ex}}{\partial r_p}. \quad (4.64)$$

When Eq. (4.64) is substituted into Eq. (4.63), it gives rise to a model known as the pore/surface diffusion model [Yang and Doong (1986), Yang (1987), Ruthven (1984)]. However, a simpler particle model based on the linear-driving-force (LDF) approximation was applied to reduce the computational

load. The particle-volume averaged quantities are introduced to simplify the model

$$\bar{q}_i^{ex} = \frac{3}{R_p^3} \int_0^{R_p} q_i^{ex} r_p^2 dr_p, \quad (4.65)$$

$$\bar{c}_{ip} = \frac{3}{R_p^3} \int_0^{R_p} c_{ip} r_p^2 dr_p. \quad (4.66)$$

By integrating Eq. (4.63) with respect to r_p and using the particle-averaged quantities, one has

$$\rho_p \frac{\partial \bar{q}_i}{\partial t} + \frac{3}{R_p} (N_{ir})_{r_p=R_p} = 0. \quad (4.67)$$

To further simplify the model, one assumes that the concentration profiles within the particle are parabolic [Yang (1987); Yang and Doong (1985, 1986)]. Since the parabolic concentration profile must satisfy the boundary conditions,

$$\begin{cases} \frac{\partial c_{ip}}{\partial r_p} = 0, & \text{for } r_p = 0, \\ c_{ip} = c_{ip}^s & \text{for } r_p = R_p, \end{cases} \quad (4.68)$$

where c_{ip}^s is the value of c_{ip} at $r_p = R_p$, then c_{ip} can be expressed as

$$c_{ip} = E_i + F_i r_p^2, \quad (4.69)$$

where

$$E_i = c_{ip}^s - F_i R_p^2, \quad F_i = (c_{ip}^s - \bar{c}_{ip}) \frac{5}{2R_p^2}, \quad (4.70)$$

and therefore,

$$\left(\frac{\partial c_{ip}}{\partial r_p} \right)_{r=R_p} = \frac{5}{R_p} (c_{ip}^s - \bar{c}_{ip}). \quad (4.71)$$

Inside the pores, $\bar{q}_i$ is a function of T and of $\bar{c}_{ip}$ approximated by the adsorption isotherm. The intraparticle flux at the particle surface is

$$(N_{ir})_{r_p=R_p} = - \left(D_{ik} \frac{\partial c_{ip}}{\partial r_p} \right)_{r_p=R_p} - \rho_p \left[D_{is} \sum_j^n \frac{\partial q_i^{ex}}{\partial \bar{c}_{jp}} \left(\frac{\partial c_{jp}}{\partial r_p} \right) \right]_{r_p=R_p}. \quad (4.72)$$

The adsorbed gas is assumed to be in thermal equilibrium with the adsorbent and hence, there are no temperature gradients inside the particle. Substituting Eqs. (4.71, 4.72) into Eq. (4.67) one gets

$$\rho_p \frac{\partial \bar{q}_i}{\partial t} = \frac{15}{R_p^2} D_{ik} (c_{ip}^s - \bar{c}_{ip}) + \frac{15}{R_p^2} \rho_p D_{is} \sum_j^n \frac{\partial q_i^{ex}}{\partial \bar{c}_{jp}} (c_{jp}^s - \bar{c}_{jp}), \quad (4.73)$$

which can be rewritten as

$$\rho_p \frac{\partial \bar{q}_i}{\partial t} = \frac{15}{R_p^2} D_{ik} (c_{ip}^s - \bar{c}_{ip}) + \frac{15}{R_p^2} \rho_p D_{is} (q_i^s - \bar{q}_i)^{ex} = \rho_p k_i (q_i^s - \bar{q}_i), \quad (4.74)$$

with k_i the LDF coefficient for component i , and q_i^s the excess adsorbed concentration of component i in equilibrium with the gas mixture of composition $(c_{1p}^s, \dots, c_{np}^s)$ at temperature T . The equilibrium adsorbed concentrations q_i^s are computed according to the multicomponent adsorption isotherm model.

The surface diffusivity depends on the fractional loading of component i , $\theta = \sum_i q_i / q_i^\infty$, as suggested by the Higashi model [G. L. Haller and Yang (1973)]

$$\frac{D_s}{D_{s,\theta=0}} = \frac{1}{1 - \theta}, \quad (4.75)$$

where q_i^∞ is the saturation loading of component i . At zero loading, the correlation by K. J. Sladek and Baddour (1974) can be employed

$$D_{s,\theta=0} = 1.6 \times \exp(-0.45 Q_s / mRT), \quad (4.76)$$

where Q_s is the isosteric heat of adsorption. The value of m is 1 for physical adsorption on carbon.

The Knudsen diffusivity, D_k (in m^2/s), is estimated using the following equation [Karger and Ruthven (1992)]

$$D_k = 9.7 \times 10^{-9} r_\mu \sqrt{T/M_w}, \quad (4.77)$$

with r_μ the mean pore radius in Å and T the temperature in K.

Hence, using the experimental breakthrough experimental conditions, the starting point in the modeling work consisted on the determination of the LDF coefficients, k_i . If the system kinetics is not too fast, it is possible to distinguish between both Knudsen and surface contributions.

It is important to point out that the LDF approximation is only valid when the operation process obeys the restriction

$$k_i t / 15 > 0.1. \quad (4.78)$$

The diffusion time constant $D_e / R_p^2 = k_i / 15$ for activated carbon is in the order of 10^{-1} . This restriction is usually met in fixed bed adsorption experiments and standard PSA/VSA and TSA cyclic processes [S. U. Rege and Yang (1998); Yang (1987)]. However, if this condition is no longer valid, it is still possible to employ Eq. (4.74) and replace the factor 15 by a time dependent relationship

[N. S. Raghavan and Ruthven (1986); Nakao and Suzuki (1983)].

From Eq. (4.74) and for a binary mixture of components 1 and 2, the differential material balances inside the sorbent particle are, respectively,

$$\rho_p \frac{\partial \bar{q}_1}{\partial t} = \frac{k_{1k}}{RT} (y_{1p}^s P - \bar{P}_{1p}) + k_{1s} \rho_p (q_1^s - \bar{q}_1)^{ex}, \quad (4.79)$$

$$\rho_p \frac{\partial \bar{q}_2}{\partial t} = \frac{k_{2k}}{RT} [(1 - y_{1p}^s) P - \bar{P}_{2p}] + k_{2s} \rho_p (q_2^s - \bar{q}_2)^{ex}, \quad (4.80)$$

where

$$k_{ik} = \frac{15\varepsilon_p D_{ik}}{\tau R_p^2}, \quad k_{is} = \frac{15\varepsilon_p D_{is}}{\tau R_p^2}. \quad (4.81)$$

From Eq. (4.77) one can rewrite the LDF equations as

$$\rho_p \frac{\partial \bar{q}_i}{\partial t} = \frac{k_{ik}^*}{RT^{1/2}} (y_{ip}^s P - \bar{P}_{ip}) + k_{is} \rho_p (q_i^s - \bar{q}_i)^{ex}, \quad (4.82)$$

with

$$k_{ik}^* = \frac{15\varepsilon_p}{\tau R_p^2} \frac{9.7 \times 10^{-9} r_\mu}{M_{wi}^{1/2}}. \quad (4.83)$$

A further simplification can be performed if one considers an adsorbate (1) plus an inert carrier (2), where Eq. (4.82) reduce to

$$\rho_p \frac{\partial \bar{q}_1}{\partial t} = \frac{k_{1k}^*}{RT^{1/2}} (y_{1p}^s P - \bar{P}_{1p}) + k_{1s} \rho_p (q_1^s - \bar{q}_1)^{ex}, \quad (4.84)$$

$$\rho_p \frac{\partial \bar{q}_2}{\partial t} = \frac{k_{2k}^*}{RT^{1/2}} [(1 - y_{1p}^s) P - \bar{P}_{2p}]. \quad (4.85)$$

Since q_2^s is no longer needed and

$$\bar{q}_2 = W_s \frac{\bar{P}_{2p}}{RT}, \quad (4.86)$$

the LDF equation for the second component can be rewritten as

$$\rho_p \frac{\partial \bar{q}_2}{\partial t} = \frac{k_{2k}^*}{RT^{1/2}} \left[(1 - y_{1p}^s) P - \frac{\bar{q}_2 RT}{W_s} \right]. \quad (4.87)$$

Notice that the fluid and adsorbed phase concentrations are constrained by the conditions of thermodynamic equilibrium, i.e.,

$$\bar{q}_i^{ex} = q_{ieq}(\bar{P}_{1p}, \bar{P}_{2p}, T), \quad (4.88)$$

$$q_i^{s,ex} = q_{ieq}(y_1^s P, (1 - y_1^s) P, T). \quad (4.89)$$

All that remains to be defined is the value of y_i^s . One assumed that there is no external film mass transfer resistance compared with the one in the micropores of the sorbent, and therefore $y_i^s = y_i$.

2. Energy balance equation

It is assumed that both gas and adsorbent phases are in thermal equilibrium, i.e., that the heat transfer resistances are negligible between the solid and the nearby gas. Hence, the energy balance can be written as

$$\begin{aligned} \varepsilon_b \left[\frac{\partial(H_g c)}{\partial t} - \frac{\partial P}{\partial t} \right] + (1 - \varepsilon_b) \rho_p \left[\frac{\partial(H_a \bar{q})}{\partial t} + C_{ps} \frac{\partial T}{\partial t} \right] \\ + \varepsilon_b \frac{\partial}{\partial z} \left(H_g c v - D_h \frac{\partial T}{\partial z} \right) = \frac{2h_w}{R_b} (T_w - T), \end{aligned} \quad (4.90)$$

where H_g is the gas enthalpy, H_a is the enthalpy of the adsorbed phase, h_w is the wall heat transfer coefficient at the inner wall, C_{ps} is the heat capacity of the solid and T_w is the wall temperature. For nonisothermal conditions, it is a good approximation for most systems to assume that all heat transfer resistance is concentrated at the external surface and the temperature is essentially uniform throughout the adsorbent sample [Ruthven (1984)]. The equation can be reformulated as

$$\begin{aligned} [\bar{C}_{pg} \varepsilon_b c + (1 - \varepsilon_b) \rho_p (C_{pa} \bar{q} + C_{ps})] \frac{\partial T}{\partial t} - \varepsilon_b \frac{\partial P}{\partial t} \\ - (1 - \varepsilon_b) \rho_p \sum_i^n Q_i \frac{\partial \bar{q}_i}{\partial t} + \varepsilon_b \bar{C}_{pg} c v \frac{\partial T}{\partial z} - \varepsilon_b \frac{\partial}{\partial z} \left(D_h \frac{\partial T}{\partial z} \right) = \frac{2h_w}{R_b} (T_w - T), \end{aligned} \quad (4.91)$$

where $\bar{C}_{pg}$ is the heat capacity of the gas mixture, Q_{is} is the isosteric heat of adsorption of component i and C_{pa} is the heat capacity of the adsorbed phase. The specific heat of each adsorbed species is assumed to be equal to that of the same species in the gas phase. Since

$$\varepsilon_b \bar{C}_{pg} c v \frac{\partial T}{\partial z} = \frac{\varepsilon_b \bar{C}_{pg} P}{R} \frac{v}{T} \frac{\partial T}{\partial z} = \frac{\varepsilon_b \bar{C}_{pg} P}{R} \left[\frac{\partial v}{\partial z} - T \frac{\partial(v/T)}{\partial z} \right] \quad (4.92)$$

and taking into account the global material balance, the energy equation can be rewritten as

$$\begin{aligned} \Omega_p (C_a \bar{q} + C_{ps}) \frac{\partial T}{\partial z} + (\bar{C}_{pg} - R) \frac{\partial P}{\partial t} + \Omega_p \sum_i^n (\bar{C}_{pg} T - Q_i) \frac{\partial \bar{q}_i}{\partial t} \\ + P \bar{C}_{pg} \frac{\partial v}{\partial z} - R \frac{\partial}{\partial z} \left(D_h \frac{\partial T}{\partial z} \right) = \psi_w (T_w - T), \end{aligned} \quad (4.93)$$

where $\psi_w = \frac{2h_w R}{\varepsilon_b R_b}$. The effective heat dispersion coefficient, D_h , is given by

$$D_h = \frac{D_{to}}{\varepsilon_b} + (0.5 \sim 0.75) \frac{k_g}{\varepsilon_b} Pr Re, \quad (4.94)$$

where k_g is the gas thermal conductivity and the Prandtl number is defined as $Pr = \bar{C}_{pg}\mu/k_g$ [Funazkri and Wakao (1978), Yang (1987)]. This coefficient can be rewritten as

$$D_h = \frac{D_{to}}{\varepsilon_b} + (0.5 \sim 0.75)D_p\bar{C}_{pg}c|v|. \quad (4.95)$$

3. Auxiliary variables

In order to get the cumulative terms relative to the molar quantities of feed/product in the PSA streams at each step of the cycle, it was defined

$$N_i = \frac{\varepsilon_b A_{bed} dz}{R} \sum_j^n \left(\frac{Py_j}{T} + \frac{R\rho_p(1 - \varepsilon_b)}{\varepsilon_b} q_j \right). \quad (4.96)$$

The moles at the inlet and exit streams of the PSA bed are given, respectively, by

$$\frac{\partial N_0}{\partial t} = \varepsilon_b A_{bed} v_0 P \frac{y_0}{RT_0}, \quad \frac{\partial N_L}{\partial t} = \varepsilon_b A_{bed} v_L P \frac{y_L}{RT_L}. \quad (4.97)$$

The purge to feed ratio, P/F , is defined as the inert gas amount in the feed that is consumed in the LPG step,

$$P/F = \frac{N_{in,2} \text{ used in LPG}}{N_{in,2} \text{ inlet in HPA}}, \quad (4.98)$$

assuming the subscripts 1 and 2 the heavier and lighter adsorbates, respectively.

The component purities and recoveries, regarding the PSA cycle schematically shown in Figure (4.36), are defined as

$$\text{Recovery}_1 = \frac{N_{out,1} \text{ exit in (LBD + LPG)}}{N_{in,1} \text{ inlet in (PR + HPA)}}, \quad (4.99)$$

$$\text{Recovery}_2 = \frac{N_{out,2} \text{ exit in (HPA + HBD)} - N_{in,2} \text{ used in LPG}}{N_{in,2} \text{ inlet in (PR + HPA)}}, \quad (4.100)$$

$$\text{Purity}_1 = \frac{N_{out,1} \text{ exit in (LBD + LPG)}}{N_{out} \text{ exit in (LBD + LPG)}}, \quad (4.101)$$

$$\text{Purity}_2 = \frac{N_{out,2} \text{ exit in (HPA + HBD)} - N_{in,2} \text{ used in LPG}}{N_{out} \text{ exit in (HPA + HBD)} - N_{in} \text{ used in LPG}}. \quad (4.102)$$

4. Boundary conditions

A set of complex inlet ($z = 0$)/outlet ($z = L$) boundary conditions for the flow, composition, pressure and temperature, were defined in order to perform the periodic process. In the validation of the breakthrough and blowdown experiments, only the adsorption and blowdown steps of the PSA cycle were activated and scheduled in the model. For the PSA cycle implemented as in Figure (4.36), all the steps are active and the boundary conditions for each consecutive step are defined. Thus, the boundary conditions (BC) for the pressurization stage (PR) are

$$\left\{ \begin{array}{ll} T_0 = T_f, \quad y_0 = y_f & \text{for } z = 0, \\ v_0 = v_{HPA} P_H / P & \text{for } z = 0, \\ v_L = 0, \quad \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L, \end{array} \right. \quad (4.103)$$

with subscripts f relative to the regular feed inlet conditions, $i = 1, \dots$, NoC components. For the high-pressure adsorption step, the BCs are

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = 0 & \text{for pressure dynamics,} \\ T_0 = T_f, \quad y_0 = y_f & \text{for } z = 0, \\ v_0 = v_{HPA} & \text{for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L. \end{array} \right. \quad (4.104)$$

The boundary conditions for the breakthrough cocurrent blowdown are

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = 0 & \text{for pressure dynamics,} \\ T_0 = T_f, \quad y_0 = y_{MS} & \text{for } z = 0, \\ v_0 = v_{HPA} & \text{for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L, \end{array} \right. \quad (4.105)$$

where subscript MS denotes the feed inlet conditions relative to the pure weakly adsorbed component. At a constant pressure, this component displaces the more strongly adsorbed one through the column, allowing its desorption.

The boundary conditions for the cocurrent blowdown step (HBD) are

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = a + bt + ct^2 & \text{for pressure dynamics,} \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = 0, \\ v_0 = 0 & \text{for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L. \end{array} \right. \quad (4.106)$$

For the counter-current blowdown step (LBD), the BC are defined as

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = a + bt + ct^2 + dt^3 & \text{for pressure dynamics,} \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L, \\ v_L = 0 & \text{for } z = L. \end{array} \right. \quad (4.107)$$

Finally, for the low-pressure purge step (LPG), one has

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = 0 & \text{for pressure dynamics,} \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = 0, \\ T_L = T_f, \quad y_L = y_{LPG} & \text{for } z = L, \\ v_L = -v_{LPG} & \text{for } z = L, \end{array} \right. \quad (4.108)$$

where v_{LPG} is the inlet LPG gas velocity, and y_{LPG} is the inlet LPG gas composition, enriched in the less adsorbed component and obtained from the HPA product.

5. Initial conditions

Concerning the breakthrough runs, at time zero, the sorbent column is saturated with the inert or the weakly adsorbed component at P_H and at feed temperature T_f . The modeling runs start with the following initial conditions at $t = 0, \forall z$:

$$P = P_H, \quad \text{for starting bed pressure,} \quad (4.109)$$

$$T = T_f, \quad \text{for starting bed temperature,} \quad (4.110)$$

$$q_1 = 1 \times 10^{-4}, \quad q_2 = \frac{(1 - 1 \times 10^{-4})W_s P_H}{RT_f}, \quad (4.111)$$

$$N_0, N_L = 0, \quad y_1 = 1 \times 10^{-4}, \quad (4.112)$$

with $i = 1, 2$ subscripts representing the strongly and weakly adsorbed components, respectively.

When one is dealing with the entire PSA cycle, the modeling starts with the inert or the weakly adsorbed component at P_L and at feed temperature T_f . The initial conditions are given below, at $t = 0, \forall z$:

$$P = P_L, \quad \text{for starting bed pressure,} \quad (4.113)$$

$$T = T_f, \quad \text{for starting bed temperature,} \quad (4.114)$$

$$\frac{\partial q_i}{\partial t} = 0, \quad (4.115)$$

$$N_0, N_L = 0, \quad y_1 = 1 \times 10^{-4}. \quad (4.116)$$

6. Numerical solution method

In this work, the modeling and simulation work is carried out using gPROMS (general PROcess Modeling System), a software package for the modeling and simulation of processes with both discrete and continuous as well as lumped and distributed characteristics. More information on gPROMS, its concepts and language, can be found in PSE (2004), Nilchan (1997), Barton and Pantelides (1994), Barton (1992) and Oh (1995).

As shown above, the periodic adsorption processes are mathematically represented by a system of partial differential and algebraic equations (PDAEs). These PDAEs are highly coupled, which makes it impossible to obtain analytical solutions. Thus, the simulation of such processes relies on numerical methods employing space and time discretizations [Nilchan (1997)]. The spatial discretization converts the original equations into a mixed system of ordinary differential and algebraic equations (DAEs) with respect to time. The simultaneously time discretization results directly in a set of nonlinear algebraic equations (AEs).

The spatial derivatives in the bed are discretized using the control-volume formulation [Patankar (1980); Waterson and Deconinck (1995), Alhumaizi (2004)] and are converted into a large system of differential-algebraic equations (DAEs) to which the efficient stiff-DAE solver built into gPROMS is applied. In order to prevent non-physical oscillations of the solution, the convective terms are spatially discretized using the van Leer harmonic flux-limited scheme implemented in the form advocated by Waterson and Deconinck (1995). The high-order correction, applied to the convective terms, is expressed as a weighted average of the centered and upwind gradients in the solution. The non-linear average function give high-order accuracy and ensures that some prescribed boundedness criterion is fulfilled. A total of 50 control volumes of length dz are applied. Time intervals smaller than 1 s are used, depending on the sharpness of the concentration wavefronts, to ensure stability and accuracy of the solution. With the input information on equilibrium adsorption and the transport properties, the model can be numerically solved through Eqs. (4.45, 4.56, 4.62, 4.74, 4.93).

4.3.4.3 Breakthrough and Blowdown

Figures (4.44) and (4.45) show the results obtained from the diluted CO₂/He breakthrough and blowdown simulations for different temperatures, and their comparison with the experimental data. Carbon dioxide is present in helium at very low concentrations, ensuring an isothermal behavior. Thus, the temperature effects in the bed due to CO₂

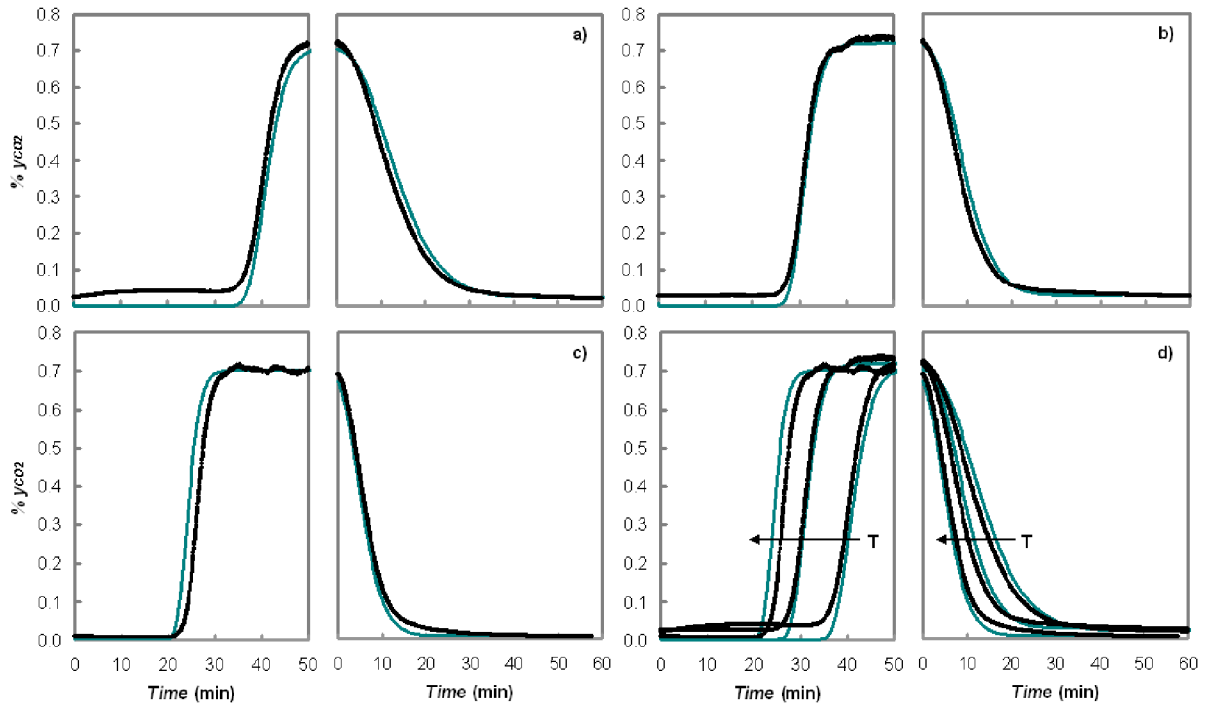


Figure 4.44: Breakthrough and blowdown simulations and their comparison with the experimental data for the diluted mixture of CO_2/He 0.7/99.3% (v/v). Black symbols are the experimental CO_2 composition history at the PSA exit stream, whereas the green lines denote the predicted CO_2 composition history. Figures a), b) and c) report the operating temperatures of 26.6°C , 36.8°C and 46.2°C , respectively. d) presents a comparison of the CO_2 effluent composition histories at the three different temperatures.

adsorption can be neglected. The only possible mass transfer resistances are the diffusivity coefficient, the film mass transfer and the axial dispersion coefficient. The flow rate was considered high enough to assume negligible film mass transfer resistance. The LDF coefficient values [Eq. (4.74)] used for the fitting of the experimental curves are reported in Table (4.26).

As one can see in Figure (4.44), the model predictions show good agreement with the laboratory experiments. Note that with temperature increase, the CO_2 breakthrough occurs earlier, as expected.

Since the adsorption is exothermic and the heat of sorption must be dissipated by heat transfer, generally, there is a temperature difference between the adsorbent and the ambient fluid, when sorption takes place. Although the dissipation of heat from the

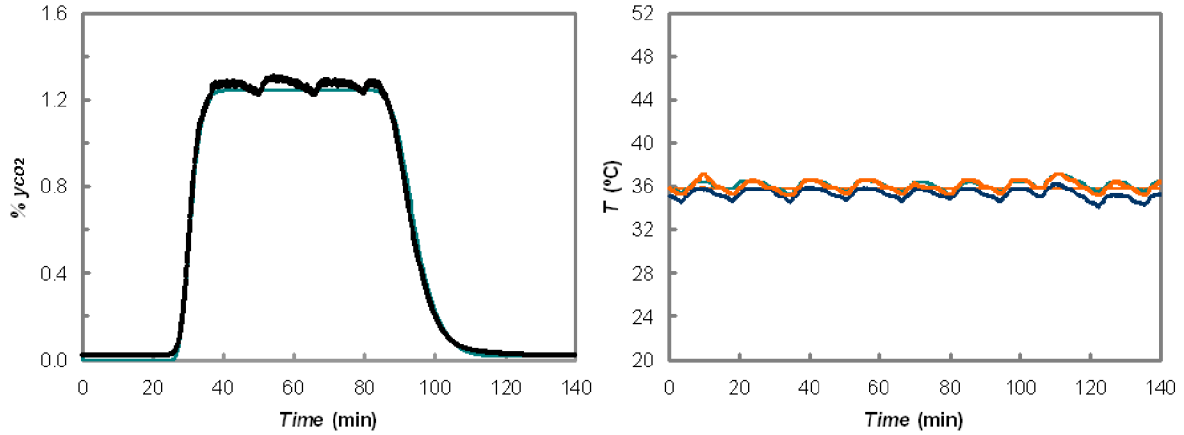


Figure 4.45: Breakthrough and blowdown simulations and their comparison with the experimental data for the diluted mixture of CO₂/He 1.2/98.8% (v/v) at 35.8°C. Left figure reports the CO₂ composition history. Black symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right figure presents the temperature histories at three measuring points inside the bed. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

external surface of the adsorbent, rather than the conduction of heat within the adsorbent, is generally the rate-limiting heat transfer process, under these experimental conditions, the heat transfer resistance is neglected, and the system is treated as isothermal. The temperature difference between the adsorbent and the ambient fluid when sorption takes place is insignificant.

At 46°C the component goes out of the column faster than it does at 26°C, due to the

Table 4.26: LDF coefficients, k_i , obtained from the fitting of the diluted CO₂ (0.7% v/v in He) breakthrough and blowdown experimental curves.

Gas	T (°C)	LDF coefficient	Diffusivity
		k_i (s ⁻¹)	D_i (m ² /s)
CO ₂	26.6	0.0796	9.0E-08
	36.8	0.1149	1.3E-07
	46.2	0.1768	2.0E-07

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.27: LDF, k_i , the diffusivity, D_i , and the wall heat transfer, h_w , coefficients, obtained from the fitting of the concentrated CO₂/He breakthrough and blowdown experimental curves.

Mixture	T	LDF coefficient	Diffusivity	Wall heat transfer coefficient
CO ₂ /He (% v/v)	(°C)	k_i (s ⁻¹)	D_i (m ² /s)	h_w (W/m ² K)
0.7/99.3	26.6	0.0796	9.0E-08	-
	36.8	0.1149	1.3E-07	-
	46.2	0.1768	2.0E-07	-
1.2/98.8	35.8	0.1149	1.3E-07	-
30/70	25.8	0.0884	1.0E-07	63.0
	37.0	0.1149	1.3E-07	59.0
	36.9	0.1149	1.3E-07	65.0
	47.4	0.1768	2.0E-07	63.0
50/50	27.6	0.0796	9.0E-08	63.0
	37.2	0.1149	1.3E-07	60.0
	46.7	0.1768	2.0E-07	65.5
80/20	26.0	0.0796	9.0E-08	65.0
	46.9	0.1768	2.0E-07	65.0

higher loading and adsorption effect in the latter case. After the sorbent saturation, the equilibrium capacity is reached and all curves tend to the same gas concentration, i.e., the CO₂ inlet concentration at each experiment.

A coherent behavior is observed during the CO₂ desorption. At 46°C the loading effect is lower than at 26°C, thus the component desorbs faster from the bed in the former case. The column is clean of CO₂, after a shorter period of time.

Figure (4.45) presents a similar CO₂ concentration history as in Figure (4.44), illustrating the isothermal behavior at diluted conditions, through the temperature histories at three locations inside the bed. The small temperature oscillations (± 1 -2°C) are simply due to the On/Off response of the in-line temperature controllers.

Figures (4.46-4.49) present the results obtained from the more concentrated CO₂/He breakthrough and blowdown simulations (30/70, 50/50 and 80/20% v/v) and their comparison with the experimental data. Carbon dioxide is now present at higher concentrations in helium. Thus, the temperature effects in the bed due to CO₂ adsorption can no longer be neglected. Table (4.27) reports the LDF, k_i , the diffusivity, D_i , and wall heat transfer, h_w , coefficients, obtained from the fitting of each experiment performed according to the operating conditions given in Tables (4.19-4.21).

It can be seen that the model can describe reasonably well the full set of data, based only on pure-component adsorption equilibria and kinetics previously measured.

From Figure (4.46) one can conclude, as expected, that the temperature variations

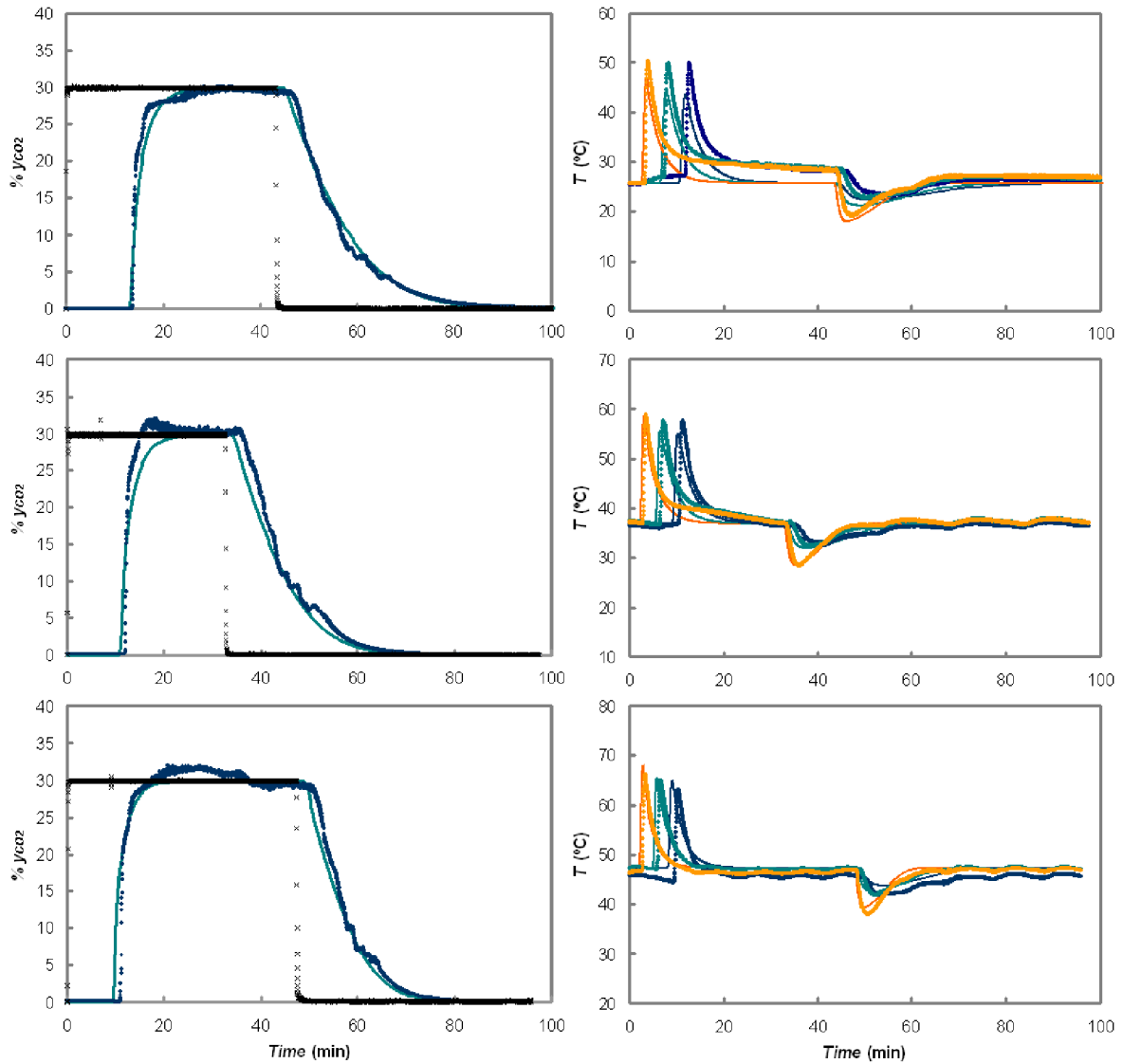


Figure 4.46: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO₂/He 30/70% (v/v) mixture at 10 bar. Top, middle and bottom figures are the results at 25.8°C, 37.0°C and 47.4°C, respectively. Left: Black symbols denote CO₂ concentration at the PSA inlet stream. Blue symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

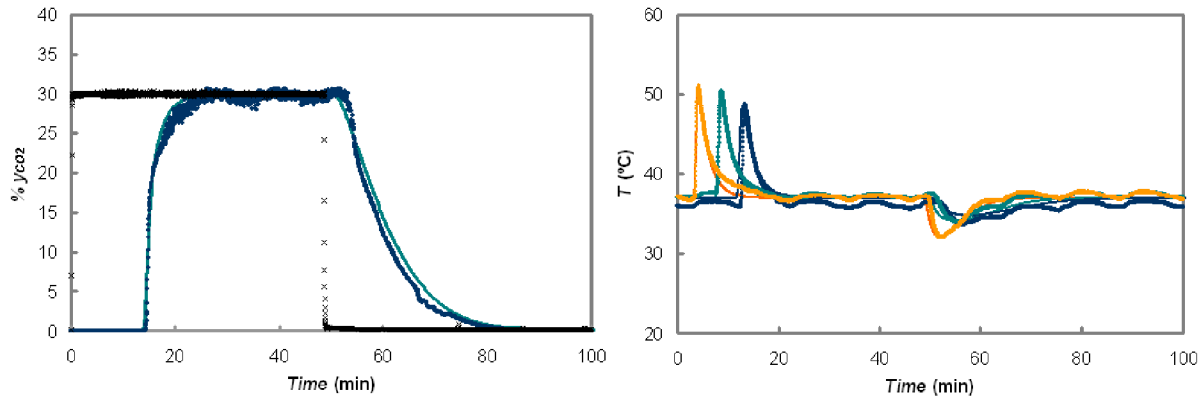


Figure 4.47: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO₂/He 30/70% (v/v) mixture at 36.9°C and 5 bar. Left: Black symbols denote CO₂ concentration at the PSA inlet stream. Blue symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

due to adsorption are larger than 25°C in the experiment made at the lower temperature (26°C). At the three points of the bed, the temperature peaks predicted are in accordance with the experimental ones, showing the same order of magnitude. Due to the sorption equilibria of CO₂ at 46°C, the temperature variation resulting from adsorption/desorption is significantly lower.

Comparing the CO₂/He 30/70% (v/v) runs, both at approximately 37°C, from Figures (4.46) and (4.47), one can see that the higher the pressure is, the higher the amount of gas adsorbed in the column and the higher the temperature variations due to the sorption effect.

Figures (4.46), (4.48) and (4.49) show the effect of the feed composition variation on the breakthrough/blowdown curves and on the temperature histories inside the sorbent bed. Note that, maintaining both temperature and total volumetric flow, increasing the ratio strongly/weakly adsorbed component, widens the breakthrough and temperature profiles. For the 80/20% (v/v) run, the loading increment in the CO₂ adsorption induces higher temperature increments in the adsorption step and higher temperature drops in

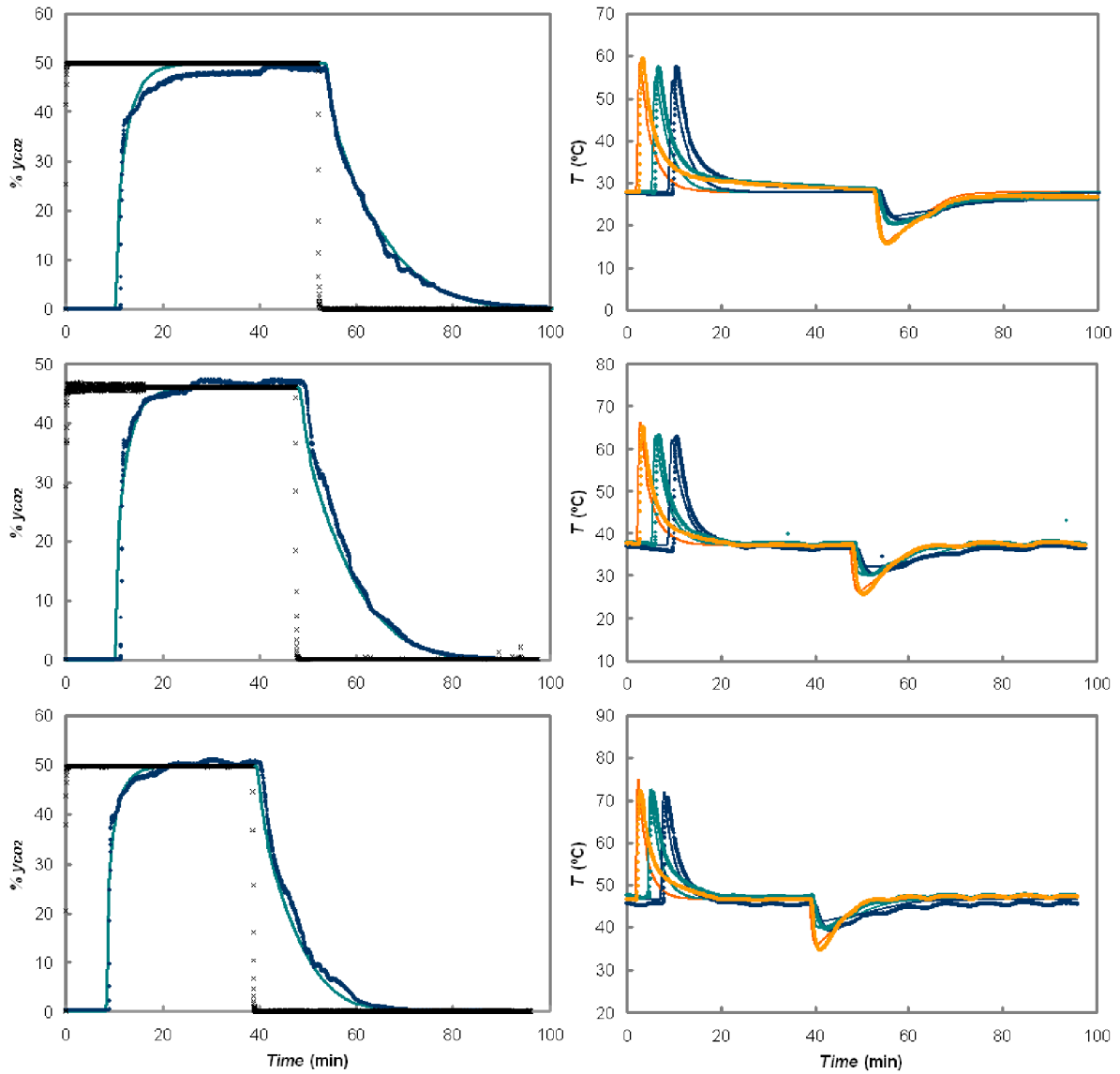


Figure 4.48: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO₂/He 50/50% (v/v) mixture. Top, middle and bottom figures are the results at 27.6°C, 37.2°C and 46.7°C, respectively. Left: Black symbols denote CO₂ concentration at the PSA inlet stream. Blue symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

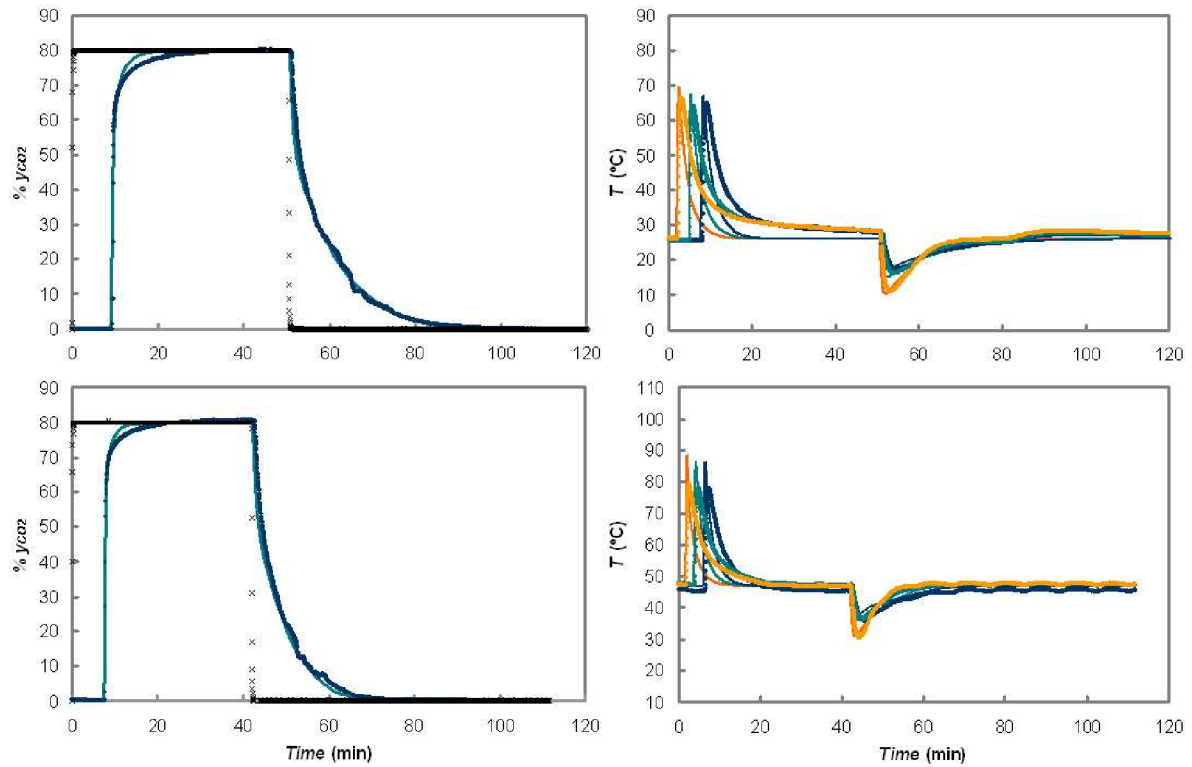


Figure 4.49: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO₂/He 80/20% (v/v) mixture. Top and bottom figures are the results at 26.0°C and 46.9°C, respectively. Left: Black symbols denote CO₂ concentration at the PSA inlet stream. Blue symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

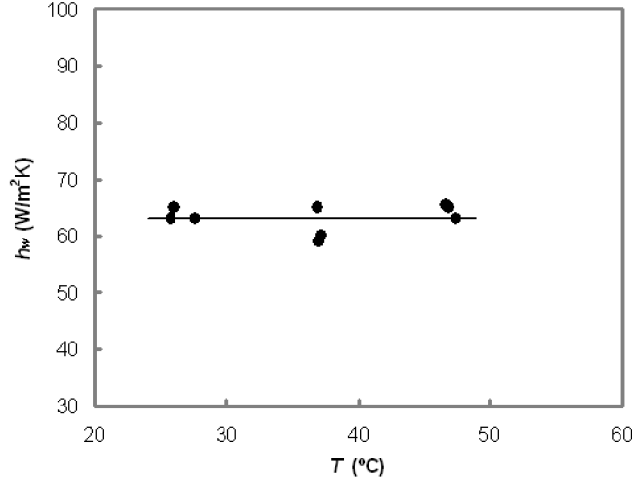


Figure 4.50: Temperature effect in the wall heat transfer coefficient, obtained from the CO₂/He 30/70, 50/50 and 80/20% (v/v) mixtures, at the average temperatures of 26°C, 37°C and 47°C, each.

the desorption stage.

From Table (4.27) and Figure (4.50), one can assume an average value of 63.2 W/m²K for the wall heat transfer coefficient, h_w .

The diffusion mechanism is an activated process, i.e.,

$$D = D_o e^{-E/RT} \quad (4.117)$$

where E is the diffusional activation energy, generally smaller than the heat of adsorption, and D_o is a parameter. Therefore, the contribution of the overall diffusivity generally increases with increasing temperature. From Table (4.26), one can see the referred temperature dependence of CO₂ diffusivity in the carbon sample.

For modeling purposes, one also needs both N₂ and CH₄ diffusivities, D_{N_2} and D_{CH_4} , respectively. As a first approximation one assumes that the surface diffusion is the predominant contribution to the LDF coefficients, k_i . The choice made revealed to be a corrected one as it will be shown later in this section. Sladek et al. have developed a general correlation, based on Eq. (4.117), that may be used to estimate the surface diffusivity, D_i [Yang (1987)]. Hence, using the component heat of adsorption reported on Table (4.17), one determined the diffusivities of CO₂, N₂ and CH₄, in order to obtain the D_{N_2}/D_{CO_2} and D_{CH_4}/D_{CO_2} ratios. Thereafter, knowing the experimental CO₂ diffusivity, and maintaining that same ratios, one calculated both N₂ and CH₄ diffusivities,

Table 4.28: Diffusivity coefficients, D_i , of CO₂, N₂ and CH₄ at the average experimental temperatures of 26°C, 37°C and 47°C.

T (°C)	$10^3/T$ (K ⁻¹)	N ₂	CH ₄	CO ₂
		D_{N_2} (m ² /s)	D_{CH_4} (m ² /s)	D_{CO_2} (m ² /s)
26	3.34	5.62E-07	3.24E-07	1.00E-07
36	3.23	6.52E-07	3.84E-07	1.30E-07
46	3.13	8.34E-07	5.02E-07	2.00E-07
D_{oi}	m ² /s	0.0003	0.0003	0.0159
E_i	J/mol	1.8742	2.0939	3.6193

for the three experimental temperatures. Table (4.28) and Figure (4.51) presents the results obtained from this approximation, showing the correlation of component diffusivity coefficients against temperature.

Considering Eqs. (4.74) and (4.77), and the LDF coefficient values obtained experimentally as shown in Table (4.27), the next step was to distinguish between both Knudsen and surface diffusivity contributions. From the CO₂/He and CO₂/N₂ experiments at each temperature, the term (dq_i/dP) was determined at the feed CO₂ partial pressure. Since

$$(q_i^s - \bar{q}_i) \approx \left(\frac{dq_i}{dP} \right)_{P=y_i P_H} (P_{ip}^s - \bar{P}_{ip}), \quad (4.118)$$

the LDF coefficient can be expressed as

$$k_i = k_{is} + \frac{k_{ik}}{\rho_p R T \left(\frac{dq_i}{dP} \right)_{P=y_i P_H}}, \quad (4.119)$$

with k_{ik} and k_{is} defined by Eqs. (4.81). Table (4.29) presents the Knudsen and surface diffusion contributions in the LDF coefficient, for the CO₂/He and CO₂/N₂ systems, performed at the experimental conditions described in Tables (4.19, 4.21) and considering the Sips isotherm equilibria described in Table (4.18). The predominant contribution to diffusion results from the surface diffusivity term.

The next set of results refers to binary mixtures of CO₂/N₂ at approximately 10 bar, at an average temperature of 36°C and at different total volumetric feeds, i.e., distinct inlet gas velocities. These runs are important to the design of the PSA process, confirming that the isosteric heats of adsorption, determined from the multicomponent extended Sips model, are correctly applied in the energy balance, and thus describing correctly the multicomponent adsorption equilibria in the fixed-bed.

As one can see from Figures (4.52-4.54), the predicted curves are reasonably in accordance with the composition and temperature experimental histories. Dynamic simulations

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.29: CO₂ and N₂ Knudsen and surface diffusion contributions for CO₂/He and CO₂/N₂ systems, at each average experimental temperatures.

Mixture	T (°C)	P _H (bar)	LDF coefficient		Knudsen contrib.		Surface contrib.	
			k _i (s ⁻¹)	k _{is} (s ⁻¹)	k _{ik} /P _P RT(dq _i /dP _i) (s ⁻¹)	k _{is} (s ⁻¹)	k _{ik} /P _P RT(dq _i /dP _i) (s ⁻¹)	k _{is} (s ⁻¹)
CO ₂ /He (% v/v)	26.6	4	0.0796	2.024E-04				0.0794
	36.8	4	0.1149	2.085E-04				0.1147
	46.2	4	0.1768	2.125E-04				0.1766
	35.8	4	0.1149	2.320E-04				0.1147
	25.8	10	0.0884	6.189E-04				0.0790
30/70	37.0	10	0.1149	6.212E-04				0.1143
	36.9	4.99	0.1149	4.968E-04				0.1144
	47.4	10	0.1768	6.237E-04				0.1762
50/50	27.6	10	0.0796	7.675E-04				0.0788
	37.2	10	0.1149	7.405E-04				0.1142
	46.7	10	0.1768	7.667E-04				0.1761

Mixture	T (°C)	P _H (bar)	v _{HPA} (cm/s)	LDF coef.		Knudsen contrib.		Surface contrib.	
				k _i (s ⁻¹)	k _{is} (s ⁻¹)	k _{ik} /P _P RT(dq _i /dP _i) (s ⁻¹)	k _{is} (s ⁻¹)	k _{ik} /P _P RT(dq _i /dP _i) (s ⁻¹)	k _{is} (s ⁻¹)
CO ₂ /N ₂ (% v/v)	36.8	9.98	2.53	0.1149	8.315E-04		0.1141	5.625E-03	0.5709
	36.4	9.98	2.53	0.1149	1.073E-03		0.1139	4.666E-03	0.5718
	37.4	9.98	2.54	0.1149	1.501E-03		0.1134	3.695E-03	0.5728

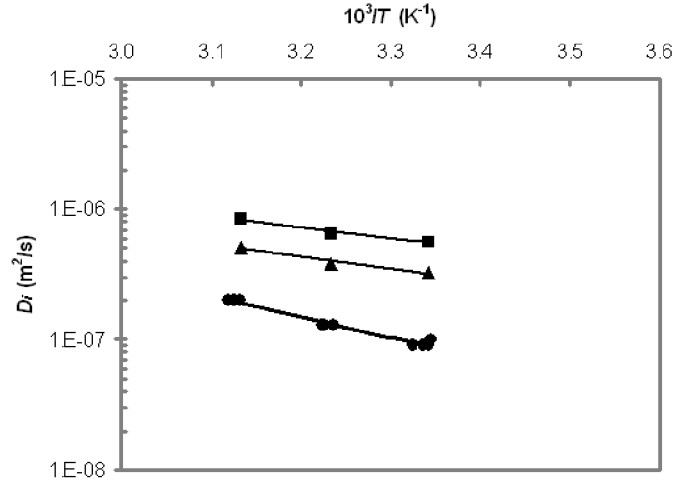


Figure 4.51: Correlation of diffusivity coefficients of CO_2 , N_2 and CH_4 against the average experimental temperatures of 26°C , 37°C and 47°C . $\bullet$, $\blacktriangle$ and $\blacksquare$ corresponds to CO_2 , CH_4 and N_2 , respectively.

are performed for base case values given in Tables (4.21, 4.24). The discretized system involves 670 ordinary differential and algebraic equations. Its simulation takes approximately less than 10 seconds on a Intel Pentium M 1.5 GHz PC with 512 MB of RAM. To point out that in some experiments, the first temperature peak (150 mm from the bottom of the bed) shows irregularities, possibly explained by experimental errors in the respective temperature probe. Nevertheless, the simulated profiles are quite satisfactory, showing the correct behavior of the fixed-bed adsorption.

The breakthrough and temperature histories take approximately three times less time to appear by triplicating the total gas feed flow. For higher feed flows, the loading capacity of the column is increased, increasing the temperature effects during feed and blowdown.

4.3.4.4 PSA Cycle Steps Experiments

The PSA experiments for the CO_2/N_2 gas separation, at three distinct compositions, were validated against the model prediction results. The dynamic simulation of the PSA process is performed to predict both the initial transient and the cyclic steady state behavior. Starting from given initial conditions, the performance of the system is simulated over a number of cycles until the system reaches the cyclic steady state (CSS). Dynamic simulations are performed for base case values given in Table (4.23, 4.24). The discretized system involves 670 ordinary differential and algebraic equations. Its simulation over 10

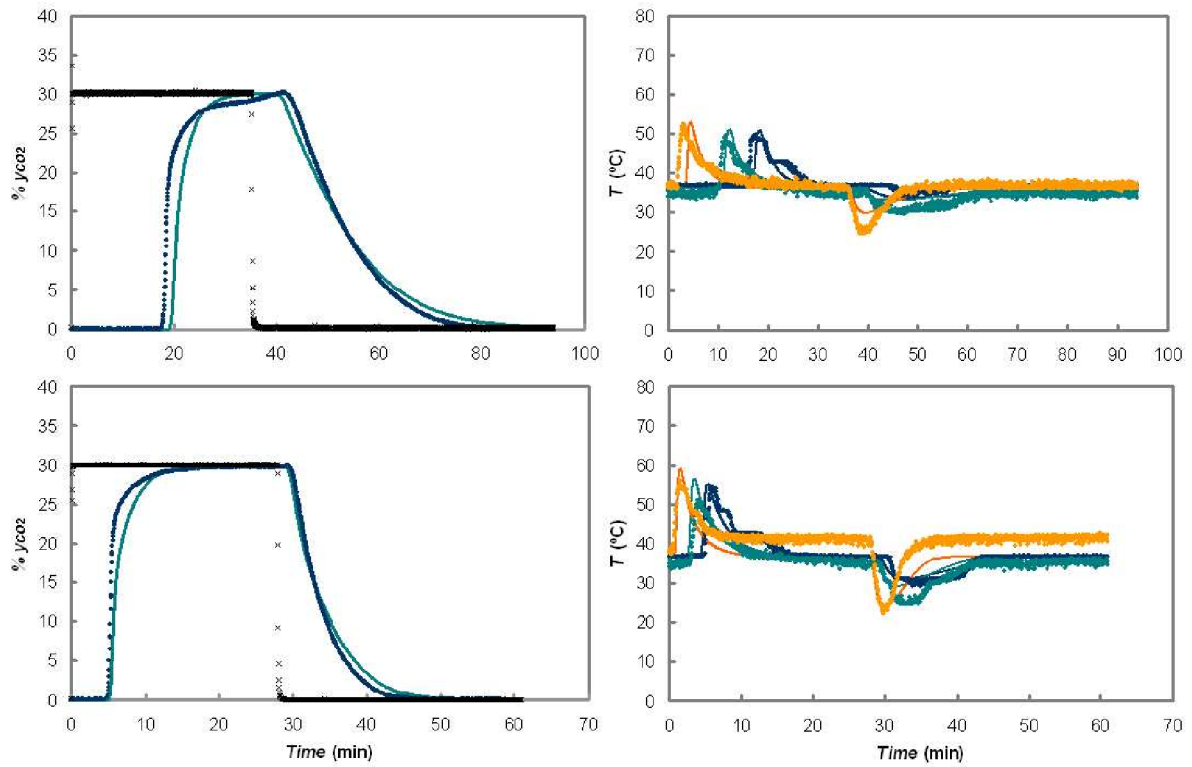


Figure 4.52: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO₂/N₂ 30/70% (v/v) mixture. Top figure shows the results at 36.14°C and 1.6914 slpm. Bottom figure presents the results at 36.75°C and 5.0497 slpm, respectively. Left: Black symbols denote CO₂ concentration at the PSA inlet stream. Blue symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

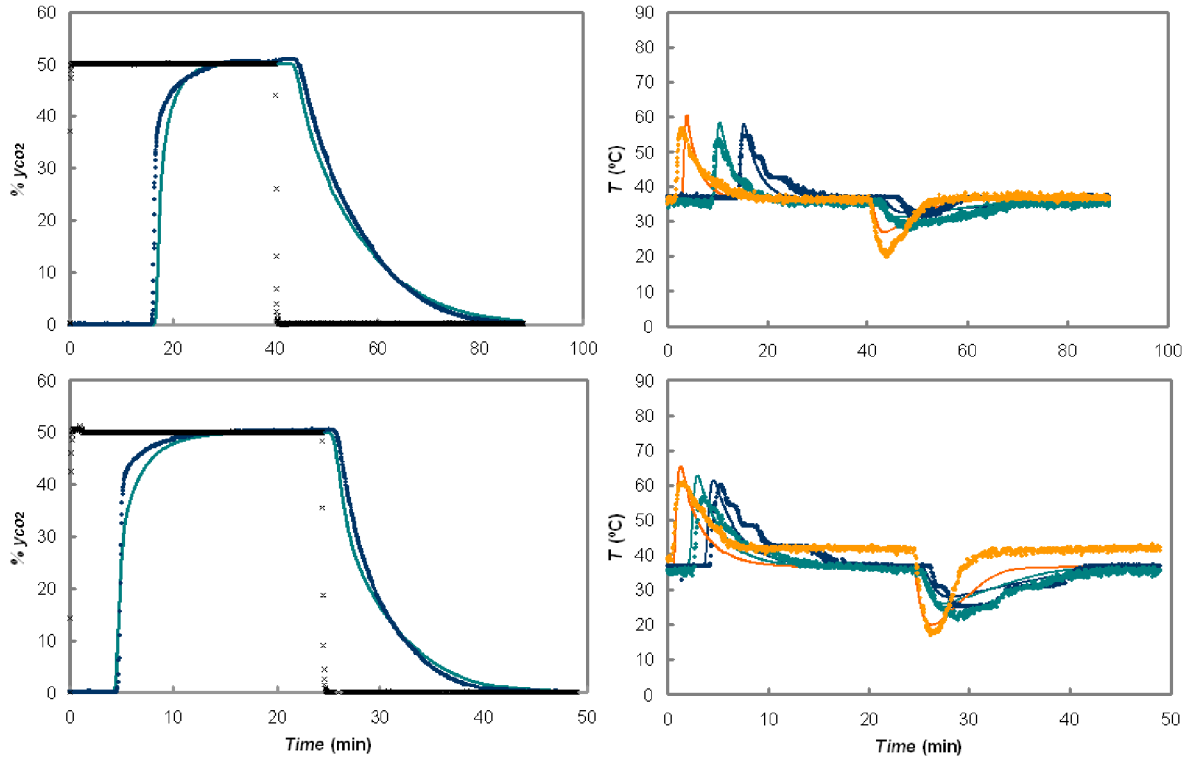


Figure 4.53: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO₂/N₂ 50/50% (v/v) mixture. Top figure shows the results at 36.17°C and 1.6810 slpm. Bottom figure presents the results at 36.38°C and 5.0508 slpm, respectively. Left: Black symbols denote CO₂ concentration at the PSA inlet stream. Blue symbols are the experimental CO₂ composition profile at the PSA exit stream, whereas the green lines denote the predicted CO₂ composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

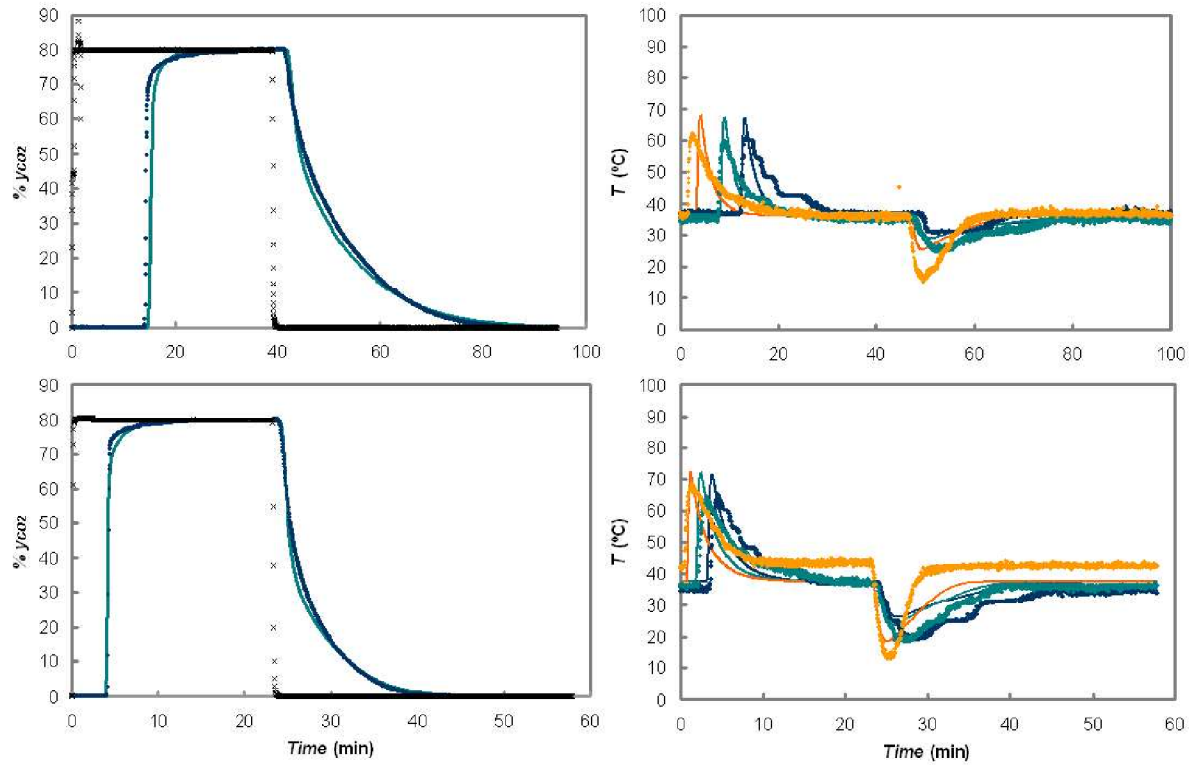


Figure 4.54: Breakthrough and blowdown simulations and their comparison with the experimental data for the CO_2/N_2 80/20% (v/v) mixture. Top figure shows the results at 35.09°C and 1.6837 slpm. Bottom figure presents the results at 37.43°C and 5.0541 slpm, respectively. Left: Black symbols denote CO_2 concentration at the PSA inlet stream. Blue symbols are the experimental CO_2 composition profile at the PSA exit stream, whereas the green lines denote the predicted CO_2 composition history. Right: Symbols denote the experimental temperature histories and lines report the predicted results. Orange, green and dark blue represent the bottom, middle and top temperature histories at 150, 350, and 550 mm from the bottom of the column, respectively.

cycles takes approximately less than 48 seconds, and less than 5 seconds for a simple CSS cycle on a Intel Pentium M 1.5 GHz PC with 512 MB of RAM.

Table (4.30) shows the gas separation performance for each PSA run, at CSS conditions, for the operating conditions of Table (4.23). Except for the feed gas composition, all other experimental conditions were approximately maintained. The step times of HPA, HBD, LBD and LPG are similar for the three runs, but the time period of pressurization up to P_H was dictated by the total volumetric feed flowrate. The higher the CO₂ loading at feed, the higher the time needed to pressurize the column up to P_L .

The cycle is schematically represented in Figure (4.36), although experimentally the N₂ purge, fed to the system, is not a real portion of the HPA product, but an external simulated stream at approximately the same composition. The separation performance, at approximately 36°C, for CO₂/N₂ mixtures at three different feed compositions are reported. It is clear that the model is reasonably capable of predicting all effects caused by various gas feed compositions.

The P/F ratio, i.e., the N₂ amount in the feed step (HPA) that is consumed in the low-pressure purge (LPG), increases with increasing CO₂ concentration, since the aim is to maintain constant the same N₂ gas velocity and concentration in the purge step. The differences between the composition and temperature histories of the three runs are mostly due to the distinct loadings of both components into the system. The main functions of the purge step are stripping the adsorbed CO₂ from the bed and increasing its product purity as well as its recovery. It cleans the bed for the next cycle at the expense of the N₂ product previously obtained. The final N₂ product purity is also increased. However, upon an excessive P/F ratio, the N₂ recovery will decrease with dilution of the CO₂ product.

Run 2 loaded with the lower CO₂ concentration, shows a significant N₂ purity product, higher than 99%, with a component recovery of 64%, while the CO₂ product was 99.5% recovered, but at a poor purity (54%). In contrast, Run 3 loaded with more CO₂, gives a CO₂ product purity of 92% at a recovery of 83%, although 69% N₂ was recovered at a poor purity (51%). The performance of Run 1 results in an intermediate situation, where 66% N₂ and 98% CO₂ were recovered at the product purities of 97% and 74%, respectively.

Figures (4.55), (4.57) and (4.59) present the comparison of the simulated results with the ones experimentally obtained for a typical PSA experiment, at CSS, performed with the described procedure and the cycle conditions described in Table (4.23). Figures (4.56), (4.58) and (4.60) show the experimental process operation until CSS is reached and its comparison with the predicted pressure, composition and temperature histories.

After the HPA step, the co-current depressurization (HBD) of Runs 1, 2 and 3 takes place up to an intermediate pressure of 3.2 bar. This pressure value is the lower limit

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

Table 4.30: PSA modeling results obtained using dynamic simulation for the CO₂/N₂ systems at CSS (NoCycle = 11).

Run		Predicted ^a					
		1		2*		3*	
Step	Avg. CO ₂ in %	50.21	(50.31)	30.21	(30.21)	80.10	(80.10)
I	Total Amt. in (LSTP)	7.770	(8.298)	6.723	(7.076)	10.258	(10.824)
Step	Avg. CO ₂ in %	50.21	(50.31)	30.21	(30.21)	80.10	(80.10)
II	Total Amt. in (LSTP)	4.002	(3.615)	3.910	(3.622)	4.487	(3.689)
	Avg. N ₂ out %	98.94		99.65		86.74	
	Total Amt. out (LSTP)	2.331		2.773		1.941	
Step	Avg. N ₂ out %	94.39		98.69		32.53	
III	Total Amt. out (LSTP)	1.901		2.112		2.582	
Step	Avg. CO ₂ out %	73.17		53.32		91.93	
IV	Total Amt. out (LSTP)	7.058		5.612		9.234	
Step	Avg. N ₂ in %	99.88	(99.88)	99.74	(99.74)	97.33	(97.33)
V	Total Amt. in (LSTP)	0.257	(0.256)	0.121	(0.112)	0.506	(0.507)
	Avg. CO ₂ out %	83.29		70.53		89.39	
	Total Amt. out (LSTP)	0.738		0.288		1.495	
	PIF	0.129		0.049		0.552	
Total Feed per cycle (LSTP) ^b		12.03	(12.17)	10.75	(10.81)	15.25	(15.02)
CO ₂ Purity (%)		74.13		54.16		91.58	
N ₂ Purity (%)		96.71		99.23		50.55	
CO ₂ Recovery (%)		97.78		99.46		83.18	
N ₂ Recovery (%)		65.59		63.71		69.20	

* Runs executed approximately at the same experimental conditions as in Run1, except for the feed gas composition.

^a Values in brackets are estimated ones from the experimental conditions.

^b Is defined as the total amount per cycle fed to the PSA during PR, HPA and LPG steps. STP (0°C, 1 atm)

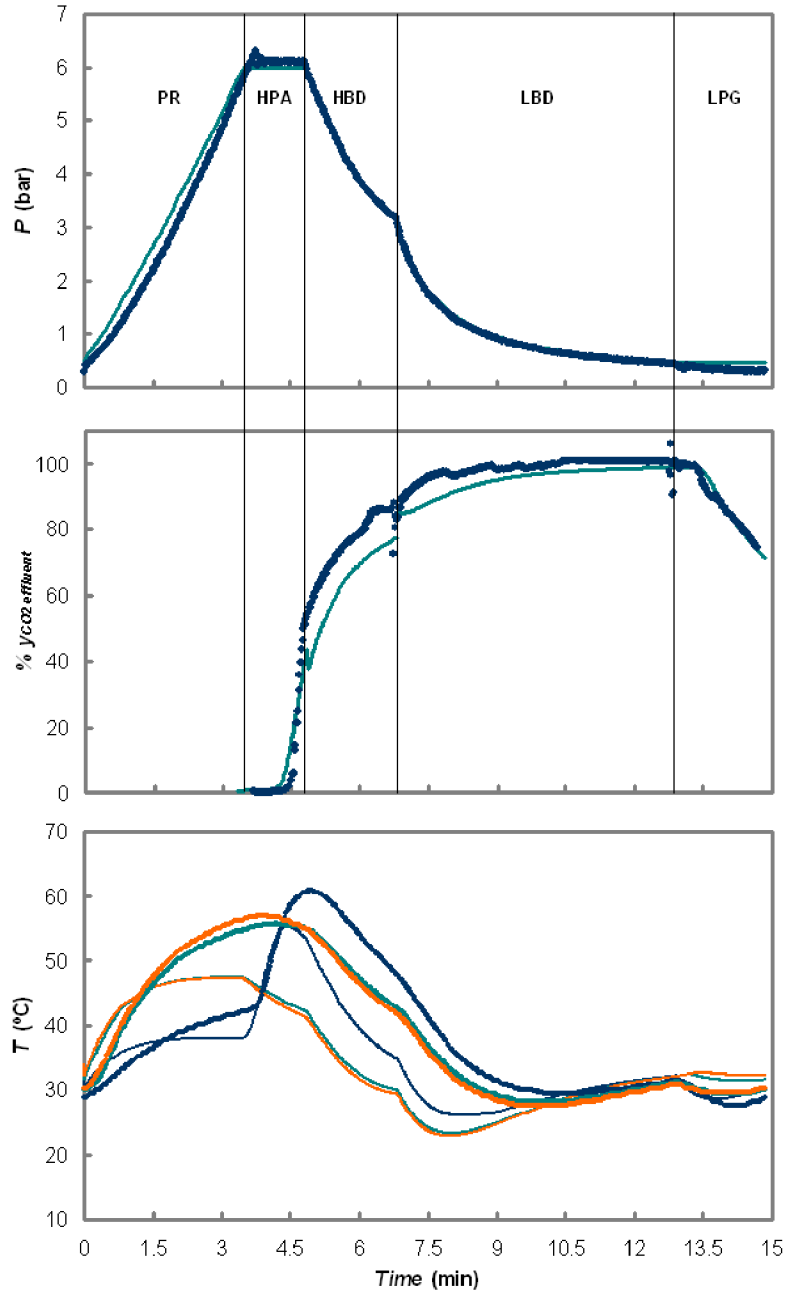


Figure 4.55: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical PSA experiment at CSS (NoCycle = 11). Corresponds to a CO_2/N_2 80/20 % (v/v) mixture at an average T_{run} of $34.14^\circ C$, a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: $0^\circ C$, 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

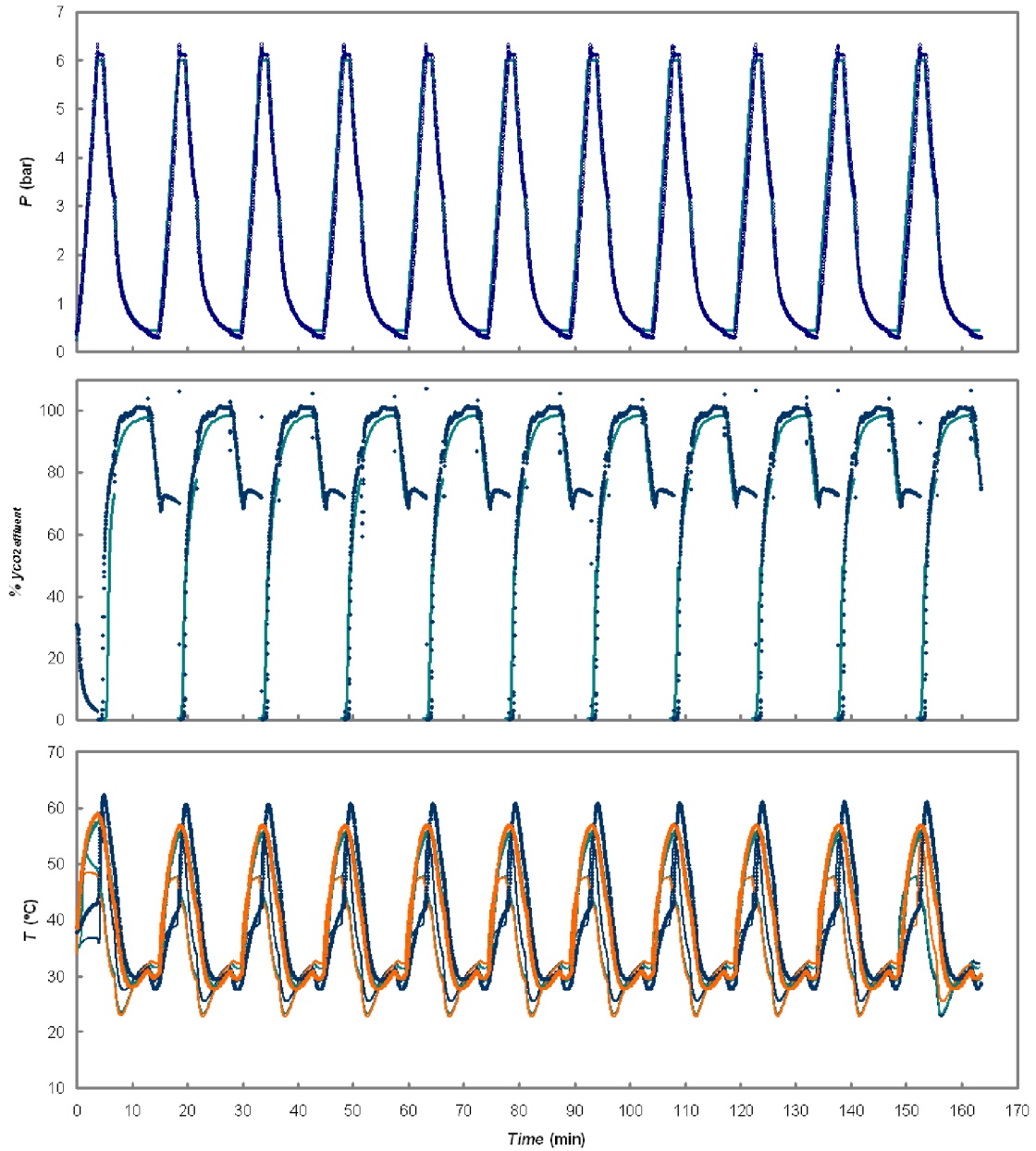


Figure 4.56: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical PSA experiment up to the CSS condition. Corresponds to a CO_2/N_2 80/20 % (v/v) mixture at an average T_{run} of 34.14°C , a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: 0°C , 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

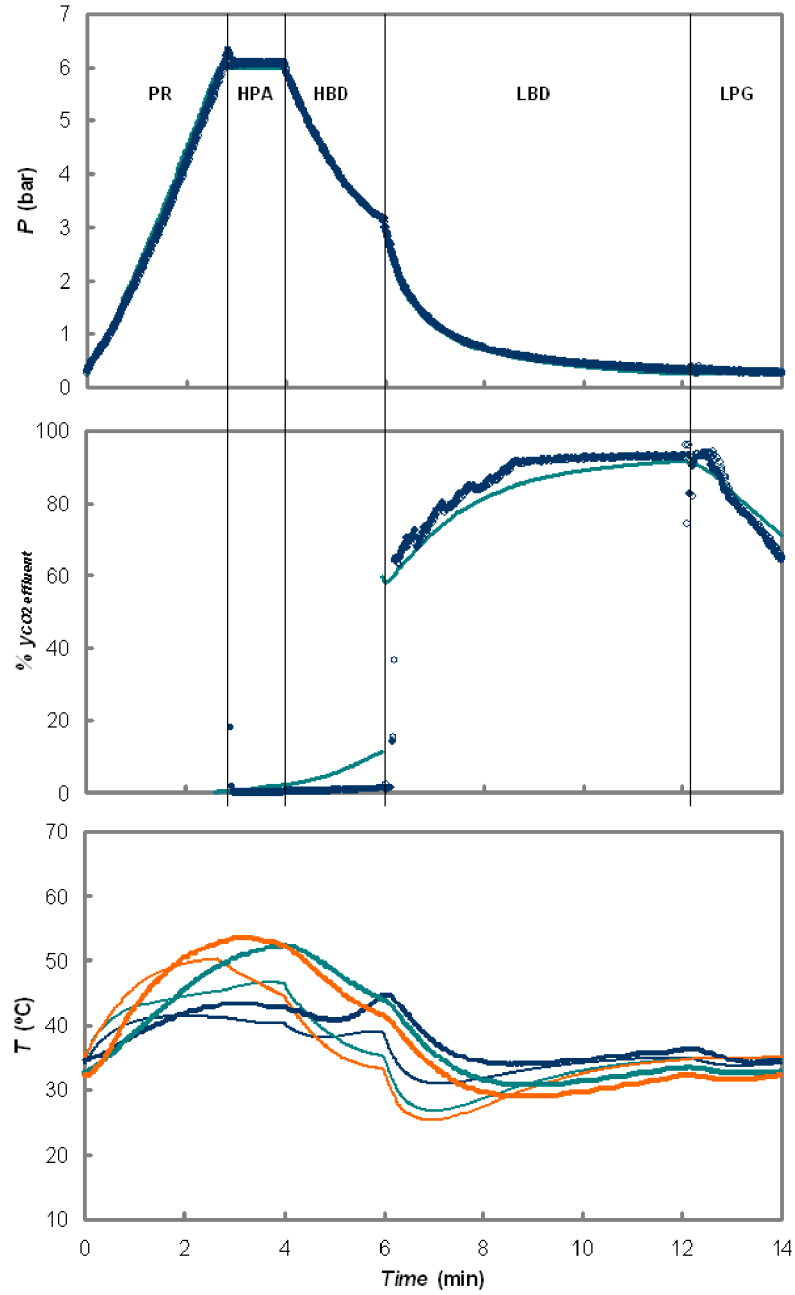


Figure 4.57: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical PSA experiment at CSS (NoCycle = 11). Corresponds to a CO_2/N_2 50/50 % (v/v) mixture at an average T_{run} of 33.04°C , a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: 0°C , 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

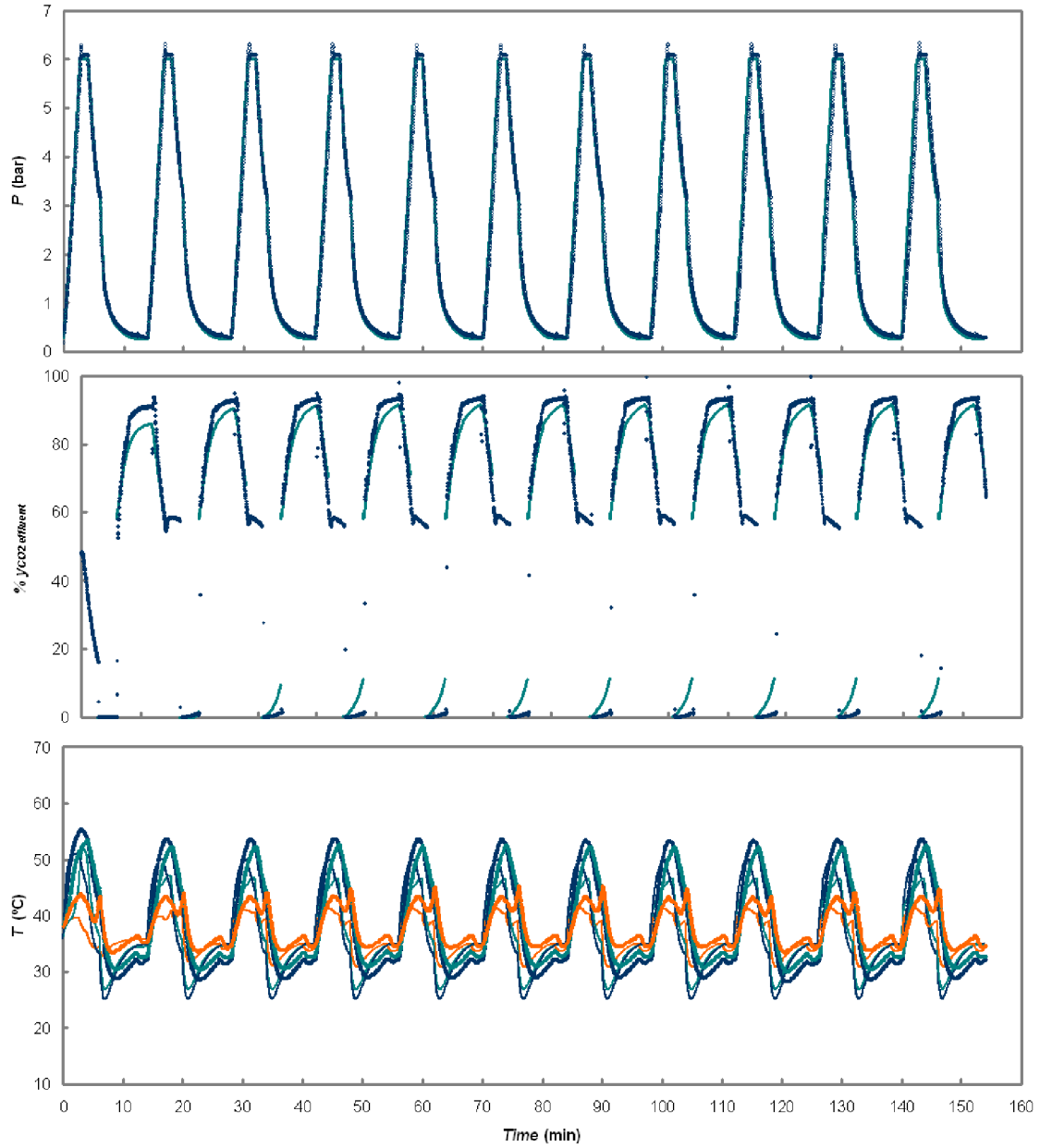


Figure 4.58: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical PSA experiment up to the CSS condition. Corresponds to a CO_2/N_2 50/50 % (v/v) mixture at an average T_{run} of $33.04^\circ C$, a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: $0^\circ C$, 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

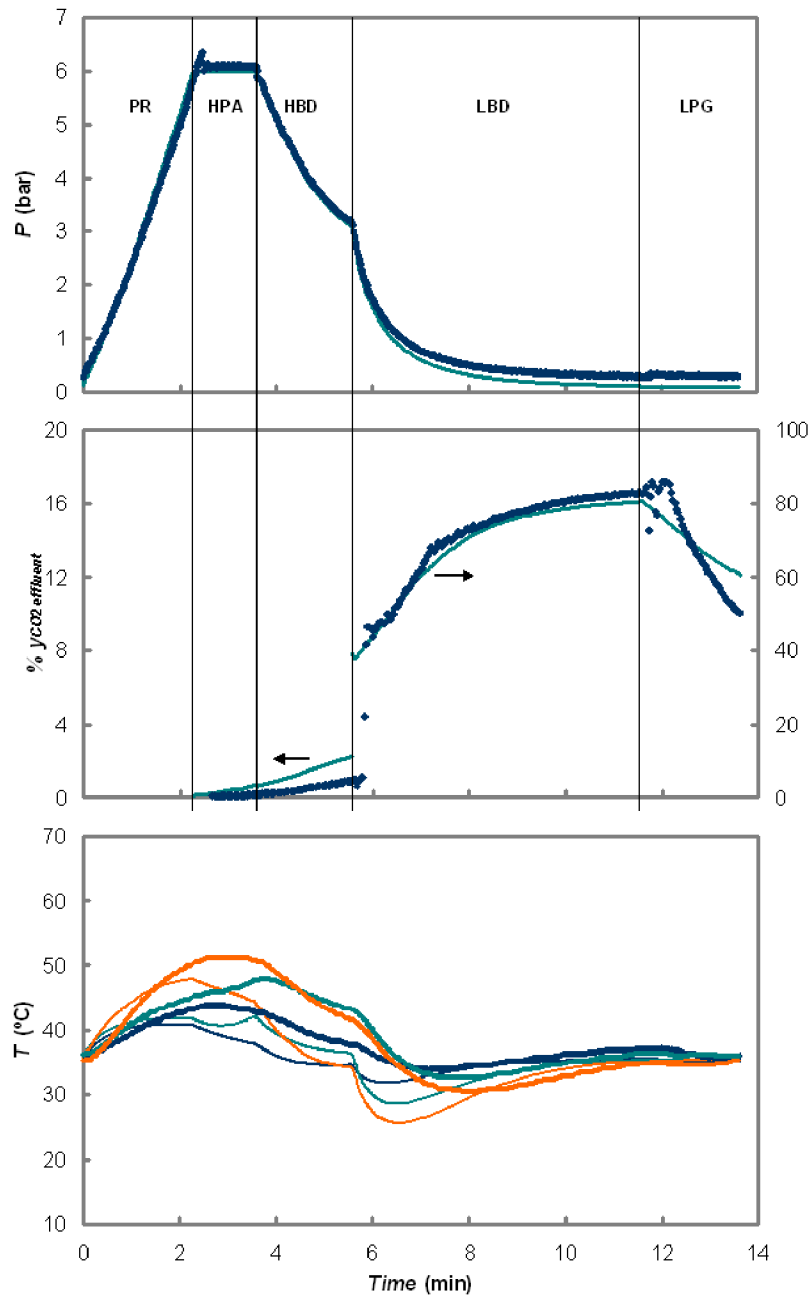


Figure 4.59: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical PSA experiment at CSS (NoCycle = 11). Corresponds to a CO_2/N_2 30/70 % (v/v) mixture at an average T_{run} of $35.85^\circ C$, a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: $0^\circ C$, 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

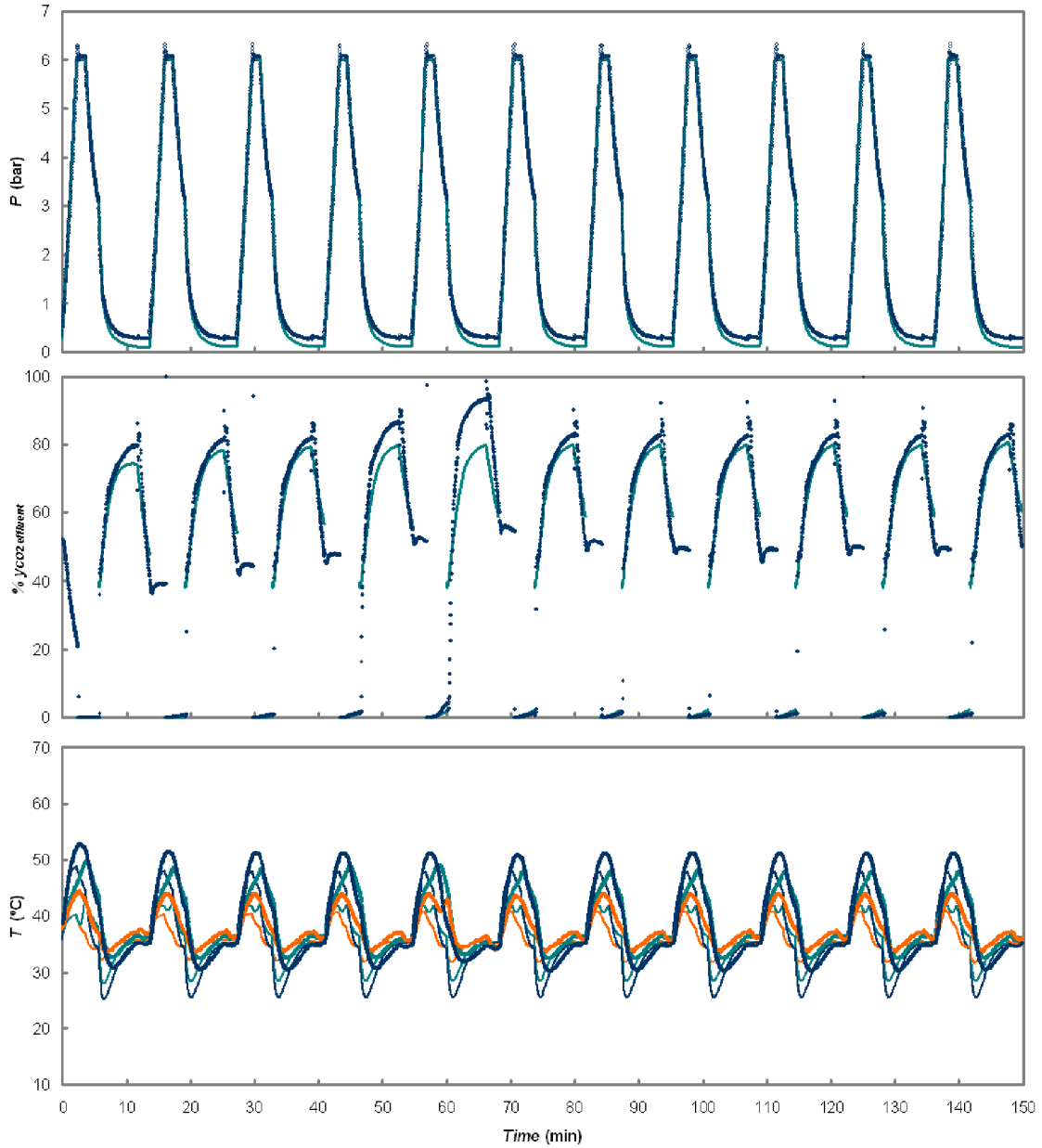


Figure 4.60: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical PSA experiment up to the CSS condition. Corresponds to a CO_2/N_2 30/70 % (v/v) mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric flow of 3.0 slpm (STP: 0°C , 1 atm). Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively.

experimentally possible with the available back-pressure controller. The HBD elutes the N_2 out of the concentration wavefront, thus increasing the CO_2 loading in the bed. It is specially important in bulk separation, rather than in trace separation, since it increases the less adsorbed product recovery, as well as the strongly adsorbed product purity. However, breakthrough of the CO_2 composition wavefront will occur if an excessive HBD is performed. This seems to be the situation in Run 3, where an excessive low end pressure, P_{HBD} , induces CO_2 breakthrough as shown in Figure (4.55). Consequently, the N_2 purity and the CO_2 recovery both decrease drastically. This effect is also illustrated by the significantly low average N_2 product composition at the end of the HBD step.

Comparing the three runs, one can conclude that, although each system is not fully optimized in terms of its variables, Run 2 probably should be applied when the target product is N_2 , whereas Run 3 should be used to obtain CO_2 as primary product. Fully parametric analysis is necessary in order to study more each separation process and carefully predict all process characteristics. Instead, this kind of analysis will be performed in the next chapter for the hybrid process developed. Nonetheless, results have shown that PSA can be used for the bulk separation process developed in this section.

The model predictions show a fair agreement with the laboratory experiments with promising separation performance on the ANGUARD carbon sample analyzed. However, there are some local discrepancies between the simulated and the experimental compositions and temperature histories, namely for the CO_2/N_2 30/70 and 50/50% (v/v) mixtures. The comparison of the experimental and model prediction temperature histories, at the three locations along the bed, are not quantitatively good, since it generally shows a lower magnitude variation due to the sorption effect. Nevertheless, they easily follow the temperature trend of the experimental values. Concerning the composition histories, the predicted values describe a distinct behavior from the experimental one, specially during the high pressure adsorption and co-current blowdown PSA cycle steps. The predicted CO_2 effluent concentrations, during HPA and HBD, are slightly higher than the one obtained experimentally, suggesting that the real N_2 product purity is indeed higher than the one predicted by the simulation model.

In order to investigate and solve the discrepancies observed, the predictions for equilibrium adsorption from mixtures using the Ideal Adsorbed Solution Theory (IAST) were also performed. The Ideal Adsorbed Solution theory is the most successful thermodynamically consistent method for predicting multicomponent adsorption equilibrium from single-component isotherm data [Myers (1989), G. Gamba and Morbidelli (1989)]. Since its introduction, various versions of the IAS theory have been presented [Do (1998)]. The

success of the IAST calculations depends on how well the single component data are fitted, specially in the low pressure region, as well as at the high pressure region, where the pure hypothetical pressure lies.

This theory involves a standard or hypothetical state. When such an approach is adopted for solving a dynamic adsorption model, the most efficient way of applying the IAS method in the numerical model is to consider the spreading pressure of the gas mixture, Π , as a dependent variable, just like temperature or partial pressure of each adsorbate. In a fixed-bed, $\Pi = \Pi(t, z)$, where t is time and z is the axial position in the bed. The analog Raoult's law for an ideal adsorption system is

$$Py_i = P_i = x_i P_i^0(\Pi), \quad (4.120)$$

and

$$\sum_{j=1}^N x_j = 1, \quad (4.121)$$

for $i = 1, 2, \dots, N$ components, where y_i is the mole fraction of component i in the gas phase, x_i is the i^{th} mole fraction in the adsorbed phase, derived from the values of Π , temperature and partial pressures, and $P_i^0(\Pi)$ is the hypothetical pressure at which the pure-component adsorption equilibrium gives the same spreading pressure, Π , as that of the mixture at temperature T . $P_i^0(\Pi)$ is calculated from the Gibbs adsorption isotherm equation

$$\frac{A\Pi}{RT} = \int_0^{P_i^0} \frac{q_i^0(P_i, T)}{P_i} dP_i, \quad (4.122)$$

with A the surface area of adsorbent and q_i^0 the adsorption isotherm of pure component i at the hypothetical pressure P_i^0 . Knowing the mole fractions in the adsorbed phase, x_i , and the hypothetical pressure of the pure component, P_i^0 , the total amount adsorbed can be calculated from the equation

$$\frac{1}{q_t} = \sum_{j=1}^N \frac{x_j}{q_j^0}. \quad (4.123)$$

Finally, the amount adsorbed contributed by the component i is given by

$$q_i = x_i q_t. \quad (4.124)$$

Eqs. (4.120-4.124) form the set of powerful equations for the IAS theory. The estimation of the spreading pressure was taken from the pure component Sips isotherm equation,

$$\frac{A\Pi}{RT} = nq_{so} \ln[1 + (bP^0)^{1/n}]. \quad (4.125)$$

Note that the spreading pressure has the units of the adsorbed concentration and it increases logarithmically with the pure component hypothetical pressure. To ensure a

good fitting of the pure component isotherm and the well-defined isotherm equation in the region where the pure hypothetical pressures lies, the experimental equilibrium data covered a higher range of pressure, although the PSA and breakthrough experiments were performed at pressures lower than 10 bar.

Figures (4.61-4.63) present the comparison between the predicted results using the IAS theory, the simulation results previously obtained, and the experimental data.

The steady state PSA results, using the two different models, were indeed very close, both showing a deviation from the experimental data. The computation time to reach the CSS, for the PSA model using IAST, was approximately 64% longer than using the model with the Sips isotherm extended to n components. The computation time for the CSS PSA cycle was approximately 45% longer applying the IAST. This is due to the iteration time needed to determine the Π_i values.

An extrapolation to solve the differences observed between the experimental and the simulated results can eventually be done if one accounts for the interactions between adsorbate molecules in the adsorption of mixed species. In other words, if one account for the interspecies (N_2 , CO_2) interactions through a modified single-gas energy parameter, $b_{i\eta}$, in the isotherm adsorption model. Yang (1987), Yang and Doong (1986) and Ritter and Yang (1987) report some work performed in this field for binary and ternary mixtures and for the Langmuir and Sips isotherm models.

Through an empirical approach based on the Langmuir-type equation, instead of the usual single-gas energy parameter, b , known from the applied Sips isotherm [Eqs. (4.26), (4.27), (4.28), (4.29)], an interaction parameter, η_i , is introduced

$$b_{i\eta} = \frac{b_i}{\eta_i}. \quad (4.126)$$

For the CO_2/N_2 50/50% (v/v) run, η_{CO_2} and η_{N_2} were determined through the fitting of the simulated CO_2 composition history to the experimental one, having as start-up point the parameters of Ritter and Yang (1987). Thus, one obtained the values of 0.76 and 1.04 for η_{CO_2} and η_{N_2} , respectively. Although these values are close to unity, they are enough to improve the model predictions compared with CO_2/N_2 experimental results.

The IAS theory was also modified by using the empirical interaction parameters. Figures (4.64) and (4.65) illustrate the comparison of effluent concentration predicted by using different methods for predicting equilibrium mixed gas adsorption.

A comparison between the previously obtained performance results, shown in Table (4.30), and the predictions now using the Sips isotherm model with the interaction parameters was made. The differences in the separation performances are not very significant, where for the 30/70 separation, a N_2 purity and recovery of 99.61% and 63.56% were obtained against 99.23% and 63.71%. CO_2 purity and recovery of 54.18% and 99.99%

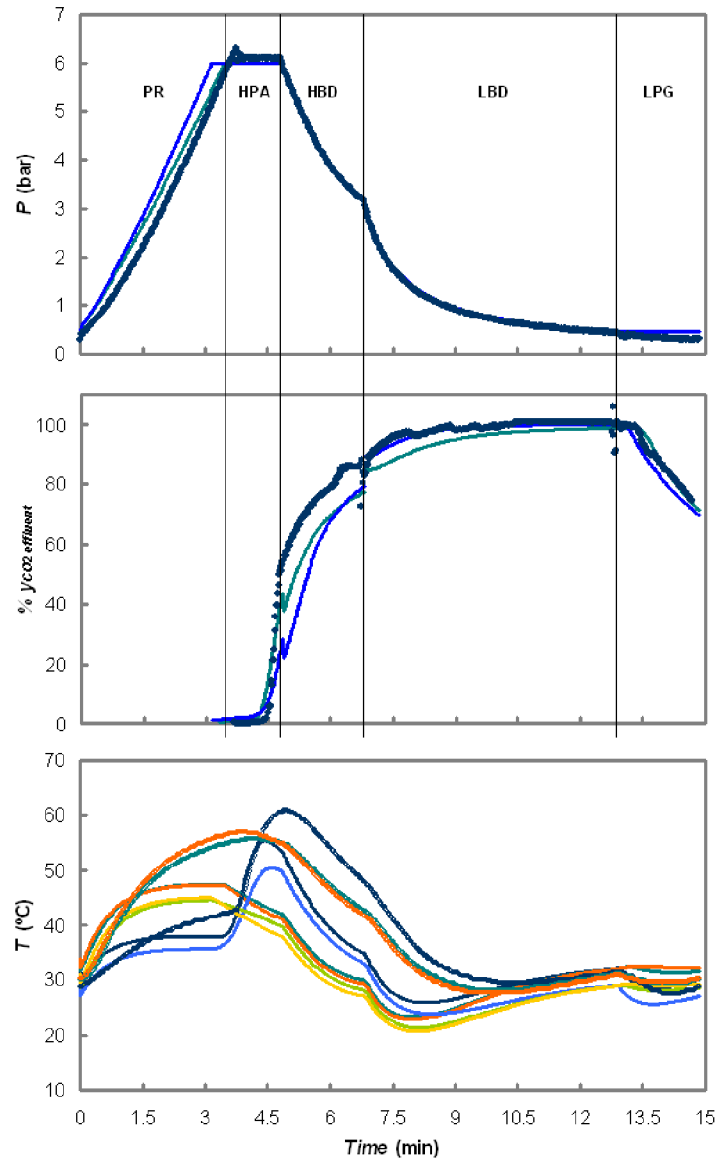


Figure 4.61: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO₂ effluent composition and temperature histories inside the bed for a CO₂/N₂ 80/20 % (v/v) typical PSA experiment at CSS (NoCycle = 11). Top and middle figure: green lines represent the model predictions using the Sips isotherm and light blue denotes the predictions using the IAST. Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively; orange, green and blue lines represent the model predictions using the Sips isotherm and the light orange, green and blue lines denote the predictions using the IAST.

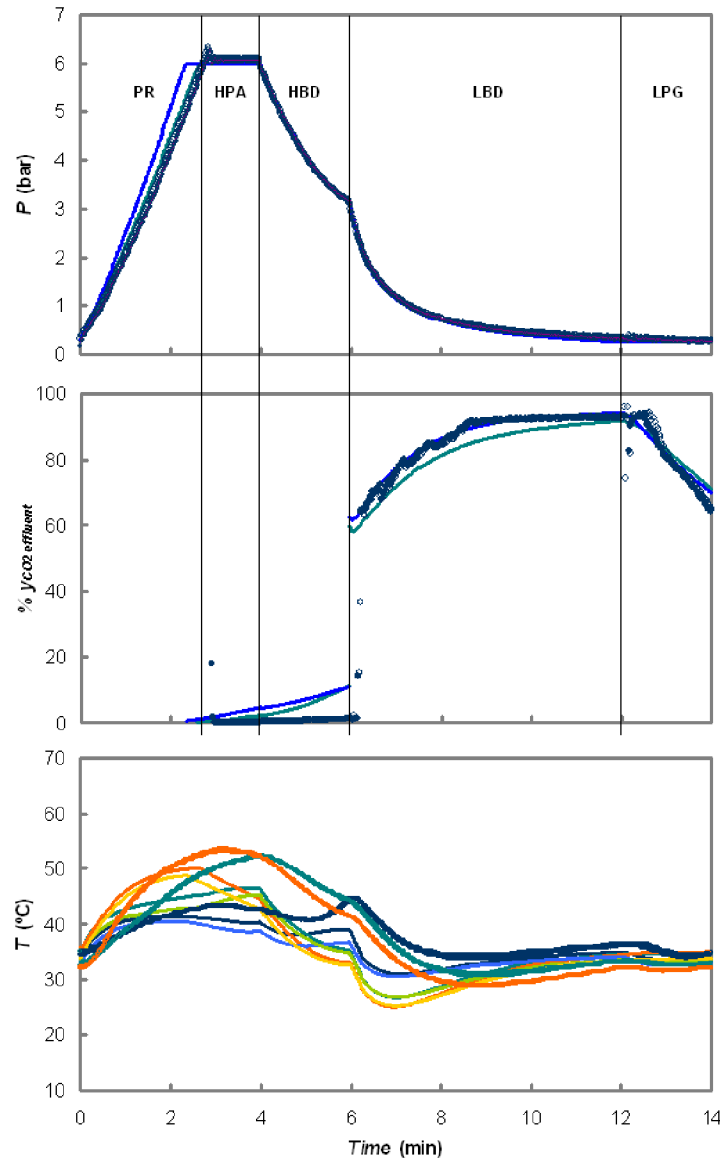


Figure 4.62: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO₂ effluent composition and temperature histories inside the adsorbent bed for a CO₂/N₂ 50/50 % (v/v) typical PSA experiment at CSS (NoCycle = 11). Top and middle figure: green lines represent the model predictions using the Sips isotherm and light blue denotes the predictions using the IAST. Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively; orange, green and blue lines represent the model predictions using the Sips isotherm and the light orange, green and blue lines denote the predictions using the IAST.

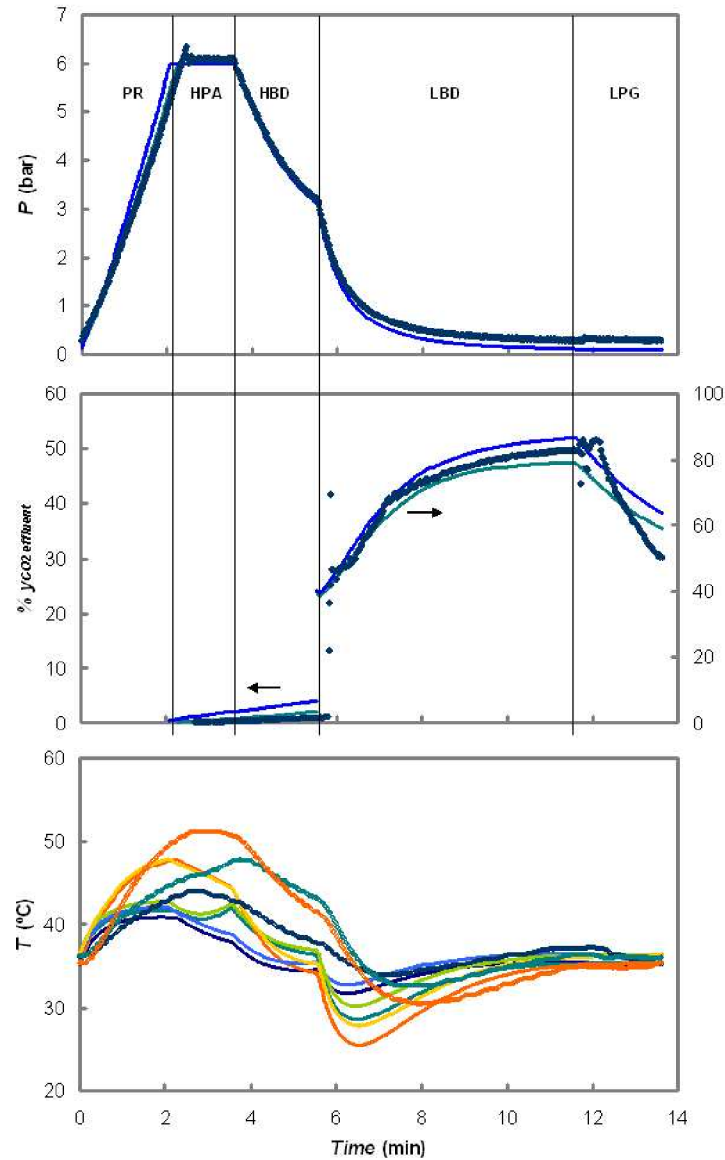


Figure 4.63: Comparison between the predicted (lines) and the experimental (symbols) pressure, CO_2 effluent composition and temperature histories inside the adsorbent bed for a typical CO_2/N_2 30/70 % (v/v) PSA experiment at CSS (NoCycle = 11). Top and middle figure: green lines represent the model predictions using the Sips isotherm and light blue denotes the predictions using the IAST. Bottom figure: orange, green and blue symbols correspond to the temperature probes located at 150, 350 and 550 mm from the bottom of the bed, respectively; orange, green and blue lines represent the model predictions using the Sips isotherm and the light orange, green and blue lines denote the predictions using the IAST.

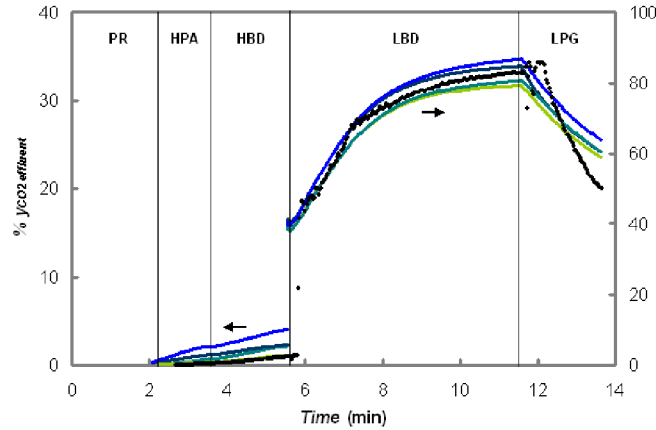


Figure 4.64: Comparison between the predicted (lines) and the experimental (symbols) CO_2 effluent composition histories inside the adsorbent bed for a CO_2/N_2 30/70 % (v/v) typical PSA experiment at CSS (NoCycle = 11). Light and dark blue lines denote the model using IAST and IAST with interaction parameter η_i , respectively. Light and dark green correspond to Sips isotherm with and without the interaction parameters η_i , respectively.

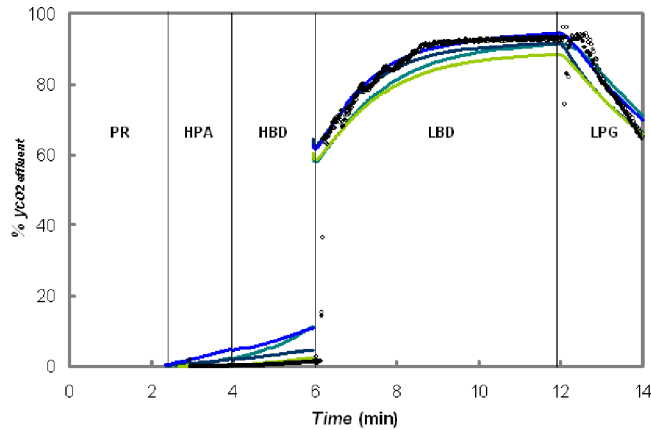


Figure 4.65: Comparison between the predicted (lines) and the experimental (symbols) CO_2 effluent composition histories inside the adsorbent bed for a CO_2/N_2 50/50 % (v/v) typical PSA experiment at CSS (NoCycle = 11). Light and dark blue lines denote the model using IAST and IAST with interaction parameter η_i , respectively. Light and dark green correspond to Sips isotherm with and without the interaction parameters η_i , respectively.

were obtained against 54.16% and 99.23%. For the 50/50 separation, a N₂ purity and recovery of 99.26% and 62.70% were obtained against 96.71% and 65.59%. CO₂ purity and recovery of 72.90% and 99.51% were obtained against the previously 74.13% and 97.78%.

The values of η_i depend on the species present, and it may also depend on temperature and composition of the adsorbed phase. η_i is a fitting parameter for a given mixture and varies for different mixtures, being usually close to unity. Hence, one should not forget that η_i is highly empirical, and this extrapolation was merely an attempt to explain the discrepancies of the predicted results.

Also the experimental values obtained are affected by the dynamic of the back pressure and of the mass flow controllers, the vacuum pump working during the depressurization and purge steps, and the multi-control valve system which makes possible the PSA operation. The numerical simulations are performed through the input values given exactly by the respective experimental run, but in contrast they do not include those experimental interferences. Consequently, some deviations can be expected when switching from one PSA step to another in the experimental curves compared with the predicted ones.

The major distinction between the breakthrough results and the PSA dynamic behavior is due to the adsorbed amount that has accumulated in the bed at a cyclic steady-state. In order to provide a basic understanding of the dynamics of the PSA process, the model using the Sips isotherm, extended to n components with the interaction parameters, was selected.

Figures (4.66-4.68) illustrate the transient behavior of PSA cycles for the CO₂/N₂ 30/70 %(v/v) typical PSA experiment, through CO₂ and N₂ gas- and adsorbed- phase compositions and temperature profiles inside the bed with 60 cm length, at the end of each step. As seen, steady state was attained after approximately 9 cycles. The 11th cycle was considered at cyclic steady state.

As one can see, during the first two PSA steps, the column is loaded with the feed mixture. While CO₂ continuously saturates the sorbent, N₂ is forced to exit the column during the HPA and HBD steps. Simultaneously, a positive temperature swing wave in direction of the flow is observed. During the LBD and LPG steps, the N₂ gas-phase concentration drops while CO₂ is recovered as the heavy product. Through the depressurization, the CO₂ desorption is accompanied by a temperature decrease inside the column.

Figure (4.69) shows the transient behavior for the PSA CO₂/N₂ 30/70 %(v/v) run, from start-up with a clean bed. On both HPA and HBD, the CO₂ concentration increases undesirably in the N₂ product while approaching steady state. For the LBD and LPG steps, the CO₂ product concentration increases while approaching steady state. These transient behaviors are due to the gradual build up of contamination in the bed.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

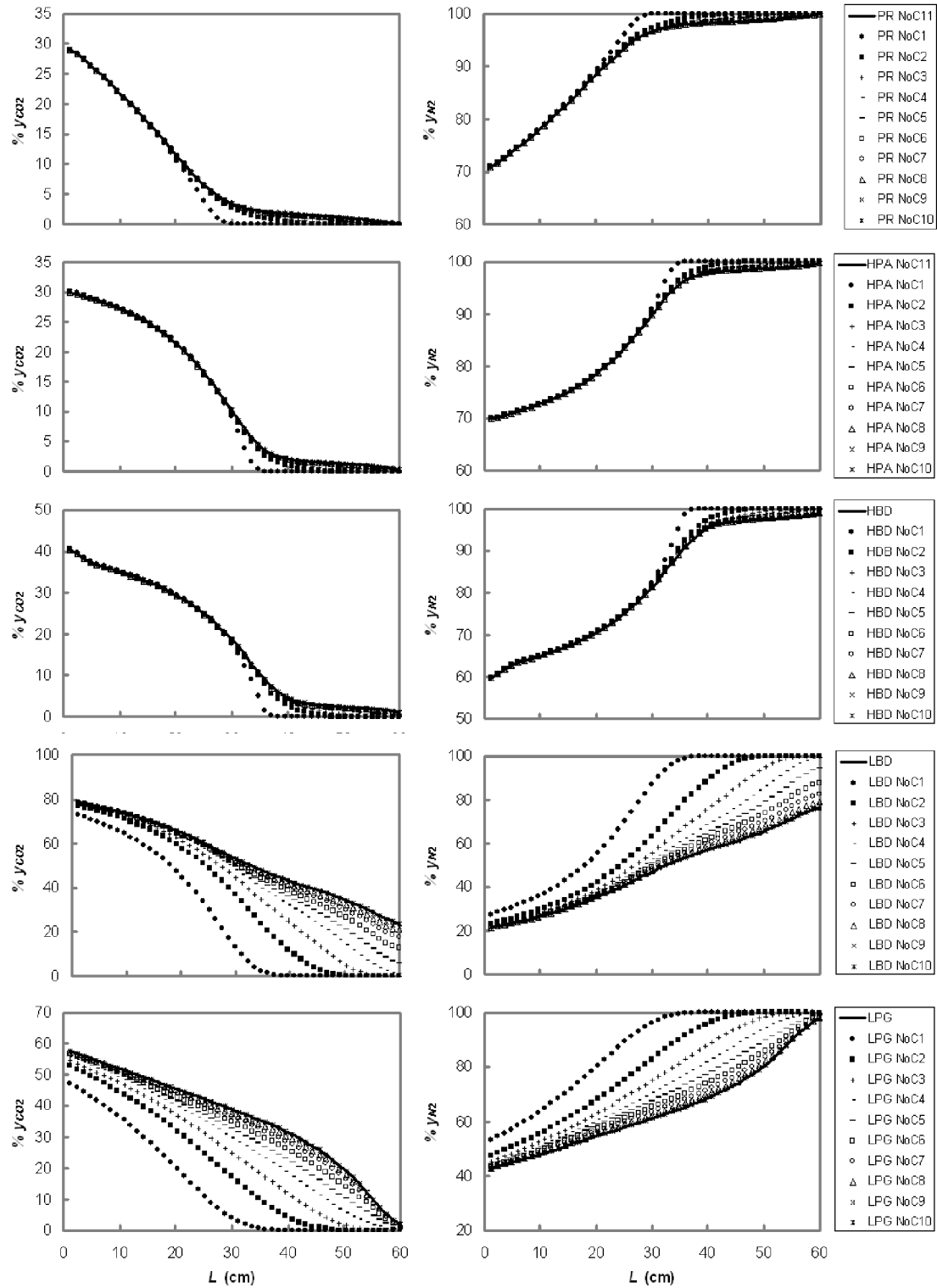


Figure 4.66: Dynamic behavior of PSA cycles for the CO₂/N₂ 30/70 %(v/v) run, through the evolution of CO₂ and N₂ gas-phase compositions inside the bed versus axial distance z at the end of each step, until CSS is reached.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

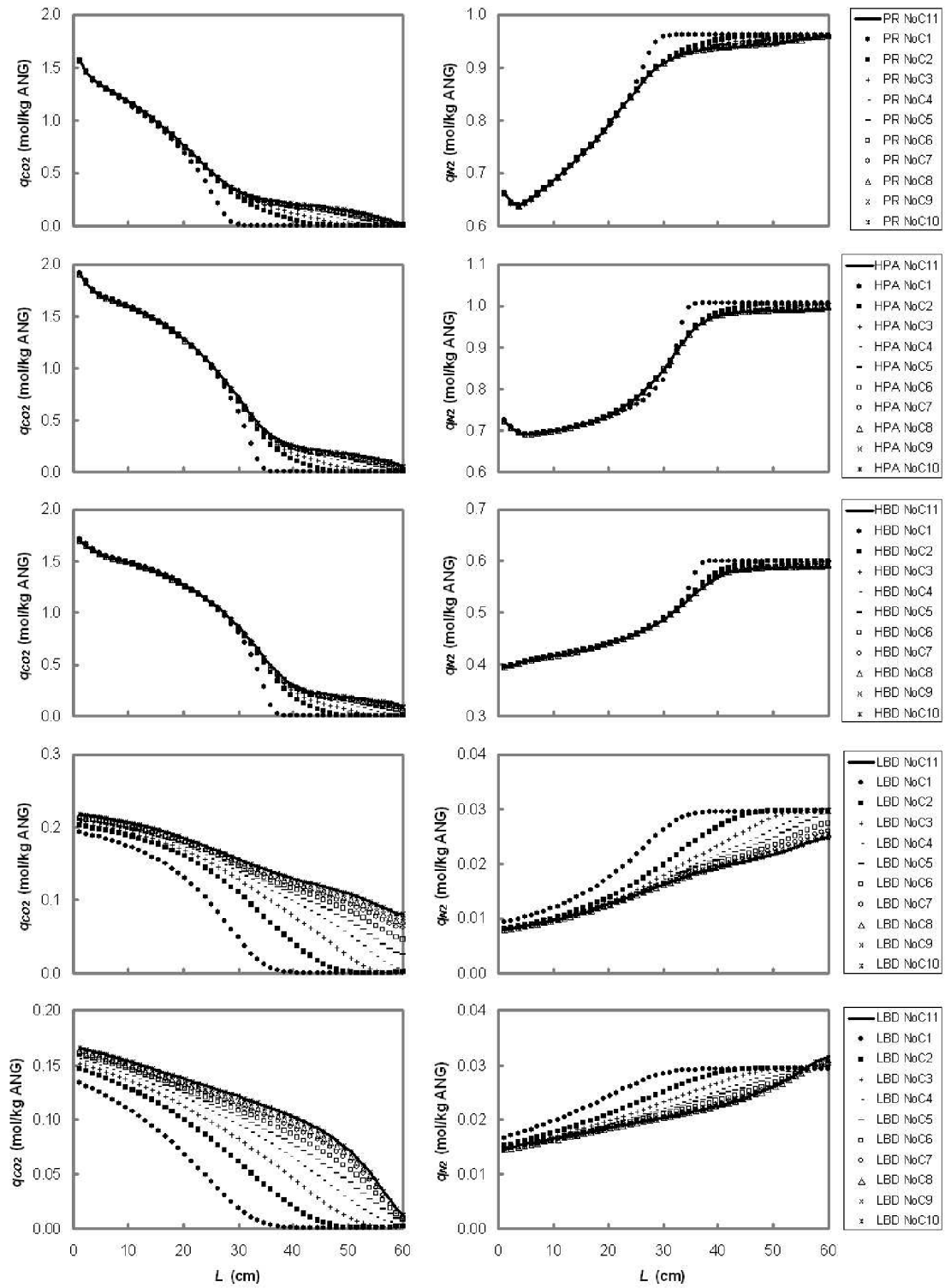


Figure 4.67: Dynamic behavior of PSA cycles for the CO₂/N₂ 30/70 %(v/v) run, through the evolution of CO₂ and N₂ adsorbed-phase compositions inside the bed versus axial distance z at the end of each step, until CSS is reached.

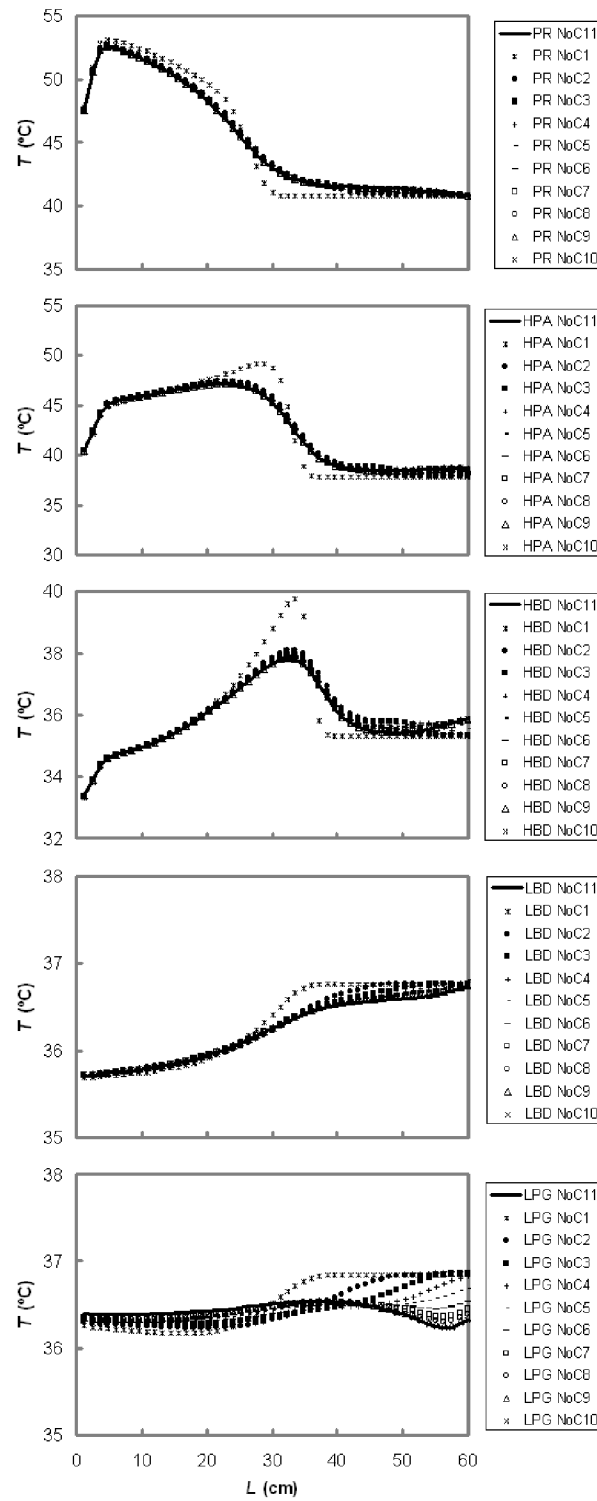


Figure 4.68: Dynamic behavior of PSA cycles for the CO₂/N₂ 30/70 %(v/v) run, through the evolution of the temperature profiles inside the bed versus axial distance z at the end of each step, until CSS is reached.

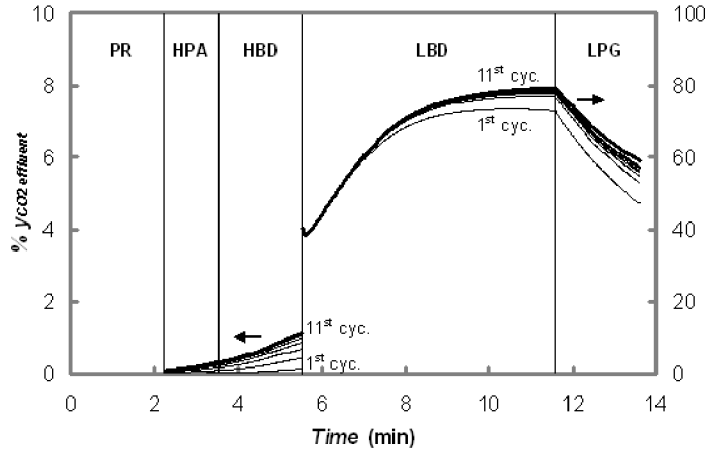


Figure 4.69: Dynamic behavior of PSA cycles for the CO_2/N_2 30/70 % (v/v) run, showing the CO_2 effluent concentration history in each step, until CSS is reached.

To better understand the PSA process, Figures (4.70) and (4.71) present the component compositions in both gas- and adsorbed- phases during each step versus the axial distance z , along a complete steady state cycle. Figure (4.72) shows the temperature inside the bed and the superficial gas velocity axial profiles for each step, along a complete steady state cycle.

As one can see, N_2 moves through the column and exits the bed at high purity (99.7%) during the HPA step, while CO_2 remains adsorbed and is kept inside. A maximum temperature near the inlet is observed indicating the loading effect during the feed. The LBD and LPG intend to eliminate the CO_2 present in the bed. CO_2 is obtained only with 80% purity by the end of LBD, since N_2 also leaves the column, diluting the product. The average CO_2 product purity in this step is low due to the dilution with N_2 . From Figure (4.71), one see a significantly reduction of the CO_2 and N_2 amounts adsorbed during the LBD step. During the LPG, N_2 is fed to the column and, hence, by the end of this step CO_2 withdraw is still diluted in N_2 . Nevertheless, an enrichment of the CO_2 exit stream concentration is observed, i.e., the average CO_2 purity during this step is 70.5%. The effect of the CO_2 desorption from the sorbent is reflected by the minimum temperature values near the exit end of the column, namely for the LBD step. Temperature variations of 11°C are observed during LBD, whereas a variation of 0.6°C is seen during the LPG step. The last PSA step (LPG) reflects the contamination amount remaining before the next cycle.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

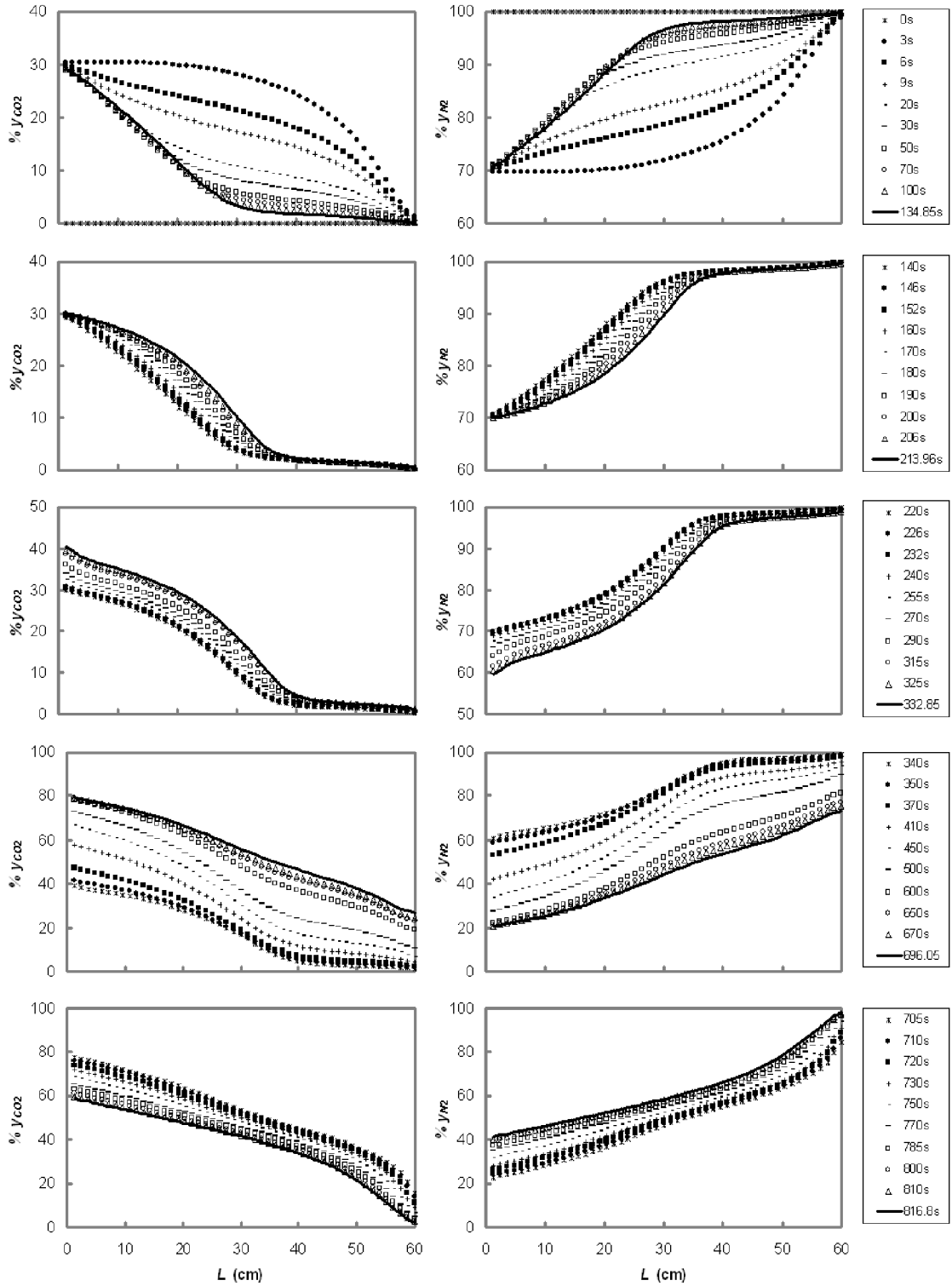


Figure 4.70: Evolution of the gas-phase composition during each step versus axial distance z , along a complete steady state cycle (NoCycle = 11) for the CO_2/N_2 30/70 %(v/v) PSA run. From top to bottom: PR/HPA/HBD/LBD/LPG.

4.3 Pressure Swing Adsorption (PSA) Experiments and Modeling

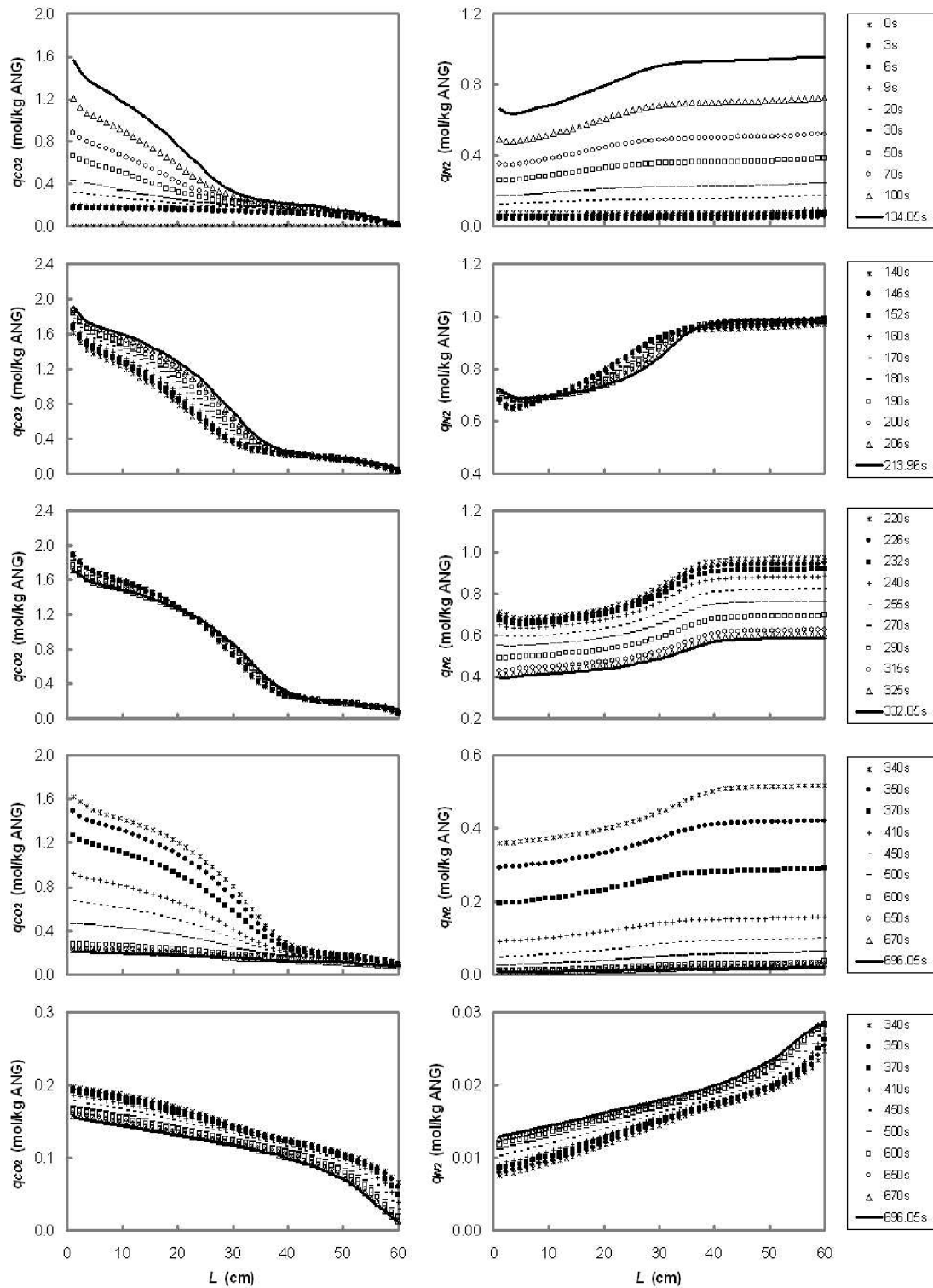


Figure 4.71: Evolution of the adsorbed-phase composition during each step versus axial distance z , along a complete steady state cycle (NoCycle = 11) for the CO₂/N₂ 30/70 %(v/v) PSA run. From top to bottom: PR/HPA/HBD/LBD/LPG.

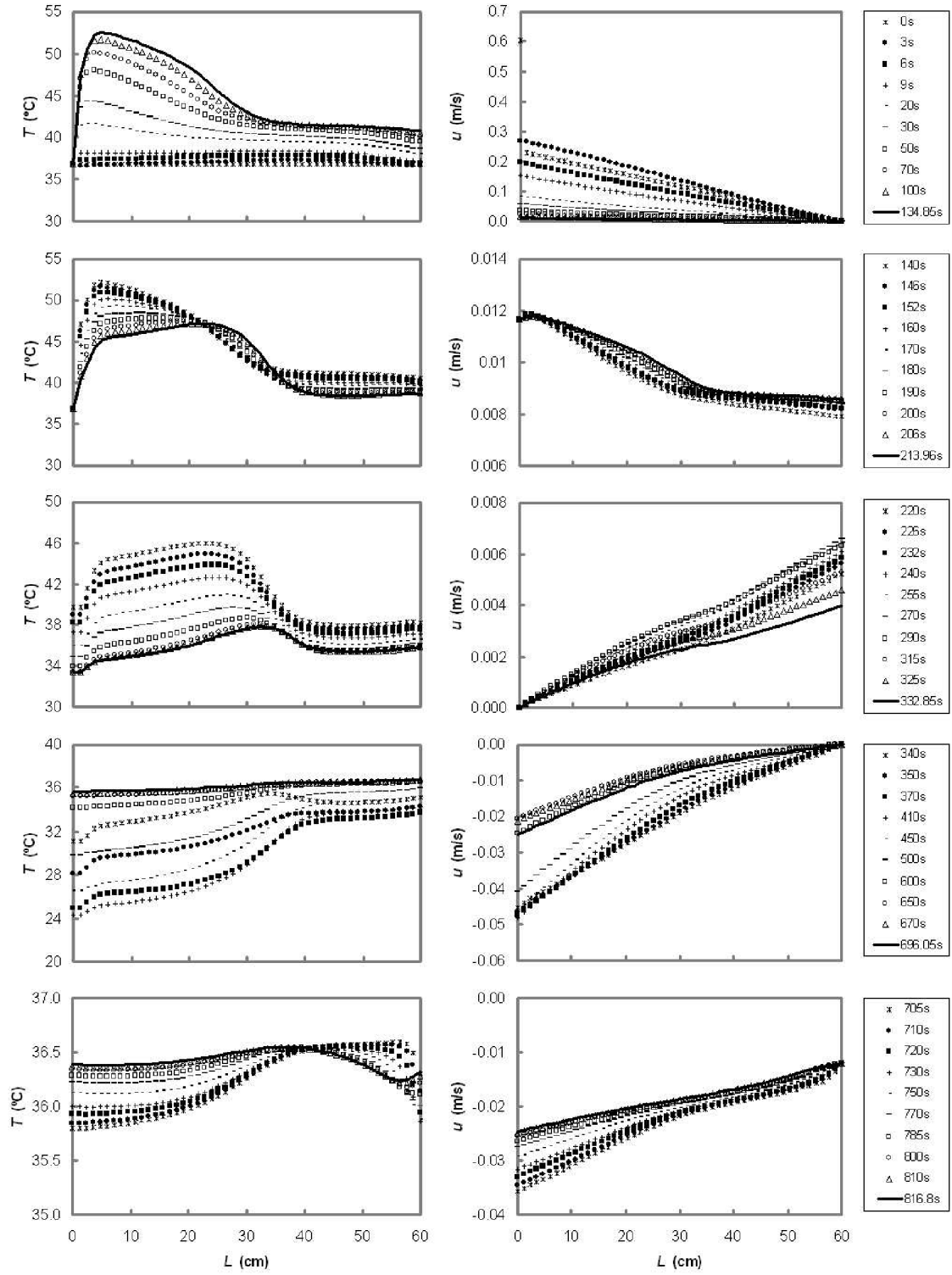


Figure 4.72: Temperature evolution profiles inside the bed and evolution of the superficial gas velocity during each step versus axial distance z , along a complete steady state cycle ($\text{NoCycle} = 11$) for the CO_2/N_2 30/70 % (v/v) PSA run. From top to bottom: PR/HPA/HBD/LBD/LPG.

4.3.5 Summary

A pressure swing adsorption unit was built and experimental breakthrough and blowdown measurements were performed in order to characterize the unit, to study the adsorption kinetics of several binary-component systems and to validate the modeling work developed. The control of the unit was fully implemented using an in-house developed software, built in Labview. An illustrative PSA cycle was implemented in order to prove the operationally of both the apparatus and the control protocol. Physical and thermodynamic properties of the adsorbent bed were also determined.

Using both adsorption equilibria data and diffusion mechanism, analyzed experimentally, the model prediction results were validated by the implemented PSA cycle. The simulations show a reasonable agreement with the laboratory experiments, with promising separation performance on the carbon sample analyzed.

Based on breakthrough and blowdown experiments, a five-step PSA was designed for the CO₂/N₂ separation with the main objectives of: 1) producing high purity products, desirably with high recoveries; 2) validating the modeling work against the experimental cycle implemented; and 3) analyzing the process characteristics and the experimental apparatus for feasible applications. The five-step PSA cycle includes:

- pressurization step (PR) with feed from the lower pressure P_L (0.3 bar) up to the maximum operating pressure P_H (6 bar), with 3 slpm of a 30/70, 50/50 or 80/20% (v/v) CO₂/N₂ mixture, from the bottom to the top of the column;
- high-pressure adsorption step (HPA) at constant pressure P_H , where feed enters the column at 3 slpm, CO₂ is retained in the solid-phase and N₂ is withdraw as product. PR plus HPA total time is approximately 240s;
- high-pressure blowdown step (HBD), co-current to the feed, where the pressure is lowered up to the intermediate pressure P_M (3.2 bar) during 120s, and where the excess of N₂ remaining in the bed is withdrawn with CO₂ gas-phase enrichment;
- low-pressure blowdown step (LBD), counter-current to the feed, where the pressure is further reduced up to P_L during approximately 360s. The heavy product is obtained.
- low-pressure purge step (LPG) with N₂ at constant pressure P_L during 120s, where further CO₂ product is withdrawn at the expense of decrease in the HPA product recovery.

The column packed with the pelletized carbon sample produced an enriched N₂ stream with purities up to 99% and recoveries up to 69%. A CO₂ product stream is obtained with purities up to 92% and recoveries up to 99%. The process variables and operating conditions to be used depend on the target separation performance. The cyclic steady-state condition was achieved after 11 cycles. The simulation model implemented in gPROMS followed the main behavior of the experiments.

It should be pointed out that the adsorbent was formulated for ANG applications and was not optimized for the specific PSA application. Although the separation performance obtained for a CO₂/N₂ separation on the activated carbon is reasonably good, given certain operating conditions, it is often reported in the literature that zeolite 13X is the material more suitable for CO₂ sequestration on testing several adsorbents for sorption-based separation, due to its relatively high capacity and desirable sorption characteristics [Gomes and Yee (2002), Harlick and Tezel (2004), J. H. Park and Cho (2002), K. T. Chue and Yang (1995)]. Nonetheless, the heat of adsorption of CO₂ on activated carbon is lower than on zeolite, so that the use of activated carbon in a PSA process may result in less severe heat effects on the PSA performance. Also, a double adsorbent bed filled with silica gel and fed with a 19/81% CO₂/N₂ mixture, at about 30°C and 10 bar, was reported to produce a CO₂ purity of 93.5% and recovery of 72.3% [Z. Zhang and Ye (1998)]. A revised rapid pressure swing adsorption (RPSA) process was used to obtain a pure CO₂ product. The advantage of this process is the operating period that is about several seconds, while for the conventional PSA is about several minutes.

Chapter 5

Membrane/PSA Processes for Gas Separation - Insights and Modeling

From the work described in the previous chapters, one can conclude that the design of sorption systems is based on a few underlying principles. First, knowledge of sorption equilibrium is required. The selection of the sorbent material with an understanding of its equilibrium properties is of primary importance. Second, the dynamic behavior of the process has to be understood. Fixed-bed processes approach a periodic state or cyclic steady state (CSS) in which the conditions at the end of each cycle are identical to those at its start, and with several different feed steps constituting a cycle. Thus, some knowledge of how transitions travel through a bed is required, which introduces both time and space into the analysis. Finally, many practical aspects such as understanding of dispersive phenomena at the bed scale and knowing the aging characteristics of the adsorbent with consequent changes in sorption equilibrium, must be included in design for the process to perform well.

For PSA separations, generally one wants a linear to slightly favorable isotherm, although purifications can operate economically with more strongly favorable isotherms. For the favorable isotherm, the composition profile inside the bed under the influence of mass transfer resistances is called a constant pattern. This behavior is shown in Figure (5.1).

Design of sorption systems often relies on the concept of the mass-transfer zone (MTZ), which closely resembles the constant pattern [Figure (5.2)]. The length of this zone together with stoichiometry can be used to predict accurately how long a bed can be utilized prior to breakthrough. This was performed during the breakthrough and blowdown experiments.

Upstream of the MTZ, the adsorbent is in equilibrium with the feed. Downstream, the adsorbent is in its initial state. Within, the mass-transfer zone equilibrium with

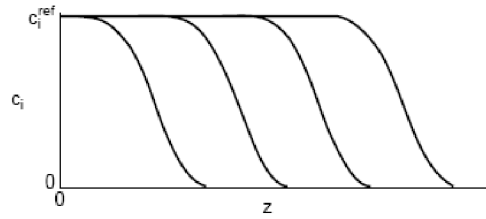


Figure 5.1: Limiting fixed-bed behavior: constant pattern for favorable isotherm [Perry and Green (1999)].

the feed is not attained, and the fluid-phase concentration drops from the feed value to the initial, pre-saturation state. As a result, the full capacity of the bed is not utilized. Obviously, the broader the MTZ, the greater the extent of unused capacity. Also the length of the equivalent equilibrium section (LES) and the length of equivalent unused bed (LUB) can be defined. The length of the MTZ is divided between these two. The effluent concentration history is called the breakthrough curve.

Design methods for PSA cycles rely on mathematical modeling and pilot-scale experiments as one saw in the last chapter. Periodic adsorption processes are overall characterized by mixed systems of partial differential and algebraic equations (PDAEs). The approach to the determination of cyclic steady state (CSS) establishment is based on replacing the initial condition specification by a periodicity condition demanding that the system state at the end of each cycle be identical to that at its start. By doing this, the partial differential and algebraic equations are directly reduced to algebraic equations [Nilchan (1997)].

Mathematical models constructed to analyze the wave compositions development, the incorporation of multiple sorbates and several cycle steps can be complex. It is comprehensible then, that coupling other separative technology like a membrane module, will increase even more the modeling work necessary to synchronize both systems and to operate the cyclic hybrid unit for the desired separation. The integrated membrane/PSA process developed tried to take advantage of the separating abilities of a membrane module and the pressure swing adsorption technology, using the pressure difference of the PSA unit as the driving force for permeation, assisting the pressurization and adsorption steps of the cycle with the effluent streams of the membrane unit.

The feasibility of the integrated process presented here is assessed through the effect of the various operating parameters on separation performance. One developed an integrated gas separation model and studied its feasibility compared with the conventional PSA stand-alone unit. This integration effort is the basis of the work one purposed to do.

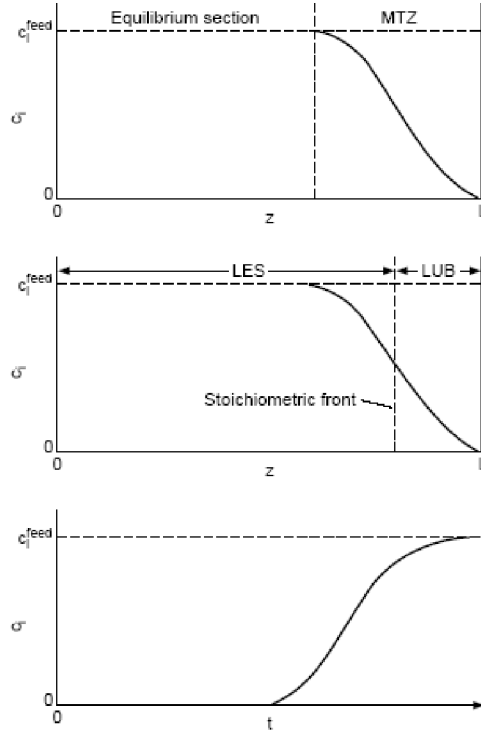


Figure 5.2: Bed profiles (top and middle) and breakthrough curve (bottom). The bed profiles show the mass-transfer zone (MTZ) and equilibrium section at breakthrough. The stoichiometric front divides the MTZ into two parts with contributions to the length of equivalent equilibrium section (LES) and the length of equivalent unused bed (LUB). [Perry and Green (1999)].

Figure (5.3) illustrates the modeling work developed. The separation of a general binary gas mixture A/B at different compositions was studied applying firstly the stand-alone units. After analyzing and validating each system against literature data, an hybrid membrane/PSA concept was implemented. Two integrated schemes were developed. A parametric system analysis was then followed for several case studies.

To point out that, with a large number of variables and nonlinear equilibria involved, it is usually not beneficial to make all variables in such models dimensionless. By doing so does not help appreciably in making comparisons with other systems. Hence, all the mathematical modeling developed and described in this chapter is not dimensionless.

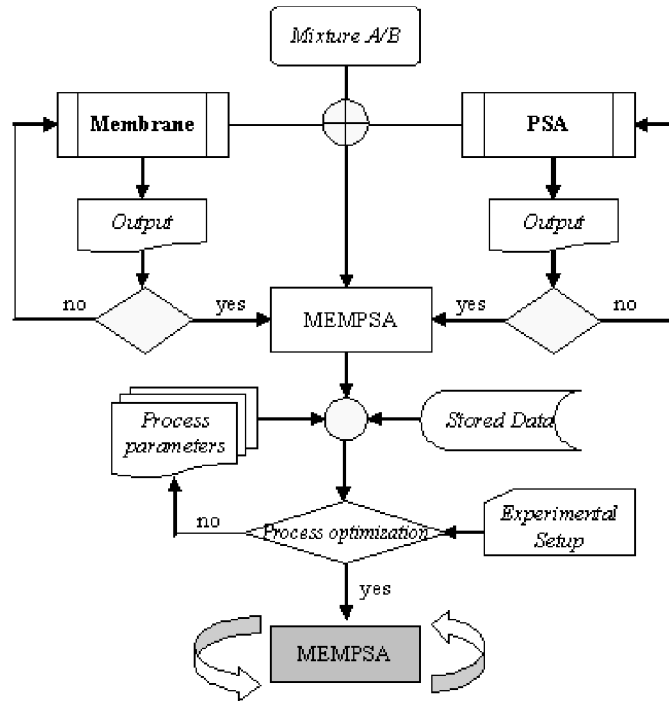


Figure 5.3: Schematic flowchart illustrating the modeling work developed.

5.1 Hybrid Membrane/PSA Processes

5.1.1 Introduction

The research was developed in order to build operational schemes for a truly synergistically integrated process, capable of operating under a wide range of conditions. The main principles are:

- The operating pressure of the PSA unit is used as the driving force for permeation, which assists the pressurization and adsorption steps of the pressure swing unit. The modeling work intends to prove that the coupled process increases the efficiency of the pressurization and high-pressure adsorption steps, thereby improving the separation performance as compared to the stand-alone units.
- Using the different enriched streams from the membrane, the aim of these integration steps is to sharpen the composition wavefronts in order to decrease the dispersive forces and to obtain high purity products, enhancing process performance.

The synchronization of the membrane with the different steps of the PSA, during each cycle, was studied in order to investigate the performance enhancement of the hybrid system compared with the standalone units. For simplicity reasons, the separation of

a general binary gas mixture A/B at different compositions was studied with this new process. The feasibility of the integrated process presented is assessed through the effect of the various operating parameters on separation performance. Hence, parametric analysis of the process variables and parameters were performed at CSS: total feed per cycle, adsorption pressure (P_H), adsorption velocity, time steps, percentage of purge and dimensionless permeation flow were analyzed in terms of the performance definitions of recovery, purity and productivity. Processes have been applied successfully to the separation of H_2/CH_4 , CO_2/CH_4 and CO_2/N_2 gas mixtures at different feed compositions and operating conditions.

5.1.2 Process Description

The hybrid process developed was called MEMPSA. The concept was implemented under two main structural conditions:

- MEMPSA – CASE A, where the more permeable component is the least adsorbed one in the PSA bed,
- MEMPSA – CASE B, where the more permeable component is the more adsorbed one in the PSA bed.

Instead of the regular A/B binary feed mixture, the PSA is fed with a mixture which is progressively enriched in the more adsorbed component during the pressurization and high pressure adsorption steps of a PSA cycle. Let us assume that A and B are, respectively, the less and more strongly adsorbed species in the sorbent bed. Figure (5.4) presents a schematic diagram of the hybrid separation processes developed.

5.1.2.1 MEMPSA – CASE A

This process involves the following cyclic steps:

- Incomplete pressurization (PR_1) of PSA bed with permeate until pressure equalization between a temporary storage tank and the column
- Secondary pressurization (PR_2) of PSA bed with regular feed up to P_H
- Permeation / High pressure adsorption (HPA)
- Co-current blowdown (CD)
- Counter-current blowdown (BD)

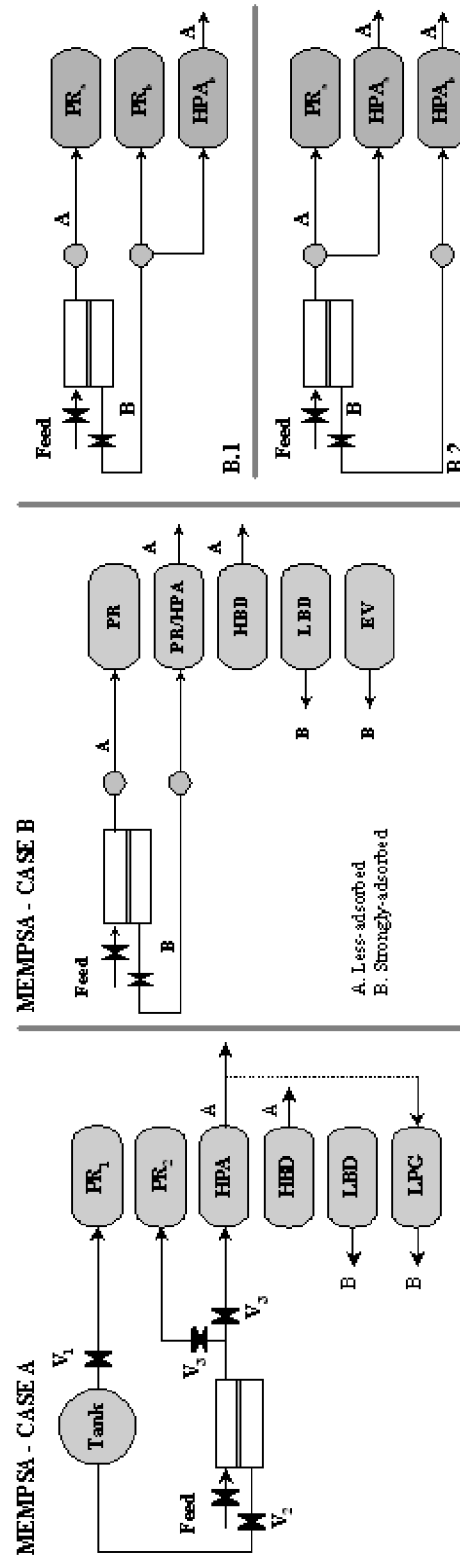


Figure 5.4: Two hybrid schemes developed: MEMPSA - CASE A and MEMPSA - CASE B. The cases B.1 and B.2 at the top are the possible operational situations under the CASE B.

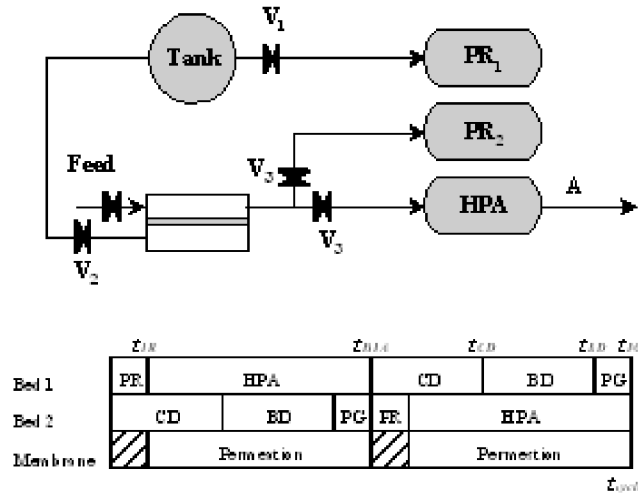


Figure 5.5: Main integration steps of MEMPSA - CASE A.

- Purge (PG)

Figure (5.5) shows a schematic diagram of the main integration steps of the hybrid cyclic process developed for bulk separation of a $H_2(A)/CH_4(B)$ binary mixture, using a membrane module and a dual-bed PSA unit. The membrane performs most of the bulk separation, operating in countercurrent flow mode to maximize the average driving force, and therefore providing the most efficient arrangement.

A membrane for H_2 purification is coupled with the PSA unit. For the simulations, the membrane permeance values are commonly those expected for a polysulfone membrane with 0.1 mm thick effective separating layer [D. T. Coker and Fleming (1998)]. Usually the membrane is a hollow fiber module for H_2 separation which is fed in the shell-side and is obtained in the permeate stream, at a lower pressure than the feed.

Permeate and residue streams are fed to the PSA at different steps for higher purity and enhanced recovery. Although the residue stream is sent directly to the PSA, the permeate stream is stored in an intermediate tank, before being sent to the adsorbent unit. The integrated process, as presented here, operates under the assumption that component A permeates faster and is the least adsorbed.

The cycle starts with an incomplete pressurization (PR_1) of one of the PSA beds with the permeate stream, which is stored in the intermediate tank and is enriched in component A. This stream was obtained during the previous high-pressure adsorption step (HPA), operating on other bed. In step PR_1 , valve V_1 is kept opened and valves V_2 and V_3 stay closed until pressure equalization between the tank and the PSA bed is established.

Then, the tank outlet is closed by shutting valve V_1 . To complete the pressurization step (PR_2), valve V_3 is opened and the adsorbent bed is pressurized with regular feed gas, which is less rich in component A than the permeate stream employed in step PR_1 . During step PR_2 , the membrane behaves as an empty tube, since both permeate and residue sides are at feed pressure P_H .

The HPA step is initiated by opening valve V_2 and feeding the PSA with the residue stream from the membrane, at a prescribed flow rate. The residue stream is enriched in the strongly adsorbed component B, while permeate is stored in the intermediate tank to be employed in the next cycle. During the HPA step, the residue pressure is kept constant at the high-pressure value P_H , whereas the permeate pressure increases with time due to gas build-up in the tank.

Ultimately, the PSA cycle proceeds with the following steps: co-current blowdown (CD) to recover the residual amount of component A, which was pushed to the end of the bed during the HPA step; counter-current blowdown (BD) and purge (PG) to recover component B and to regenerate the bed for the next cycle. During these steps the membrane module is operating with other PSA bed in order to provide continuity of flow. Although the operation of each bed is batchwise, the system as a whole is a continuous one that is operated in cyclic steady state. The membrane module behaves similarly because of its coupling to the PSA cycle.

The main principles to retain here are:

- The permeation occurs in a cyclic fashion, because of the coupling to the sequential steps of the PSA cycle. Unlike conventional membrane operation where the pressure is kept constant, the cyclic adsorption process makes the permeate pressure change as the permeation proceeds with time.
- The PSA is fed with a mixture which is progressively enriched in the least permeable/more strongly adsorbed component. The composition wavefronts are sharpened, thereby enhancing the process performance.

5.1.2.2 MEMPSA – CASE B

This process involves the following cyclic steps:

- Permeation at constant pressures on both sides of the membrane / Pressurization (PR_a) of the PSA bed with residue stream
- Secondary pressurization (PR_b), if needed, up to the adsorption pressure P_H with permeate; or first stage of high pressure adsorption step (HPA_a) with residue

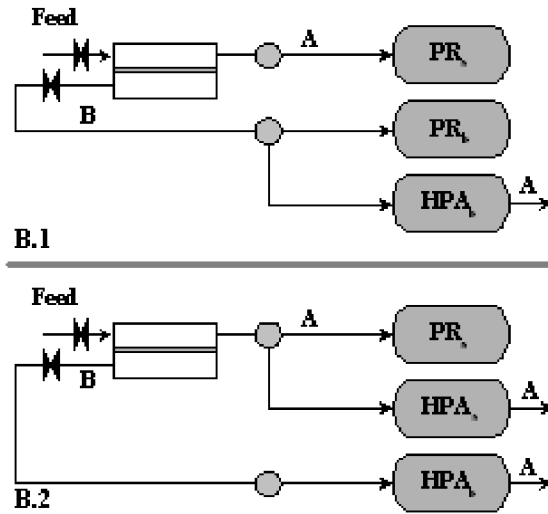


Figure 5.6: Main integration steps of MEMPSA - CASE B.

- Secondary high pressure adsorption (HPA_b) with permeate at P_H
- Cocurrent blowdown (CD) up to the intermediate pressure P_M
- Countercurrent blowdown (BD) up to P_L
- Evacuation (EV) or Purge (PG) steps

Figure (5.6) shows a schematic diagram of the hybrid cyclic process developed for gas separation of the $\text{CH}_4(\text{A})/\text{CO}_2(\text{B})$ binary mixture, using a membrane module and a PSA unit. The membrane performs most of the bulk separation, operating in countercurrent flow mode to maximize the average driving force, and therefore providing the most efficient arrangement.

The membrane-type applied in this process can be a typical cellulose acetate membrane, which has a selectivity of 12-15 under normal operating conditions. These values are significantly below the selectivity calculated from pure gas measurements and can reflect the effect of membrane plasticization by CO_2 . Despite this fact, these type of membranes are only now being slowly replaced by polyimide and polyaramide membranes with selectivities of 20-25 [Baker (2002), Ho and Sircar (1992)].

This specific arrangement was the one applied in the CO_2/N_2 separation analysis performed on the previous chapter. In this case, one selected a membrane separating ability close to the one experimentally used, i.e, a membrane module containing a PES/PI (polyethersulfone Sumikaexcel/polyimide Matrimid 5218) blend.

Unlike the previous example, the more strongly adsorbed component in the adsorbent bed is the more permeable one in the membrane. Also pressures on both side of the membrane are kept constant along the permeation time. Although the residue stream is sent directly to the PSA, the permeate stream can either be used for complete pressurization or be sent directly to the bed in the adsorption step.

The integration varies with the range of the total feed amount admitted per cycle that is assumed. The membrane is fed with the gas mixture A/B and a preliminary separation is performed with simultaneously feeding to the PSA bed with each one of the exit streams of the membrane. The PSA follows the typical steps of the Skarstrom cycle, but considers two possible steps for pressurization and high-pressure adsorption with different feed compositions, blowdowns co- and counter-current to the feed step, a possible purge with part of the adsorption product or/and an evacuation at sub-atmospheric pressure.

The integrated process, as presented here, operates under the assumption that component A is the less permeable one and is the least adsorbed. The integrated cycle starts with a permeation step with the high-pressure side of the membrane at $P_1 = P_H$ and the low-pressure at $P_2 = P_L$. Simultaneously, a first pressurization stage (PR_a) takes place with the residue effluent stream from the membrane, enriched in component A, until pressure equalization between the membrane and the PSA bed is established. Two situations can occur:

- If pressure in the bed is lower then the adsorption pressure, P_H , the residue was not enough and thus, to complete the pressurization step, the bed is pressurized with permeate gas, enriched in the more strongly adsorbed component B . In this case B.1, after PR_a , the membrane is no longer operational for this adsorbent bed. The HPA step (HPA_b) is initiated feeding the PSA with the rest of the permeate stream obtained from the membrane at a prescribed flow rate. During this stage the permeate pressure is kept constant at the high-pressure value P_H .
- If the adsorption pressure in the bed is reached during permeation and there is residue left from the membrane, the cycle proceeds with a HPA step (HPA_a) using that stream, enriched in the lighter component A . After HPA_a the membrane is no longer operational for this bed. The bed pressure is kept constant (P_H) and HPA is then completed using the permeate streams enriched in the more strongly adsorbed component B .

The PSA cycle proceeds with the blowdowns co- and counter-current to the feed, to recover the residual amount of component A which was pushed to the end of the bed during the HPA step, and to start collecting the component B, which is present in the feed end of the bed. The bed depressurization occurs from P_H to an intermediate pressure,

P_M and then to P_L . Finally, a low-pressure purge (LPG) at P_L with HPA product may occur to recover component B and to regenerate the bed for the next cycle.

Using the different enriched streams from the membrane, the aim of these integration steps is again to sharpen the composition wavefronts in order to decrease the dispersive forces and to obtain high purity for both products, if possible without using part of them to enhance the process performance. It is fair to point out that a pressurization of the permeate up to P_H is required, prior to being fed to the bed, which increases the power consumption of the system. The eventual performance enhancement has to be evaluated against the other potential system costs.

Tables (5.1) and (5.2) present the process simulation parameters employed in both MEMPSA – CASES A and B.

5.1.3 Theoretical Model

Component material balance, overall material balance and energy balance equations are written for each unit. Unless stated the following model description is referred to both MEMPSA – CASES developed.

Firstly, the membrane governing equations are described. To simplify the computational model, the following assumptions are considered for the membrane unit:

- Ideal gas law applies.
- Shell side pressure change is negligible.
- Shell side feed and countercurrent contacting are assumed.
- Negligible temperature gradients.
- Negligible time lag due to passage of gas molecules through the membrane, i.e., a permeate stream is obtained instantaneously as the high pressure feed is supplied to the membrane.
- Axial dispersion is considered and constant permeances are assumed.

The molar flux of component i due to permeation is given by Eq. (3.13). A dimensionless permeation flow parameter was defined as

$$F_m = \wp_j A_{mem} (P_H - P_L) / F_f, \quad (5.1)$$

where $\wp_j$ is the permeance of the more permeable component, $A_{mem} = A_f L_F$ is the total surface area available for permeation, and F_f is a reference molar flow per cycle fed to HPA step. For both membrane zones 1 and 2, i.e., for the high- and low-pressure sides of the module, the following equations were considered:

Table 5.1: Process simulation parameters employed in both MEMPSA – CASE A.

MEMPSA - CASE A	
Physical properties - PSA	
Bed inside radius, R_b (cm)	2.05
Bed length, L (cm)	60.0
Particle size, R_p (cm)	0.028
Bulk density, ρ_b (g/cm ³)	0.498
Particle density, ρ_p (g/cm ³)	0.850
Bed porosity, ε_b	0.43
Intraparticle void fraction, ε_p	0.61
Total voidage, ε	0.78
Heat capacity of carbon, C_{ps} (cal/g/°C)	0.250
Heat capacity of wall, C_{pw} (cal/g/°C)	0.110
Avg. heat capacity of gas mix., C_{pg} (cal/mol/°C)	7.647
Physical properties - Membrane	
Cross-section relation, V_k - volume of k side of the membrane	$V_k = 0.02 V_c$
Membrane selectivity, $\alpha_{H_2(A)/CH_4(B)}$	35
H ₂ Permeance, θ_{H_2} (GPU)	100
Permeation flow parameter ^b , F_m	5.15 - 51.54
System properties	
Feed temperature, T_f (K)	293.15
Feed pressure, P_H (bar)	25.45 - 35.45
Blowdown pressure, P_m (bar)	4.73 - 14.73
Low pressure purge, P_L (bar)	1.21
Feed molar fractions, y_{if} (%)	
CH ₄ (B)	50
H ₂ (A)	50
Parameters from Sips isotherm ^a	
$q_{m H_2(A)/CH_4(B)}$ (mol/kg)	$1.795/T; 0.308T^{-0.59}$
$B_{H_2(A)}$ (psi ⁻¹)	$3.8 \times 10^{-5} \exp(1.73 \times 10^3/T)$
$B_{CH_4(B)}$ (psi ⁻¹)	$4.23 \times 10^{-6} \exp(1.23 \times 10^3/T)$
$n_{H_2(A)/CH_4(B)}$	1; 0.96
Total feed amount per cycle, $Feed$ (L STP)	47.7 - 80
Purge to Feed ratio, P/F	0.06 - 0.22
Volume of the intermediate tank, V_c (L)	0.25 - 2.5
Step time (s)	
t_{PR} (s)	30
t_{HPA} (s)	180
t_{CD} (s)	90
t_{BD} (s)	90
t_{PG} (s)	30
t_{cycle} (min)	7.0
Wall thickness, e_w (m)	0.001
Particle tortuosity, τ	10
Avg. effective diffusivity, D_e (m ² /s)	2E-08
Thermal dispersion parameter, D_{to} (J/m/s/°C)	0.106
Molecular diffusivity, $P D_m \approx P D_{H_2-CH_4(288K)}$ (m ² bar/s)	6.85E-05
Wall heat transfer coefficient, h_w (cal/m ² /°C/s)	30
Wall conductivity, k_w (W/m/K)	43.3
Wall density, ρ_w (g/cm ³)	8.22

^a Yang and Doong (1985)

^b Calculated with a mean reference molar flow, F_r , fed to the HPA step, applied in the simulation runs (≈ 2.1 slpm, STP: 0°C, 1 atm)

Table 5.2: Process simulation parameters employed in both MEMPSA – CASE B.

MEMPSA - CASE B	
Physical properties - PSA	
Bed inside radius, R_b (cm)	2.05
Bed length, L (cm)	40.0
Particle size, R_p (cm)	0.028
Bulk density, ρ_b (g/cm ³)	0.498
Particle density, ρ_p (g/cm ³)	0.850
Bed porosity, ε_b	0.43
Intraparticle void fraction, ε_p	0.61
Total voidage, ε	0.78
Heat capacity of carbon, C_{ps} (cal/g/°C)	0.250
Heat capacity of wall, C_{pw} (cal/g/°C)	0.110
Avg. heat capacity of gas mix., C_{pg} (cal/mol/°C)	7.647
Physical properties - Membrane	
Cross-section relation, V_k - volume of k side of the membrane	$V_k = 0.1 V_{PSA}$
Membrane selectivity, $\alpha_{CO_2(B)/CH_4(A)}$	20
CO ₂ Permeance, θ_{CO_2} (GPU)	60
Permeation flow parameter ^b , F_m	0.47 - 2.76
System properties	
Feed temperature, T_f (K)	298.15
Feed pressure, P_H (bar)	6.9 - 11.9
Co-current blowdown pressure, P_{CD} (bar)	2.5 - 5.5
Counter-current blowdown pressure, P_{BD} (bar)	1.0 - 2.0
Low pressure, P_L (bar)	0.34
Feed molar fractions, $y_{f, CH_4/CO_2}$ (%)	50/50; 85/15
Parameters from Sips isotherm ^a	
$q_{mi} = k_1 + k_2 T$ (mol/kg), T in K; $Bi = k_3 \exp(k_4/T)$	
$k_1, CH_4(A)/CO_2(B)$	9.67; 16.9
$k_2, CH_4(A)/CO_2(B)$	-1.25E-2; -1.49E-2
$k_3, CH_4(A)/CO_2(B)$	3.8E-3; 3.67E-5
$k_4, CH_4(A)/CO_2(B)$	1731; 1893
$n, CH_4(A)/CO_2(B)$	1.0
$\eta, CH_4(A)/CO_2(B)$	1.2; 0.84
Heat of adsorption, Q_i (cal/mol)	5000
Total feed amount per cycle, $Feed$ (L STP)	20.65 - 180.65
Purge to Feed ratio, P/F	0 - 0.8
Pressurization fluid velocity, v_{PR} (m/s)	0.025 - 0.75
HPA, PG fluid velocities, $v_{HPA, PG}$ (m/s)	0.025 - 0.125
Step time (s)	
t_{CD} (s)	30 - 120
t_{BD} (s)	30 - 120
t_{EV} (s)	90; 180
t_{cycle} (min)	6.8 - 56.1
Wall thickness, e_w (m)	0.001
Particle tortuosity, τ	50
Effective surface diffusivity for $\theta=0$, $D_{s,i}$ (m ² /s)	7.4E-10
Effective Knudsen diffusivity for, $D_{s, CH_4/CO_2}$ (m ² /s)	4.2E-9 / 2.5E-9
Thermal dispersion parameter, D_{to} (J/m/s/°C)	0.106
Molecular diffusivity, $P D_m$ (m ² bar/s)	6.85E-05
Wall heat transfer coefficient, h_w (cal/m ² /°C/s)	30
Wall conductivity, k_w (W/m/K)	43.3
Wall density, ρ_w (g/cm ³)	8.22

^a Yang and Doong (1986)

^b Calculated with the reference molar flow, F_f , fed to the HPA step, applied in the simulation runs (≈ 6.1 slpm, STP: 0°C, 1 atm)

1. Membrane – Material balance equations

• Global material balance

The global material balance equations in both residue ($k = 1$) and permeate ($k = 2$) sides of the membrane are given by Eq. (3.18), which can be simplified to

$$\frac{\partial P_k}{\partial t} - \frac{\partial(v_k P_k)}{\partial z} = (2k - 3) \frac{A_f R T_k}{A_k} N_{1 \rightarrow 2}, \quad (5.2)$$

with A_f the surface area of active layer per unit of membrane length, A_k the cross-section area of each membrane zone, v the gas velocity, t the time and z the distance. The pressure on the feed side is taken to be constant and equal to the feed pressure. For CASE A, in the permeate side, the pressure changes during permeation due to the gas build-up in the intermediate tank. Hence, while the pressure in zone 1 is constant,

$$\frac{dP_1}{dz} = 0, \quad t \geq 0, \quad (5.3)$$

the pressure dynamics in the permeate side is given by

$$P_2 = P_v(t), \quad t \geq 0, \quad (5.4)$$

where P_v is the instantaneous pressure in the tank. In CASE B, pressure is kept constant on both sides of the membrane.

• Individual material balance

The differential material balance equations to component i in both zones of the membrane are given by Eq. (3.22), which is simplified to

$$\frac{\partial P_{ik}}{\partial t} + \frac{\partial(v_k P_{ik})}{\partial z} - \frac{\partial}{\partial z} \left(k_k \frac{\partial P_{ik}}{\partial z} \right) = (2k - 3) \frac{A_f R T_k}{A_k} N_{i,1 \rightarrow 2}, \quad (5.5)$$

with $i = 1, \dots, \text{NoC}$, and k_k the axial dispersion coefficient, which accounts for molecular diffusion and hydrodynamic dispersion.

2. Membrane – Auxiliary variables

The following auxiliary variables were defined in order to analyze the performance of the unit. The inlet ($z = 0$) and exit ($z = L$) molar flows at both zones of the membrane were defined as

$$\frac{\partial N_{ok}}{\partial t} = (3 - 2k) \frac{A_k v_{ok} P_{ik}}{R T_k}, \quad \frac{\partial N_{Lk}}{\partial t} = (3 - 2k) \frac{A_k v_{Lk} P_{ik}}{R T_k}, \quad (5.6)$$

where $k = 1$ and $k = 2$ for residue and permeate sides of the unit, respectively.

3. Membrane – Initial conditions

The initial conditions defined for MEMPSA – CASE A, at $t = 0, \forall z$ are

$$P_1 = P_H, \quad P_{1i} = y_{in}P_H, \quad (5.7)$$

$$P_2 = P_L, \quad P_{2i} = y_{in}P_L, \quad (5.8)$$

$$N_{ok} = 0, \quad N_{Lk} = 0, \quad (5.9)$$

with P_H the feed pressure, P_L the low-operating pressure, (1, 2) the subscripts for the high- and low-pressure sides of the membrane, respectively, and *in* subscripts denoting the feed conditions. The initial conditions defined for MEMPSA – CASE B, at $t = 0, \forall z$ are

$$P_1 = P_H, \quad P_{1i} = y_{in}P_H, \quad (5.10)$$

$$P_2 = P_{BD}, \quad P_{2i} = y_{in}P_L, \quad (5.11)$$

$$N_{ok} = 0, \quad N_{Lk} = 0, \quad (5.12)$$

with P_{BD} the pressure at the end of BD step.

Concerning the PSA unit, the following assumptions were considered as follows:

- Ideal gas law applies.
- Non-isothermal model and variable-velocity axially dispersed plug flow model is considered, with negligible pressure loss inside the PSA bed.
- A pore diffusion model governs mass transfer inside the adsorbent particles.
- Thermal equilibrium between the fluid and the particles is assumed.
- No variation exists in the radial direction for both concentration and temperature.
- Transport (diffusivity) and physical (C_{pg} , ρ) properties are assumed constant and independent of temperature, due to the narrow temperature range of the process.
- No kinetic interaction between the components for adsorption on the particles.
- Multicomponent adsorption equilibrium is modeled by Langmuir-Freundlich (LF, also called Sips) isotherm model.

1. PSA – Material balance equations

- **Global material balance**

For all the components $i = 1, \dots, \text{NoC}$, the global material balance is given by

$$\varepsilon_b \frac{\partial c}{\partial t} + (1 - \varepsilon_b) \varepsilon_p \frac{\partial \bar{c}_p}{\partial t} + (1 - \varepsilon_b) \rho_p \frac{\partial \bar{q}}{\partial t} + \varepsilon_b \frac{\partial (cv)}{\partial z} = 0, \quad (5.13)$$

where $c = \sum_i^n c_i$ is the total molar concentration of the gas mixture, c_i is the molar concentration of component i in the gas, $\bar{q} = \sum_i^n \bar{q}_i$ is the total average excess amount of gas adsorbed (the superscript *ex* is dropped to simplify the notation), $\bar{c}_{ip}$ is the total average concentration of component i inside the pores of the adsorbent particles, v is the interstitial velocity, ε is the total bed void fraction, t is time and z is bed axial position, i.e., the temporal and spatial domains, respectively. Considering that

$$c = \frac{P}{RT}, \quad \bar{c}_p = \frac{\bar{P}_p}{RT}, \quad (5.14)$$

and $P = P(t)$, the global material balance can be rewritten as

$$\frac{\partial}{\partial t} \left(\frac{P}{T} \right) + \Lambda_p \frac{\partial}{\partial t} \left(\frac{P_p}{T} \right) + \frac{\partial}{\partial z} \left(\frac{vP}{T} \right) + \Omega_p \frac{\partial \bar{q}}{\partial t} = 0, \quad (5.15)$$

where

$$\Lambda_p = \frac{\varepsilon_p(1 - \varepsilon_b)}{\varepsilon_b}, \quad \Omega_p = \frac{\Lambda_p \rho_p R}{\varepsilon_p}. \quad (5.16)$$

- **Individual material balance**

For a differential volume element dz , the mass balance for component i is given by

$$\varepsilon_b \frac{\partial c_i}{\partial t} + (1 - \varepsilon_b) \varepsilon_p \frac{\partial \bar{c}_{ip}}{\partial t} + (1 - \varepsilon_b) \rho_p \frac{\partial \bar{q}_i}{\partial t} + \varepsilon_b \frac{\partial}{\partial z} \left(c_i v - D_L c \frac{\partial y_i}{\partial z} \right) = 0, \quad (5.17)$$

$$\begin{aligned} \frac{P}{T} \left(\frac{\partial y_i}{\partial t} + \Lambda_p \frac{\partial \bar{y}_{ip}}{\partial t} \right) + \Omega_p \frac{\partial \bar{q}_i}{\partial t} + \frac{y_i + \Lambda_p \bar{y}_{ip}}{T} \left[\frac{\partial P}{\partial t} - \frac{P}{T} \frac{\partial T}{\partial t} \right] \\ + P \frac{\partial}{\partial z} \left(\frac{y_i v}{T} - \frac{D_L}{T} \frac{\partial y_i}{\partial z} \right) = 0, \end{aligned} \quad (5.18)$$

with $\bar{y}_{ip} = \bar{P}_{ip}/P$ the mole fraction of component i in the sorbent particle, and D_L the axial dispersion coefficient defined according to Eq. (4.59).

- **Individual material balance inside the pores of the adsorbent particle**

For MEMPSA – CASE A, the individual material balance inside the pores of the solid particle is given by

$$\varepsilon_p \frac{\partial c_{ip}}{\partial t} + \rho_p \frac{\partial q_i}{\partial t} + \frac{1}{r_p^2} \frac{\partial}{\partial r_p} (r_p^2 N_{ir}) = 0, \quad \forall r_p \in (0, R_p), \quad t \geq 0, \quad (5.19)$$

with ε_p the intraparticle void fraction, r_p the radial coordinate inside the particle (assumed spherical) of radius R_p . The sorption rates may be related to the fluxes at the particle surface through [Yang and Doong (1985)]

$$N_i^s = (N_{ir})_{r_p=R_p} = y_{ip}^s \sum_i^n N_i^s - D_e c \left(\frac{\partial y_{ip}}{\partial r_p} \right)_{r_p=R_p}. \quad (5.20)$$

Integrating Eq. (5.19) in order to r_p and using the particle volume averaged quantities, Eqs. (4.65, 4.66), one has

$$\varepsilon_p \frac{\partial \bar{c}_{ip}}{\partial t} + \rho_p \frac{\partial \bar{q}_i}{\partial t} + \frac{3}{R_p} (N_{ir})_{r_p=R_p} = 0, \quad (5.21)$$

$$\sum_i^n N_i^s = -\frac{R_p \rho_p}{3} \sum_i^n \frac{\partial \bar{q}_i}{\partial t} - \frac{R_p \varepsilon_p}{3R} \frac{\partial}{\partial t} \left(\frac{P}{T} \right). \quad (5.22)$$

Assuming parabolic concentration profiles within the sorbent particle, as defined by Eqs. (4.69) and (4.70), one combines Eqs. (5.19), (5.20), (5.22) and (4.71), into

$$\frac{\varepsilon_p}{R} \frac{\partial}{\partial t} \left(\frac{\bar{y}_{ip} P}{T} \right) + \rho_p \frac{\partial \bar{q}_i}{\partial t} + \frac{3}{R_p} \left[y_{ip}^s \sum_i^n N_i^s - \frac{P}{RT} D_e \left(\frac{\partial y_{ip}}{\partial r_p} \right)_{r_p=R_p} \right] = 0, \quad (5.23)$$

to obtain the final form of the individual material balance inside the pores of the solid particle

$$\begin{aligned} \frac{\partial \bar{y}_{ip}}{\partial t} - (y_i - \bar{y}_{ip}) \left(\frac{1}{P} \frac{\partial P}{\partial t} - \frac{1}{T} \frac{\partial T}{\partial t} + \frac{15 D_e}{\varepsilon_p R_p^2} \right) \\ + \frac{\rho_p R T}{\varepsilon_p P} \left(\frac{\partial \bar{q}_i}{\partial t} - y_i \sum_i^n \frac{\partial \bar{q}_i}{\partial t} \right) = 0, \end{aligned} \quad (5.24)$$

where $y_{ip}^s \approx y_i$ and D_e is the intraparticle effective diffusivity of sorbate.

In CASE B, a pore and surface diffusion model is considered, as in Yang and Doong (1986), where instead of an effective diffusivity two fluxes contribute to the pore diffusion: surface and gas-phase. Hence, the material balance for each component inside the pores of a spherical carbon particle can be written as in Eq. (5.19). The intraparticle flux N_{ir} of component i comprises pore and surface diffusion. The pore diffusion is dominated by Knudsen diffusion with a constant diffusivity D_{ik} . By integrating Eq. (5.19) with respect to r_p and using the particle-averaged quantities, one have Eq. (5.21). The intraparticle flux at the particle surface is defined as in Eq. (4.72). The adsorbed gas is

assumed to be in thermal equilibrium with the adsorbent and hence, there are no temperature gradients inside the particle. Finally, substituting Eqs. (4.71, 4.72) into Eq. (5.21) one obtains

$$\varepsilon_p \frac{\partial}{\partial t} \left(\frac{\bar{P}_{ip}}{T} \right) + \rho_p R \frac{\partial \bar{q}_i}{\partial t} - \frac{15 D_{ik}}{R_p^2 T} (y_{ip}^s P - \bar{P}_{ip}) - \frac{15 D_{is} R \rho_p}{R_p^2 T} (q_i^s - \bar{q}_i) = 0, \quad (5.25)$$

with the surface diffusivity D_{is} defined from Eq. (4.75) and the Knudsen diffusivity estimated from Eq. (4.77). q_i^s is the excess adsorbed concentration of component i in equilibrium with the gas mixture of composition $(c_{1p}^s, \dots, c_{np}^s)$ at temperature T . The equilibrium adsorbed concentrations q_i^s and $\bar{q}_i$ are computed according to the multicomponent adsorption isotherm model, as in Eqs. (4.88, 4.89).

2. PSA – Energy balance equation

For both hybrid models developed, the energy balance in the bed accounts for the total particle porosity and is given by

$$\begin{aligned} [\varepsilon \bar{C}_{pg} c + (1 - \varepsilon_b) \rho_p C_{pa} \bar{q} + (1 - \varepsilon_b) \rho_p C_{ps}] \frac{\partial T}{\partial t} - \varepsilon \frac{\partial P}{\partial t} - (1 - \varepsilon_b) \rho_p \sum_i^n Q_i \frac{\partial \bar{q}_i}{\partial t} \\ + \varepsilon_b \bar{C}_{pg} c v \frac{\partial T}{\partial z} - \varepsilon_b D_h \frac{\partial^2 T}{\partial z^2} = \frac{2h_w}{R_b} (T_w - T), \end{aligned} \quad (5.26)$$

with the heat dispersion coefficient, D_h , defined by Eq. (4.95). This equation can be further developed and rewritten as

$$\begin{aligned} \left[\bar{C}_{pg} \frac{P}{T} + \Lambda_p \bar{C}_{pg} \frac{P}{T} + \Omega_p C_{pa} \bar{q} + \Omega_p C_{ps} \right] \frac{\partial T}{\partial t} - R(1 - \Lambda_p) \frac{\partial P}{\partial t} - \Omega_p \sum_i^n Q_i \frac{\partial \bar{q}_i}{\partial t} \\ + \bar{C}_{pg} \frac{P v}{T} \frac{\partial T}{\partial z} - D_h R \frac{\partial^2 T}{\partial z^2} = \psi_w (T_w - T), \end{aligned} \quad (5.27)$$

where $\psi_w = 2h_w R / \varepsilon_b R_b$ and C_{pa} is the heat capacity of the adsorbed phase. The specific heat of each adsorbed species is assumed to be equal to that of the same species in the gas phase. Since

$$P \frac{\partial}{\partial z} \left(\frac{v}{T} \right) = \frac{P}{T} \frac{\partial v}{\partial z} - \frac{P v}{T^2} \frac{\partial T}{\partial z}, \quad (5.28)$$

and from the global material balance, one gets

$$\begin{aligned} \bar{C}_{pg} \frac{P v}{T} \frac{\partial T}{\partial z} &= \bar{C}_{pg} P \frac{\partial v}{\partial z} - \bar{C}_{pg} P T \frac{\partial}{\partial z} \left(\frac{v}{T} \right) \\ &= \bar{C}_{pg} P \frac{\partial v}{\partial z} + \bar{C}_{pg} T \Omega_p \frac{\partial \bar{q}}{\partial t} + \bar{C}_{pg} T (1 + \Lambda_p) \frac{\partial}{\partial t} \left(\frac{P}{T} \right). \end{aligned} \quad (5.29)$$

Rearranging, the energy balance can be finally rewritten as

$$\begin{aligned}
 & (\bar{C}_{pg} - R)(1 + \Lambda_p) \frac{\partial P}{\partial t} + \Omega_p (\bar{C}_{pg} \bar{q} + C_{ps}) \frac{\partial T}{\partial t} + \bar{C}_{pg} P \frac{\partial v}{\partial z} \\
 & + \Omega_p \sum_i^n (\bar{C}_{pg} T - Q_i) \frac{\partial \bar{q}_i}{\partial t} - D_h R \frac{\partial^2 T}{\partial z^2} = \psi_w (T_w - T).
 \end{aligned} \tag{5.30}$$

The differential energy balance applied to the steel cylinder wall, which is assumed to be externally insulated, is given by

$$\rho_w C_{pw} \frac{\partial T_w}{\partial t} = k_w \frac{\partial^2 T_w}{\partial z^2} + \frac{h_w}{e_w} (T - T_w), \tag{5.31}$$

where ρ_w is the wall density, h_w is the wall heat transfer coefficient, k_w is the wall thermal conductivity, C_{pw} is the volumetric heat capacity of the metal and e_w is the thickness of the cylinder wall. The first RHS term is relative to axial conduction energy in the column wall and the second term is concerned with the convective heat between the gas and the wall.

3. PSA – Adsorption rate equation

For MEMPSA – CASE A, the equilibrium data was fitted by the Sips equation, using the parameters of [Yang and Doong \(1985\)](#) described in Table (5.1). The adsorption rate equation for each component i was extended to the multicomponent form. For the MEMPSA – CASE B, the equilibrium data was also fitted by the multicomponent Sips equation, and its parameters are presented in Table (5.2) and are the same as the ones reported in [Yang and Doong \(1986\)](#).

4. Auxiliary variables

To be able to schedule the cyclic steps, the cumulative terms relative to the molar quantities of feed/products in the PSA streams at each step of the process were defined as in Eq. (4.96). The moles at the inlet and exit streams of the PSA bed are given, respectively, by Eqs. (4.97).

The same way as before, the performance of the separation process is measured, but now considering the PSA integration with the membrane unit. Hence, the component purities and recoveries are defined as follows:

$$\text{Recovery}_A = \frac{N_{out,A} \text{ exit in (HPA + HBD)} - N_{in,A} \text{ used in LPG}}{N_{in,A} \text{ inlet in (PR + HPA)}}, \text{ for CASE A,} \tag{5.32}$$

$$\text{Recovery}_A = \frac{N_{out,A} \text{ exit in (HPA + HBD)} - N_{in,A} \text{ used in LPG}}{N_{in,A} \text{ inlet in PR}_a}, \text{ for CASE B,} \tag{5.33}$$

$$\text{Recovery}_B = \frac{N_{out,B}}{N_{in,B}} \frac{\text{exit in (LBD + LPG)}}{\text{inlet in (PR + HPA)}}, \text{ for CASE A,} \quad (5.34)$$

$$\text{Recovery}_B = \frac{N_{out,B}}{N_{1in,B}} \frac{\text{exit in (LBD + LPG + EV)}}{\text{inlet in PR}_a}, \text{ for CASE B,} \quad (5.35)$$

$$\text{Purity}_A = \frac{N_{out,A}}{N_{out}} \frac{\text{exit in (HPA + HBD)} - N_{in,A} \text{ used in LPG}}{\text{exit in (HPA + HBD)} - N_{in} \text{ used in LPG}}, \quad (5.36)$$

$$\text{Purity}_B = \frac{N_{out,B}}{N_{out}} \frac{\text{exit in (LBD + LPG)}}{\text{exit in (LBD + LPG)}}, \text{ for CASE A,} \quad (5.37)$$

$$\text{Purity}_B = \frac{N_{out,B}}{N_{out}} \frac{\text{exit in (LBD + LPG + EV)}}{\text{exit in (LBD + LPG + EV)}}, \text{ for CASE B,} \quad (5.38)$$

assuming the subscripts A and B the lighter and heavier adsorbates, respectively. The purge to feed ratio, P/F , is defined as the gas amount of component A in the feed that is consumed in the LPG step,

$$P/F = \frac{N_{in,A} \text{ used in LPG}}{N_{in,A} \text{ inlet in HPA}}. \quad (5.39)$$

The productivity of component i , i.e., the net amount of high purity product obtained per kilogram of adsorbent and total cycle time, is given by

$$\eta_i = \frac{N_{out,i,produced}}{M_c t_{cycle}}, \quad (5.40)$$

where M_c is the adsorbent amount used and t_{cycle} is the total cycle time. The stage-cut, i.e., the fraction of feed gas permeating through the membrane, is defined as

$$\theta = \frac{N_{out,permeate}}{N_{in,feed}}. \quad (5.41)$$

5. Boundary conditions

A set of complex inlet ($z = 0$)/outlet ($z = L$) boundary conditions for the flow, composition, pressure and temperature, are usually defined in order to perform the conventional periodic process. Thus, for the hybrid modeling an even more extended set of boundary conditions have to be fulfilled in order to operate the system.

For MEMPSA – CASE A, the following additional boundary conditions were considered:

- Global material balance for the intermediate tank during the HPA stage:
For all the components $i = 1, \dots, \text{NoC}$, the global material balance for the intermediate tank is obtained

$$\frac{V_c}{T_v} \frac{dP_v}{dt} = -A_2 v_{20} \frac{P_2}{T_2}, \quad (5.42)$$

where V_c is the tank volume, T_v is the temperature in the tank, P_v is the total pressure in the tank, and subscript 2 correspond to the permeate side of the membrane.

- Individual material balance for the intermediate tank during the HPA stage:
The material balance to the i^{th} component of the n component gas mixture is

$$V_c P_v \frac{\partial y_{iv}}{\partial t} = T_v A_2 \frac{P_2}{T_2} v_{20} (y_{iv} - y_{2i_0}), \quad (5.43)$$

where y_{iv} is the mole fraction of component i in the tank and y_{2i_0} is the permeate mole fraction of i in at the exit end of the membrane.

- Global material balance for the intermediate tank during the PR₁ stage:
For all the components $i = 1, \dots, \text{NoC}$, the global material balance for the intermediate tank is obtained

$$\frac{V_c}{T_v} \frac{\partial P_v}{\partial t} = -A_{bed} \varepsilon_b v_0 \frac{P}{T_0}. \quad (5.44)$$

- Individual material balance for the intermediate tank during the PR₁ stage:
The material balance to the i^{th} component of the n component gas mixture is

$$\frac{\partial y_{iv}}{\partial t} = 0. \quad (5.45)$$

- Global material balance for the intermediate tank during the other stages:
For all the components $i = 1, \dots, \text{NoC}$, the global material balance for the intermediate tank is obtained

$$\frac{dP_v}{dt} = 0. \quad (5.46)$$

- Individual material balance for the intermediate tank during the other stages:
The material balance to the i^{th} component of the n component gas mixture is

$$\frac{\partial y_{iv}}{\partial t} = 0. \quad (5.47)$$

Thus, for the CASE A, the rest of the boundary conditions (BCs) for membrane/PSA operation were defined for the pressurization PR₁:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0, & y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, & \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ v_{20} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = \frac{P_H - P}{t_{PR}} & & \text{for bed pressure dynamics,} \\ T_0 = T_v, & y_{i_0} = y_{i_v} & \text{in bed, for } z = 0, \\ v_L = 0, & \frac{\partial T}{\partial z} = 0, & \frac{\partial y_i}{\partial z} = 0 \text{ in bed, for } z = L, \end{array} \right. \quad (5.48)$$

with subscripts f relative to the regular feed inlet conditions, $i = 1, \dots$, NoC components, and t_{PR} the time of the complete pressurization step. For the pressurization step PR_2 , the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0, & y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ A_1 v_{1L} P_1 = A_{bed} \varepsilon_b v_0 P, & \frac{\partial^2 y_{1i}}{\partial z^2} = 0 & \text{in residue zone (1), for } z = L, \\ v_{20} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = \frac{P_H - P}{t_{PR}} & & \text{for bed pressure dynamics,} \\ T_0 = T_1, & y_{i_0} = y_{1i_L} & \text{in bed, for } z = 0, \\ v_L = 0, & \frac{\partial T}{\partial z} = 0, & \frac{\partial y_i}{\partial z} = 0 \text{ in bed, for } z = L, \end{array} \right. \quad (5.49)$$

For the high-pressure adsorption step (HPA), the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0, & y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ A_1 v_{1L} P_1 = A_{bed} \varepsilon_b v_0 P, & \frac{\partial^2 y_{1i}}{\partial z^2} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial P_2}{\partial t} = \frac{\partial P_v}{\partial t}, & \frac{\partial^2 y_{2i}}{\partial z^2} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = -\gamma(P - P_H) & & \text{for bed pressure dynamics,} \\ T_0 = T_1, & y_{i_0} = y_{1i_L} & \text{in bed, for } z = 0, \\ v_L = v_{HPA}, & \frac{\partial^2 T}{\partial z^2} = 0, & \frac{\partial^2 y_i}{\partial z^2} = 0 \text{ in bed, for } z = L, \end{array} \right. \quad (5.50)$$

with the parameter $\gamma = 0.152$ and v_{HPA} the inlet gas velocity. For the co-current

blowdown step (CD), the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0, & y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, & \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ v_{20} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = -\alpha(P - w), & w = \frac{P_M - P \exp(-\alpha t_{CD})}{1 - \exp(-\alpha t_{CD})} & \text{for bed pressure dynamics,} \\ v_0 = 0, & \frac{\partial T}{\partial z} = 0, & \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = 0, \\ \frac{\partial^2 T}{\partial z^2} = 0, & \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.51)$$

with the parameter $\alpha = 0.01$. For the counter-current blowdown step (BD), the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0, & y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, & \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ v_{20} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = -\beta(P - z), & z = \frac{P_L - P \exp(-\beta t_{BD})}{1 - \exp(-\beta t_{BD})} & \text{for bed pressure dynamics,} \\ \frac{\partial^2 T}{\partial z^2} = 0, & \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{in bed, for } z = 0, \\ v_L = 0, & \frac{\partial T}{\partial z} = 0, & \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.52)$$

with the parameter $\beta = 0.05$. Finally, for the purge step (PG), the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial P_1}{\partial t} = 0, & y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, & \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ v_{20} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, & \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = 0 & & \text{for bed pressure dynamics,} \\ \frac{\partial^2 T}{\partial z^2} = 0, & \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{in bed, for } z = 0, \\ v_L = -v_{PG}, & T_L = T_{1f}, & y_{iL} = y_{i_{PG}} & \text{in bed, for } z = L, \end{array} \right. \quad (5.53)$$

with v_{PG} the purge gas velocity and $y_{i_{PG}}$ the inlet purge mole fraction of component i . v_{PG} is obtained by the purge to feed ratio imposition and $y_{i_{PG}}$ is determined from the modeling cycle, at the end of the HPA step.

The scheme described below was implemented between the permeate side of the membrane and the intermediate tank, in order to account for the hybrid operation during the HPA step. The total molar amount of gas in the permeate side of the membrane is given by

$$N_2^{(0)} = \frac{P_2^{(0)} V_2}{RT_2} = \frac{P_2^{(0)} A_2}{RT_2}. \quad (5.54)$$

The individual molar amount of component i^{th} in the permeate side of the membrane is given by

$$N_{2i}^{(0)} = \frac{P_2^{(0)} A_2}{RT_2} \int_0^L y_{2i}(z) dz = \frac{P_2^{(0)} A_2 \Delta z}{RT_2} \sum_{j=1}^{NoP} y_{2i}(j), \quad (5.55)$$

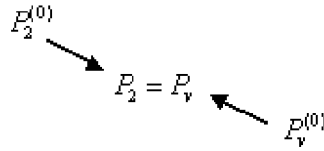
with $\Delta z = L/NoP$, where L is the bed length and NoP is the number of control-volume elements considered. The total amount of gas present inside the tank is

$$N_v^{(0)} = \frac{P_v^{(0)} V_c}{RT_v}, \quad (5.56)$$

and the individual molar amount of component i^{th} in the tank is

$$N_{i_v}^{(0)} = \frac{P_v^{(0)} y_{i_v}^{(0)} V_c}{RT_v}. \quad (5.57)$$

Since an equalization occurs between pressures of both permeate side and intermediate tank, P_2 and P_v , respectively, and assuming as approximation that the molar



fractions profiles are maintained in permeate zone, after pressure equalization, i.e., $y_{2i}(z) = y_{2i}^{(0)}(z)$, the total gas amount transported to the tank is given by

$$\Delta N = N_2^{(0)} - N_2 = \frac{(P_2^{(0)} - P_2) A_2 L}{RT_2}. \quad (5.58)$$

The respective individual molar amount of component i^{th} transported is

$$\Delta N_i = \frac{(P_2^{(0)} - P_2) A_2 \Delta z}{RT_2} \sum_{j=1}^{NoP} y_{2i}(j). \quad (5.59)$$

The new pressure in the tank will be given by

$$P_v = \frac{(N_v^{(0)} - \Delta N) RT_v}{V_c}, \quad (5.60)$$

and since $P_2 = P_v$, then the new permeate pressure will be

$$P_2 = \left(\frac{P_v^{(0)} V_c}{RT_v} + \frac{(P_2^{(0)} - P_2) A_2 L}{RT_2} \right) \frac{RT_v}{V_c}, \quad (5.61)$$

$$P_2 = \frac{P_v^{(0)} V_c T_2 + P_2^{(0)} A_2 L T_v}{T_2 V_c + A_2 L T_v}. \quad (5.62)$$

Consequently, the new molar fractions in the intermediate tank are given by

$$y_{i_v} = \frac{N_{i_v}^{(0)} + \Delta N_i}{N_v^{(0)} + \Delta N}, \quad (5.63)$$

Substituting Eq. (5.60) into Eq. (5.63), one obtains

$$y_{i_v} = \frac{(N_{i_v}^{(0)} + \Delta N_i) RT_v}{P_2 V_c}, \quad (5.64)$$

and using Eqs. (5.57, 5.59) into Eq. (5.64), one finally gets

$$y_{i_v} = \frac{1}{P_2 V_c} \left(P_v^{(0)} y_{i_v}^{(0)} V_c + \frac{(P_2^{(0)} - P_2) A_2 T_v \Delta z}{T_2} \sum_{j=1}^{NoP} y_{2i}(j) \right). \quad (5.65)$$

For MEMPSA – CASE B, the BCs for the pressurization PR_a are defined as:

$$\left\{ \begin{array}{ll} y_{1i_0} = y_{if} & \text{in residue zone (1), for } z = 0, \\ v_{1L} = v_{PR}, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ T_0 = T_1, \quad y_{i_0} = y_{1i_L}, \quad v_0 = \frac{A_1 P_H}{\varepsilon_b A_{bed} P} v_{1L} & \text{in bed, for } z = 0, \\ v_L = 0, \quad \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.66)$$

with subscripts f relative to the regular feed inlet conditions, $i = 1, \dots$, NoC components, and v_{PR} the gas velocity during the pressurization step. For the pressurization step PR_b , the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ T_0 = T_2, \quad y_{i_0} = y_{2i_{out}}, \quad v_0 = \frac{A_2 P_H}{\varepsilon_b A_{bed} P} v_{PR} & \text{in bed, for } z = 0, \\ v_L = 0, \quad \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.67)$$

with $y_{2i_{out}}$ the average permeate molar fraction obtained at PR. For the high-pressure adsorption step HPA_a , the BCs are given by

$$\left\{ \begin{array}{ll} y_{1i_0} = y_{i_f} & \text{in residue zone (1), for } z = 0, \\ v_{1L} = \frac{\varepsilon_b A_{bed} P}{A_1 P_H} v_0, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = 0 & \text{for bed pressure dynamics,} \\ T_0 = T_1, \quad y_{i_0} = y_{1i_L}, \quad v_0 = v_{HPA} & \text{in bed, for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.68)$$

For the high-pressure adsorption step HPA_b , the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = 0 & \text{for bed pressure dynamics,} \\ T_0 = T_2, \quad y_{i_0} = y_{2i_{out}}, \quad v_0 = v_{HPA} & \text{in bed, for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.69)$$

For the co-current blowdown step (CD), the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = \alpha_1 + \alpha_2 P, \quad \alpha_1 = \frac{\alpha_2 (P \exp(\alpha_2 t_{CD}) - P_{CD})}{1 - \exp(\alpha_2 t_{CD})} & \text{for bed pressure dynamics,} \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0, \quad v_0 = 0 & \text{in bed, for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.70)$$

with the parameter $\alpha_2 = -0.02$. For the counter-current blowdown and evacuation

steps (BD, EV), the BCs are given by

$$\left\{ \begin{array}{ll} \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = \alpha_1 + \alpha_2 P, \quad \alpha_1 = \frac{\alpha_2 (P \exp(\alpha_2 t_{BD, EV}) - P_{BD, EV})}{1 - \exp(\alpha_2 t_{BD, EV})} & \text{for bed pressure dynamics,} \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = 0, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0, \quad v_L = 0 & \text{in bed, for } z = L, \end{array} \right. \quad (5.71)$$

with the parameter $\alpha_{2, BD} = -0.01$ or/and $\alpha_{2, EV} = -0.02$. Finally, for the the purge step (PG), the BCs are:

$$\left\{ \begin{array}{ll} \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = 0, \\ v_{1L} = 0, \quad \frac{\partial y_{1i}}{\partial z} = 0 & \text{in residue zone (1), for } z = L, \\ \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = 0, \\ v_{2L} = 0, \quad \frac{\partial y_{2i}}{\partial z} = 0 & \text{in permeate zone (2), for } z = L, \\ \frac{\partial P}{\partial t} = 0, \quad \alpha_1 = \frac{\alpha_2 (P \exp(\alpha_2 t_{BD}) - P_{BD})}{1 - \exp(\alpha_2 t_{BD})} & \text{for bed pressure dynamics,} \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{in bed, for } z = 0, \\ T = T_f, \quad y_L = y_{i_{PG}}, \quad v_L = -v_{PG} & \text{in bed, for } z = L, \end{array} \right. \quad (5.72)$$

with v_{PG} the purge gas velocity and $y_{i_{PG}}$ the inlet purge mole fraction of component i , determined from the modeling cycle, at the end of the HPA step. This step stops when the inlet condition imposed by both v_{PG} and purge to feed ratio is satisfied. Note that when the feed per cycle admitted is insufficient to pressurize the bed up to the adsorption pressure, P_H , the model is able to stop, and an error message appears, alerting for this situation.

6. Initial conditions

For each case the following initial conditions were defined. Hence, For the membrane unit of MEMPSA - CASE A it were considered

$$P_1 = P_H, \quad P_{1i} = y_{in} P_H \quad \text{for membrane high-pressure side,} \quad (5.73)$$

$$P_2 = P_L, \quad P_{2i} = y_{in} P_L \quad \text{for membrane low-pressure side,} \quad (5.74)$$

$$N_{0k}, N_{Lk} = 0. \quad (5.75)$$

For the intermediate tank, one has

$$P_v = P_H, \quad y_{vi} = y_{in}, \quad (5.76)$$

and for the PSA bed

$$P = P_L, \quad T = T_f, \quad \frac{\partial q_i}{\partial t} = 0, \quad (5.77)$$

$$N_0, N_L = 0, \quad y_{CH_4} = y_{CH_4,p} = 1 \times 10^{-4}. \quad (5.78)$$

For MEMPSA - CASE B, the following initial conditions were assumed for the membrane unit:

$$P_1 = P_H, \quad P_{1i} = y_{in}P_H \quad \text{for membrane high-pressure side,} \quad (5.79)$$

$$P_2 = P_{BD}, \quad P_{2i} = y_{in}P_L \quad \text{for membrane low-pressure side,} \quad (5.80)$$

$$N_{0k}, N_{Lk} = 0. \quad (5.81)$$

For the PSA, one has

$$P = P_L, \quad T = T_f = T_w, \quad \frac{\partial q_i}{\partial t} = 0, \quad (5.82)$$

$$N_0, N_L = 0, \quad y_{CH_4} = 1 - 1 \times 10^{-4}, \quad (5.83)$$

$$P_{CH_4,p} = (1 - 1 \times 10^{-4})P_L, \quad P_{CO_2,p} = 1 \times 10^{-4}P_L. \quad (5.84)$$

5.1.4 Model Validation, Results and Analysis

The modeling results concerning both the hybrid concept and the conventional PSA operation were obtained and compared. Hence, the MEMPSA – CASE A was compared with the conventional stand-alone PSA cycle similar to the one cited in [Yang and Doong \(1985\)](#). The hybrid CASE B was compared with a stand-alone PSA operation at the same operating conditions. In this case, the membrane unit was simply deactivated, i.e., its operation was turned off and the periodic cycle proceeded as a single PSA unit.

The MEMPSA CASES were named according to their chronological development. CASE A was implemented prior to CASE B. Since the experimental PSA cycle falls into the later CASE if one included a membrane unit coupled to the process, the following results and analysis are firstly presented for MEMPSA – CASE B.

5.1.4.1 MEMPSA – CASE B

Case Study: CO₂/N₂ Separation Based on the Experimental Work

An hybrid membrane/PSA model for the separation of a CO₂/N₂ gas mixture was performed in order to study the effect of the inclusion of an additional membrane unit into the implemented experimental PSA process. The integration of both technologies was made and its results were obtained and compared with the stand-alone PSA performance for the CO₂/N₂ 30/70% (v/v) mixture. On both situations, the equilibrium relationship between the fluid phase and the adsorbed phase concentrations were given by the Sips isotherm, extended to n components and englobing its interaction parameters.

Concerning the membrane, one assumed a unit with a separating ability (component permeances, selectivity) similar to the one of the experimental module used, since this membrane was specially designed for the CO₂/N₂ separation. The addition of a membrane with that same selectivity towards the CO₂ most permeating species, would engender serious effects to the feed conditions of a single PSA process operation.

Is this integrated process feasible and enough to enhance the final product purity and recovery? This is the question that we will answer in this chapter.

The hybrid membrane/PSA model developed adds a gPROMS model for the membrane unit and an extra model for the complex set of boundary conditions that are able to operate and integrate the membrane operation with the cyclic steps of the PSA process. Then, a redefined gPROMS task performs the schedule sequence of the system. Figure (5.6) presents the membrane/PSA process developed when the least permeable component, N₂ in the present case, is the least adsorbed species in the sorbent bed (MEMPSA - CASE B). The hybrid results obtained are compared with the stand-alone PSA as follows.

The integrated process, as presented here, operates under the assumption that component A is the less permeable and the least adsorbed one, i.e., A and B correspond to N₂ and CO₂, respectively. The input parameters given in the model are membrane selectivity and surface permeation area, A_{mem} . The membrane physical characteristics (cross-section areas) are defined in the model to give the minimum impact on the PSA operation. At steady-state, the accumulation terms in the membrane are minimized relative to the PSA, in order to avoid interference of the membrane with the adsorption process. For example, the membrane cross-section areas, A_k ($k = 1, 2$, with 1 - residue, 2 - permeate), are scaled with V_{PSA}/L_f to allow the accumulation in the membrane to be equal to 10% of that in the PSA. V_{PSA} and L_f are the PSA bed volume and the membrane length, respectively.

Table (5.3) presents the preliminary hybrid simulation performance results in order to check the integrity of the integrated model, to study the effects of the dimensionless per-

meation flow parameter, F_m , and to compare it with the stand-alone PSA results relative to the 30/70% (v/v) CO₂/N₂ run, using the Sips adsorption isotherm with the component interaction parameters. Except for the integrated boundary conditions imposed to perform the membrane/PSA linkage, all the operating conditions are maintained on both single PSA and hybrid systems. The hybrid model reached the CSS at the 11th cycle. Therefore, the membrane did not slow down the convergence to the CSS. The discretized system involves 1154 ordinary differential and algebraic equations. For runs A–C, a simulation over 10 cycles takes approximately less than 750 seconds, and less than 12 seconds for the CSS cycle on an Intel Pentium M 1.5 GHz PC with 512 MB of RAM.

As one can see, the comparison of the product purities and recoveries between the previously stand-alone PSA run and the hybrid one, actually do not show a large improvement on the global performance when applying this latter system. Nevertheless, for the hybrid run C, the CO₂ purity increases about 4.5%, while the N₂ recovery increases 5.6%, for approximately the same CO₂ recovery and N₂ purity. Figure (5.7) shows the pressure and CO₂ effluent concentration histories for the runs A, B and C.

An exhaustive parametric analysis was performed in this CASE B-type of hybrid process, for the CO₂/CH₄ separation and is fully described later in this section. That research allowed the prediction of the hybrid system behavior under certain operating conditions, such as the total feed per cycle admitted, the dimensionless permeation flow parameter, the P/F ratio, etc. Hence, the next step was to change one of that variables for this specific integrated separation process, in order to see if the same performance trend is maintained and if the enhancements are verified when compared with the obtained single PSA process.

For both stand-alone PSA and integrated systems, the total volumetric feed admitted per cycle was changed, maintaining all other conditions. Nonetheless, note that to reproduce the conditions of the initial reference stand-alone PSA experiment, both composition and velocity of the purge stream were maintained the same. This means that the P/F ratio was not equal for all simulations, as one can observe in Table (5.3). These simulation results are also presented on Table (5.3), through runs D–L. Runs A to F are relative to the hybrid process, and runs G to L correspond to an equivalent stand-alone PSA. Figure (5.8) illustrates the effect of the total volumetric feed admitted per cycle, through the gas-phase composition profiles inside the bed at the end of each step, for runs C–F. As observed and expected, moving from run C to F, increasing the feed throughput, the sharp CO₂ wavefront is displaced along the bed, towards the exit end, where a more pure component is obtained. In other words, the bed utilization, defined as the fraction of bed covered by the heavy component wavefront during the adsorption step, increases, and the fraction of clean bed decreases. From the LBD and LPG steps, a purer N₂ product

Table 5.3: Process performance results obtained using both single PSA and hybrid membrane/PSA dynamic simulations for the 30/30% (v/v) CO₂/N₂ separation at CSS (No-Cycle = 11).

RUN	stand-alone PSA	A	B	C	D	E	F	G	H	I	J	L
Total Feed per cycle*	LSTP	11.171	11.171	11.171	20.200	40.200	50.200	8.478	14.319	17.502	37.496	47.494
F_m	-	0.53	0.36	2.13	2.13	2.13	2.13	-	-	-	-	-
Y_{CO2} in residue	%	15.42	23.96	8.36	8.36	8.36	8.37	-	-	-	-	-
Y_{N2} in residue	%	84.58	76.04	91.64	91.64	91.64	91.63	-	-	-	-	-
Y_{CO2} in permeate	%	89.00	91.48	85.29	85.29	85.29	85.29	-	-	-	-	-
Y_{N2} in permeate	%	11.00	8.52	14.71	14.71	14.71	14.71	-	-	-	-	-
t_{PRA}	s	134.85	68.04	71.78	64.69	64.69	64.69	138.08	138.12	138.14	138.13	138.15
t_{HPAa}	s	-	68.52	81.93	57.55	190.77	485.98	633.61	-	-	-	-
t_{HPAb}	s	79.11	33.65	14.74	49.93	100.35	212.04	267.89	34.07	152.93	217.67	828.04
t_{HBD}	s	118.89	118.89	118.89	118.89	118.89	118.89	118.89	141.52	141.52	141.52	141.52
t_{LBD}	s	363.20	363.20	363.20	363.20	363.20	363.20	363.20	363.20	363.20	363.20	363.20
t_{PG}	s	120.75	120.75	120.75	120.75	120.75	120.75	120.75	120.75	120.75	120.75	120.75
t_{cycle}	min	13.61	12.88	12.85	12.92	15.98	22.76	26.15	13.29	15.28	23.14	26.53
PIF		0.04347	0.06697	0.06450	0.06943	0.02173	0.00863	0.00662	0.01611	0.00351	0.00242	0.00064
CO₂ Purity	%	54.18	56.19	55.54	56.61	75.11	93.84	95.97	49.04	64.58	70.47	80.90
N₂ Purity	%	99.62	99.28	99.16	99.43	98.31	96.21	92.77	99.94	99.86	99.81	82.80
CO₂ Recovery	%	99.99	98.86	98.69	99.05	96.58	91.14	82.27	99.91	99.76	99.64	54.70
N₂ Recovery	%	63.56	66.63	65.80	67.14	86.15	97.41	98.51	55.06	76.32	81.93	92.87
* Is defined as the total amount per cycle fed to the PSA during PR, HPA and LPG steps STP(0°C, 1 atm)												

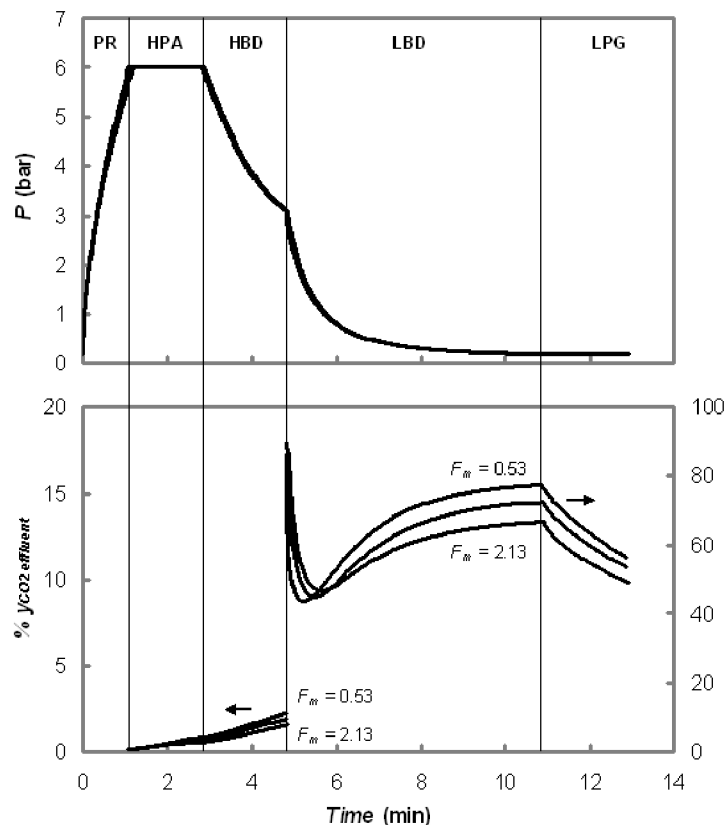


Figure 5.7: Pressure and CO_2 effluent concentration histories for the runs A, B and C, inside the adsorbent bed at CSS (NoCycle = 11). Corresponds to a CO_2/N_2 30/70 % (v/v) feed mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric feed flow of 3.0 slpm (STP: 0°C , 1 atm).

is obtained in run C, at the cost of a lower recovery. Note that, especially for runs E and F the performance enhancement is significant, when compared with the equivalent stand-alone runs J and L, although the cycle time for these runs is twice that for runs A–C. Table (5.4) presents with more detail the modeling results comparison between runs E and J. Instead of the regular 30/70 mixture fed to the PSA, a feed stream with only 16.8% CO_2 on average enters the bed in the hybrid process. The PR step and the first stage of the HPA are performed with a feed stream enriched in the lighter component, N_2 , which is the first to be withdrawn from the column as product. This first product is then obtained at higher purity. The HPA_b occurs with a feed stream now enriched in the more adsorbed component, simultaneously with recovery of high purity N_2 . The HBD step continues to produce a purer N_2 stream than that obtained in the stand-alone PSA process. Finally, the CO_2 product is collected in LBD and LPG steps, at an higher

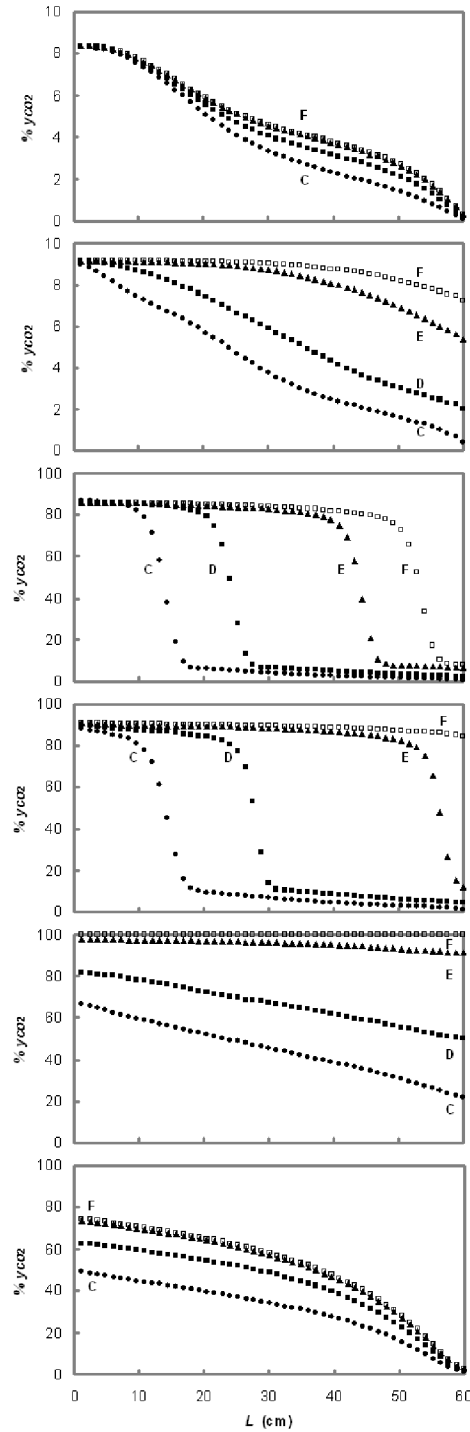


Figure 5.8: CO_2 gas-phase composition profiles inside the bed at the end of each step, for runs C–F at CSS (NoCycle = 11). CO_2/N_2 30/70 % (v/v) feed mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric feed flow of 3.0 slpm (STP: 0°C , 1 atm). From top to bottom: $\text{PR}_a/\text{HPA}_a/\text{HPA}_b/\text{HBD}/\text{LBD}/\text{LPG}$.

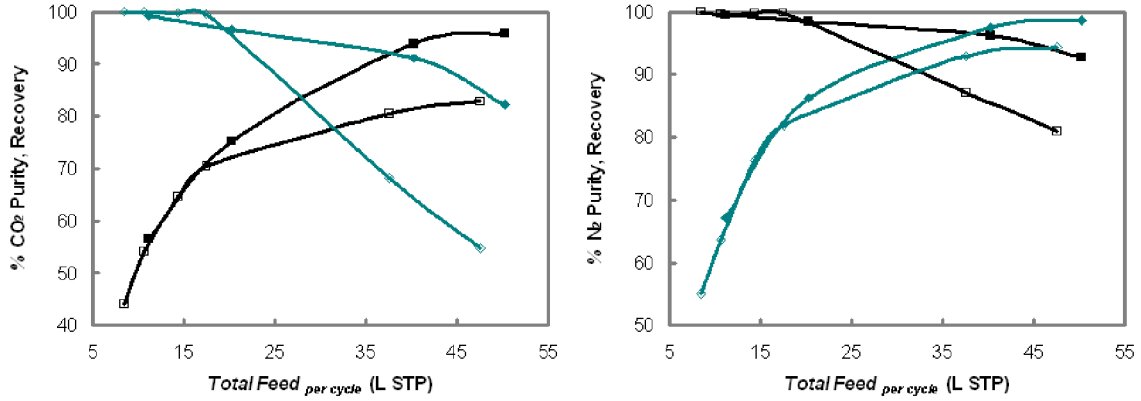


Figure 5.9: Impact of the membrane on PSA for the 30/70 CO₂/N₂ separation: performance curve for the hybrid system with a total feed per cycle variation. Green and black denotes recoveries and purities, respectively. Filled and open symbols correspond to membrane on and membrane off, respectively.

average purity for the integrated case.

Figure (5.9) shows the impact of the membrane on PSA through the characteristic curve for the both systems with total feed per cycle variation. As one can see, the enhancement of the integrated process when compared with the stand-alone PSA increases significantly with the increase of the total feed admitted per cycle. Thus, for high feed throughputs the hybrid process developed has a clearly advantage. This trend is as expected, since the same behavior was obtained from the base-CASE B parametric analysis that will be described next for the CO₂/CH₄ system.

Figures (5.10–5.13) illustrate the comparison between runs E (hybrid process) and J (stand-alone PSA) relative to the evolution of the CO₂ gas- and adsorbed-phases compositions, temperature profiles and superficial gas velocity inside the bed, during each cycle step, versus axial distance z along a complete steady state-cycle. It is notorious the stiffness of the composition wavefronts inside the bed during the HPA and HBD steps. The temperature profile also follows a behavior corresponding to the cycle modification imposed by the inclusion of the membrane unit.

To better understand the membrane operation during the PR and HPA_a steps of Run E, Figure (5.14) presents the gas composition and velocity profiles at each side of the membrane, versus the axial distance z along a steady-state cycle. During permeation time, the residue is enriched in the least adsorbed component, while the permeate is enriched in the more strongly adsorbed one, which is the more permeable species.

5.1 Hybrid Membrane/PSA Processes

Table 5.4: Modeling results at CSS (NoCycle = 11) obtained for Runs E and J, the hybrid process and the stand-alone PSA simulations, respectively. The feed is the regular 30/30% (v/v) CO₂/N₂ mixture.

Run			Predicted	Run			Predicted
E				J			
Step	Memb. Avg. CO ₂ in %		30.21	Step	Avg. CO ₂ in %		30.21
Ia	Memb.Total Amt. in (LSTP)		7.087	I	Total Amt. in (LSTP)		6.787
	Memb. Avg. CO ₂ permeate out %		88.10				
	Memb.Total Amt. permeate out (LSTP)		1.385				
	PSA Avg. CO ₂ in %		16.18				
	PSA Total Amt. in (LSTP)		5.702				
Step	Memb. Avg. CO ₂ in %		30.21	Step	Avg. CO ₂ in %		30.21
Ila	Memb.Total Amt. in (LSTP)		32.913	II	Total Amt. in (LSTP)		30.690
	Memb. Avg. CO ₂ permeate out %		85.82		Avg. N ₂ out %		89.87
	Memb.Total Amt. permeate out (LSTP)		9.033		Total Amt. out (LSTP)		24.563
	PSA Avg. CO ₂ in %		9.17				
	PSA Total Amt. in (LSTP)		23.879				
	PSA Avg. N ₂ out %		97.06				
	PSA Total Amt. out (LSTP)		22.083				
Step	PSA Avg. CO ₂ in %		86.12	Step	Avg. N ₂ out %		66.70
Ilb	PSA Total Amt. in (LSTP)		10.419	III	Total Amt. out (LSTP)		3.352
	PSA Avg. N ₂ out %		94.09				
	PSA Total Amt. out (LSTP)		4.750				
Step	Avg. N ₂ out %		91.27	Step	Avg. CO ₂ out %		80.36
III	Total Amt. out (LSTP)		1.631	IV	Total Amt. out (LSTP)		9.457
Step	Avg. CO ₂ out %		94.23				
IV	Total Amt. out (LSTP)		11.015				
Step	Avg. N ₂ in %		99.74	Step	Avg. N ₂ in %		99.74
V	Total Amt. in (LSTP)		0.200	V	Total Amt. in (LSTP)		0.019
	Avg. CO ₂ out %		87.85		Avg. CO ₂ out %		94.03
	Total Amt. out (LSTP)		0.720		Total Amt. out (LSTP)		0.124
	P/F		0.009		P/F		0.001
Total Feed per cycle (LSTP) ^a			40.20	Total Feed per cycle (LSTP) ^b			37.50
CO ₂ Purity (%)			93.84	CO ₂ Purity (%)			80.54
N ₂ Purity (%)			96.21	N ₂ Purity (%)			87.08
CO ₂ Recovery (%)			91.14	CO ₂ Recovery (%)			68.16
N ₂ Recovery (%)			97.41	N ₂ Recovery (%)			92.87

^a Is defined as the total amount per cycle fed to the PSA during PR, HPA and LPG steps.
STP (0°C, 1 atm)

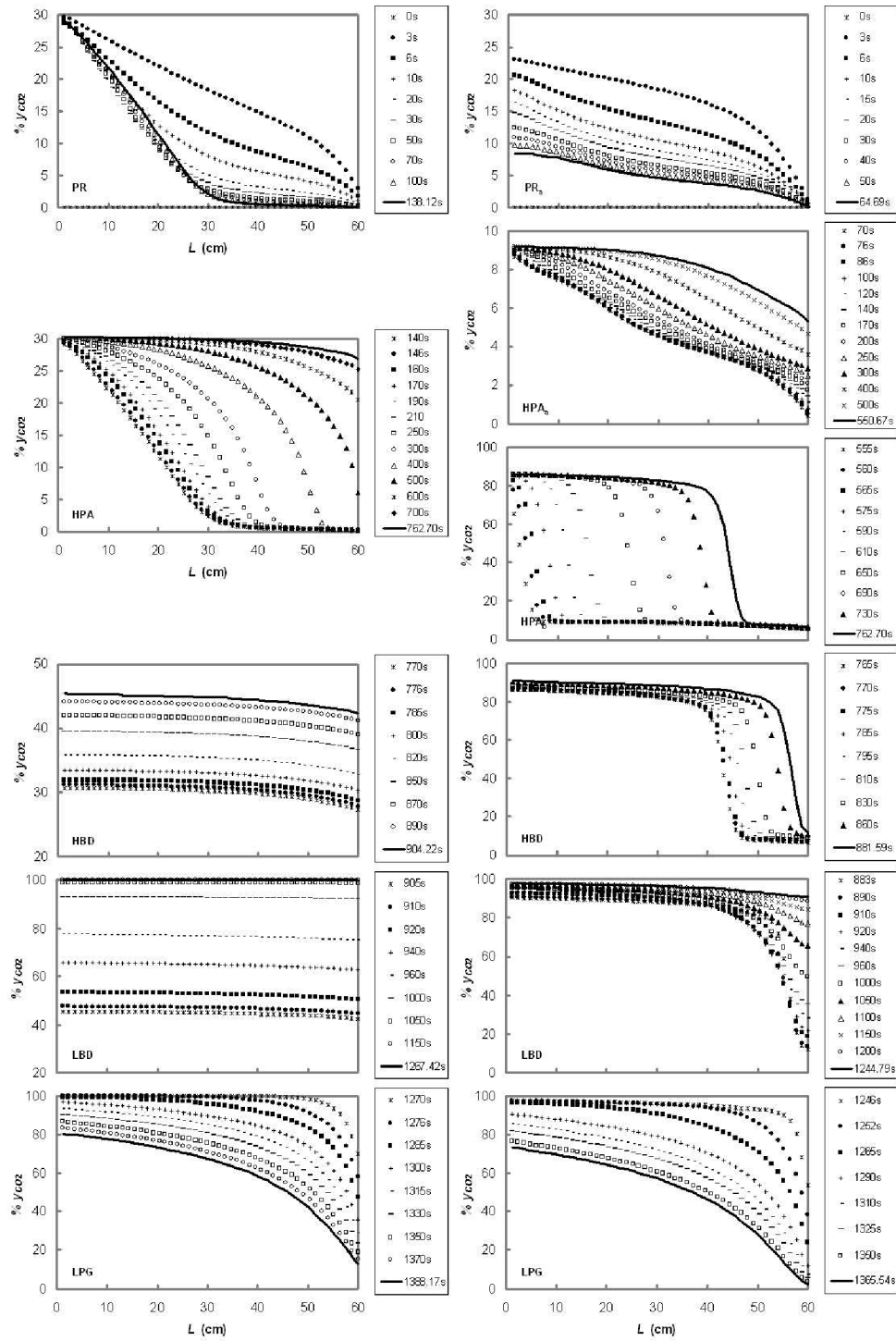


Figure 5.10: CO₂ gas-phase composition profiles inside the bed at the end of each step, for runs E and J at CSS (NoCycle = 11). CO₂/N₂ 30/70 % (v/v) feed mixture at an average T_{run} of 35.85°C, a pressure P_H of 6 bar and a total volumetric feed flow of 3.0 slpm (STP: 0°C, 1 atm). From top to bottom: PR_a/HPA_a/HPA_b/HBD/LBD/LPG. From left to right: Runs J/E.

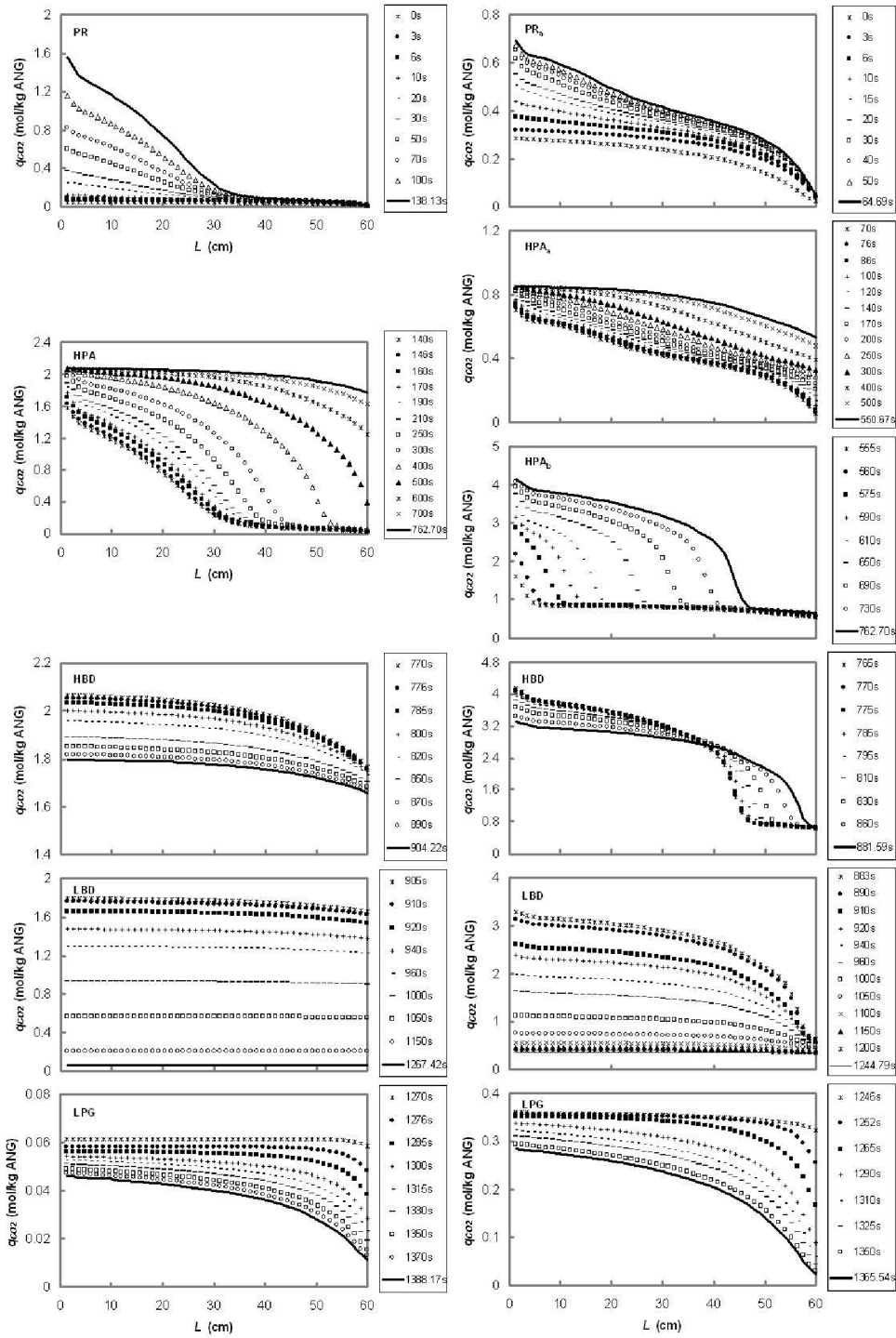


Figure 5.11: CO_2 adsorbed-phase composition profiles inside the bed at the end of each step, for runs E and J at CSS (NoCycle = 11). CO_2/N_2 30/70 % (v/v) feed mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric feed flow of 3.0 slpm (STP: 0°C , 1 atm). From top to bottom: $\text{PR}_a/\text{HPA}_a/\text{HPA}_b/\text{HBD}/\text{LBD}/\text{LPG}$. From left to right: Runs J/E.

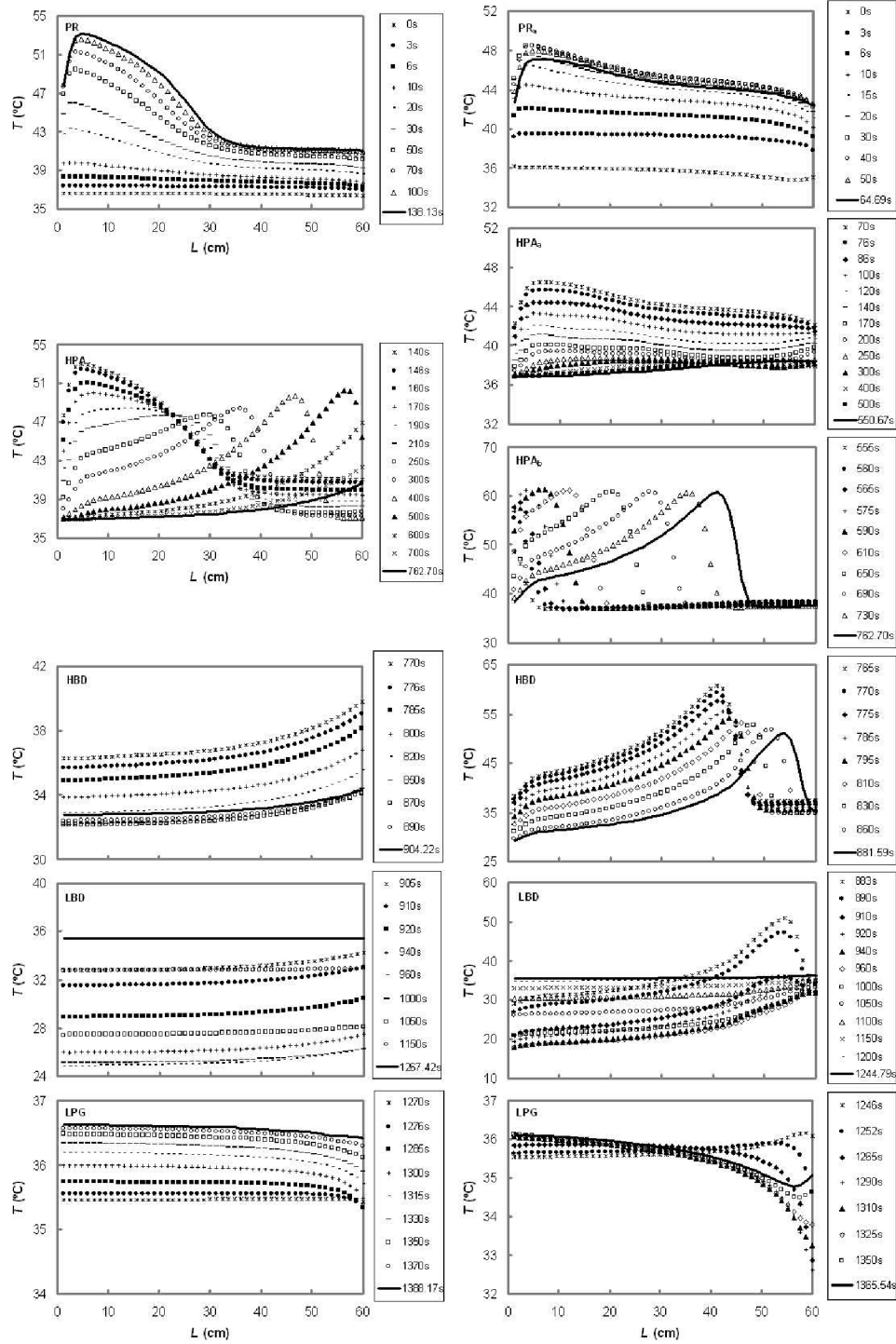


Figure 5.12: Temperature profiles inside the bed at the end of each step, for runs E and J at CSS (NoCycle = 11). CO_2/N_2 30/70 % (v/v) feed mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric feed flow of 3.0 slpm (STP: 0°C , 1 atm). From top to bottom: $\text{PR}_a/\text{HPA}_a/\text{HPA}_b/\text{HBD}/\text{LBD}/\text{LPG}$. From left to right: Runs J/E.

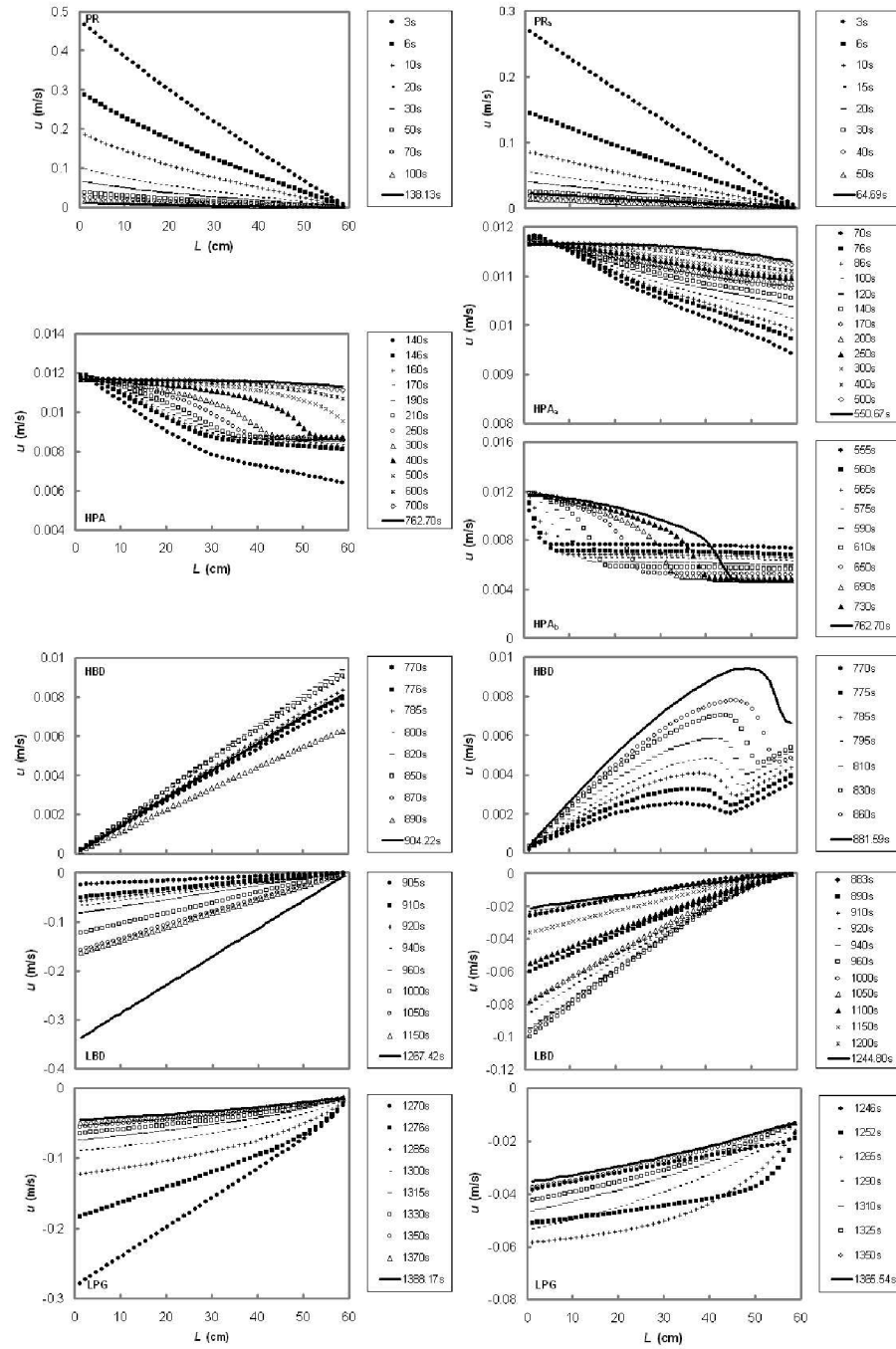


Figure 5.13: Evolution of the superficial gas velocity during each step versus axial distance z , for runs E and J at CSS (NoCycle = 11). CO_2/N_2 30/70 % (v/v) feed mixture at an average T_{run} of 35.85°C , a pressure P_H of 6 bar and a total volumetric feed flow of 3.0 slpm (STP: 0°C , 1 atm). From top to bottom: $\text{PR}_a/\text{HPA}_a/\text{HPA}_b/\text{HBD}/\text{LBD}/\text{LPG}$. From left to right: Runs J/E.

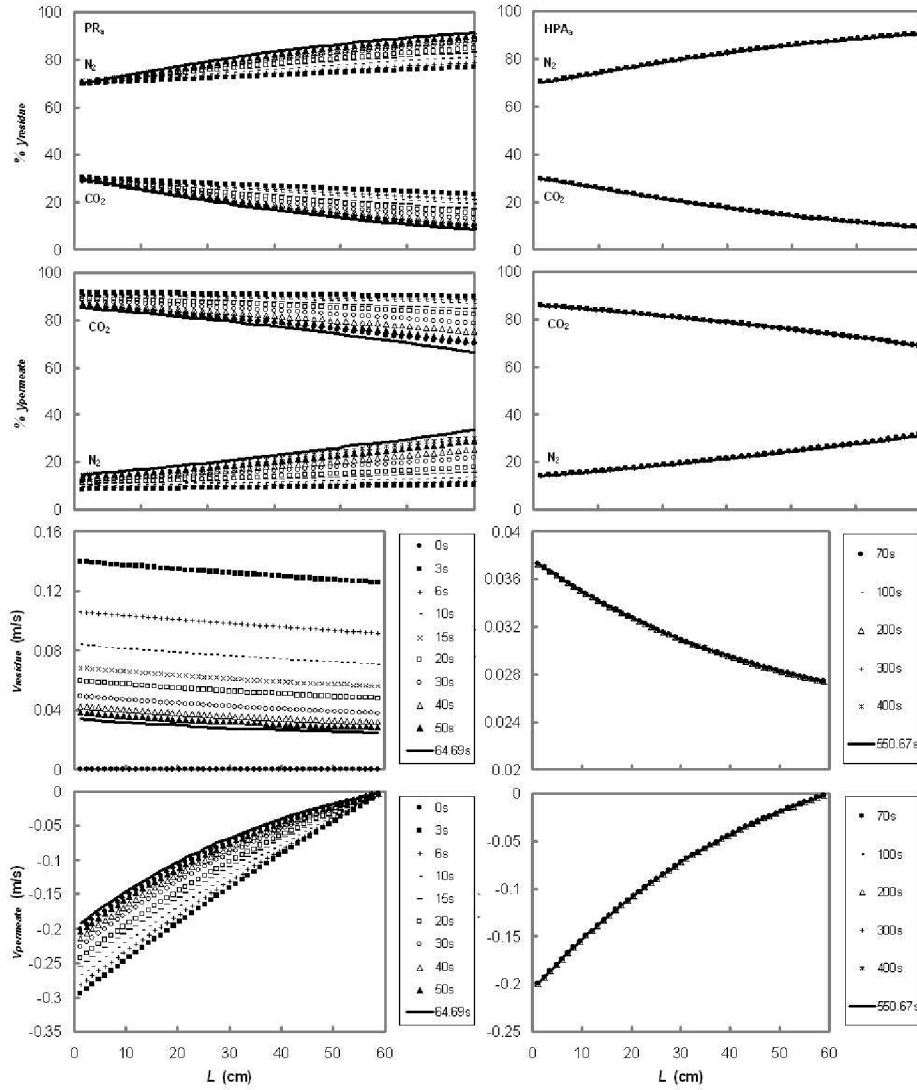


Figure 5.14: Evolution of the gas composition and velocity at each side of the membrane, during each step, versus axial distance z , for run E at CSS (NoCycle = 11).

Case Study: CO_2/CH_4 Separation

The simulation runs performed were selected for assessment of the hybrid process performance. The PSA employs activated carbon as the adsorbent coupled to a membrane with a typical gas selectivity α_{CO_2/CH_4} of 20, where the CO_2 and CH_4 permeances were assumed 60 GPU and 3 GPU, respectively. The periodic hybrid cycle is composed by: Pressurization (PR_a , PR_b) / High-pressure adsorption (HPA_a , HPA_b) / Co-current blowdown (HBD or CD) / Counter-current blowdown (LBD or BD) / Purge (LPG) and Evacuation (EV). The standard operating conditions considered and its performance re-

sults are described in Table (5.2). The hybrid model reached the CSS at the 51th cycle. The simulations for the CSS cycle take approximately 73 seconds for a 15 minutes cycle time, on a Intel Pentium PC with 500 MB of RAM.

For the CH₄(A)/CO₂(B) separation, the following parameters were analyzed: F_m , total feed/cycle, P_H , $P_{CD,BD}$, $t_{CD/BD/EV}$, %PG (amount of HPA product fed to the bed in PG step), purities, recoveries and component productivities. As stated before, the integration varies with the range of the total feed amount admitted per cycle that is assumed. Thus, the initial simulations focused on the determination of the turning point, where the CASE B.1 switched to CASE B.2. The total feed admitted per cycle was varied and results showed that for values higher than 40.65 L(STP) per cycle, the MEMPSA process switches from B.1 to B.2.

To analyze the dynamic behavior of both CASES B, for a 50/50%(v/v) CH₄(A)/CO₂(B) separation, let's consider a total feed per cycle of 30.65 and 40.65 L(STP) for cases B.1 and B.2, respectively. Table (5.5) reports the simulation performance results concerning the variation of several operating parameters. Increasing the cycle time, t_{cycle} , the product productivity is decreased. This is shown comparing, for example, runs 21 and 22.

Figure (5.15) presents the characteristic curve relative to the effect of the intermediate pressure, P_{CD} , variation. At CSS, one obtains CH₄ recoveries up to 88% with purities up to 92%. For CO₂ purities up to 88% are obtained with recoveries up to 96%. As expected, the higher the product recoveries, the lower its purities. Figure (5.16) reports the same performance results, but with P_{CD} in the x axis. The performance trend with P_{CD} variation described the expected system behavior.

For these simulation runs, the membrane inlet and exit streams were analyzed in order to check the separating ability of this unit. Hence, the following membrane performance parameters were defined:

- Product recovery: amount of component i that is obtained, either in the residue or in the permeate exit streams of the membrane, divided by the amount of the same component present in the feed stream.

$$\text{Recovery}_A = \frac{N_{out,A} \text{ in residue}}{N_{in,A} \text{ in feed}}, \quad (5.85)$$

$$\text{Recovery}_B = \frac{N_{out,B} \text{ in permeate}}{N_{in,B} \text{ in feed}}, \quad (5.86)$$

- Product purity: fraction of component i that is obtained in each product stream.

$$\text{Purity}_A = \frac{N_{out,A} \text{ in residue}}{N_{out} \text{ in residue}}, \quad (5.87)$$

$$\text{Purity}_B = \frac{N_{out,B} \text{ in permeate}}{N_{out} \text{ in permeate}}, \quad (5.88)$$

Table 5.5: Simulation performance results concerning the variation of several operating parameters. CH_4/CO_2 50/50 % (v/v) feed mixture at 25°C , $F_m = 1.38$, and total feed amount per cycle which excludes the PG amount fed per cycle.

No.	Feed _{cycle} L STP	L_{bed} cm	P_H bar	P_{CO} bar	P_{LO} bar	P_L bar	%PG	t_{CO} s	t_{EO} s	t_{EG} s	t_{EV} s	t_{cycle} min	V_{PR} m/s	V_{HFA} m/s	V_{RG} m/s	N_{in} L STP	%Purity CH_4	%Purity CO_2	%Recovery CH_4	%Recovery CO_2	Productivity (mol/kg h) CH_4	Productivity (mol/kg h) CO_2
1	30.65	40.0	9.9	2.5	1.5	0.34	0	90	90	0.0	180	21.1	0.025	0.025	0.00	0.000	86.56	78.34	75.60	88.21	0.093	0.109
2	30.65	40.0	9.9	3.5	1.5	0.34	0	90	90	0.0	180	21.0	0.025	0.025	0.00	0.000	89.56	71.73	63.52	92.55	0.078	0.114
3	30.65	40.0	7.9	5.5	1.5	0.34	0	90	90	0.0	180	19.4	0.025	0.025	0.00	0.000	92.05	63.29	44.24	96.13	0.059	0.129
4	30.65	40.0	7.9	4.5	1.5	0.34	0	90	90	0.0	180	19.5	0.025	0.025	0.00	0.000	90.99	67.19	53.79	94.63	0.072	0.126
5	30.65	40.0	7.9	3.5	1.5	0.34	0	90	90	0.0	180	19.5	0.025	0.025	0.00	0.000	89.31	72.23	64.53	92.23	0.086	0.123
6	30.65	40.0	7.9	2.5	1.5	0.34	0	90	90	0.0	180	19.6	0.025	0.025	0.00	0.000	86.36	79.04	76.70	87.84	0.102	0.116
7	40.65	40.0	7.9	2.5	1.5	0.34	0	90	90	0.0	180	20.2	0.025	0.025	0.00	0.000	83.53	82.54	88.31	87.60	0.150	0.141
8	40.65	40.0	7.9	3.5	1.5	0.34	0	90	90	0.0	180	20.2	0.025	0.025	0.00	0.000	87.16	88.17	80.06	81.56	0.137	0.151
9	40.65	40.0	7.9	4.5	1.5	0.34	0	90	90	0.0	180	20.1	0.025	0.025	0.00	0.000	89.03	91.06	72.23	76.64	0.124	0.156
10	40.65	40.0	7.9	5.5	1.5	0.34	0	90	90	0.0	180	20.1	0.025	0.025	0.00	0.000	90.19	92.87	65.16	72.72	0.112	0.159
11	30.65	40.0	7.9	3.5	1.5	0.34	5	90	90	11.5	180	19.7	0.025	0.025	0.025	0.222	89.47	92.40	62.34	71.53	0.083	0.122
12	30.65	40.0	7.9	3.5	1.5	0.34	10	90	90	23.0	180	19.9	0.025	0.025	0.025	0.442	89.64	92.57	60.24	70.86	0.081	0.121
13	30.65	40.0	7.9	3.5	1.5	0.34	20	90	90	45.6	180	20.3	0.025	0.025	0.025	0.879	89.96	92.89	56.25	69.59	0.076	0.119
14	30.65	40.0	7.9	3.5	1.5	0.34	30	90	90	68.2	180	20.7	0.025	0.025	0.025	1.313	90.26	93.18	52.49	68.39	0.071	0.118
15	30.65	40.0	7.9	3.5	1.5	0.34	50	90	90	113.3	180	21.4	0.025	0.025	0.025	2.181	90.81	93.73	45.47	66.12	0.062	0.115
16	30.65	40.0	7.9	3.5	1.5	0.34	50	90	90	221.8	180	23.3	0.025	0.025	0.0125	2.135	90.12	93.27	45.39	65.91	0.057	0.105
17	40.65	40.0	7.9	3.5	1.5	0.34	5	90	90	30.7	180	20.7	0.025	0.025	0.025	0.591	87.73	88.81	75.61	79.89	0.129	0.148
18	40.65	40.0	7.9	3.5	1.5	0.34	10	90	90	61.2	180	21.2	0.025	0.025	0.025	1.178	88.26	89.41	71.41	78.33	0.122	0.146
19	40.65	40.0	7.9	3.5	1.5	0.34	20	90	90	121.8	180	22.2	0.025	0.025	0.025	2.344	89.21	90.45	63.58	75.43	0.109	0.142
20	40.65	40.0	7.9	3.5	1.5	0.34	30	90	90	182.0	180	23.2	0.025	0.025	0.025	3.503	90.04	91.34	56.37	72.73	0.097	0.138
21	40.65	40.0	7.9	3.5	1.5	0.34	50	90	90	302.0	180	25.1	0.025	0.025	0.025	5.813	91.40	92.80	43.51	67.82	0.075	0.130
22	40.65	40.0	7.9	3.5	1.5	0.34	50	90	90	601.1	180	30.2	0.025	0.025	0.0125	5.785	90.35	91.90	43.42	67.53	0.063	0.107
23	40.65	50.0	7.9	3.5	1.5	0.34	0	90	90	0.0	180	19.9	0.025	0.025	0.00	0.000	89.54	74.94	69.27	91.87	0.120	0.159

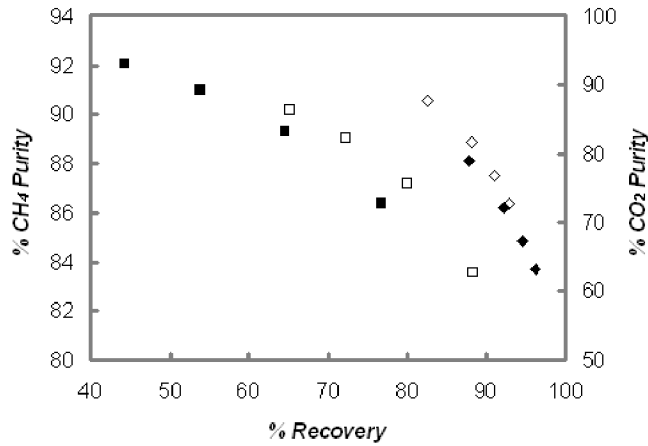


Figure 5.15: Characteristic curve relative to the effect of the intermediate blowdown pressure, P_{CD} , variation on the performance of the integrated system, at CSS (NoCycle = 51). CH₄/CO₂ 50/50 %(v/v) feed mixture at 25°C, $P_H = 7.9$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA,PG} = 0.025$ m/s, no purge (PG) step, and total amount feed per cycle of 30.65 L STP ($\square/\diamond$, CH₄/CO₂) and 40.65 L STP ($\blacksquare/\blacklozenge$, CH₄/CO₂). STP: 0°C, 1 atm.

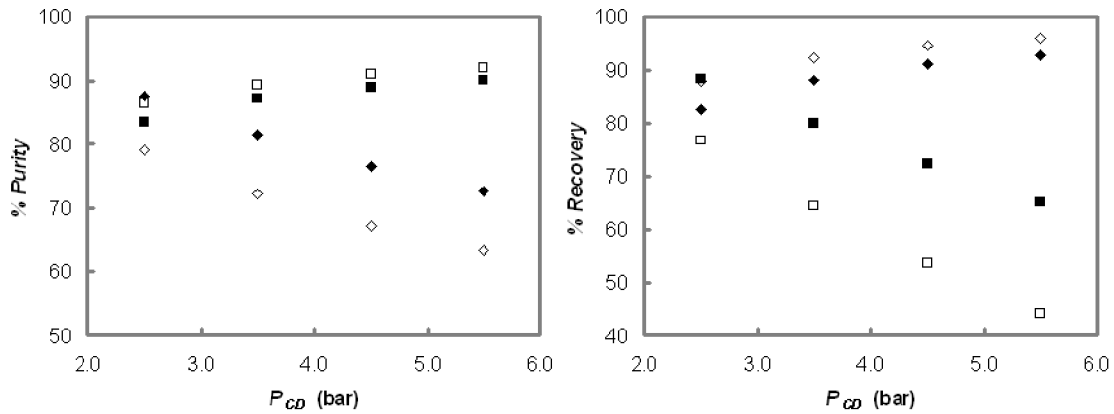


Figure 5.16: Effect of the intermediate blowdown pressure, P_{CD} , variation on the performance of the integrated system, at CSS (NoCycle = 51). CH₄/CO₂ 50/50 %(v/v) feed mixture at 25°C, $P_H = 7.9$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA,PG} = 0.025$ m/s, no purge (PG) step, and total amount feed per cycle of 30.65 L STP and 40.65 L STP. $\square/\diamond$, CH₄/CO₂ at 30.65 L STP; $\blacksquare/\blacklozenge$, CH₄/CO₂ at 40.65 L STP (STP: 0°C, 1 atm).

Table (5.6) illustrates the average composition and component recoveries on both sides of the membrane, for the previous simulations performed, when the P_{CD} variation effect was analyzed. A residue enriched in CH_4 and a permeate stream enriched in CO_2 are obtained, which will enter the PSA bed on pressurization and adsorption steps of the integrated cycle. These average component compositions contrast with the ones obtained for the membrane performance in MEMPSA – CASE A [Figure (5.33)], in the 50/50 (v/v) $\text{A}(\text{H}_2)/\text{B}(\text{CH}_4)$ separation, where for $V_c = 2.5$ L a permeate $\approx 84\%$ enriched in $\text{A}(\text{H}_2)$ is fed to the PR_1 step, while only a $\approx 57\%$ $\text{B}(\text{CH}_4)$ enriched residue is fed during HPA.

Figure (5.17) presents the effect of the feed purge amount variation on the performance of the integrated process, at CSS. The %PG is the amount of $\text{A}(\text{CH}_4)$ product, obtained in HPA, used to purge the column during the PG step. As one can see, for the given operating conditions, the increase of the amount of feed purge, do not significantly improve the CH_4 and CO_2 purity and recovery, respectively, compared with the loss of CH_4 and dilution of CO_2 product.

Table (5.7) presents the simulation performance results concerning t_{CD} , t_{BD} , t_{EV} and v_{PG} variation. As seen, increasing the cycle time both product productivities are decreased. In other words, decreasing the co-current blowdown time, t_{CD} , the CH_4 purity and CO_2 recovery are increased marginally, but both CH_4 recovery and CO_2 purity slightly decrease, with increment of the productivities, because of the reduction of the total cycle time, t_{cycle} . This is verified through the comparison of runs 1 – 3 with runs 7 – 9 and 13 – 15. The same productivity trend is observed with the variation of the evacuation time, t_{EV} , and the counter-current blowdown time, t_{BD} .

The separation of the 50/50% (v/v) CH_4/CO_4 mixture and its results, under the hybrid concept developed, were described. The primary objective here was to analyze the dynamic behavior of MEMPSA – CASE B, its ability to predict the separation performance and its capability to switch between cases B.1 and B.2, whenever a certain total feed amount is imposed per cycle.

Table 5.6: Average composition and component recoveries on both sides of the membrane, for the simulations results obtained in Figures (5.15, 5.16).

Membrane Streams	% Average Composition (v/v)		% Product Recovery
	CH_4	CO_2	
Feed	50.0	50.0	
Residue	83.3	16.7	84.8
Permeate	15.3	84.7	82.9

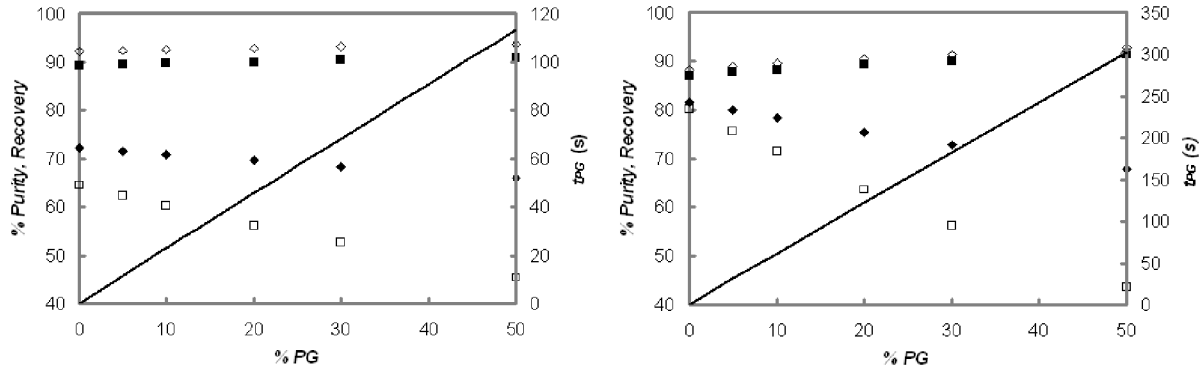


Figure 5.17: Effect of the feed purge amount variation on the performance of the integrated process, at cyclic steady state conditions (NoCycle = 51). CH_4/CO_2 50/50 % (v/v) feed mixture at 25°C , $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA,PG} = 0.025$ m/s, and total amount feed per cycle of 30.65 L STP (left) and 40.65 L STP (right). The total amount feed per cycle excludes the PG amount fed per cycle. $\square/\diamond$, CH_4/CO_2 recoveries; $\blacksquare/\blacklozenge$, CH_4/CO_2 purities. STP: 0°C , 1 atm.

A second CH_4/CO_4 mixture, with a 85/15% (v/v) composition, was studied and the integrated results were then compared with the conventional stand-alone PSA unit. The periodic hybrid cycle is composed by: Pressurization (PR_a , PR_b) / High-pressure adsorption (HPA_a , HPA_b) / Co-current blowdown (HBD or CD) / Counter-current blowdown (LBD or BD) / Purge (LPG) and Evacuation (EV). The standard operating conditions considered are described in Table (5.2). The hybrid model reached the CSS at the 51th cycle. The simulations for the CSS cycle take on average 116 seconds for a 22.1 minutes cycle time, on a Intel Pentium(r) II PC with 262 MB of RAM.

Figure (5.18) shows the transient behavior for the PSA CH_4/CO_2 85/15 % (v/v) run without a PG step, from start-up with a clean bed. On both HPA and HBD (or CD), the CO_2 concentration readjusts itself while approaching steady state. For the LBD (or BD) and EV steps, the CO_2 product concentration decreases while approaching steady state. These transient behaviors are due to the gradual build up of contamination in the bed.

Figure (5.19) shows the characteristic curve relative to the effect of the total feed per cycle variation. For the 85/15 mixture, excluding the purge step from the cycle, one obtain recoveries of CH_4 well above 90% (94.8%) with purities up to 97%. For CO_2 it is possible to obtain purities in the order of 62.7% with recoveries up to 92.2%. The higher

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Table 5.7: Simulation performance results concerning $t_{CD,BD,EV}$ and v_{PG} variation. CH₄/CO₂ 50/50 %(v/v) feed mixture at 25°C, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $v_{PR,HPA} = 0.025$ m/s, and total feed amount per cycle of 40.65 L STP, which excludes the PG amount fed per cycle.

No.	%PG	t_{CD}	t_{BD}	t_{PG}	t_{EV}	t_{cycle}	v_{PG}	N_{in}	%Purity		%Recovery		Productivity (mol/(kg h))	
		s	s	s	s	min	m/s	PG L STP	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
1	0	90	90	0.0	180	20.2	0.0000	0.000	87.16	81.56	80.06	88.17	0.137	0.151
2	30	90	90	182.0	180	23.2	0.0250	3.503	90.04	72.73	56.37	91.34	0.097	0.138
3	30	90	90	542.3	180	29.3	0.0083	3.480	88.82	72.20	56.02	90.26	0.076	0.108
4	0	90	90	0.0	90	18.6	0.0000	0.000	85.70	82.12	81.18	86.41	0.151	0.160
5	30	90	90	187.5	90	21.7	0.0250	3.609	89.60	73.18	57.00	90.77	0.105	0.147
6	30	90	90	559.6	90	28.0	0.0083	3.590	88.13	72.56	56.61	89.42	0.081	0.112
7	0	50	90	0.0	180	19.4	0.0000	0.000	87.86	81.06	79.19	89.02	0.140	0.158
8	30	50	90	183.4	180	22.5	0.0250	3.530	90.62	72.22	55.30	91.97	0.098	0.143
9	30	50	90	546.1	180	28.6	0.0083	3.504	89.31	71.64	54.89	90.83	0.076	0.111
10	0	90	50	0.0	180	19.4	0.0000	0.000	87.44	82.03	80.63	88.38	0.143	0.157
11	30	90	50	183.2	180	22.5	0.0250	3.527	90.27	72.90	56.51	91.52	0.100	0.142
12	30	90	50	545.3	180	28.6	0.0083	3.499	88.94	72.32	56.12	90.34	0.078	0.111
13	0	30	90	0.0	180	19.1	0.0000	0.000	88.27	80.31	78.02	89.60	0.141	0.162
14	30	30	90	184.3	180	22.1	0.0250	3.548	90.97	71.57	54.10	92.41	0.098	0.146
15	30	30	90	548.7	180	28.3	0.0083	3.521	89.63	70.97	53.64	91.27	0.076	0.113
16	0	90	120	0.0	180	20.7	0.0000	0.000	87.00	81.31	79.75	88.04	0.133	0.147
17	30	90	120	181.3	180	23.7	0.0250	3.491	89.89	72.63	56.29	91.22	0.095	0.135
18	30	90	120	540.8	180	29.8	0.0083	3.470	88.74	72.14	55.96	90.19	0.075	0.106

the recoveries, the smaller the purities.

The effective performance enhancement of the hybrid process, for the range of operating conditions considered, is verified when a comparison with the stand-alone PSA separation is made. For this later system, recoveries of CH₄ reach 95.3% with purities up to 91.4%, which are not very different from the ones obtained by the integration. But for CO₂, the results show that the single unit only give purities up to 41.5% with recoveries up to 87.6%. Again, the recovery/purity trade-off is maintained.

The effect of the purge amount fed to the system was then analyzed, for a fixed total feed amount admitted per cycle to the system. Figure (5.20) presents the feed purge amount variation on the performance of the integrated process at CSS. %PG is defined as the percentage of product amount produced during the HPA step that is used to purge the bed. Once again, the hybrid process is advantageous relative to the conventional

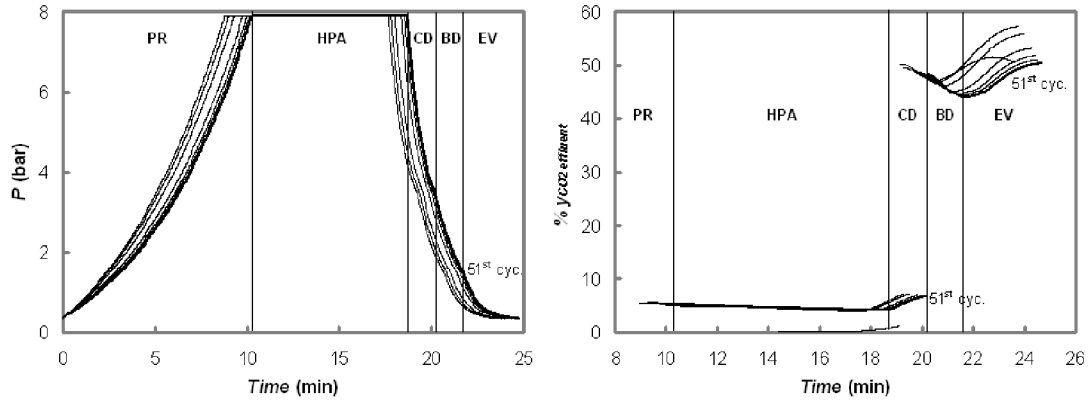


Figure 5.18: Dynamic behavior of PSA cycles for the CH_4/CO_2 85/15 % (v/v) run without a PG step, showing the pressure CO_2 effluent concentration histories in each step until CSS is reached. Feed mixture at $25^\circ C$, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA} = 0.025$ m/s, and total amount feed per cycle of 70.65 L STP.

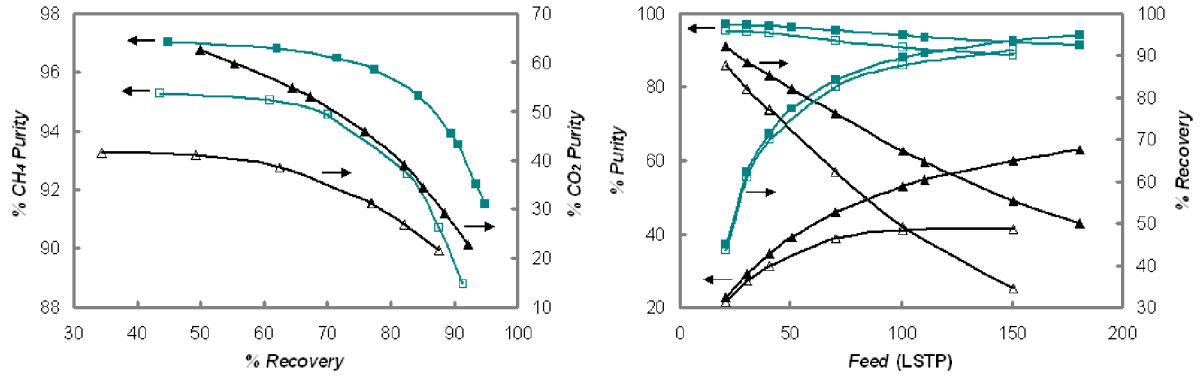


Figure 5.19: Effect of the total feed per cycle variation (right) on the performance of the integrated process, at CSS (NoCycle = 51), and respective performance characteristic curve (left). CH_4/CO_2 85/15 % (v/v) feed mixture at $25^\circ C$, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA} = 0.025$ m/s and no purge (PG) step. Symbols: filled, membrane on ($\blacksquare/\blacktriangle$, CH_4/CO_2); open, membrane off ($\square/\triangle$, CH_4/CO_2). STP: $0^\circ C$, 1 atm.

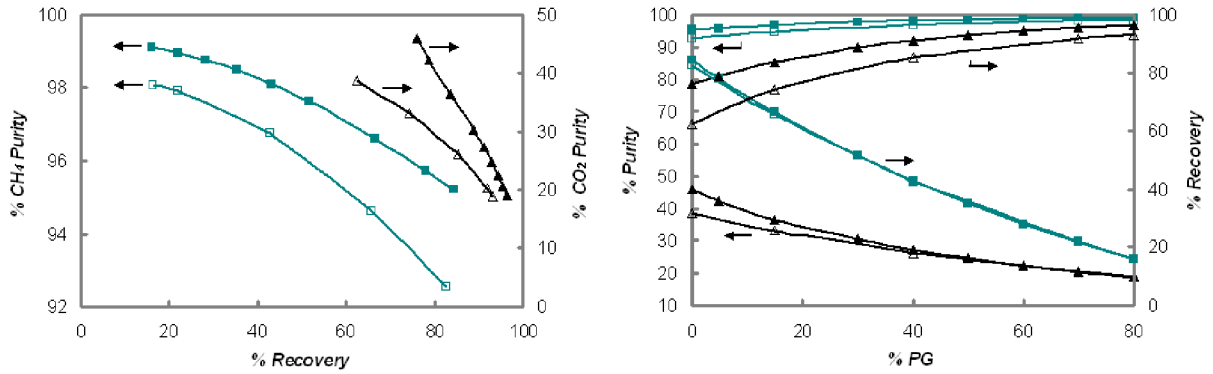


Figure 5.20: Effect of the feed purge amount variation on the performance (right) of the integrated process, at CSS (NoCycle = 51), and respective performance characteristic curve (left). CH₄/CO₂ 85/15 % (v/v) feed mixture at 25°C, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA,PG} = 0.025$ m/s, and total amount feed per cycle of 70.65 L STP. The total amount feed per cycle excludes the PG amount fed per cycle. Symbols: filled, membrane on (■/▲, CH₄/CO₂); open, membrane off (□/△, CH₄/CO₂). STP: 0°C, 1 atm.

separation system. One obtains CO₂ purities up to 45.9% and recoveries up to 96.3%, against 38.7% and 93.1% for the stand-alone PSA unit, respectively. The CH₄ product is recovered up to 84.3% at purities up to 99.1%, while in the single PSA, one get 82.5% and 98.1%, respectively.

Figure (5.21) shows the impact of both the feed amount admitted per cycle and the feed purge amount variations onto the total integrated cycle time and the CO₂ and CH₄ productivities. Increasing the %PG, the total cycle time increases and the component productivities decrease. In contrast, increasing the total feed admitted per cycle, the total cycle time increases and both component productivities increase, tending to stabilized values. In this later case, namely for CH₄, the amount of product obtained overcomes the effect of t_{cycle} increase, which by the productivity definition [Eq. (5.40)], explains the variation observed.

The inlet fluid velocity at the high-pressure adsorption step, v_{HPA} , and the residue exit gas velocity imposed in the membrane during the bed pressurization, v_{PR} were changed, in order to observe their effect on the process behavior. Figure (5.22) presents the results obtained in terms of component productivities and total cycle time evolution for two different values of total feed per cycle admitted into the hybrid system, which correspond

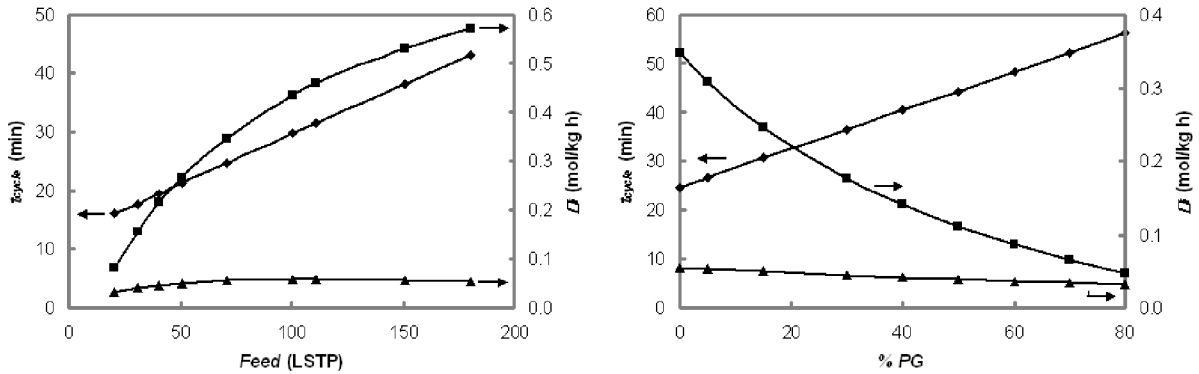


Figure 5.21: Impact of the feed amount admitted per cycle (left) and the feed purge amount (right) variations on the total integrated cycle time and the CO_2 and CH_4 productivities, at CSS (NoCycle = 51). CH_4/CO_2 85/15 % (v/v) feed mixture at $25^\circ C$, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD,BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA,PG} = 0.025$ m/s, and total amount feed per cycle of 70.65 L STP. The total amount feed per cycle excludes the PG amount fed per cycle. Symbols: $\blacklozenge$, t_{cycle} ; $\blacksquare$, η_{CH_4} ; $\blacktriangle$, η_{CO_2} . STP: $0^\circ C$, 1 atm.

to the two distinct cases (B.1 and B.2) of the integrated process developed. Increasing the gas velocities, the total cycle time decreases and the component productivities increase.

For the given range of operation, v_{PR} , v_{HPA} and v_{PG} were changed for each case in order to reach the minimum cycle time, below which there is no further increase in the productivity for the given operating conditions and total feed per cycle assumed. Figure (5.23) presents the simulation results obtained. Although the separation performance is marginally maintained at all times, for values of v_{PR} , v_{HPA} and v_{PG} higher than 0.25, 0.05 and 0.125 m/s, respectively, the productivity does not increase further. Thus, under these conditions, one has reached the minimum total cycle time that gives the maximum component productivities.

One way to understand why the concentration wavefronts on the column are improved in the MEMPSA process, is shown in Figure (5.24). Instead of a regular 85/15% (v/v) $CH_4(A)/CO_2(B)$ mixture fed to the column, a feed stream progressively enriched in the more adsorbed component is admitted to the PSA. As one can see, in the conventional situation, one has always the same feed composition during both pressurization (PR) and high-pressure adsorption (HPA) steps of the cycle. In contrast, in the hybrid concept, a CH_4 more enriched stream is fed to the bed during the PR and first stage of HPA (HPA_a)

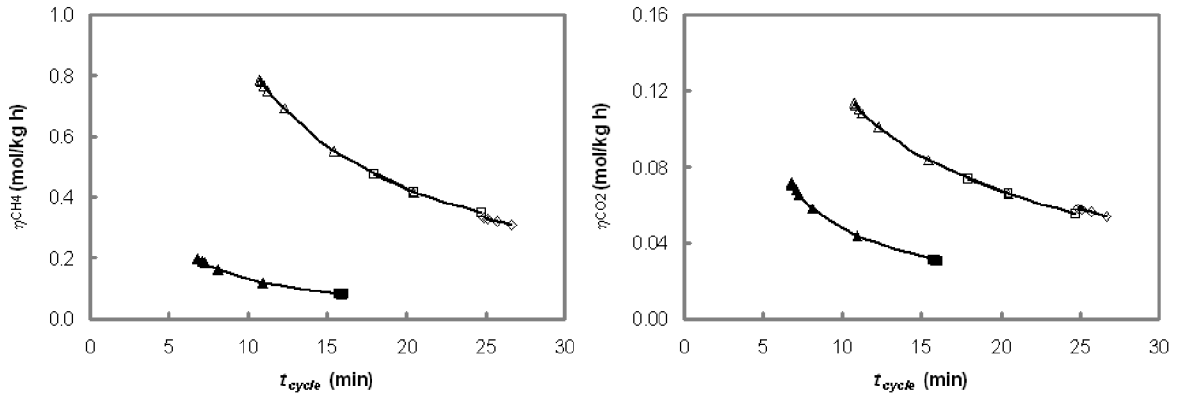


Figure 5.22: Effect of the variation of the inlet fluid velocity at the high-pressure adsorption step, v_{HPA} , and the residue exit gas velocity imposed in the membrane during the bed pressurization, v_{PR} , on component productivities and total cycle time, at CSS (NoCycle = 51). CH_4/CO_2 85/15 % (v/v) feed mixture at $25^\circ C$, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD,BD} = 90$ s, $t_{EV} = 180$ s, and total amount feed per cycle of 70.65 L STP and 20.65 L STP. When PG is included, %PG = 5%. Symbols: $\diamond$, v_{PG} variation for a feed per cycle of 70.65 L STP; $\triangle$, v_{PR} variation for a feed per cycle of 70.65 L STP; $\blacktriangle$, v_{PR} variation for a feed per cycle of 20.65 L STP; $\square$, v_{HPA} variation for a feed per cycle of 70.65 L STP; $\blacksquare$, v_{HPA} variation for a feed per cycle of 20.65 L STP. STP: $0^\circ C$, 1 atm.

steps. In this CASE B.2, the HPA_b occurs consequently with a feed stream now more enriched in CO_2 , the more adsorbed component.

Table (5.8) illustrates the average composition and component recoveries on both sides of the membrane, for the previous simulations, when the feed purge amount variation effect was analyzed. It is obtained a residue enriched in CH_4 and a permeate stream enriched in CO_2 , which will enter the PSA bed on the pressurization and adsorption steps of the integrated cycle.

Concerning the membrane operation, Figure (5.25) presents the effect of the dimensionless permeation flow parameter, F_m , on the membrane performance. Increasing the parameter F_m , which is proportional to the product of membrane area and CO_2 permeance [Eq. (5.1)], increases the recovery of the permeate enriched in CO_2 , but at a lower purity, whereas the residue stream, enriched in CH_4 , is obtained at higher purity, but at a lower recovery. This means that a trade-off between the membrane component purities

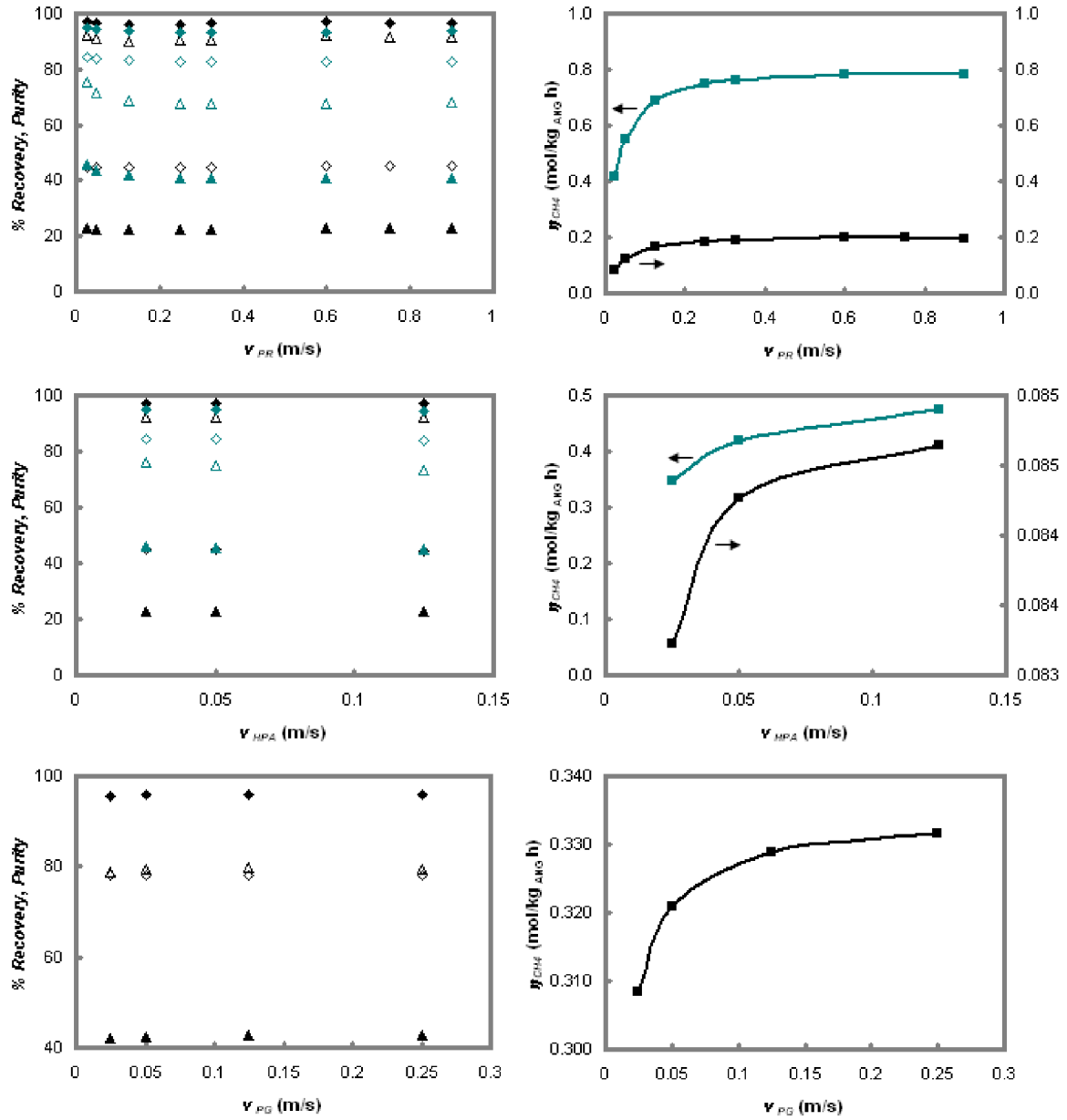


Figure 5.23: Effect of the variation of the inlet fluid velocity in the bed at the high-pressure adsorption step, v_{HPA} , the residue exit gas velocity imposed in the membrane during the bed pressurization, v_{PR} , and the inlet purge gas velocity, on component productivity, at CSS (NoCycle = 51). CH_4/CO_2 85/15 % (v/v) feed mixture at 25°C , $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA,PG} = 0.025$ m/s, and total amount feed per cycle of 70.65 L STP (green symbols) and 20.65 L STP (black symbols). When PG is included, %PG = 5%. Symbols: $\blacksquare$, CH_4 productivity, $\blacklozenge$, CH_4 Purity; $\blacklozenge$, CH_4 Recovery; $\blacktriangle$, CO_2 Purity; $\triangle$, CO_2 Recovery; variation for a total amount feed per cycle of 70.65 L STP. STP: 0°C , 1 atm.

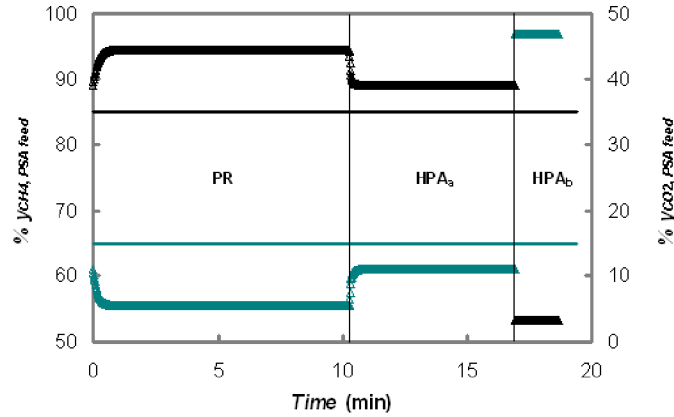


Figure 5.24: Impact of the membrane on the bed inlet composition of CO_2 (green symbols) and CH_4 (black symbols) for the hybrid system during the pressurization and adsorption steps of the cycle, at CSS (NoCycle = 51). CH_4/CO_2 85/15 % (v/v) feed mixture at 25°C , $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $F_m = 1.38$, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA} = 0.025$ m/s, no purge step, and total amount feed per cycle of 70.65 L STP. Δ , membrane on; —, membrane off. STP: 0°C , 1 atm.

dictate the feed composition of both pressurization and high-pressure adsorption steps on the integrated PSA bed.

Table (5.9) resumes the data results at CSS, described above. Table (5.10) reports the simulation performance results at CSS, concerning the $P_{H,CD,BD}$ variation. For the specified operating conditions, increasing the maximum operating pressure, P_H [runs 7-9 in Table (5.10)], induces a decrease in the cycle time and an increase in the component productivities. Increasing P_{CD} (runs 1-4), the global recovery of CO_2 increases at the expense of the CH_4 recovery and dilution of the CO_2 final product. If one includes a PG step with %PG of 30% (runs 10-12), for example, less CH_4 product is recovered, but at a

Table 5.8: Average composition and component recoveries on both sides of the membrane, for the simulations results obtained in Figure (5.20).

Membrane	% Average Composition (v/v)		% Product
Streams	CH_4	CO_2	Recovery
Feed	85.0	15.0	
Residue	90.7	9.3	90.5
Permeate	53.0	47.0	47.6

Table 5.9: Simulation conditions and data results obtained for the MEMPSA process used for the CH_4/CO_2 85/15 % (v/v) separation. Feed mixture at 25°C , $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar and $P_L = 0.34$ bar. The total amount feed per cycle excludes the PG amount fed per cycle.

No.	Feed L/STP	F _m	%PG	t _{CO} s	t _{BD} min	t _{EV} s	t _{cycle} min	V _{reg} m ³	V _{total} m ³	V _{prod} m ³	N _{LSTP}	% Global Purity		% Global Recovery		% Membrane Purity		% Membrane Recovery		Productivity (mol (kg h))	
												CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
1	20.65	1.38	0	90	90	0	180	16.0	0.025	0.000	0.00	97.05	22.77	44.80	92.20	94.43	44.07	83.88	71.96	0.083	0.030
2	36.65	1.38	0	90	90	0	180	17.7	0.025	0.000	0.00	96.63	23.19	62.15	88.40	93.10	44.80	86.12	63.85	0.156	0.039
3	46.65	1.38	0	90	90	0	180	19.5	0.025	0.000	0.00	96.47	34.51	71.47	85.16	92.08	45.53	87.93	52.15	0.215	0.045
4	56.65	1.38	0	90	90	0	180	21.2	0.025	0.000	0.00	96.07	38.98	77.33	82.05	91.48	46.09	89.08	52.99	0.268	0.050
5	70.65	1.38	0	90	90	0	180	24.7	0.025	0.000	0.00	95.20	45.98	84.25	75.94	90.79	46.92	90.41	46.05	0.348	0.055
6	100.65	1.38	0	90	90	0	180	29.8	0.025	0.000	0.00	93.92	53.02	88.50	67.18	90.28	47.71	91.45	44.21	0.436	0.058
7	110.65	1.38	0	90	90	0	180	31.5	0.025	0.000	0.00	93.53	54.74	90.59	64.50	90.17	47.91	91.68	43.37	0.459	0.058
8	150.65	1.38	0	90	90	0	180	36.2	0.025	0.000	0.00	92.22	59.84	93.45	55.29	88.88	48.48	92.29	41.11	0.531	0.055
9	180.65	1.38	0	90	90	0	180	43.2	0.025	0.000	0.00	91.48	62.69	94.75	49.99	89.74	48.78	92.58	40.05	0.571	0.053
10	70.65	1.38	80	90	90	31.9	180	56.1	0.025	0.025	36.80	99.10	19.01	15.05	96.27	90.68	47.08	90.63	47.22	0.047	0.032
11	70.65	1.38	70	90	90	27.9	180	52.2	0.025	0.025	32.18	98.95	20.61	21.81	95.43	90.69	47.06	90.61	47.29	0.065	0.034
12	70.65	1.38	60	90	90	23.9	180	48.2	0.025	0.025	27.57	98.75	22.47	28.14	94.34	90.70	47.05	90.59	47.37	0.086	0.036
13	70.65	1.38	50	90	90	19.9	180	44.3	0.025	0.025	22.96	98.47	24.66	35.13	92.94	90.71	47.03	90.57	47.47	0.111	0.039
14	70.65	1.38	40	90	90	15.9	180	40.4	0.025	0.025	19.37	98.10	27.25	42.88	91.10	90.73	47.01	90.54	47.57	0.141	0.042
15	70.65	1.38	30	90	90	11.9	180	36.4	0.025	0.025	13.78	97.62	30.36	51.50	88.69	90.74	46.99	90.50	47.69	0.176	0.045
16	70.65	1.38	15	90	90	6.0	180	30.6	0.025	0.025	6.90	96.61	36.47	68.39	83.53	90.77	46.95	90.45	47.89	0.246	0.050
17	70.65	1.38	5	90	90	2.0	180	26.7	0.025	0.000	2.31	95.70	42.16	77.89	76.74	90.79	46.92	90.42	48.02	0.308	0.054
18	70.65	2.76	0	90	90	0	180	14.3	0.050	0.000	0.00	95.55	45.18	83.30	78.01	90.76	46.96	90.47	47.81	0.594	0.098
19	70.65	2.76	0	90	90	0	180	14.6	0.050	0.000	0.00	95.42	45.63	83.77	77.20	90.77	46.96	90.46	47.84	0.593	0.095
20	70.65	2.76	0	120	90	0	180	15.8	0.050	0.000	0.00	95.06	45.92	84.38	75.15	90.78	46.94	90.44	47.94	0.543	0.085
21	70.65	2.76	0	90	90	0	180	14.3	0.050	0.000	0.00	95.39	46.57	84.43	76.87	90.76	46.96	90.47	47.81	0.602	0.097
22	70.65	2.76	0	90	90	0	180	14.6	0.050	0.000	0.00	95.33	46.34	84.35	76.58	90.77	46.96	90.46	47.65	0.587	0.094
23	70.65	2.76	0	90	120	0	180	15.8	0.050	0.000	0.00	95.10	45.64	84.14	75.45	90.78	46.94	90.44	47.93	0.542	0.086
24	70.65	2.76	0	90	90	0	90	13.8	0.050	0.000	0.00	94.99	46.23	84.67	74.68	90.74	46.99	90.51	47.69	0.627	0.098
25	70.65	2.76	30	90	90	6.0	180	20.1	0.050	0.050	13.81	98.37	30.51	50.67	92.34	90.70	47.05	90.59	47.37	0.314	0.084
26	70.65	2.76	30	90	90	6.0	180	21.7	0.050	0.050	13.78	98.11	30.86	51.70	91.05	90.72	47.02	90.56	47.50	0.298	0.077
27	70.65	2.76	30	90	90	6.0	180	20.2	0.050	0.050	13.81	98.29	31.05	51.59	91.89	90.70	47.04	90.59	47.39	0.320	0.084
28	70.65	2.76	30	90	90	6.0	180	21.7	0.050	0.050	13.85	98.13	30.84	51.50	91.16	90.72	47.02	90.56	47.49	0.297	0.077
29	70.65	2.76	30	90	90	6.0	90	19.6	0.050	0.050	13.88	98.27	31.15	51.72	91.76	90.69	47.07	90.61	47.28	0.329	0.086
30	70.65	1.38	0	90	90	0	180	20.5	0.025	0.050	0.00	95.05	45.59	84.17	75.14	89.47	46.54	92.19	38.55	0.419	0.066
31	70.65	1.38	0	90	90	0	180	18.0	0.025	0.125	0.00	94.72	44.72	83.98	73.45	88.55	45.53	93.33	31.60	0.476	0.073
32	20.65	1.38	0	90	90	0	180	15.8	0.025	0.050	0.00	97.06	22.77	44.79	92.24	94.43	44.07	83.88	71.96	0.084	0.031
33	20.65	1.38	0	90	90	0	180	15.7	0.025	0.125	0.00	97.03	22.72	44.68	92.16	94.43	44.07	83.86	71.96	0.085	0.031
34	70.65	1.38	5	90	90	1.0	180	25.7	0.025	0.050	2.31	95.84	42.46	77.97	79.40	90.78	46.93	90.42	47.99	0.321	0.056
35	70.65	1.38	5	90	90	0.4	180	25.1	0.025	0.125	2.31	95.89	42.60	79.01	79.67	90.78	46.93	90.43	47.97	0.329	0.058
36	70.65	1.38	5	90	90	0.2	180	24.8	0.025	0.250	2.31	95.88	42.59	78.02	79.60	90.78	46.93	90.43	47.96	0.332	0.058
37	20.65	1.38	0	90	90	0	180	10.9	0.050	0.000	0.00	96.98	22.46	44.66	90.89	90.92	46.70	90.99	46.46	0.122	0.044
38	20.65	1.38	0	90	90	0	180	8.1	0.125	0.000	0.00	96.27	22.33	44.69	90.10	87.71	52.14	96.17	23.67	0.164	0.058
39	20.65	1.38	0	90	90	0	180	7.2	0.250	0.000	0.00	96.36	22.40	44.77	90.34	86.59	53.19	97.79	14.20	0.185	0.066
40	20.65	1.38	0	90	90	0	180	7.0	0.325	0.000	0.00	96.46	22.47	44.82	90.59	86.35	53.34	98.13	12.14	0.190	0.068
41	20.65	1.38	0	90	90	0	180	6.8	0.600	0.000	0.00	97.04	22.68	45.17	92.15	85.99	53.16	98.61	8.94	0.199	0.072
42	20.65	1.38	0	90	90	0	180	6.8	0.750	0.000	0.00	96.92	22.79	45.08	91.82	86.00	53.23	98.59	9.08	0.198	0.071
43	20.65	1.38	0	90	90	0	180	6.8	0.900	0.000	0.00	96.78	22.69	44.99	91.44	86.05	53.31	98.54	9.48	0.197	0.071
44	70.65	1.38	0	90	90	0	180	20.5	0.025	0.000	0.00	95.05	45.59	84.17	75.14	89.47	46.54	92.19	38.55	0.419	0.066
45	70.65	1.38	0	90	90	0	180	15.4	0.050	0.000	0.00	94.38	43.67	83.66	71.78	88.34	50.41	94.97	29.99	0.552	0.084
46	70.65	1.38	0	90	90	0	180	12.3	0.125	0.000	0.00	93.75	41.74	83.10	68.60	87.37	52.46	96.67	20.82	0.680	0.100
47	70.65	1.38	0	90	90	0	180	11.3	0.250	0.000	0.00	93.53	40.95	82.81	67.55	87.00	52.80	97.21	17.66	0.749	0.108
48	70.65	1.38	0	90	90	0	180	11.0	0.325	0.000	0.00	93.50	40.80	82.73	67.43	86.91	52.82	97.32	16.97	0.763	0.110
49	70.65	1.38	0	90	90	0	180	10.8	0.600	0.000	0.00	93.53	40.72	82.63	67.58	86.81	52.78	97.47	16.06	0.781	0.113
50	70.65	1.38	0	90	90	0	180	10.7	0.900	0.000	0.00	93.60	40.84	82.63	67.96	86.78	52.75	97.50	15.84	0.785	0.114
51	70.65	2.76	0	90	90	0	180	15.3	0.050	0.000	0.00	95.20	45.93	84.22	75.94	90.77	46.95	90.45	47.90	0.560	0.089
52	20.65	2.76	0	90	90	0	180	10.9	0.050	0.000	0.00	97.03	22.82	45.01	92.14	94.43	44.07	83.88	71.96	0.122	0.044
53	70.65	0.69	0	90	90	0	180	15.5	0.050	0.00											

Table 5.10: Simulation conditions and data results, concerning the $P_{H,CD,BD}$ variation, obtained for the MEMPSA process used for the CH_4/CO_2 85/15 % (v/v) separation. Feed mixture at 25°C , $P_L = 0.34$ bar, $F_m = 2.76$, $v_{PR,HPA,PG} = 0.025$ m/s, and total amount feed per cycle of 70.65 L STP. The total amount feed per cycle excludes the PG amount fed per cycle.

No.	P_H bar	P_{CO} bar	P_{80} bar	% PG	t_{CD} s	t_{EO} s	t_{EG} min	t_{EV} s	t_{cycle} min	$N_{in,PG}$ L STP	% Global Purity CH_4	% Global Purity CO_2	% Global Recovery CH_4	% Global Recovery CO_2	% Membrane Purity CH_4	% Membrane Purity CO_2	% Membrane Recovery CH_4	% Membrane Recovery CO_2	Productivity CH_4 (mol/kg h)	Productivity CO_2 (mol/kg h)
1	7.9	2.5	1.5	0	90	90	0.0	180	15.3	0.00	94.57	50.77	87.78	71.42	90.78	46.94	90.43	47.95	0.584	0.084
2	7.9	3.5	1.5	0	90	90	0.0	180	15.3	0.00	95.20	45.93	84.22	75.94	90.77	46.95	90.45	47.90	0.560	0.069
3	7.9	4.5	1.5	0	90	90	0.0	180	15.3	0.00	95.57	42.51	81.23	78.67	90.77	46.95	90.46	47.87	0.541	0.062
4	7.9	5.5	1.5	0	90	90	0.0	180	15.3	0.00	95.81	39.94	78.63	80.52	90.76	46.96	90.46	47.84	0.524	0.065
5	7.9	3.5	1.0	0	90	90	0.0	180	15.2	0.00	95.76	47.47	84.62	78.78	92.59	51.11	90.01	59.16	0.566	0.093
6	7.9	3.5	2.0	0	90	90	0.0	180	15.4	0.00	94.63	44.40	83.86	73.04	89.26	42.53	90.94	37.99	0.556	0.085
7	6.9	3.5	1.5	0	90	90	0.0	180	15.4	0.00	94.52	44.66	84.18	72.33	89.95	45.19	90.91	42.45	0.523	0.079
8	9.9	3.5	1.5	0	90	90	0.0	180	13.7	0.00	96.05	47.26	84.17	80.38	92.09	49.12	89.70	56.33	0.624	0.105
9	11.9	3.5	1.5	0	90	90	0.0	180	12.7	0.00	96.53	47.79	84.02	82.86	93.08	50.30	89.11	62.43	0.676	0.118
10	7.9	2.5	1.5	30	90	90	6.0	180	21.2	13.79	97.81	32.73	54.52	89.31	90.72	47.02	90.55	47.52	0.321	0.078
11	7.9	3.5	1.5	30	90	90	6.0	180	21.2	14.20	98.19	30.91	51.53	91.42	90.71	47.03	90.57	47.46	0.304	0.079
12	7.9	5.5	1.5	30	90	90	6.0	180	21.1	13.79	98.55	29.32	46.87	93.48	90.70	47.04	90.59	47.39	0.277	0.081
13	7.9	3.5	1.0	30	90	90	9.0	180	24.1	13.84	98.88	31.70	51.73	94.63	92.51	51.27	90.17	58.60	0.269	0.072
14	7.9	3.5	2.0	30	90	90	4.5	180	19.8	13.76	97.45	30.09	51.34	87.96	89.22	42.57	91.03	37.67	0.324	0.083
15	6.9	3.5	1.5	30	90	90	6.1	180	22.4	14.20	97.76	30.23	50.81	89.34	89.90	45.25	91.02	42.06	0.284	0.074
16	9.9	3.5	1.5	30	90	90	5.7	180	19.3	13.10	98.67	31.65	52.73	93.76	92.02	49.23	89.84	55.83	0.398	0.089
17	11.9	3.5	1.5	30	90	90	5.4	180	18.0	12.52	98.91	32.49	53.72	94.95	93.00	50.43	89.26	61.92	0.367	0.086

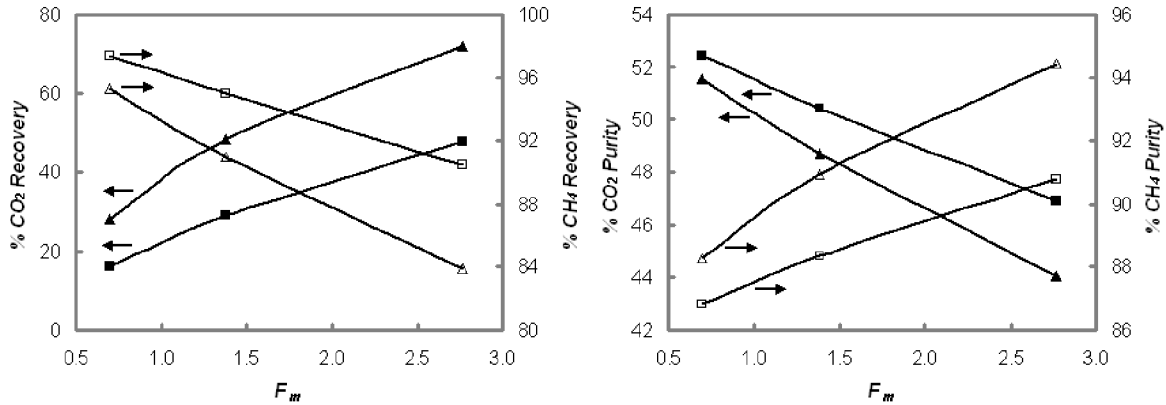


Figure 5.25: Effect of the dimensionless permeation flow parameter, F_m , on the membrane performance (left, recovery; right, purity), at CSS (NoCycle = 51). CH₄/CO₂ 85/15 %(v/v) feed mixture at 25°C, $P_H = 7.9$ bar, $P_{CD} = 3.5$ bar, $P_{BD} = 1.5$ bar, $P_L = 0.34$ bar, $t_{CD} = t_{BD} = 90$ s, $t_{EV} = 180$ s, $v_{PR,HPA} = 0.025$ m/s, no purge step, and total amount feed per cycle of 70.65 L STP and 20.65 L STP. CO₂: ■/▲, 70.65/20.65 L STP; CH₄: □/△, 70.65/20.65 L STP. STP: 0°C, 1 atm.

higher purity, and the CO₂ global recovery is increased with product dilution. Increasing P_{BD} (runs 2, 5, 6) the global recovery of CO₂ decreases with no significant variation of the rest of the performance definitions. Once again, the inclusion of 30% PG on a PG step (runs 11, 13, 14), for these conditions, improves both CH₄ purity and CO₂ recovery, but CH₄ recovery drops due the use of part of this product as purge. CO₂ purity is diluted.

5.1.4.2 MEMPSA – CASE A

Case Study: H₂/CH₄ Separation

MEMPSA – CASE A was compared with the conventional stand-alone PSA cycle similar to the one cited by [Yang and Doong \(1985\)](#), since the first single-PSA mathematical model coded in gPROMS was firstly validated with the work of these authors. A brief discussion concerning the main conclusions of [Yang and Doong \(1985\)](#) work and the preliminary validation results of our stand-alone PSA model is presented prior to the simulation results obtained for the MEMPSA – CASE A.

Bulk separation, where all components are wanted, was studied by [Yang and Doong \(1985\)](#), both experimentally and theoretically for a 50/50% H₂/CH₄ in activated car-

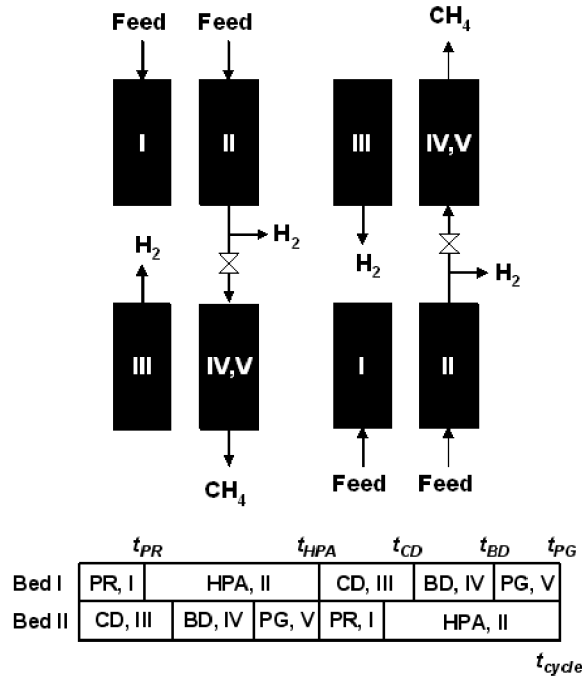


Figure 5.26: Schematic steps of a two-bed PSA process reported by Yang and Doong (1985).

bon. The theoretical model applied a pore diffusion resistance, non-isothermality and adsorption of all components. Five steps are considered in the PSA cycle:

1. Pressurization (PR)
2. High Pressure Adsorption (HPA)
3. Cocurrent Blowdown (CD)
4. Countercurrent Blowdown (BD)
5. Purge (PG)

The weakly adsorbed component, H_2 is collected during HPA (II) and CD (III) steps, and the strongly adsorbed species, CH_4 , is produced in BD (IV) and PG (V) steps. Two or more interconnected beds are operated in phase, so continuous feed and products are possible. Figure (5.26) illustrates the schematic diagram of the cycle steps in a two-bed PSA process.

In the PR step, the bed is pressurized up to the feed pressure by the feed mixture (or by the blowdown gases, which are enriched in the weakly adsorbed components). In the HPA step, the feed flows through the bed at high pressure while H_2 product is produced

Table 5.11: Cocurrent depressurization effect on a steady state PSA separation of a 50/50 H₂/CH₄ mixture, with several CD end pressures, P_m [Yang and Doong (1985)]. The total feed amount per cycle is the sum of the total amount entered per cycle in both steps I and II, at cyclic steady state operation and considering the pressurization with feed. The CD step time was fixed at 90 s.

		Experimental			Theoretical		
		E	F	G	E	F	G
CD pressure, P_m (bar)		16.86	12.72	10.31	16.86	12.72	10.31
F/F		0.085	0.090	0.096	0.085	0.090	0.096
Step II	Avg. effluent % H ₂	98.5	98.2	98.5	98.9	98.8	98.7
	Total amount (L STP)	8.8	8.7	8.8	7.97	7.93	7.90
Step III	Avg. effluent % H ₂	95.5	92.8	84.0	97.0	95.6	93.1
	Total amount (L STP)	11.7	14.8	16.0	11.0	13.6	15.4
Step IV, V	Avg. effluent % CH ₄	79.2	89.6	89.5	78.6	84.5	87.8
	Total amount (L STP)	29.7	26.8	24.1	29.6	26.8	25.0
Total Feed amount per cycle (L STP)		49.5	49.6	48.2	47.8	47.7	47.4
% H ₂ Recovery		75.6	88.5	89.4	74.6	84.2	89.4
% CH ₄ Recovery		97.2	95.1	88.9	97.4	94.9	92.1

as effluent that is used to purge a second bed at a reduced pressure. The CD step recovers the H₂ remained in the sorbent voids and allows time to desorb and diffuse CH₄ out of the porous particles in the column. This additional time is important for the subsequent recovery of CH₄. The CD step stops at an intermediate pressure and depends on the bed fraction covered by the CH₄ wavefront.

The product purity of the strongly adsorbed component depends on the use of the CD step. The cocurrent blowdown elutes the weakly adsorbed species out of the composition wavefront, increasing the loading of the strongly adsorbed component into the bed. This is possible because the bed not utilized in HPA step is used to adsorb CH₄, and much less H₂, during the CD stage. The effect of the cocurrent depressurization is illustrated in Figure (5.27) and Table (5.11), where only the pressure at the end of this step is changed, maintaining the other system conditions. The CH₄ product concentration and the H₂ product recovery are significantly increased with P_m decrease during the CD stage. Nonetheless, the excessive lowering of P_m will induce the CH₄ breakthrough and consequently degradation of both H₂ purity and CH₄ recovery. Hence, Yang and Doong (1985) reported an optimal P_m value of 12.72 bar, corresponding to run F. This same run was then chosen for validation of the PSA model built in gPROMS.

In order to produce the CH₄ product and to clean the bed for the next cycle, the

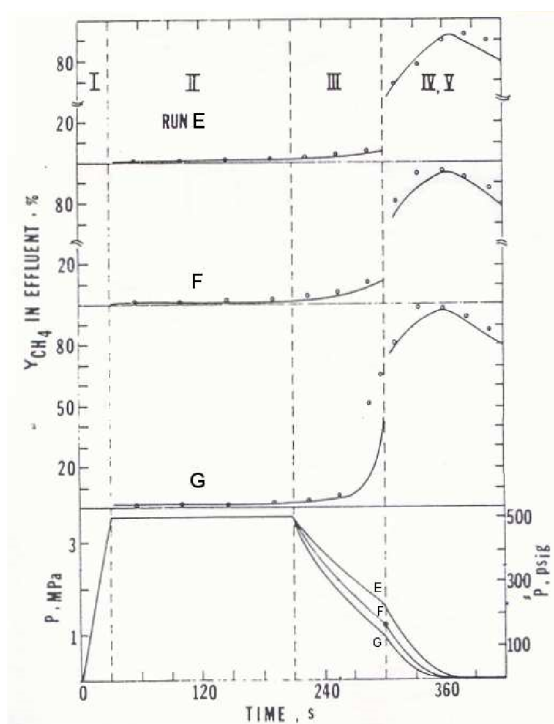


Figure 5.27: Effluent CH_4 composition and pressure histories in steady state PSA for several runs where P_m is changed. Symbols denote experimental data and lines are generated by the model [Yang and Doong (1985)].

BD and PG steps are performed countercurrently to the feed stream direction. The PG step performed with the light component is critical for the product purity of this specie. It cleans the column regenerating the sorbent for the next cycle, which consequently increases the H_2 product purity and even its recovery. It also strips the adsorbed CH_4 out of the bed and hence enriches both methane product purity and recovery. The purge effect is clearly illustrated in Figure (5.28) and Table (5.12). The optimal range of the P/F ratio found was 0.06-0.08, since a further increase will lower the H_2 recovery and dilute the CH_4 product.

Special attention was taken by Yang and Doong (1985) concerning the feed rate effect, analyzed in terms of the fraction of bed covered by the wavefront in HPA step. The higher the feed rate, i.e., the longer the bed coverage in HPA, the lower are both H_2 and CH_4 product purities, as seen in Table (5.13). This can be explained from the small fraction of bed left available for CD step. Consequently, little methane is desorbed and its concentration in bulk phase is not much enhanced, hence affecting the process performance.

Table 5.12: Purge to Feed ratio (P/F) effect on a steady state PSA separation of a 50/50 H_2/CH_4 mixture [Yang and Doong (1985)]. The total feed amount per cycle is the sum of the total amount entered per cycle in both steps I and II, at cyclic steady state operation and considering the pressurization with feed.

		Experimental				Theoretical			
		A	B	C	D	A	B	C	D
F/F		0.0	0.049	0.066	0.085	0.0	0.049	0.066	0.085
Step	Avg. effluent % H_2	9.2	93.7	97.4	98.1	89.7	97.4	98.3	99.0
II	Total amount (L STP)	12.2	13.2	13.8	14.3	11.0	11.9	12.5	13.1
Step	Avg. effluent % H_2	88.0	88.8	92.6	91.7	86.9	93.6	95.3	96.8
III	Total amount (L STP)	5.0	6.0	6.1	6.6	5.9	5.6	5.5	5.4
Step	Avg. effluent % CH_4	80.5	81.5	80.4	81.9	80.6	80.5	80.5	80.4
IV, V	Total amount (L STP)	23.1	23.9	25.6	25.4	22.4	24.7	25.5	26.4
Total Feed amount per cycle (L STP)		40.3	42.5	44.6	45.1	39.4	41.6	42.7	43.8
% H_2 Recovery		77.5	79.3	78.3	80.4	76.1	77.7	77.9	77.5
% CH_4 Recovery		92.0	92.6	96.2	96.2	91.8	95.5	96.2	96.8

Table 5.13: Flow rate effect on a steady state PSA separation of a 50/50 H_2/CH_4 mixture [Yang and Doong (1985)]. The total feed amount per cycle is the sum of the total amount entered per cycle in both steps I and II, at cyclic steady state operation and considering the pressurization with feed. The feed pressure, P_H , considered is 21.67 bar and the results are given for the same time length of feed.

		Experimental			Theoretical		
		H	I	J	H	I	J
CD pressure, P_m (bar)		5.83	9.62	13.41	5.83	9.62	13.41
F/F		0.110	0.110	0.056	0.110	0.110	0.056
Avg. Prod. in II (L/min)		1.61	4.7	7.1	1.61	4.7	7.1
Step	Avg. effluent % H_2	98.4	98.4	93.5	97.6	98.6	96.5
II	Total amount (L STP)	4.8	13.9	21.4	4.6	8.2	19.0
Step	Avg. effluent % H_2	91.9	90.3	51.9	91.3	94.0	67.1
III	Total amount (L STP)	10.7	7.8	6.1	10.8	7.6	5.9
Step	Avg. effluent % CH_4	94.8	83.2	80.2	88.4	84.9	83.2
IV, V	Total amount (L STP)	15.1	26.3	27.6	16.6	22.7	28.7
Total Feed amount per cycle (L STP)		30.1	46.4	54.0	31.2	43.9	52.5
% H_2 Recovery		94.6	83.3	80.0	89.0	87.5	81.5
% CH_4 Recovery		93.8	94.4	83.6	94.1	87.7	90.0

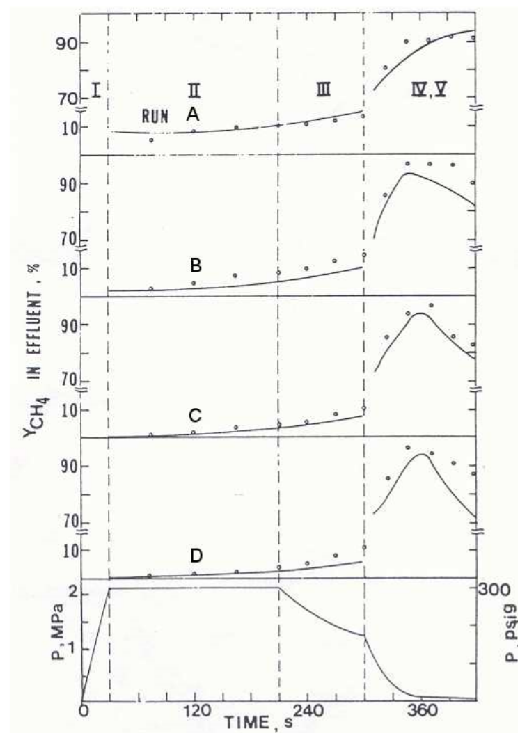


Figure 5.28: Effluent CH_4 composition and pressure histories in steady state PSA for several runs where the P/F ratio is changed. Symbols denote experimental data and lines are generated by the model [Yang and Doong (1985)].

Decreasing the feed pressure P_H to 7.9 bar for the same set of runs as in Table (5.13), allows the P/F ratio to have a diluting effect on the CH_4 product purity, since the amount of CH_4 adsorbed in HPA is smaller [Table (5.14)]. Thus, a higher bed coverage yields a higher CH_4 product concentration. If no PG step was considered, the CH_4 purity would be higher in the run with the lower bed coverage, i.e., the lower flow rate during HPA.

Yang and Doong (1985) also concluded that the pressurization by this light component enhances its product purity, instead of the regular feed mixture. In the PR step, H_2 was introduced countercurrently to the HPA step direction. Through this procedure, commonly used in industry for H_2 purification, the composition wavefronts in the bed are sharpened. For the HPA step (II), sharpening the diffuse wavefront will promote a better separation for both products. However, the complexity of the process increases, since H_2 used in the PR step is obtained from the H_2 products of the process (HPA and CD exit streams). Also the throughput or productivity is lowered, since part of H_2 product is recycled in the process. This last concept was of extreme importance in the hybrid systems development.

The theoretical model for the stand-alone PSA follows the same governing equations

Table 5.14: Flow rate effect on a steady state PSA separation of a 50/50 H₂/CH₄ mixture [Yang and Doong (1985)]. The total feed amount per cycle is the sum of the total amount entered per cycle in both steps I and II, at cyclic steady state operation and considering the pressurization with feed. The feed pressure, P_H , considered is 7.9 bar.

		Experimental			Theoretical		
		K	I	L	K	I	L
Avg. Prod. in II (L/min)		1.60	2.80	3.60	1.60	2.80	3.60
F/F		0.190	0.130	0.110	0.190	0.130	0.110
Step	Avg. effluent % H₂	97.8	96.4	92.6	97.1	96.2	95.5
II	Total amount (L STP)	4.4	8.3	10.7	4.4	7.7	10.0
Step	Avg. effluent % H₂	91.1	86.6	71.0	88.4	84.7	72.2
III	Total amount (L STP)	4.0	3.9	3.6	3.9	4.0	4.3
Step	Avg. effluent % CH₄	85.1	88.7	91.1	84.6	88.5	90.3
IV, V	Total amount (L STP)	8.71	11.20	12.70	8.80	11.00	11.40
Total Feed amount per cycle (L STP)		16.4	22.3	25.7	16.4	21.8	25.0
% H₂ Recovery		84.7	89.0	90.1	84.2	89.2	92.2
% CH₄ Recovery		94.1	92.4	86.6	90.2	89.6	82.5

as those already described for the hybrid MEMPSA – CASE A. However, the boundary conditions (BCs) considered here were quite more simpler, since there were no membrane and intermediate tank coupled to the system. Hence, the set of inlet ($z = 0$)/outlet ($z = L$) BCs were described as follows

- Pressurization step (PR)

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = \frac{P_H - P}{t_{PR}} & \text{for pressure dynamics,} \\ T_0 = T_f, \quad y_0 = y_f & \text{for } z = 0, \\ v_L = 0, & \text{for } z = L, \\ \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L, \end{array} \right. \quad (5.89)$$

with t_{PR} the pressurization step time, P_H the maximum system pressure, and subscripts f relative to the regular feed inlet conditions, and $i = 1, \dots$, NoC components.

- High pressure adsorption step (HPA)

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = \gamma(P - P_H) & \text{for pressure dynamics,} \\ T_0 = T_f, \quad y_0 = y_f & \text{for } z = 0, \\ v_L = v_{HPA}, & \text{for } z = L, \\ \frac{\partial^2 T}{\partial z^2} = 0, \quad \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{for } z = L, \end{array} \right. \quad (5.90)$$

where γ is a constant assumed equal to 0.152. From this step, the purge composition of the inlet stream to be used in the PG stage, y_{PG} , is obtained.

- Cocurrent blowdown step (CD)

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = -\alpha_1(P - \alpha_2), & \text{with } \alpha_2 = \frac{P_m - P \exp(-\alpha_1 t_{CD})}{1 - \exp(-\alpha_1 t_{CD})}, \\ v_0 = 0, \quad \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = 0, \\ \frac{\partial^2 T}{\partial z^2} = 0, \quad \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{for } z = L, \end{array} \right. \quad (5.91)$$

with $\alpha_1 = 0.01$, t_{CD} the cocurrent step time, and P_m the intermediate blowdown pressure reached at the end of the CD step.

- Countercurrent blowdown step (BD)

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = -\beta_1(P - \beta_2), & \text{with } \beta_2 = \frac{P_L - P \exp(-\beta_1 t_{BD})}{1 - \exp(-\beta_1 t_{BD})}, \\ \frac{\partial^2 T}{\partial z^2} = 0, \quad \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{for } z = 0, \\ v_L = 0, \quad \frac{\partial T}{\partial z} = 0, \quad \frac{\partial y_i}{\partial z} = 0 & \text{for } z = L, \end{array} \right. \quad (5.92)$$

where $\beta_1 = 0.05$, t_{BD} is the countercurrent step time, and P_L is the minimum system pressure.

- Purge step (PG)

$$\left\{ \begin{array}{ll} \frac{\partial P}{\partial t} = 0 & \text{for pressure dynamics,} \\ \frac{\partial^2 T}{\partial z^2} = 0, \quad \frac{\partial^2 y_i}{\partial z^2} = 0 & \text{for } z = 0, \\ v_L = -v_{PG}, & \text{for } z = L, \\ T_L = T_f, \quad y_L = y_{PG}, & \text{for } z = L, \end{array} \right. \quad (5.93)$$

with v_{PG} the inlet purge gas velocity during the purge step time t_{PG} , obtained from a specified purge to feed ratio, P/F .

At time zero, the sorbent column is clean of any adsorbed species in the solid phase. The process starts with sorbent at equilibrium with the gas phase. The following initial conditions at $t = 0, \forall z$ were assumed

$$P = P_L, \quad \text{for starting bed pressure,} \quad (5.94)$$

$$T = T_w = T_f, \quad \text{for starting bed temperature,} \quad (5.95)$$

$$\frac{\partial q_i}{\partial t} = 0, \quad (5.96)$$

Table 5.15: Adsorption bed characteristics [Yang and Doong (1985)] and system properties used in the simulations.

Physical properties	
Bed inside radius, R_b (cm)	2.05
Bed length, L (cm)	60.0
Particle size, R_p (cm)	0.028
Bulk density, ρ_b (g/cm ³)	0.498
Particle density, ρ_p (g/cm ³)	0.850
Bed porosity, ε_b	0.43
Intraparticle void fraction, ε_p	0.61
Total voidage, ε	0.78
Heat capacity of carbon, C_{ps} (cal/g/°C)	0.250
Heat capacity of wall, C_{pw} (cal/g/°C)	0.110
Avg. heat capacity of gas mix., C_{pg} (cal/mol/°C)	7.647
System properties	
Feed temperature, T_f (K)	293.15
Feed pressure, P_H (bar)	35.45
Blowdown pressure, P_m (bar)	12.72
Low pressure purge, P_L (bar)	1.21
Feed molar fractions, y_{if} (%)	
CH_4 (1)	50
H_2 (2)	50
Heat of adsorption, $-Q_i$ (kcal/mol)	
CH_4 (1)	5.00
H_2 (2)	2.88
Total feed amount per cycle, $Feed$ (L STP)	47.7
Purge to Feed ratio, P/F	0.09
Step time (s)	
t_{PR}	30
t_{HPA}	180
t_{CD}	90
t_{BD}	90
t_{PG}	30
t_{cycle} (min)	7
Wall thickness, e_w (m)	0.001
Particle tortuosity, τ	10
Avg. effective diffusivity, D_e (m ² /s)	2E-08
Thermal dispersion parameter, D_{∞} (J/m/s/°C)	0.106
Molecular diffusivity, $P D_m \approx P D_{H_2-CH_4 (288K)}$ (m ² bar/s)	6.85E-05
Wall heat transfer coefficient, h_w (cal/m ² /°C/s)	30
Wall conductivity, k_w (W/m/K)	43.3
Wall density, ρ_w (g/cm ³)	8.22

Table 5.16: Comparison between the PSA modeling results obtained for Run F and the experimental and theoretical data from Yang and Doong (1985). Steady state separation of 50/50% H₂/CH₄ mixture.

RUN		Experimental Yang's work	Theoretical Yang's work	Predicted
F				
CD pressure, P_m (bar)		12.72	12.72	12.72
P/F		0.090	0.090	0.090
Step	Avg. CH ₄ in %	50.0	50.0	50.0
I	Total amount (L STP)			38.6
Step	Avg. CH ₄ in %			50.0
II	Total amount (L STP)			8.84
	Avg. H ₂ out %	98.2	98.8	96.8
	Total amount (L STP)	8.7	7.93	5.25
Step	Avg. H ₂ out %	92.8	95.6	94.8
III	Total amount (L STP)	14.8	13.6	15.0
Step	Avg. CH ₄ out %	89.6	84.5	85.8
IV, V	Total amount (L STP)	26.8	26.8	27.5
	Total purge amount in (L STP)	0.7	0.6	0.4
Total Feed per cycle (LSTP) ^a		49.6	47.7	47.4
% H ₂ Purity		94.7	96.7	95.3
% CH ₄ Purity		89.6	84.5	85.8
% H ₂ Recovery		88.5	84.2	79.9
% CH ₄ Recovery		95.1	94.9	99.6

^a The total feed amount per cycle is the sum of the total amount entered per cycle in both steps I and II at CSS
STP (0°C, 1 atm)

$$N_0 = N_L = 0, \quad (5.97)$$

$$y_1 = y_{p,1} = 1 \times 10^{-4}, \quad (5.98)$$

with (1, 2) subscripts representing the strongly and weakly adsorbed components, respectively. The cyclic steady state was generally reached after 10 cycles.

Simulation results obtained for the stand-alone PSA are fairly in accordance with both the experimental and theoretical data reported by Yang and Doong (1985). Table (5.15) presents the adsorption bed characteristics and system properties used in the simulations. Table (5.16) shows the model results for run F at steady state conditions, which are accomplished approximately after the 10th cycle.

The concentration profiles in the bed, generated by the model, for CH₄ in the gas phase and in the sorbent pores, are presented in Figure (5.29). They report the predicted composition at the end of each step in a steady state PSA cycle. The differences between the CH₄ concentrations in the gas phase and inside the pores are smaller which indicate that the operation was nearly at equilibrium. Similar results were obtained by Yang (1987). As stated by the authors, these differences could be larger during the early period

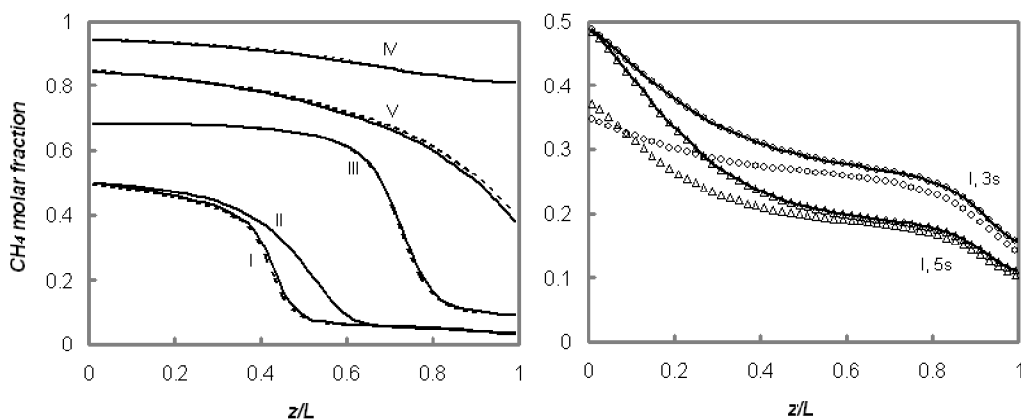


Figure 5.29: Predicted CH_4 composition profiles in the bed at the end of each step in a steady state, generated by the model, for both gas phase and inside the particle pores. At left, dashed and solid lines represent the CH_4 bulk and average pore concentrations, respectively. At right, single symbols denote CH_4 average pore concentrations.

in each step, specially in the stages involving pressure changes. This is shown through the CH_4 concentration profiles in PR step, after of 3 s and 5 s.

The pressure history of the validation run is depicted in Figure (5.30). The effluent CH_4 composition history in steady state PSA is also presented. A comparison of the generated model results is performed with the data reported in Figure (5.27) for run F. As one can see, the predicted histories are in accordance with both experimental and model results obtained by Yang and Doong (1985).

Figure (5.31) presents the simulated CH_4 composition surface during H_2 and CH_4 production steps, i.e., during (HPA + CD) and (BD + PG), respectively. The methane concentration histories and profiles with time and bed axial position at steady state are presented. On the same figure is shown the respective simulated temperature surface during the production steps. A single temperature peak accompanies the CH_4 adsorption front in the high pressure feed, while a temperature reduction is observed during the desorption steps.

For MEMPSA – CASE A, the periodic hybrid cycle is composed by: Pressurization (PR_1 , PR_2) / High-pressure adsorption (HPA) / Co-current blowdown (HBD or CD) / Counter-current blowdown (LBD or BD) / Purge (LPG). The PSA employs activated carbon as the adsorbent coupled to a membrane with a typical gas selectivity $\alpha_{\text{H}_2/\text{CH}_4}$ of 35, where the H_2 and CH_4 permeances were assumed 100 GPU and 2.86 GPU, respectively. The hybrid model reached the CSS at the 11th cycle. The simulations for the CSS cycle

take approximately 110 seconds on a Intel Pentium PC with 500 MB of RAM. The standard operating conditions considered are described in Table (5.1).

Figure (5.32) shows the pressure histories in both PSA and permeate side of the membrane, before and at cyclic steady state conditions. As said before, permeate pressure varies along permeation time, being dependent of the intermediate tank volume assumed in each simulation. As expected, the higher the volume of the intermediate tank, the lower the permeate pressure by the end of the membrane operation. Also, the evolution during permeation time will be different in the two situations, since the starting permeate pressure differs according to the tank volume assumed.

During the adsorption step, permeation occurs driven by the pressure difference between the residue side of the membrane and the storage tank. Since the permeation rate decreases as permeate pressure increases, because of gas build up in the tank, the mole fraction of $H_2(A)$ in the permeate stream decreases with time, approaching the value in the feed gas. As seen in Figures (5.33, 5.34), as the tank volume is increased, the final permeate pressure is decreased and the mole fraction of $H_2(A)$ in the permeate stream is increased. Furthermore, increasing parameter F_m , which is proportional to the product of membrane area and $H_2(A)$ permeance, the permeate pressure increases and the mole fraction of $H_2(A)$ in the permeate stream decreases.

Figure (5.35) presents the effect of total feed amount variation on product purities and recoveries for both the stand-alone PSA unit and the integrated system. The results show that for the same separation performance, the hybrid system has a higher feed

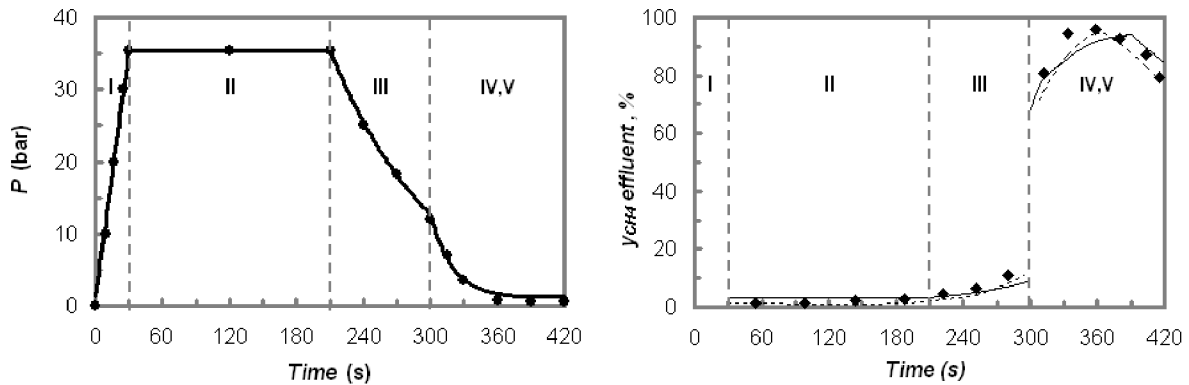


Figure 5.30: Bed pressure and CH_4 effluent concentration histories in steady-state. Symbols and dashed lines represent the experimental and predicted data for run F from Yang and Doong (1985). Solid lines denote the simulated results obtained using the conditions and simulation parameters listed in Table (5.15).

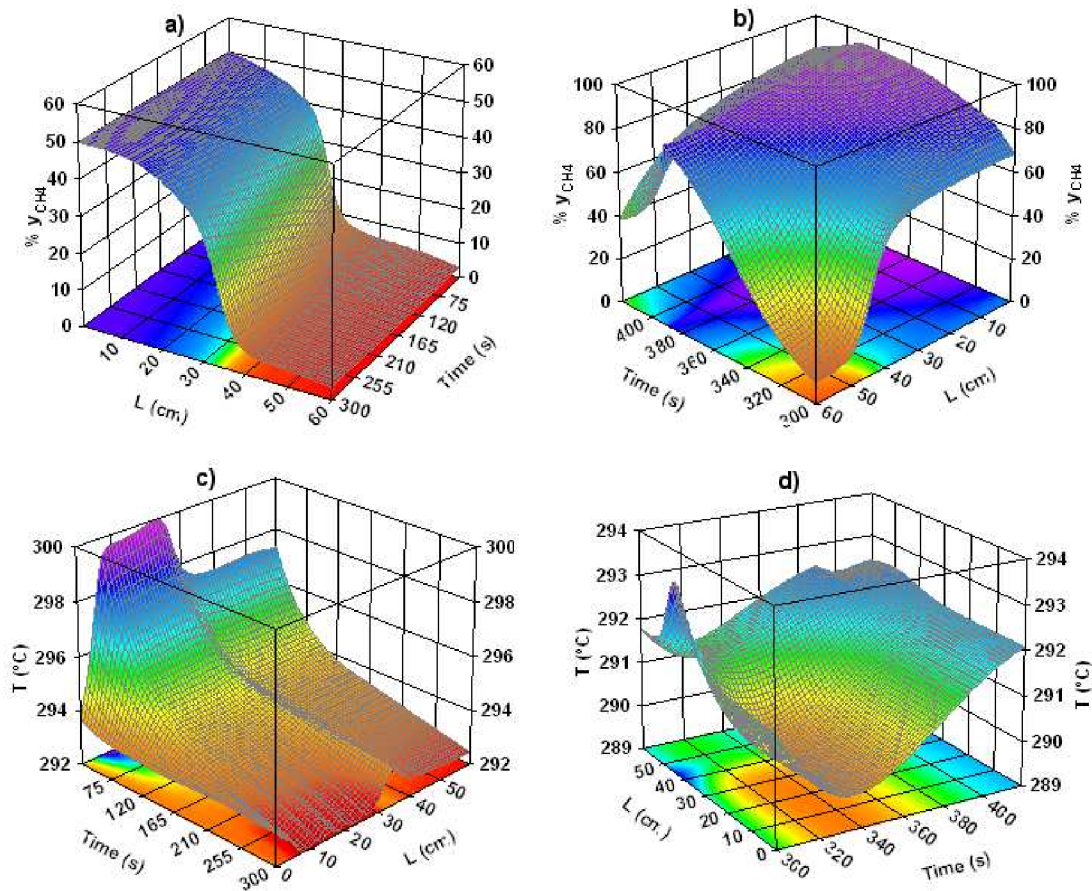


Figure 5.31: Simulated CH_4 concentration and temperature variation with the axial position and time during: a, c) H_2 production steps (HPA + CD); and b, d) CH_4 productions steps (BD + PG), at steady-state for run F.

throughput than the PSA operating alone. Increasing the feed flow rate results in longer bed coverage at the end of the high-pressure adsorption step, improving both purity and recovery. After excessive 65 L(STP) of total feed amount admitted per cycle to the system, the H_2 product is diluted with CH_4 and both H_2 purity and CH_4 recovery start to drop significantly. Nevertheless, in this region, one can see that for a given feed admitted the process enhancement of the hybrid case, compared with the conventional PSA, is clearly verified.

The purge step regenerates the bed for the next cycle and recovers the product stream enriched in CH_4 by stripping it out of the bed. As seen in Figure (5.36), increasing the purge to feed ratio, P/F , increases H_2 purity and CH_4 recovery steadily, but with loss of H_2 recovery and dilution of the CH_4 product stream. As known, the purge step is performed at the expense of the H_2 product obtained from HPA, that enters the bed

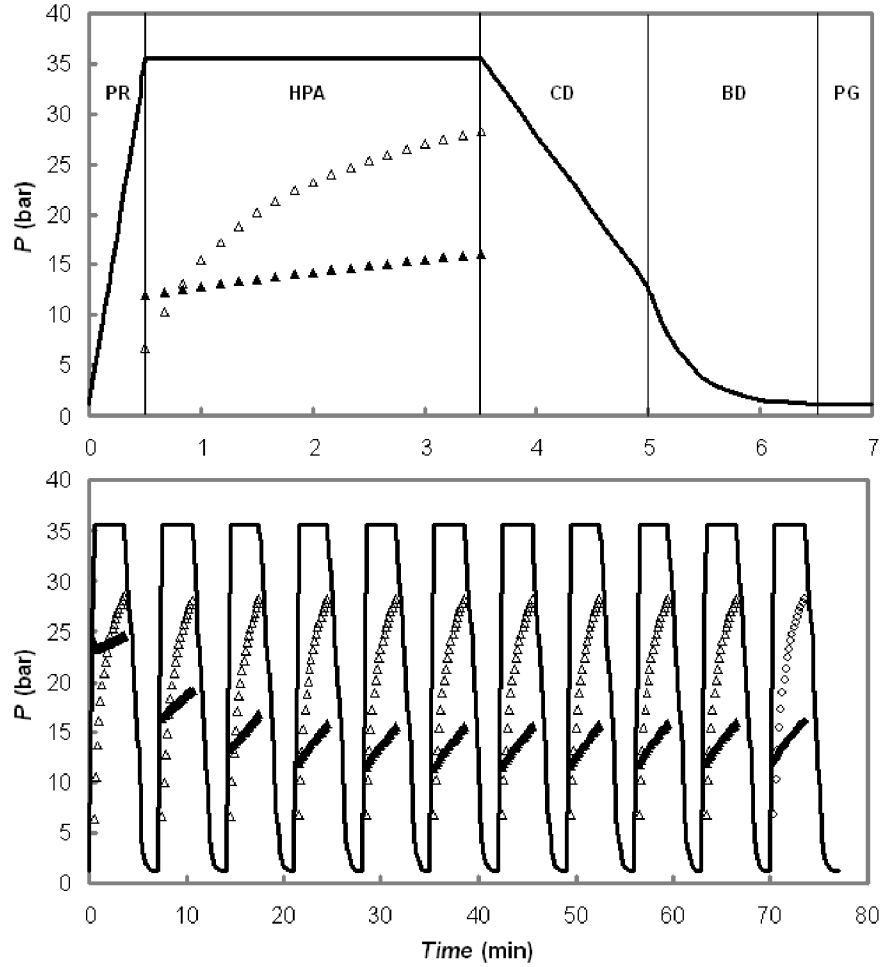


Figure 5.32: Pressure histories in both PSA and permeate side of the membrane, before (bottom) and at cyclic steady state conditions (top). Symbols: triangles represent unsteady state histories and circles denote histories at CSS (NoCycle = 11). Open and filled symbols correspond to an intermediate tank volume of 250 and 2500 cm³, respectively. H₂/CH₄ 50/50 %(v/v) feed mixture at 20°C, $P_M = 12.73$ bar, $P/F = 0.09$, $F_m = 17.18$ and a total amount fed per cycle of 47.7 L STP (STP: 0°C, 1 atm).

and dilutes the CH₄ produced in this step. It is also observed that the H₂ recovery and CH₄ purity for the integrated system are higher than those for the conventional PSA unit operating alone.

Figures (5.37, 5.38) show H₂ and CH₄ concentration profiles inside the adsorbent bed for the PSA unit alone and for the hybrid processes. The concentration profiles for the hybrid process are sharper than those for the PSA alone. This enhances the separation performance of the combined process. Unlike in a conventional PSA process, the adsorbent

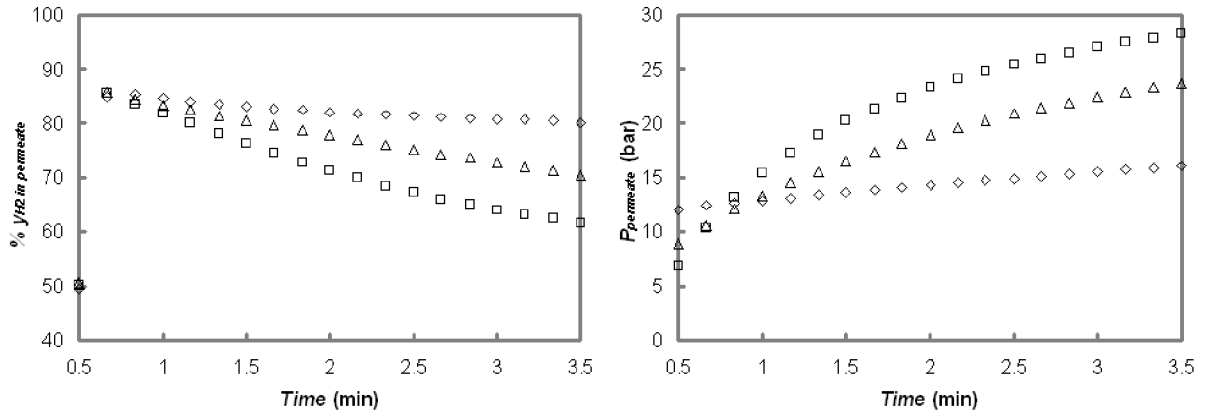


Figure 5.33: H₂ concentration (left) and pressure (right) histories in the permeate stream as a function of tank volume V_c , at CSS (NoCycle = 11). Symbols: $\square$, $V_c = 0.25$ L; $\triangle$, $V_c = 0.50$ L; $\diamond$, $V_c = 2.50$ L. H₂/CH₄ 50/50 %(v/v) feed mixture at 20°C, $P_H = 35.45$ bar, $P_M = 12.73$ bar, $F_m = 17.18$, $P/F = 0.09$ and a total amount fed per cycle of 47.7 L STP (STP: 0°C, 1 atm).

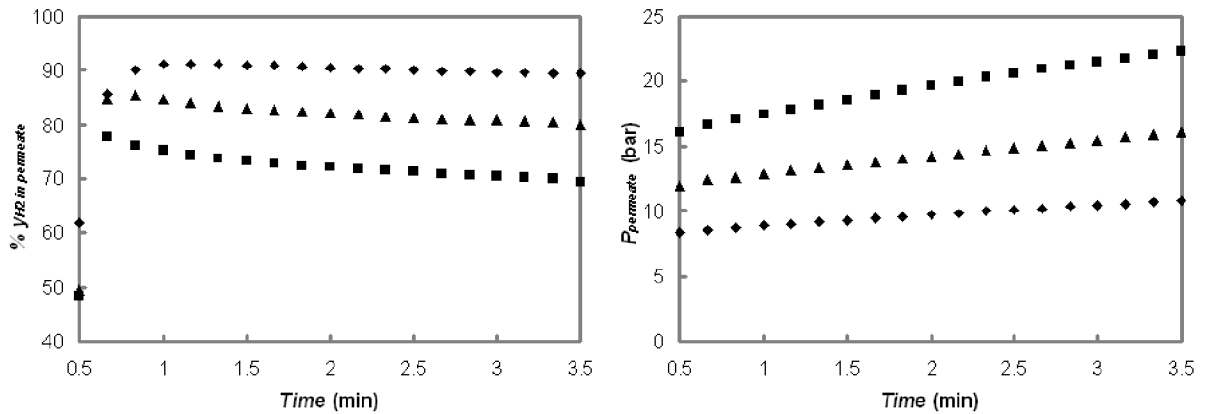


Figure 5.34: H₂ concentration (left) and pressure (right) histories in the permeate stream as a function of dimensionless permeation flow F_m , at CSS (NoCycle = 11). Symbols: $\blacksquare$, $F_m = 51.54$; $\blacktriangle$, $F_m = 17.18$; $\blacklozenge$, $F_m = 5.15$. H₂/CH₄ 50/50 %(v/v) feed mixture at 20°C, $P_H = 35.45$ bar, $P_M = 12.73$ bar, $V_c = 2.5$ L, $P/F = 0.09$ and a total amount fed per cycle of 47.7 L STP (STP: 0°C, 1 atm).

bed in the integrated system is fed with a varying-composition gas stream, initially rich in the more permeable but less adsorbed component, which is progressively enriched in the other component having opposite behavior.

Figure (5.39) presents the effect of the intermediate blowdown pressure, P_M , variation on the separation performance, for both stand-alone PSA and the integrated system, at cyclic steady state conditions. As expected, increasing the intermediate pressure, P_M , which corresponds to the bed pressure at the end of the first depressurization step, the purity of the less adsorbed component, H_2 , increases significantly, but less product is recovered. The opposite trend occurs for CH_4 , where the product is diluted while P_M increases.

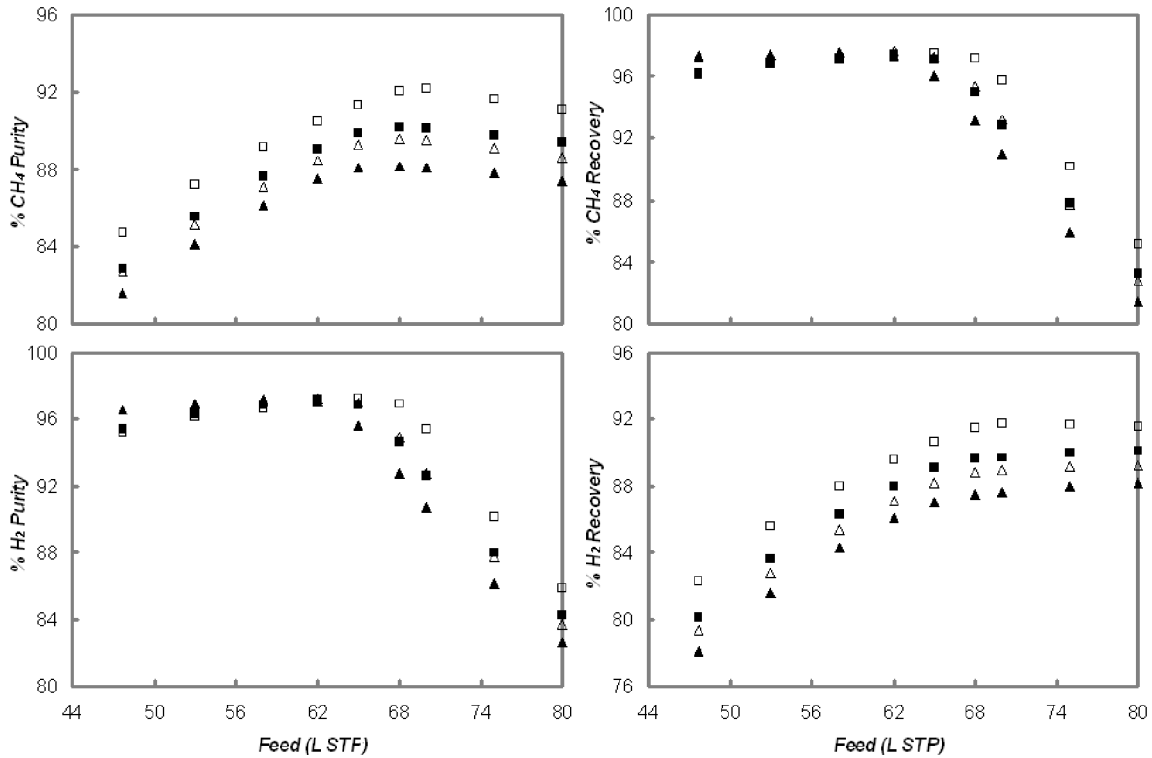


Figure 5.35: Impact of the total feed amount per cycle on CH_4 and H_2 product purities and recoveries for both stand-alone PSA ($\blacktriangle$, $P_H = 25.5$ bar; $\triangle$, $P_H = 35.5$ bar) and integrated system ($\blacksquare$, $P_H = 25.5$ bar; $\square$, $P_H = 35.5$ bar), at CSS (NoCycle = 11). H_2/CH_4 50/50 %(v/v) feed mixture at 20°C , $P_M = 12.73$ bar, $P/F = 0.09$, $F_m = 17.18$ and $V_c = 2.5$ L (STP: 0°C , 1 atm).

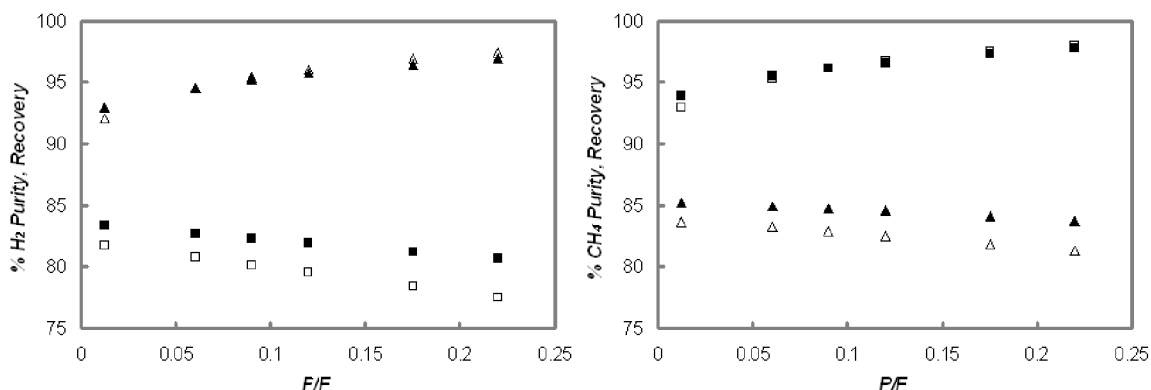


Figure 5.36: Impact of P/F ratio (amount of the component A in the feed that is consumed in the purge) on product purity and recovery for both stand-alone PSA (Δ , purity; $\square$, recovery) and integrated systems ($\blacktriangle$, purity; $\blacksquare$, recovery), at cyclic steady state conditions (NoCycle = 11). H₂/CH₄ 50/50 %(v/v) feed mixture at 20°C, $P_H = 35.45$ bar, P_M of 12.73 bar, $F_m = 17.18$, $V_c = 2.5$ L and a total amount feed per cycle of 47.7 L STP (STP: 0°C, 1 atm).

5.2 Summary

A fully detailed hybrid concept and its model development were described. Two different operational schemes for a truly synergistically integrated process were developed. They are capable of operating under a wide range of operating conditions. The main principles underlying their operation are:

- The operating pressure of the PSA unit is used as the driving force for permeation, which assists the pressurization and adsorption steps of the pressure swing unit. The modeling work proved that the coupled process increases the efficiency of the pressurization and high-pressure adsorption steps, thereby improving the separation performance as compared to the conventional stand-alone units.
- Using the different enriched streams from the membrane, the aim of these integration steps is to sharpen the composition wavefronts, in order to decrease the dispersion obtaining high purity products and enhancing the process performance.

The feasibility of the integrated process presented is assessed through the effect of the various operating parameters on separation performance. The hybrid process developed was called MEMPSA. The concept was implemented under two main structural conditions:

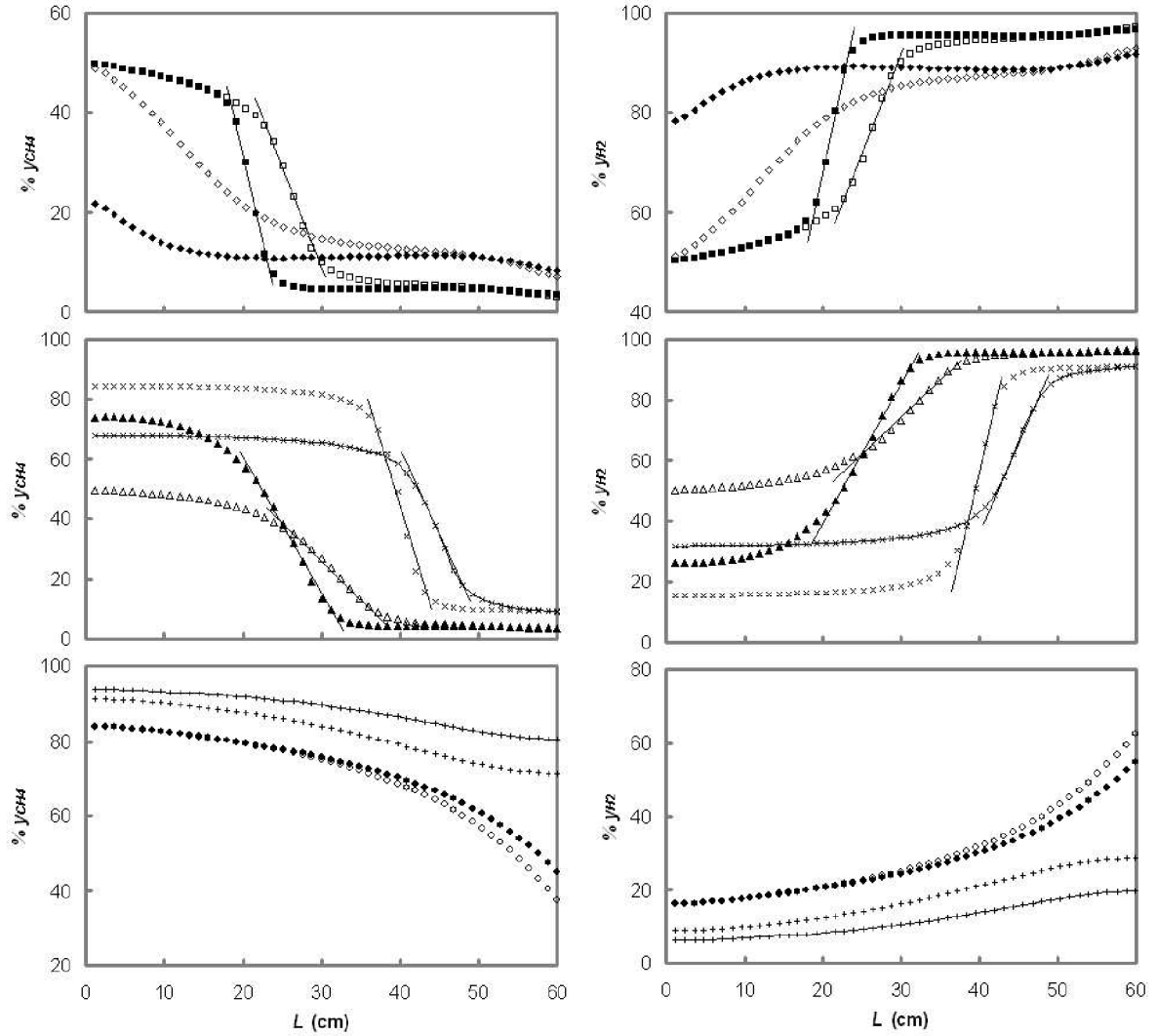


Figure 5.37: CH_4 (left) and H_2 (right) gas-phase composition profiles inside the PSA bed at the end of each step for both stand-alone PSA (open symbols) and integrated system (filled symbols), at CSS (NoCycle = 11). H_2/CH_4 50/50 % (v/v) feed mixture at 20°C , $P_H = 35.45$ bar, $P_M = 12.73$ bar, $F_m = 17.18$, $V_c = 2.5$ L, $P/F = 0.09$ and a total amount feed per cycle of 47.7 L STP (STP: 0°C , 1 atm). $\diamond/\blacklozenge$, PR_1 (9 s); $\square/\blacksquare$, PR (30 s); $\triangle/\blacktriangle$, HPA (210 s); $\ast/\times$, CD (300 s); $\mp/\pm$, BD (390 s); $\circ/\bullet$, PG (420 s).

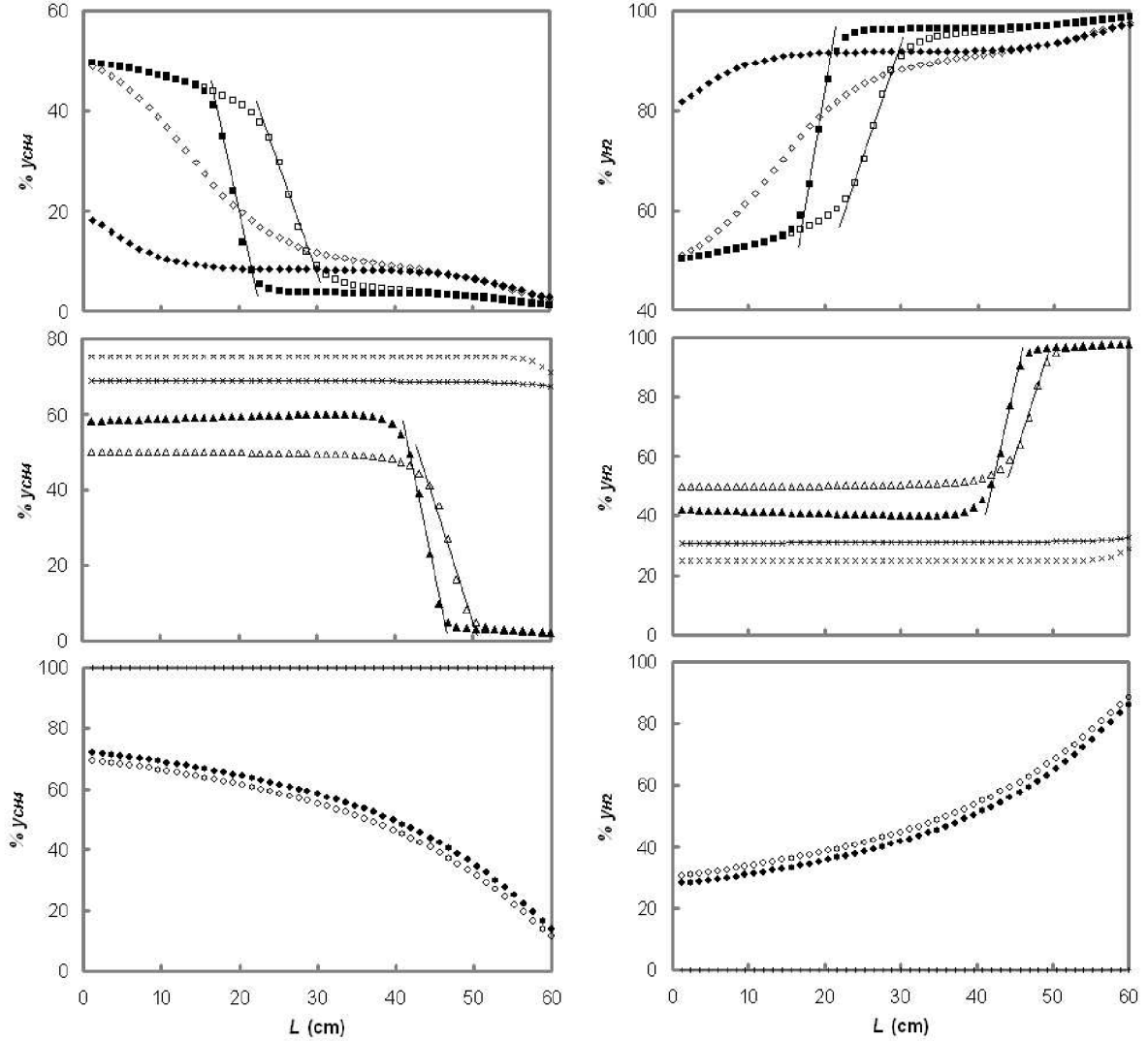


Figure 5.38: CH₄ (left) and H₂ (right) gas-phase composition profiles inside the PSA bed at the end of each step for both stand-alone PSA (open symbols) and integrated system (filled symbols), at CSS (NoCycle = 11). H₂/CH₄ 50/50 %(v/v) feed mixture at 20°C, $P_H = 35.45$ bar, $P_M = 12.73$ bar, $F_m = 17.18$, $V_c = 2.5$ L, $P/F = 0.09$ and a total amount fed per cycle of 70.0 L STP (STP: 0°C, 1 atm). $\diamond/\blacklozenge$, PR₁ (10 s); $\square/\blacksquare$, PR (30 s); $\triangle/\blacktriangle$, HPA (210 s); $\ast/\times$, CD (300 s); $\mp/\pm$, BD (390 s); $\circ/\bullet$, PG (420 s).

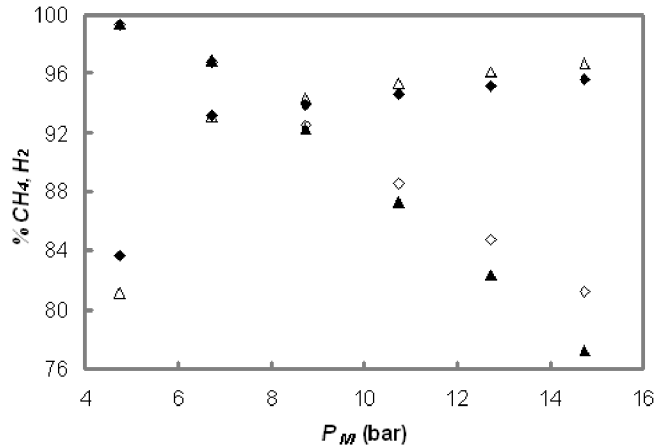


Figure 5.39: Effect of the intermediate blowdown pressure, P_{CD} , variation on CH₄ (open symbols) and H₂ (filled symbols) separation performance, for both stand-alone PSA and integrated system, at cyclic steady state conditions (NoCycle = 11). H₂/CH₄ 50/50 %(v/v) feed mixture at 20°C, $P_H = 35.45$ bar, $F_m = 17.18$, $V_c = 2.5$ L, $P/F = 0.09$ and a total amount feed per cycle of 47.7 L STP (STP: 0°C, 1 atm). $\Delta/\blacktriangle$, recovery; $\diamond/\blacklozenge$, purity.

- MEMPSA – CASE A process, where the more permeable component is the least adsorbed one in the PSA bed,
- MEMPSA – CASE B process, where the more permeable component is the more adsorbed one in the PSA bed.

Instead of the regular A/B binary feed mixture, the PSA is fed with a mixture which is progressively enriched in the more adsorbed component along the pressurization and high pressure adsorption steps of a PSA cycle.

An integrated mathematical model was implemented for both cases and results were obtained and compared with the conventional units involved. Dynamic simulations were performed for the binary separations of CO₂/N₂, CH₄/H₂ and CH₄/CO₄, at different feed compositions.

An hybrid membrane/PSA model for the separation of a CO₂/N₂ gas mixture was performed in order to study the effect of the inclusion of an additional membrane unit into the implemented experimental PSA process. The integration of both technologies was made and its results were obtained and compared with the stand-alone PSA performance for the CO₂/N₂ 30/70% (v/v) mixture. Through comparison with the experimental PSA cycle implemented, this integrated process is enough to enhance the final product purity

and recovery. Instead of the regular 30/70 mixture fed to the PSA, a feed stream more enriched in N_2 enters the bed in the hybrid process. The PR step and the first stage of the HPA are performed with a feed stream enriched in the lighter component, N_2 , which is the first to be withdrawn from the column as product. This first product is then obtained at higher purity. Consequently, the HPA_b occurs with a feed stream enriched in the more adsorbed component, simultaneously with recovery of high purity N_2 . The HBD step continues to produce a purer N_2 stream than that obtained in the stand-alone PSA process. Finally, the CO_2 product is collected in LBD and LPG steps, at an higher average purity for the integrated case. It is proven that the enhancement of the integrated process when compared with the stand-alone PSA increases significantly with the increase of the total feed admitted per cycle. Thus, for high feed throughputs the hybrid process developed have a clearly advantage.

The overall computational work done allows us to conclude that, the inclusion of a membrane module into a periodic PSA process, by a truly synergistically scheme, is indeed an innovative method to improve separation performance of several gas systems when compared with the more common stand-alone units. A pre-established PSA process, already in operation, can be eventually coupled with membrane technology, through the alternative systems described, giving rise to enhanced product purities and recoveries. If these enhancements are sufficiently high to overcome the energy and investment requirements for a particular gas system, is another research subject that has to be performed in conjunction with process development.

Chapter 6

Adsorbed Natural Gas (ANG)

Processes for Gas Storage

Applications

6.1 Introduction

This section intends to summarily describe the ANGWARD process and integrate in it the work developed in FCT/UNL.

Natural gases vary widely in composition, and the trace components are adsorbed to different extents and released at different rates. The higher the trace hydrocarbons present in most pipeline natural gases, particularly C_{5+} components and the sulphur odorants, the more strongly the retention on activated carbon with the result that the storage system becomes contaminated and gradually loses capacity.

A key requirement for adsorption storage systems is the need to be able to deliver NG from the ANG storage vessel to the same composition specification as the original pipeline gas, in other words to be able to desorb the same composition as on adsorption. The complex and variable composition of EU pipeline gases and the different adsorption behavior of the trace components, make this a formidable technical challenge.

A large-scale storage operation was considered, relevant to a UK storage scenario, involving diurnal storage for a nominal winter demand forecast.

The use of a guard bed is relatively straightforward when the main vessel is being charged, but becomes particularly complicated during discharge. The difficulties arise from the need to maintain a constant odorant concentration at guard bed outlet, which means obtaining a controlled release of the odorants from the carbon into the odorant-free

gas stream flowing from the main storage vessel. Such release of odorants can be achieved by heating the carbon in the guard bed, either directly (heat transfer by conduction), or indirectly (heating the gas and then using the hot gas to heat the carbon).

A process scheme was developed around this concept, in which the guard bed is regenerated by using only part of the exit flow from the main storage vessel during the discharge cycle. Thus, there would be a flow bypass around the guard bed, which would reduce the heat exchanger size and heating duty for guard bed regeneration. A reduction in size of the required heating equipment will reduce the cost of the complete guard bed package. This will be offset however, by the need for a more complicated flow ratio control system. The current preference for the regeneration of the guard bed during the discharge phase is via the use of indirect heating, i.e., by use of a water bath heater for heating the gas leaving the main vessel. Hot oil is used as the heat source. The heated gas then flows across the guard bed, causing the release of the odorants in a controlled manner.

Although it was recognized that indirect heating would become more expensive than direct heating, due to the loss of energy carried by the heated gas stream leaving the guard bed, this increase in cost was considered to be negligible. Furthermore, the energy loss could be greatly reduced with a heat recovery system (gas-gas heat exchanger, placed at guard bed outlet and used to pre-heat the gas leaving the main storage vessel). Direct heating by the use of an internal coil or tube bank has been dismissed for the diurnal storage application since, due to the poor carbon thermal conductivity, large temperature differences and undesirable hot spots occur within the guard bed which could lead to inadequate regeneration. However, for smaller scale applications, direct heating should not be ruled out.

A *standard* gas composition was selected for the process development and simulation work, to reflect the gas compositions prevalent throughout the EU. The composition selected was a synthetic one to represent the worst possible case in terms of C_{5+} components and odorants, so that the guard bed sizing would be appropriate to any EU natural gas scenario. This aspect was also reflected in the development of the carbon adsorbent, so that it could be applied to any gas quality across Europe. The gas is defined in Table (6.1).

Since most of the testing was conducted in the UK, it was agreed that a typical UK gas composition should be used in the cyclic experiments, although for simulation purposes, the ANGWARD composition was used so that the effect of higher levels of C_{5+} components and odorants could be modeled. The results can be easily extrapolated to all compositions.

The worst-case gas compositions across the EU, obtained in recent surveys, show that the maximum C_{6+} concentration occurs in the UK (Easington terminal) at approximately

Table 6.1: Typical composition of the Natural Gas (NG) model mixture defined as the standard based on the analysis of several european natural gases [ANGUARD (March 2004)].

Species	Mole fraction y (% vol)
N ₂	1.00
CO ₂	0.50
C ₁	88.71
C ₂	5.00
C ₃	1.20
C ₄	3.20
C ₅	0.24
C ₆	0.10
C ₇	0.04
C ₈	0.01
THT	25 (a)
TBM	25 (a)

(a) ppm, mg/Nm³

1200 ppm. The maximum odorant concentration (EU wide), components in trace amounts to odorize the NG, occurs in France with a 25 mg/m³ THT/TBM mixture.

The high-pressure diurnal storage facilities in the UK operate at maximum storage pressures from about 20 to 66 barg. However, there would be no advantage in operating ANG facilities with a maximum operating pressure greater than 40 barg. The minimum pressure again varies locally across the UK, typically between 1 to 7 barg. Use of pressure boosters could reduce the minimum pressure to lower than 1 barg.

Concerning the operating temperature, normal values for a guard bed in the diurnal storage application are likely to vary from - 20°C to + 80°C [ANGUARD (March 2004)].

The storage system has two steps: a charge phase and a discharge phase. Figure (6.1) presents the ANGUARD process developed. The guard bed containing the carbon sample (ANGUARD 5) prevents, during charge, the contamination of the main storage tank with C₆₊ and retains the odorants. Gas, flowing into the system from the high-pressure gas source, is constant throughout the charge and discharge phases.

Flow out of the storage system is via pressure control valve PCV1 [Figures (6.2) and (6.3)]. This valve opens or closes to maintain the site outlet pressure. During the charge phase, gas demand out of the site is lower than the average volumetric flow into the site so pressure rises downstream of PCV1. The heat exchanger and ratio control system are

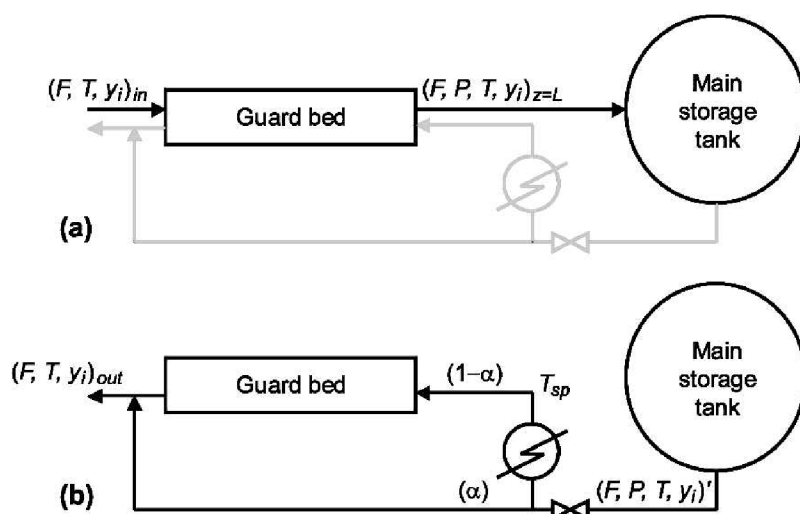


Figure 6.1: Two-step operation of the ANG system: (a) charge, (b) discharge for conceptual ANGWARD process. α is the bypass flow fraction and T_{sp} is the temperature of the heated gas; both variables can be manipulated during discharge [ANGUARD (March 2004)].

isolated via valves V1, V2 and V4. V3 is open so gas flows into the storage system as indicated in Figure (6.2).

Figure (6.4) shows the pressure and temperature histories and breakthrough curves of n -alkanes C_1 - C_5 in the outlet gas stream of guard bed during charge. It is necessary 160 min to charge the main tank. Pressure varies non-linearly with time due to the non-linear dependence with the loading. Heat of adsorption released in charge is not fully dissipated to the environment, giving rise to an increase in temperature up to nearly 60°C . This corresponds to the highest adsorption rate. The non-adsorbed gas exits the guard-bed lowering the temperature to its initial value.

In the breakthrough curves of n -alkanes during charge, composition variation of the outlet stream of the guard bed with time is shown. The bed is effective in retaining C_{6+} and odorants. C_1 and C_2 breakthrough immediately followed by C_3 and C_4 . C_5 breakthrough time is longer and increasing the bed length by a few percent it would retain also this component.

Figure (6.5) presents the state of the gas phase molar fraction profiles of the n -alkanes at the end of charge. C_1 - C_3 is moving through the bed compared with C_5 - C_8 which are being adsorbed in the adsorbent. The same plot is presented with respect to the odorants. The odorant THT adsorbs more strongly than TBM.

During the charge phase all the gas flows through the guard bed, bypassing the heat exchanger and into the main storage vessel. The desorption may be carried out in a

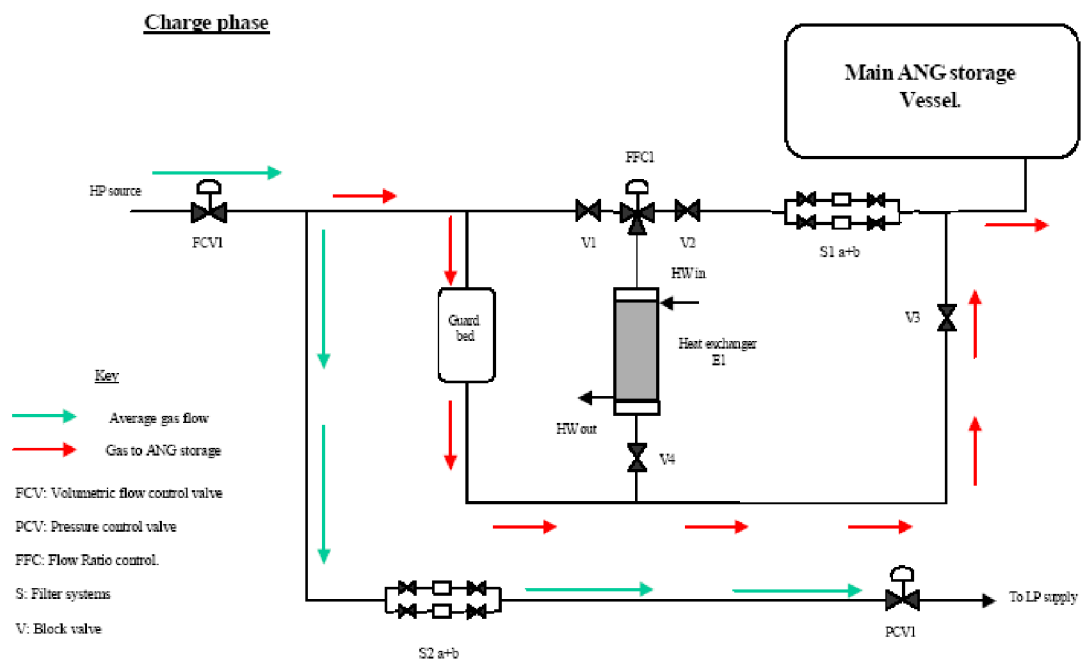


Figure 6.2: Gas Flow paths during charge for conceptual ANGWARD process [ANGUARD (March 2004)].

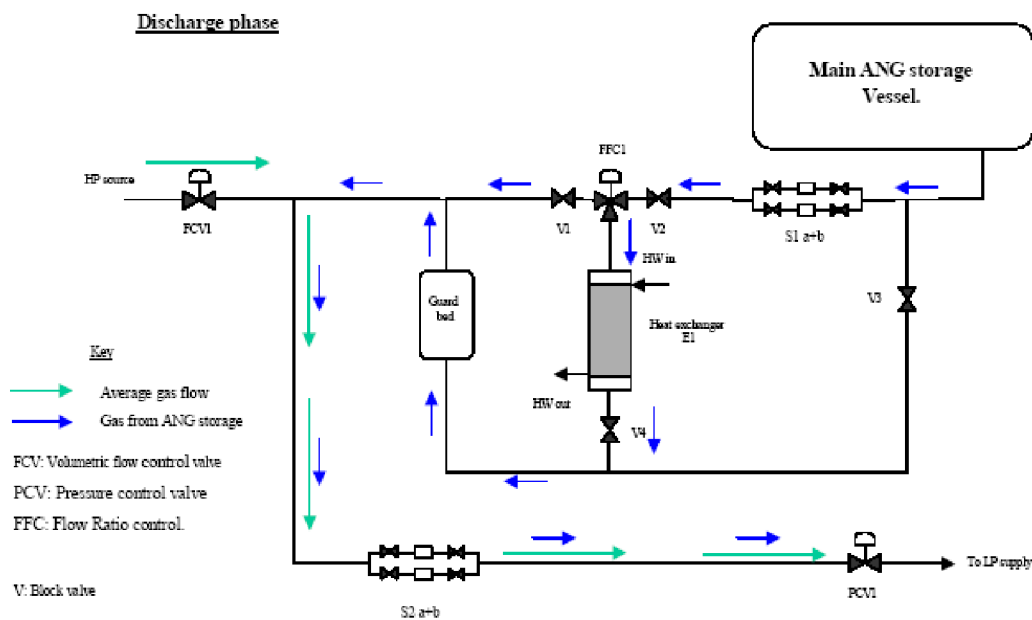


Figure 6.3: Gas Flow paths during discharge for conceptual ANGWARD process [ANGUARD (March 2004)].

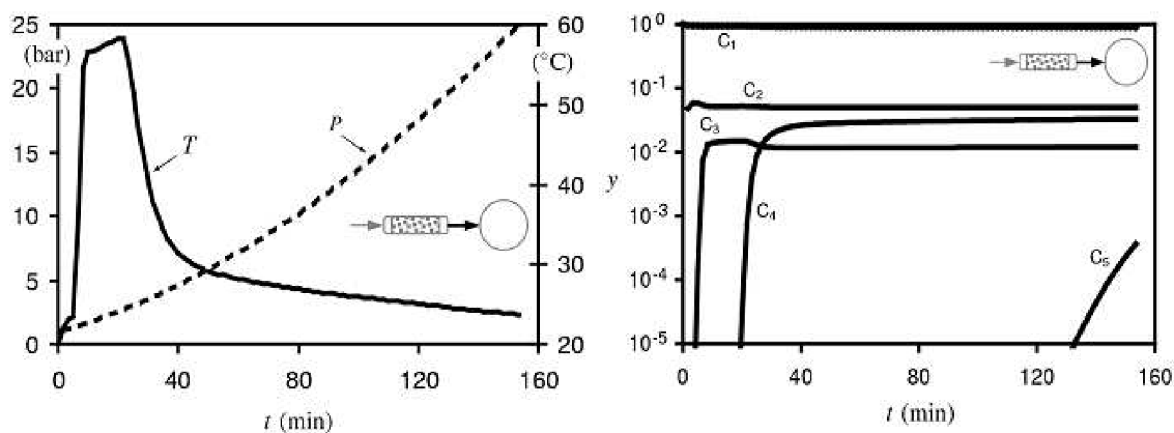


Figure 6.4: Pressure and temperature histories in outlet gas stream of guard bed during charge ($T_{feed} = 20^\circ\text{C}$, $P_1 = 1$ bar, $P_2 = 25$ bar, $F = 200$ L/min); Breakthrough curves of n -alkanes C_1 - C_5 in the outlet gas stream of guard bed during charge.

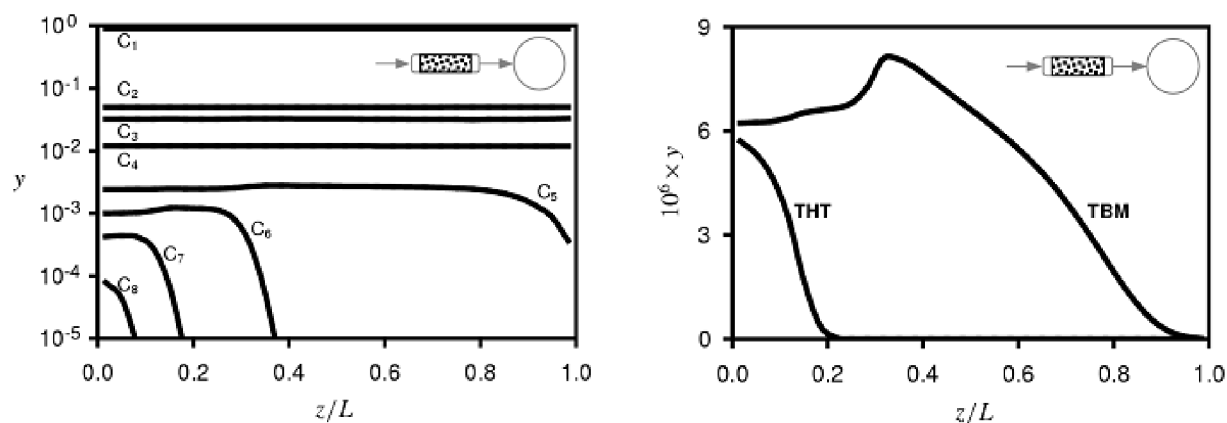


Figure 6.5: Gas-phase mole fraction profiles of n -alkanes C_1 - C_8 and of TBM and THT at the end of charge.

number of controlled phases to ensure the best delivered gas composition. Here, several schemes were considered:

1. Discharge with no gas heating. Desorption is via pressure swing only. All the gas flows through the guard bed and out to vent.
2. Discharge with gas heating. For normal operation, it is intended for all of the gas flow to be heated and to pass through the guard bed. Primary control of the odorant concentration will be achieved via gas outlet of the heat exchanger. Secondary control can be achieved by bypassing a fraction of gas flow past both the guard bed and the heat exchanger via CV1 - this option is used if the measured odorant concentration is too high. The concept of using a permanent guard bed bypass that could lead to substantial system cost savings, can also be demonstrated with this configuration if desired.
3. Discharge with no gas heating. This occurs towards the end of the discharge phase and is required to cool the guard bed in preparation for the next charge phase. All the gas flows through the guard bed and out to vent.

Figure (6.6) shows the pressure and temperature histories, and odorants TBM and THT breakthrough curves during discharge without control of odorant concentration. In this first operating model, there is no control of odorant concentration in the outlet stream of the guard bed. Pressure and temperature histories in discharge are presented. Temperature exits the tank at 24°C. Trends, as expected, are opposite to those observed in the charge phase. The odorants concentration at the outlet stream of the bed during discharge are also seen. During most of the discharge phase, the odorant concentration is much lower than the target value needed to meet the quality of an odorized NG.

Figure (6.7) presents the history of manipulated gas temperature and TBM and THT breakthrough curves during discharge with PID control of odorant concentration. This second approach was chosen and implemented. The discharge stream of the tank is heated to control the concentration release of the odorants at the exit of the guard bed. It has been tested by simulating a feedback control system using a proportional integral controller. It is assumed that the outlet stream from the bed is measured online with instant reading. The signal is sent to the controller and the deviation of concentration from the target value is used to determine the appropriate heating rate.

It is shown that odorant concentration is closer to the target values. In the top is the total odorant concentration, which is kept at the desired target value. One can conclude that the control system has improved the odorant quality of the outlet stream of the guard

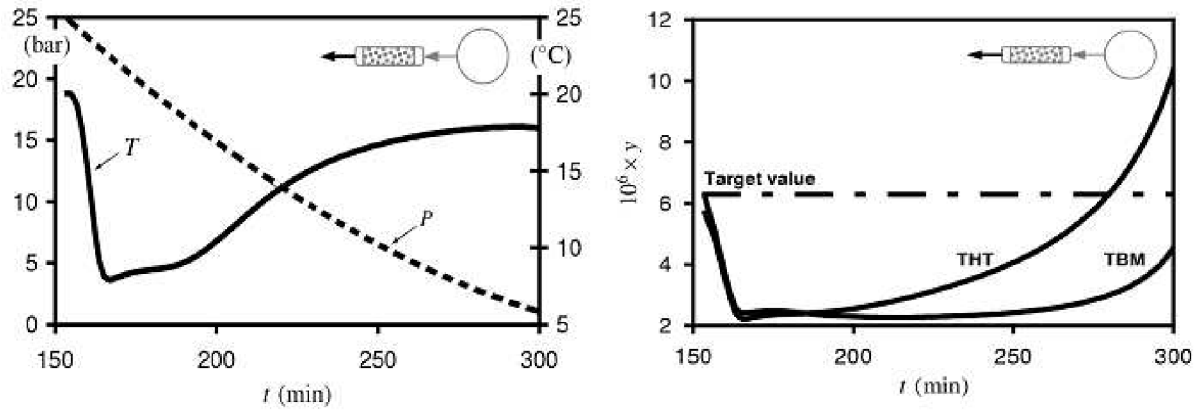


Figure 6.6: Pressure and temperature histories during discharge without control of odorant concentration; TBM and THT breakthrough curves during discharge without control of odorant concentration.

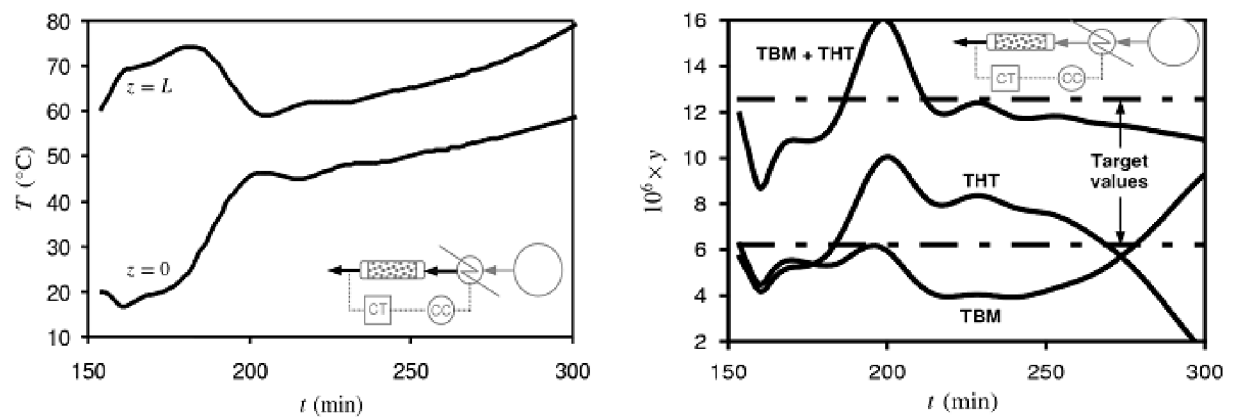


Figure 6.7: History of manipulated gas temperature and TBM and THT breakthrough curves during discharge with PID control of odorant concentration.

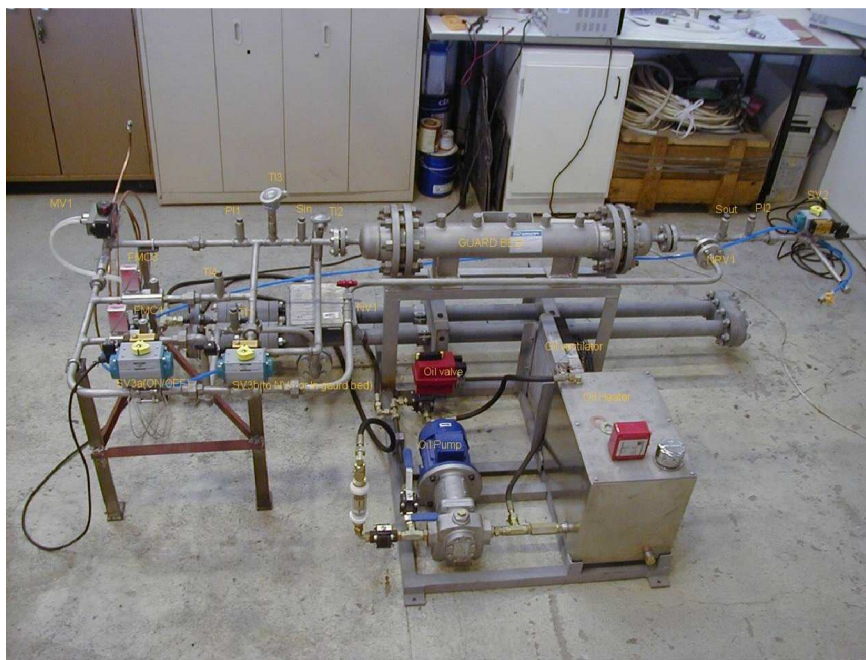


Figure 6.8: Pilot guard-bed system, oil bath, heat exchanger and ancillary instrumentation, tested by the ANGUARD group [ANGUARD (March 2004)].

bed. The required temperature is in the range 50-80°C and allows the odorization of this stream very accurately.

This second approach was the basis for the final discharge scheme developed. As referred, the current preference for the regeneration of the guard bed during the discharge phase is via the use of indirect heating, i.e. by use of a oil bath heater. During the discharge phase, gas demand out of the site is higher than the average volumetric flow into the site, so pressure downstream of FVC1 will fall. Gas flows out of the main storage vessel as indicated in Figure (6.3). The flow ratio control system routes a specified fraction of the gas through the heat exchanger. The outlet temperature of the gas leaving the heat exchanger increased over the course of the discharge phase in order to maintain the odorant concentration of the exit gas stream [Figure (6.1)].

Figure (6.8) shows a view of the pilot guard-bed system, oil bath, heat exchanger and ancillary instrumentation, tested by the ANGUARD group.

The ANGUARD guard bed was sized according to the C₅₊ components, and was scaled to the appropriate NG and carbon adsorbent. A volume of around 5.7 L was estimated to be appropriate to the 500 L main storage vessel. Thus, the guard bed is approximately 1.1% of the main bed volume. The guard bed was fabricated in stainless steel, with flanged ends for easy loading of the carbon. 1.77 kg of adsorbent (ANGUARD 5) was loaded [ANGUARD (March 2004)].

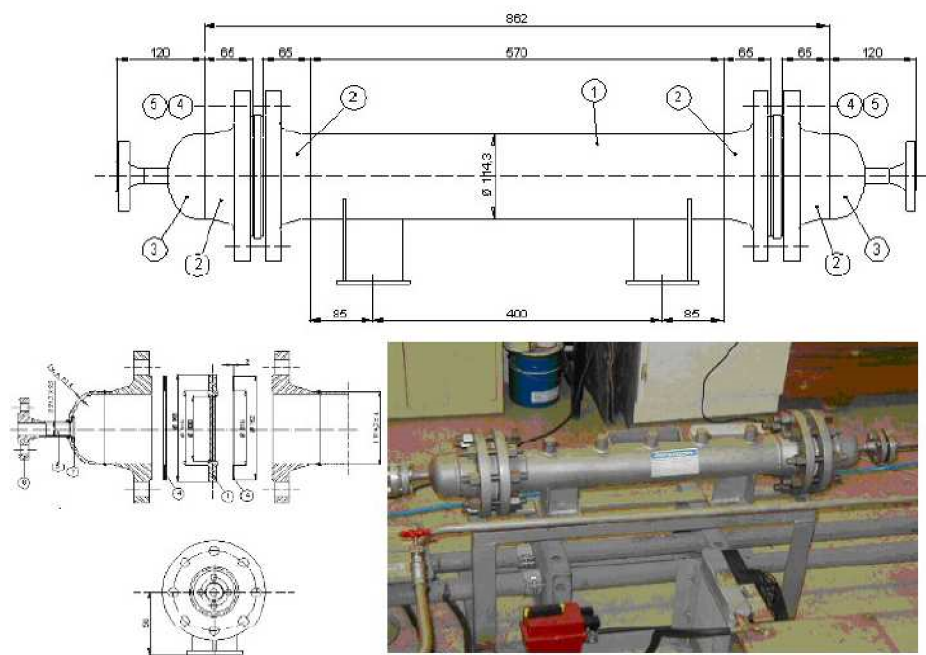


Figure 6.9: Guard bed schematic and photograph [ANGUARD (March 2004)].

The vessel is shown in Figure (6.9). Assembly, construction and initial testing was done under the supervision of ISQ, in PT. After the construction of the system, it underwent pressure testing and extensive testing of the heating system to check basic operation prior to being shipped to Advantica. The basic rig also underwent substantial considerations following a hazard and operability (HAZOP) assessment in order to gain safety approval for installing and commissioning the rig.

In order to maintain the outlet odorant concentration during discharge within a defined window of variation, a control system for the heat exchanger is required. It was anticipated that gas flow rate across the guard bed will not remain constant during discharge, depending on the gas demand by the customers. Monitoring the odorant concentration at the outlet and changing the condition of the independent variables accordingly is designed to achieve this.

Preliminary work has shown that the use of a simple PID (proportional, integral differential) control scheme may not be adequate to smoothly desorb the odorants in the required concentration, with no overshoot. The difficulty with controlling such a complex system lies with continuously changing conditions at guard bed inlet coupled with long deadtime, i.e., whenever heat is applied to obtain the required desorbed concentration, the desorption conditions will change by the time the target GB temperature is reached. The solution to this problem uses the ANGUARD advanced control strategy developed

by our research group at FCT/UNL.

In a few words, the new control scheme applies a pre-computed optimum temperature ramping to the heated gas, while simultaneously manipulating the bypass flow rate to achieve the best possible reodorization. The temperature ramping is pre-computed off-line using the dynamic simulation model coupled to a nonlinear constrained optimization package. Discrepancies between model predictions and the real process dynamics are compensated by changes to the bypass flow rate, since this variable is continuously updated in feedback mode [Figure (6.10)]. By using an optimized 4-step temperature ramp, the simulation model shows that the odorants can be desorbed smoothly in the required concentration, with very little undershoot or overshoot.

This control strategy has been incorporated into the control module of the pilot-scale guard bed system. The control module has been implemented as a dynamic linking library (DLL) and communicates with the Labview data acquisition and control software to update the values of the manipulated variables based on the measured data.

The hydrocarbon (HC) concentrations in the reodorized gas (downstream of the bypass) are measured using a mass spectrometer at discrete points in time to obtain the sampled data. The sampling time is about 15 s, which guarantees that the HC readings are updated at a much faster rate than the dynamics of the guard bed. The other state variables (pressures, temperatures, mass flows, valve positions, etc.) are measured at the same sampling rate, except for the odorant (OD) concentrations. Due to limitations on the response of the gas chromatograph (GC), the OD concentrations are updated only every 6.4 min.

In order to eliminate the effect of the time-lag of the GC on the response of the control system, an inference method was developed to predict the OD concentrations between GC readings. Basically, the method consists of associating the OD readings to that of a reference HC, whose temporal profile is employed to predict those of the odorants. The extrapolation function is updated whenever new OD readings are available [Figure (6.11)]. Preliminary tests showed that the best reference HCs are either butane (C_4) or pentane (C_5). The latter is the reference HC employed in the experimental runs carried out at Advantica.

6.2 Contribution from FCT/UNL

The key objective was to develop predictive and adaptive models for the storage and guard bed system. A multi-component adsorption model was developed suitable for both main vessel and guard bed, comprising both kinetic and equilibrium models and utilizing

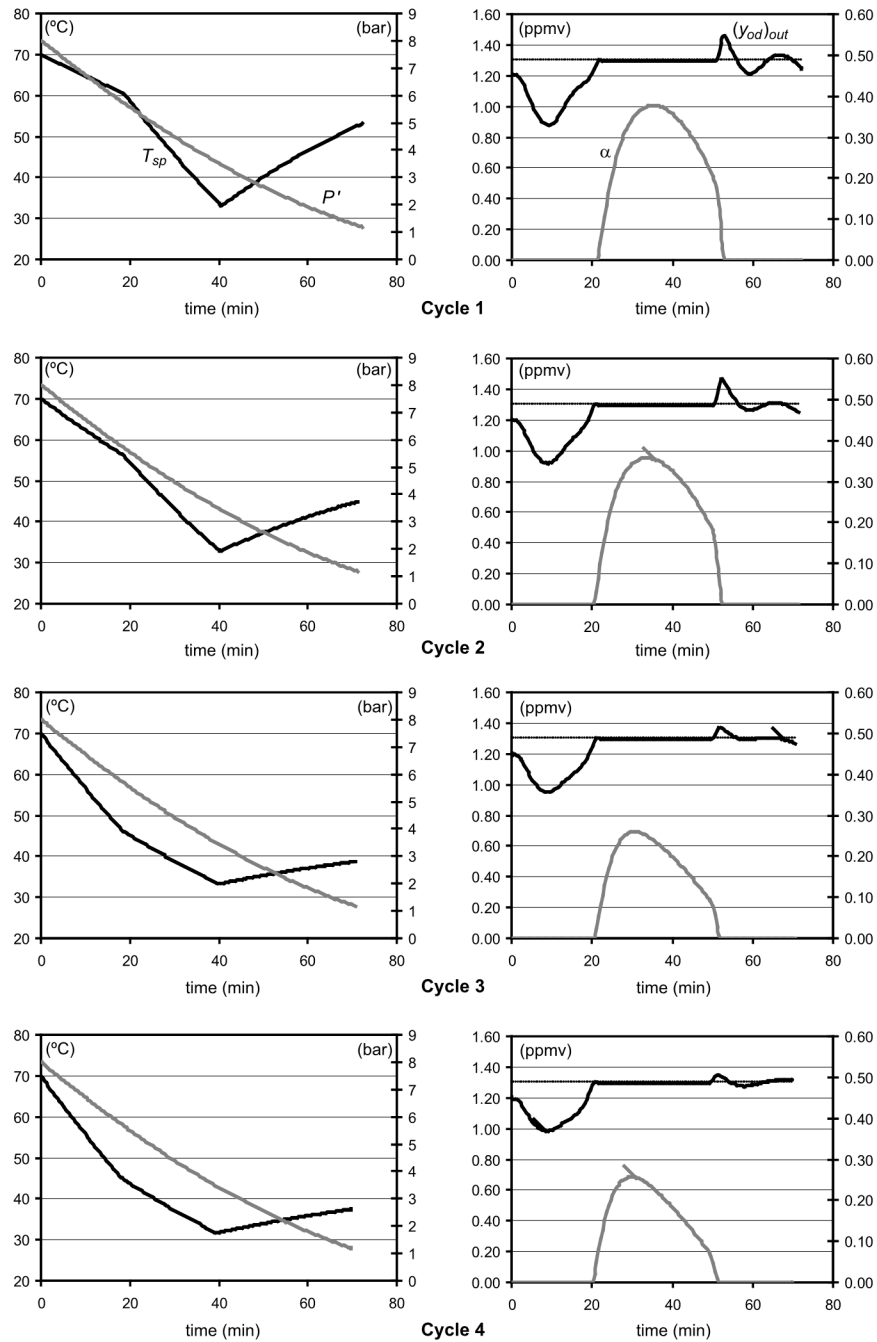


Figure 6.10: Example computed optimum temperature and bypass profiles of heated gas for cyclic operation of the ANG storage system for standard UK pipeline natural gas. Similar simulations were developed for single odorant gas and the ANGWARD standard gas. The exact optimum profile is dependent on the starting conditions for each cycle [ANGUARD (March 2004)].

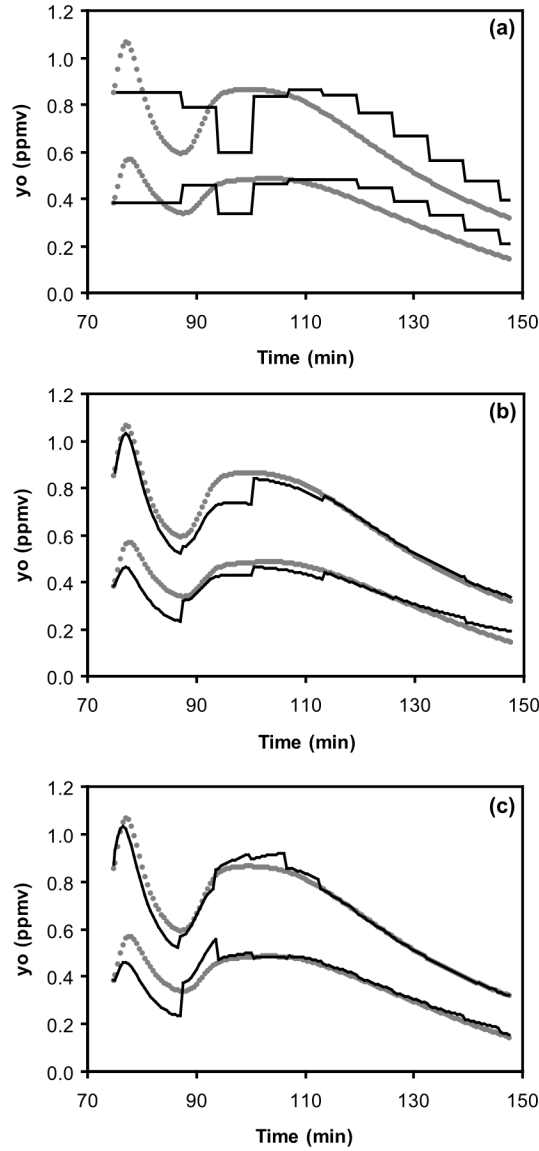


Figure 6.11: Comparison of true and inferred odorant readings for a simulated discharge. The gray circles denote true OD concentrations whereas the lines are the sampled variables: (a) raw data sent by the chromatograph, (b) zero-order extrapolation procedure, (c) first-order extrapolation procedure. Main simulation parameters: $(y_{TBM}, y_{THT})_{in} = (0.4, 0.9)$ ppmv; $F_{in/out} = 100$ L/min; $(P_{low}, P_{high}) = (0.17, 7.0)$ barg; $\alpha = 0$; $T_{z=L} = 20^\circ\text{C}$.

newly-obtained isotherm data. The approach was to develop an improved version of the Ideal Adsorbed Solution/ Adsorption Potential Theory (IAS/APT) model to describe the adsorption processes within the bed for the different molecules; to correlate results of hydrocarbon and odorant adsorption measurements made on ANGWARD carbons with the model; and to use the model to simulate the behavior of the ANGWARD system and to specify control conditions under which desorption of the NG components could be achieved to give desired gas composition on discharge from the storage system.

The dynamic cyclic model of the guard bed was used to size the guard bed and evaluate its performance relative to the 500 L storage tank that was used in actual testing of the overall system. The simulation results indicate that a 500 L storage tank with a net deliverable capacity set to 50 v/v (i.e. a 50 STP (101.325 KPa, 298 K) liters of gas stored per liter of pressure vessel internal volume was set as the storage target for ANG) requires a volume of guard bed $V_{GB} = 5.725$ L, to prevent its contamination with hydrocarbons C_{6+} and to retain the odorants in the guard bed. Thus, the computed volume of the guard bed is only 1.1% of the total volume of the main storage tank. The model was subsequently employed to demonstrate the feasibility of reodorising the delivered NG by heating the gas. The results show that this simple control scheme using a proportional-integral controller can maintain the total odourisation level of the discharged natural gas at acceptable values. More importantly, with a more complex predictive control scheme it is possible to odorize the outlet gas stream at a very accurate level.

The ANGWARD carbons were designed on the basis of their working capacity for higher hydrocarbons. When the selected carbons were delivered to Advantica for testing, it was important to characterize them for odorant performance using real NG. In preliminary laboratory tests in UK, a 25 mm tube guard bed was used for this purpose. The data obtained illustrated that, for ANGWARD 4 and 5, both odorants present in UK natural gas could be recovered with a significant proportion of this odorant being recovered by pressure swing. It also illustrated full recovery of all hydrocarbons. Recovery of all components was achieved at temperatures lower than 70°C. This once again gave confidence that an improved carbon formulation had been produced, and that the results of the adsorption measurements of single components on these carbons, made at FCT/UNL, could now be correlated with real NG behavior. This then led to final testing phase, following delivery and integration of all the ANGWARD hardware and software.

Unique experimental determinations of adsorption equilibria for the components of NG, including, methane, ethane, propane, butane, and odorant compounds tertbutyl

mercaptan (TBM) and tetrahydrothiophene (THT), carbon dioxide and nitrogen, were obtained on a newly developed carbon formulation, ANGWARD 5 carbon supplied by partner Sutcliffe Speakman Carbons Ltd (SSCL). The experimental adsorption data were successfully correlated using the Adsorption Potential Theory (APT). The experimental description and procedure, the adsorption isotherm data and the model predictions through the APT are listed in section 4.2, since the work performed under the ANGWARD project was also part of the hybrid PSA/Membrane separation process developed during the thesis.

There is experimental evidence that the analysis of the n -alkanes series on the carbon, for these applications, can be done using the Adsorption Potential Theory, as demonstrated recently by C. E. Holland and Ritter (2001b) on Westvaco BAX-1100 carbon, and assumed previously by the group [Mota (1999); Mota and Rodrigo (2000)]. The experimental data collapsed into a single temperature independent characteristic curve, plotted in Figure (4.15). The lack of scatter in the plotted data demonstrates the temperature independency of the characteristic curve and corroborates the applicability of the APT to the carbon under study.

An improved version of the Dubinin-Astakhov (DA) isotherm model was derived to model the behavior of the guard bed (see section 4.2). The parameters of the new model were obtained by regressing an extended set of experimental adsorption data. The regressed value of the specific micropore volume, W_s ($0.860 \text{ cm}^3/\text{g}$), is in excellent agreement with the total pore volume determined from the N_2 adsorption at 77 K ($0.850 \text{ cm}^3/\text{g}$) and from the mercury porosimetry ($0.881 \text{ cm}^3/\text{g}$) for the adsorbent selected (ANGWARD 5). The adsorption equilibria plots show a very good agreement between the model predictions and the experimental values for all of the adsorbates. Thus, the isotherm model should prove to be very useful for predicting the adsorption capacity of an ANG storage tank and to size and optimize the operation of a carbon-based filter for ANG applications.

6.3 Project Final Results

The experimental testing of the integrated guard bed system was performed to simulate a typical diurnal storage cycle, as shown in Figure (6.12). Through the prototype guard bed and storage vessel integration, the design and technical considerations behind it, and the control system implemented, the final outcome was the proof of the ability of the system to store and deliver gas of the required quality. Regeneration of pipeline quality of NG on discharge from the storage system, provided the final confirmation of the ANGWARD concept.

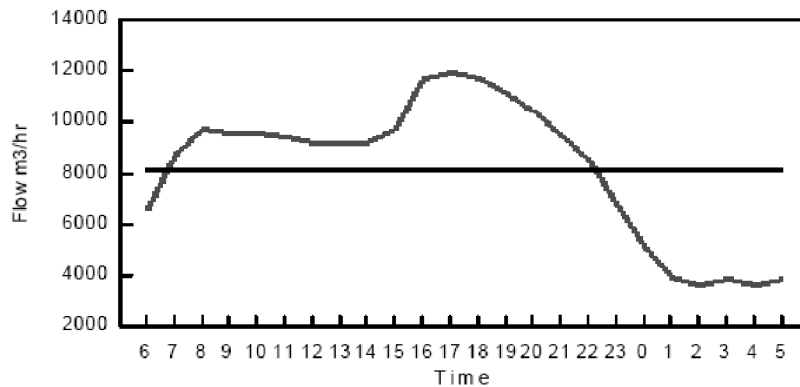


Figure 6.12: Typical diurnal flow profile for a local gas distribution system [ANGUARD (March 2004)].

In the final testing phase, the ANGUARD system, integrated with the main ANG storage vessel and gas handling system, was used. Flow rates into the vessel were designed to assume vessel fill rates which could be expected during a diurnal cycle, but were tailored such that maximum pressures never exceeded 10 bar, and allowed a fill to occur in less than 2 hours. Likewise, discharge used a range of flow rates which corresponded to typical diurnal requirements. If a full diurnal fill had been used, main vessel pressures up to 25 bar would have been needed, and excessive amounts of NG and time would have been required. The guard bed was therefore somewhat oversized for the amount of gas usually used.

Natural gas 1: Low odorant runs

A low odorant NG was used for this work. This contained no TBM, and 0.25 ppm DMS, i.e., only one odorant. All other compositions were as for standard UK natural gas. The results of these tests illustrated the sensitivity of the control system, as the original specification for the system assumed that odorant concentrations would be up to 100 times greater than used here, as for many European gases. Simulations of the expected behavior of this NG were carried out for the expected flow profiles, and the results of these simulations incorporated into the control software. Figure (6.13) illustrates the results for the 5th low odorant charge-discharge cycle.

Natural Gas 2: High odorant runs (UK pipeline quality natural gas)

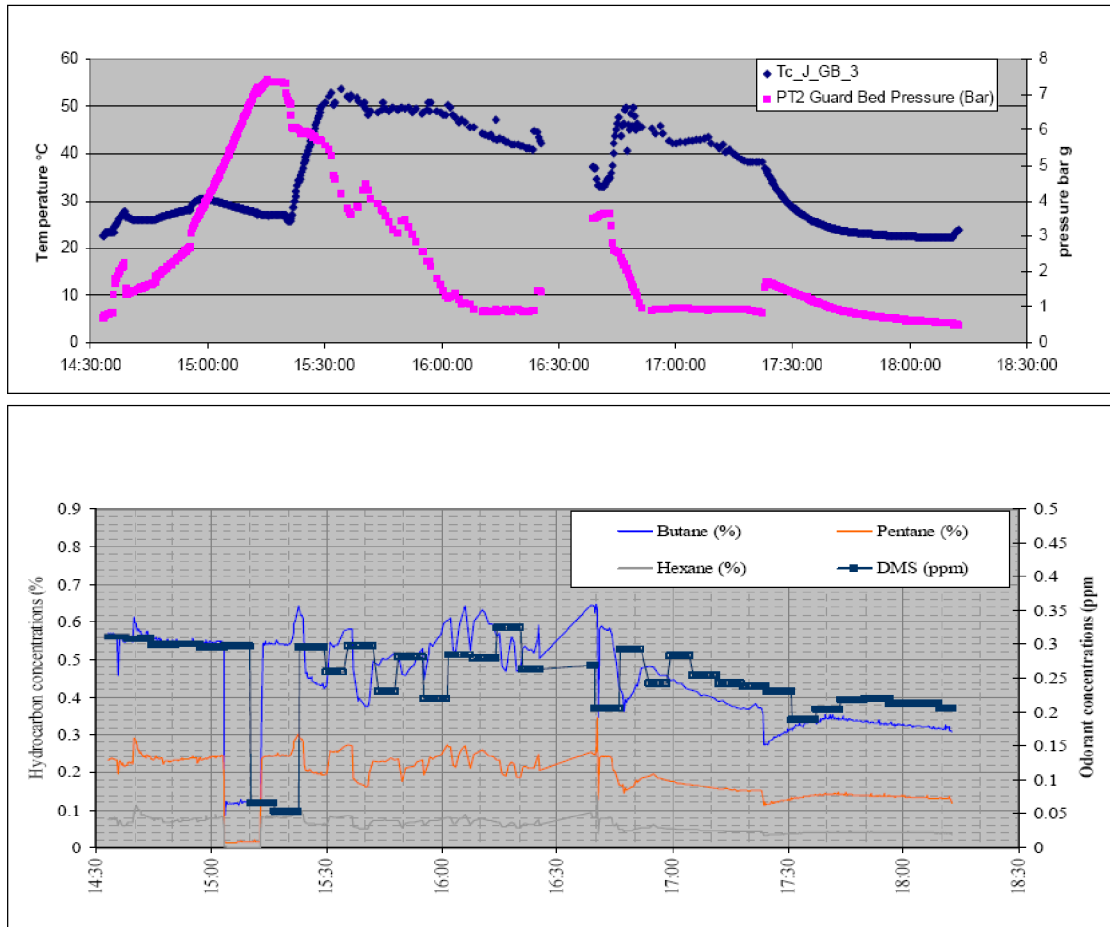


Figure 6.13: ANGWARD charge and discharge for low odorant gas. Discharge began at approximately 15:15 [ANGUARD (March 2004)].

In total, 8 runs were performed to simulate a typical diurnal charge-discharge cycle. Table (6.2) lists all the runs, although some were not completed due to continuous rig and control system improvements. Each experiment yielded a substantial set of data on gas flows, pressure and temperature throughout the system and as a result modifications were continually made to improve control response. Between the low odorant and high odorant runs, a newly written control *.dll* was installed to take into account the different expected outputs. This introduced new errors into the system which were removed during the course of the first 5 high odorant runs. Another significant change was moving the temperature control point to sample as close as possible to the front of the guard bed carbon charge, as the simulation assumed conditions at the leading edge of the guard bed. Compensation was also made for pressure differentials. The model assumed that the pressure in the guard bed would mirror exactly that in the main storage vessel. Because of the dynamics of the mass flow control chain, this was not the case; the model was

Table 6.2: Summary of high odorant (i.e., UK normal natural gas) runs.

Run	cycle number	Comment
HOR1	1	Modifications to controller and hardware to optimise output.
HOR2	2	
HOR3	3	
HOR4	4	
HOR5	5	
HOR6pt1	6	New ANGWARD dll controller installed at end of this stage
HOR6pt2	6	TBM not desorbing. Adsorbed on internal surfaces of the pipe work and valves.
HOR7	7	Excellent control, but TBM dropping (see above)
HOR8	8	Perturbation of control system by increasing temperature shows that controller was already operating correctly.

updated to take these differences into account. In fact the final system change was made at the end of the charge point of the 6th high odorant run, HOR6, which meant that gas was maintained in the system for over 24 hours during this run.

The discharge from the guard bed during run HOR6 is illustrated in Figure (6.14). The most significant feature of this run is the complete lack of any TBM in the discharge traces. This revealed that the pipe-work, despite attempts to deal with this, was not completely conditioned to prevent reaction with TBM. If this is taken into account, the results of the subsequent runs can be explained in terms of this process, and confidence is established that the control system is operating correctly.

HOR7 shows perfect response by the ANGWARD system [Figure (6.15)]. There is very high level of manipulation and control due to the model and control software functioning well together. Desorption of hydrocarbons and DMS odorant is smooth and uniform, giving exactly the required gas quality at the outlet. The TBM trace again shows the retention on the internal walls of the pipe work due to the fact that the system was inadequately pre-sulphided. Further evidence that this was indeed happening was obtained in the next run (HOR8).

HOR7 demonstrates that the seemingly impossible task of achieving a guard bed and control system that removes the required trace components and then releases them in a smooth and consistent manner, has been realised with ANGWARD. It also provides information on the preferential adsorption of TBM on clean metal surfaces and indicates the need for conditioning the internal surfaces of the system to prevent this occurrence.

Run HOR8 is presented in Figure (6.16). This illustrates the performance of the control system and illustrates that previous run HOR7 was in fact providing ideal control.

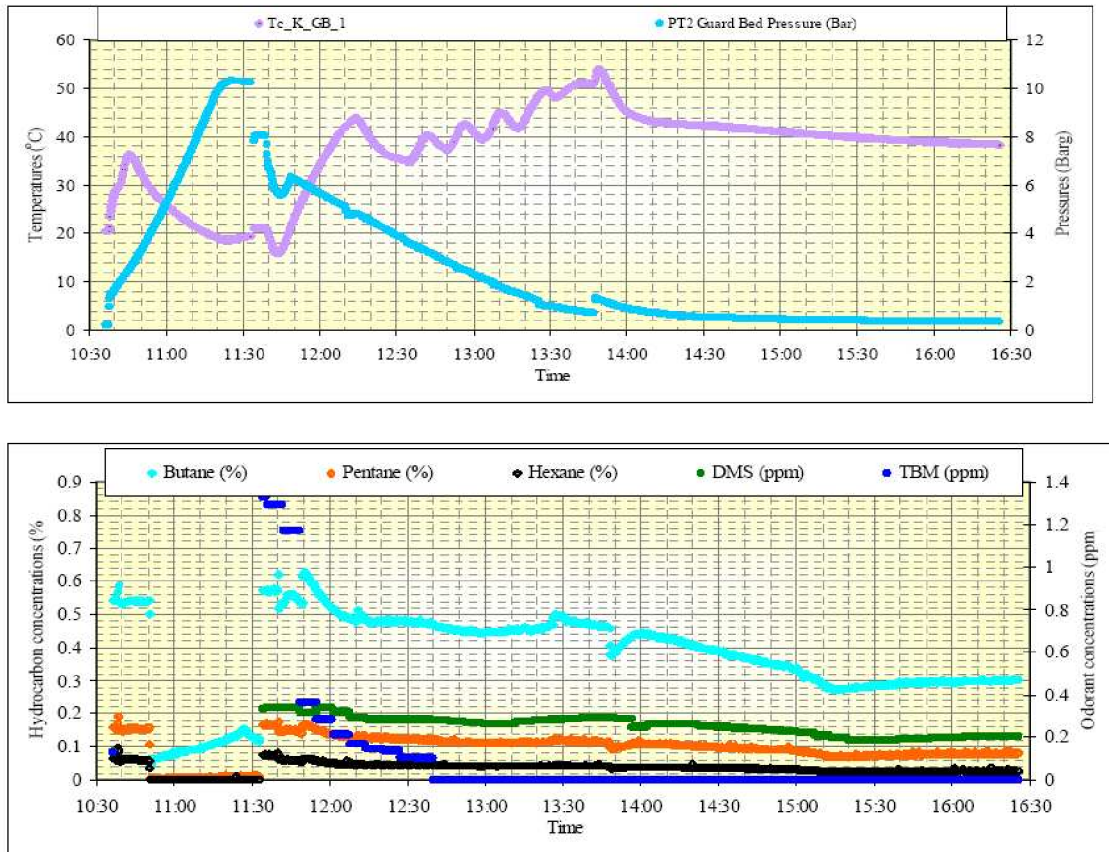


Figure 6.14: High odorant run 6. Charge on this scale appears to occur from 10:50 to 11:35, although main charge took place over 24 hours earlier, with discharge being preceded by a brief top-up. The decay in TBM reflects recovery of the small quantity of TBM added in the top-up charge [ANGUARD (March 2004)].

Upon start of discharge, the TBM desorption rate began to fall slightly, so a change was made to control temperature (actually position of control thermocouple), to get the guard bed hotter, and hence maintain the desorption rate of TBM. This also meant that concentration of other components rose above the normal controlled level, meaning that later in the discharge insufficient hydrocarbons and odorants remained to maintain the levels and therefore these (including TBM) dropped below that required. This is further evidence that the reason for the low TBM concentrations during discharge is adsorption and reaction with the pipework. The TBM is no longer available for desorption and therefore any attempt to increase its rate will reduce in overall depletion of the guard bed.

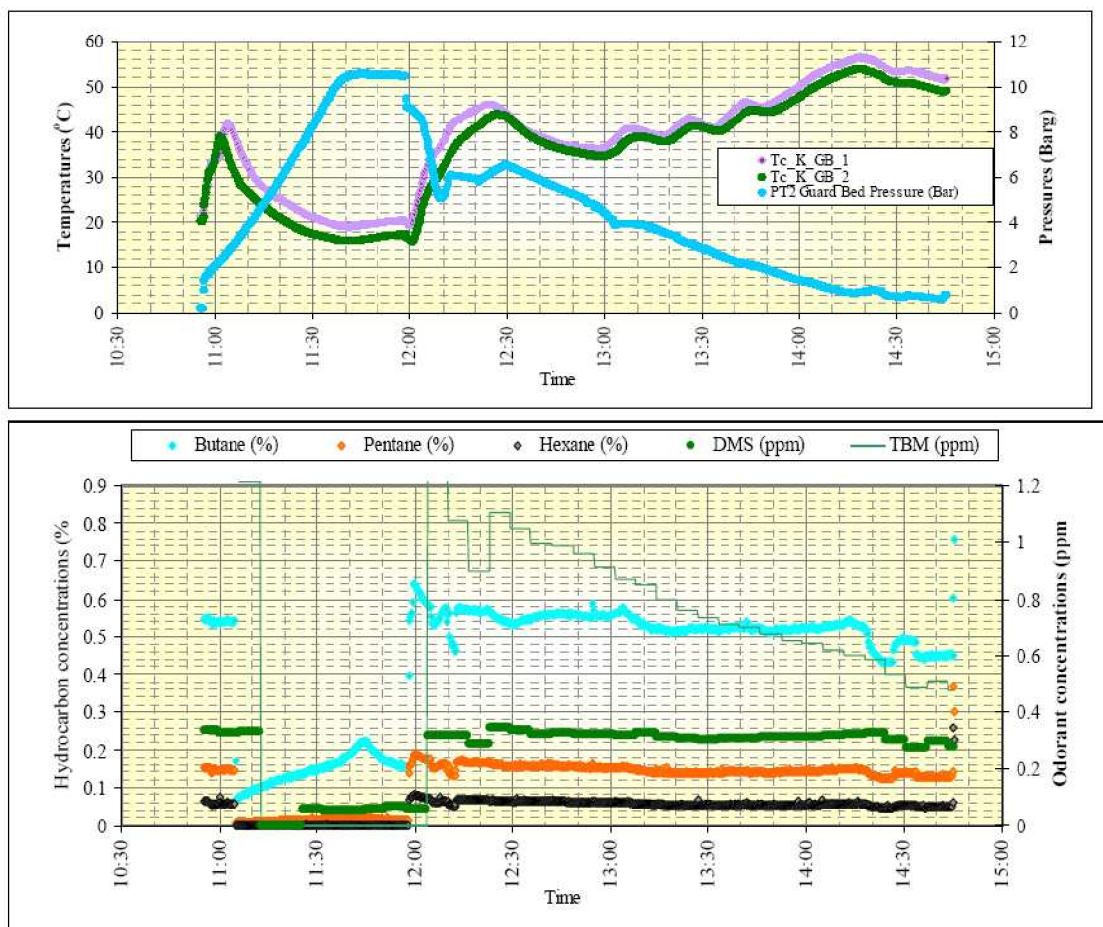


Figure 6.15: High odorant run 7. Charging of the vessel occurs between approximately 11:10 and 11:58, the subsequent time being discharge [ANGUARD (March 2004)].

6.4 Conclusions

The quantification of the success of the project can be summarized below:

- Guard bed and unique control system was developed that filters out the trace components during filling and releases them in a controlled manner during discharge. Highly efficient filtering of C_{5+} and odorants, and process completely reversible on discharge with high degree of control. Nevertheless, information on the preferential adsorption or reaction of TBM on clean metal surfaces and pipework was obtained, indicating the need for conditioning the internal surfaces of the system to prevent this occurrence. The internal wall surfaces of the rig pipe work need to be sulphide passivated so as to prevent strong adsorption of TBM odorant.
- Innovative multi-component model developed, and novel adsorption isotherms and

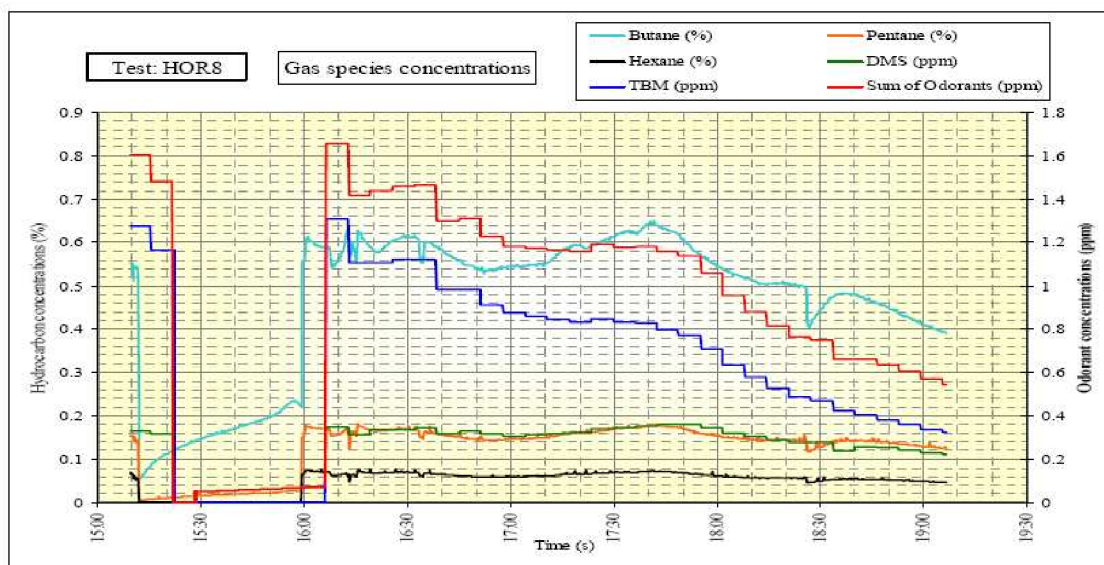


Figure 6.16: High Odorant run 8: UK Natural Gas. Charge was from 15:10 to 16:00. The system temperature was perturbed at approximately 16:55 [ANGUARD (March 2004)].

data obtained experimentally for NG components on activated carbon. The model is highly predictive of gas composition at any stage in the process and is the basis for the control system in ANGUARD.

- Integration of the guard bed with the main storage vessel completed, and proof of concept testing successfully carried out. Highly effective collaboration/synergy between the modelers, control system developers and system testers has resulted in a responsive and versatile system design that can be adapted for a range of applications and scales.

To finalize, experimental safety data have been established and quantitative safety models developed, that in combination demonstrate increased safety of storage operations by ANG. The analysis indicates the need for a carbon trap and protection of the relief valve by a filter, coupled with the use of larger carbon particles (around 10 mm diameter) to avoid ANG particle deposit build-up process and relief valve failure with ejection of gas-laden carbon from the main vessel. The use of a mesh inside the ANG vessel by the relief valve, and the use of larger particle size (around 10 mm), together improve significantly the behavior during release and reduce the risk associated with this scenario well within manageable limits. The potential guard bed hazards derive also from the presence of odorants at high concentration, and to the possibility of SO_2 formation; however, the short term exposure level (STEL) for SO_2 is 5 ppm for 5 minutes, whereas the lowest fatal exposure is 1000 ppm for 10 minutes.

Table 6.3: Application related assessment of results of ANGWARD.

Application Characteristic	Diurnal	Power Generation 40 MW	Vehicular	Measure of ANGWARD Results
Max flow rate (Nm ³ /hr)	7000	7000	400	ANGWARD system easy to scale up, using predictive model and experimental data.
Total capacity Nm ³	30000	21000 (3hrs back-up supply)	Typically up to 0.1	
Removal duty-odorants	Remove odorants. Maintain odorants within gas quality specifications on discharge.	Remove odorants.	Remove odorants on the charge, and desorb on discharge, gas quality on discharge cycle less important.	Control system flexible and adaptive ANGWARD tested and proven with most adverse gas composition. 100% removal/release.
Removal duty- Hydrocarbons	100 % C6+, replace to pipeline on discharge.	100% C6+	100% C6+	
Heating method for guard bed	Indirect. Check upper temperature limit!	Indirect	Electrical	Anguard system demonstrates control of temperature.
Pressure drop	Minimal (as not to impact on main storage vessel) <0.1 bar. Function of velocity, particle size and voidage.	Minimal (as not to impact on main storage vessel) <0.1 bar. Function of velocity, particle size and voidage.	Minimal	Pressure drop not an issue in ANGWARD system.
Temp or pressure swing?	Both. For temperature check C6+ isotherms.	Potential to swing guard bed pressure independently for high psa recovery.	Temperature	ANGWARD demonstrates carbon with minimal temperature swing and energy input.
Tank configuration	Aspect ratio. Relates to pressure drop, heat exchange, adsorption/desorption kinetics. Methods of heating.	As diurnal.	Long residence time. Aspect ratio not as critical.	
Pressure & temp. range	7 barg – 15 mbar to 40 – 7 barg. 80°C would be sufficient but 200°C would reduce guard bed volume. Need to evaluate economic benefit of upgrading to higher temp. More power required.	As diurnal.	35 bar – 15mbar	
Feedback control	Manipulated variable: heat input. Need to monitor odorant concentration with feedback control.	Feedback control on discharge not important.	Feedback control on discharge not important.	Demonstrated effectively for diurnal application.
Safety	Covered in WP8.	Covered in WP8.	Covered in WP8.	Shown that hazards are reduced compared to CNG.
Process configuration	Bypass configuration to be considered. Benefit of enhancement versus cost versus risk.	Bypass not required.	Bypass not required.	Bypass demonstrated effectively in ANGWARD.
Vessel material	Carbon steel. Poss. Carbon Manganese.	Carbon steel. Poss. Carbon Manganese.	Carbon steel. Poss. Carbon Manganese.	
Maintenance & Lifetime	Define by design margin. Diurnal storage GB can be maintained during the summer months.	Can be maintained during the summer months.	Continuous operation required.	ANGWARD addressed gas quality issues leading to increased lifetime.
Fluidised vs fixed	Variable demand profile would make this difficult. Dust would be an issue. Revisit if Fixed beds prove to be problematic.	Variable demand profile would make this very difficult. Dust would be an issue. Revisit if Fixed beds prove to be problematic.	Variable demand profile would make this very difficult. Dust would be an issue. Revisit if Fixed beds prove to be problematic.	
Fill/discharge flow profile	kinetic considerations due to differing fill and discharge profiles	As diurnal	Fast vs slow fill. Temperature profiles vs demand.	
Carbon external geometry	Granular, extrudates, monoliths. Effect on kinetics. Thermal conductivity. Availability.	Granular, extrudates, monoliths. Effect on kinetics. Thermal conductivity. Availability.	Extrudates and Monolithic forms more suited to application. Effect on kinetics. Thermal conductivity. Need highest volumetric storage performance.	

The results of the ANGWARD development show that the Consortium has achieved an innovative and flexible process for NG storage operations that makes it in principle, very amenable to a number of applications, such as diurnal storage options, power generation or vehicular applications. Table [6.3] list some applications related assessment of results of ANGWARD.

In conclusion, the following achievements have been demonstrated by completion of this project [[ANGWARD \(March 2004\)](#)]:

- Barriers to implementation of the technology have been lowered across a broad range of applications, and a new storage system has been enabled;
- System design is now possible with manageable options for odorant control;
- Tools have been developed to design a complete ANG system;
- Safety contours have been established for the entire storage system and methodologies developed to model and assess hazards associated with the technology;
- Techno-economic studies have determined that the economics of ANG storage can be highly favorable compared to alternatives.

Chapter 7

Conclusions

7.1 Sustainability of Membrane and PSA Processes - An Overview

In the near future, gas separations and the removal of contaminants from air streams will probably represent the main opportunities in membrane processes. It is certain that developments in membrane materials like ceramics, carbon, molecular sieve and polymers, and new configurations will continue to arise. From the several hundred research papers that appear monthly, it is important to remember that all the work must aim to industrial applicability. Both nanoscale and macroscopic modeling is needed to predict the separation performance of membrane materials and hybrid separation systems for several operating conditions with feasibility for industrial applications.

The capture of CO₂, one of the greenhouse gases, either from flue gases or from NG streams, is an example where gas separation technology and adsorption systems may offer efficient solutions and prove the sustainability of those processes. Several other gases like CH₄, H₂ or N₂ are valuable ones and can be obtained through the referred processes.

The sun's radiation that reaches earth's surface results in the heating of the ground surface, melting of the ice and snow, water evaporation and plant photosynthesis. The earth's hot surface acts as a radiator in the IR band and this radiation is absorbed by the greenhouse gases (ozone, CO₂, CH₄, chlorofluorocarbons (CFCs), water vapor, etc.). With the increase of the concentration of these gases, the radiated energy increases, resulting in the global earth's warming. CO₂ is responsible for half of the human contribution to this effect. This gas exists in various NG streams (Appendix C) and results from several manmade applications, like fossil fuel combustion for industry, transportation, electricity generation and cooking. It is expected that CO₂ amount will increase from the current 300-350 ppmv to 500-900 ppmv by year 2100 [P. P. Radecki and Bullock (1999)]. To contradict this tendency, UN climate change convention set up a goal to not exceed 450

ppmv of CO₂ atmospheric concentration. To achieve this results it was recommended for all industrialized nations to reduce CO₂ emissions by 20% below the 1990 levels by year 2010.

CO₂ is currently captured by physical or chemical absorption (scrubbing), where high pressure is used and hence compression is necessary, and solvent stability, concentration and regeneration are key issues associated. Cryogenic is also an expensive and a difficult process. The stand-alone adsorption process is a non-steady state system which requires cleaning the feed stream, compression and the adsorbent is a key issue due to contamination at the operations conditions. Nevertheless, the flexibility given by the gas selective membranes, already used for CO₂ removal, may be combined with adsorption processes and improve overall performance and economics.

The 1999 costs of CO₂ recovery, from various streams, range from \$35-114/ton CO₂ depending on the nature of the feed stream, chemicals used and location of the separation plant. The estimated selling price of crude CO₂ is about \$6-12/ton CO₂ depending on the volume [P. P. Radecki and Bullock (1999)]. Therefore, one can say that the major driver for CO₂ capture is the greenhouse effect, since the economic incentive to recover this gas is not at all significant. To conclude, the motivation for further developments of membrane processes is not the absolute economics of CO₂ recovery but the relative economics of the various CO₂ removal technologies. This example of application was illustrative of the sustainability of the processes described and was part of the motivation of this thesis concerning the development of integrated gas separation systems.

7.2 Economical Feasibility Analysis

7.2.1 Membrane/PSA Processes and its Integration

Cost information is rarely available for new processes under development. Thus, in this section it is given some attention to several considerations concerning the economical feasibility of both membrane and PSA units, with the ultimate goal of understanding the overall economic balance when a hybrid membrane /PSA process is proposed.

In both membrane and pressure swing adsorption processes the main operating cost is the power required to compress the feed stream. So a first estimate of comparative performance can be obtained simply by considering the power requirements [D. M. Ruthven and Kneabel (1994)].

The overall economic balance between the PSA and membrane systems depends mainly on the scale of operation. Membrane processes generally offer the best choice at very small scales, PSA processes are most economic at relatively large scales, and there is a significant intermediate range in which there are little differences in costs between

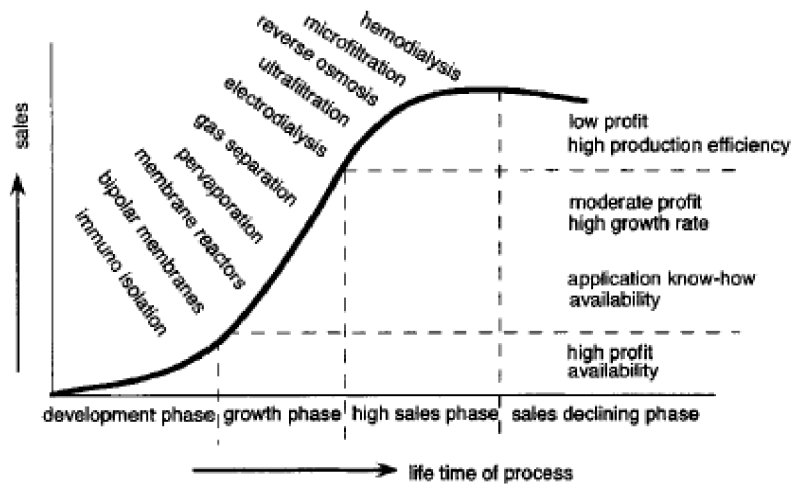


Figure 7.1: Life-cycle curve of various membrane processes.

these systems. Here, PSA and membrane processes are competitive. Membrane are efficient concentrators, but not suitable for production of a 100% purity. At higher purities and throughputs the balance of economic advantage shifts first to PSA systems, then to vacuum swing systems and finally to cryogenic distillation. Recompression costs are very important and must be included in the analysis. Hybrid systems of membrane plus another separation process, are often advantageous [D. M. Ruthven and Kneabel (1994), Wankat (1990)].

Since the capital costs of both membrane and PSA processes increase almost linearly with throughput, while the capital costs for processes such as cryogenic distillation increase less rapidly with increasing throughput, one may expect that most commercial applications of these processes will continue to be at smaller and medium throughputs, rather than at the very largest operation scales.

Concerning membrane processes, their typical life-cycle curve indicates four phases, as shown in Figure (7.1), in which the sales of different membrane processes are presented as a function of its state of development [Strathmann (2001)]. None of the membrane systems are in the declining stage yet. Gas separation is in the rapidly growing phase, showing intermediate sales and moderate profits. Its market is dominated by small segments that are generally served by smaller companies. The availability of components with the required properties and application know-how are key criteria for the sales. As seen, the mature processes have the highest sales but low profits. Here, production efficiency is of great importance because sales are determined mainly by product costs. Its market is dominated by a relatively small number of companies with a high automated and efficiency production.

The problem in membrane processes is the economic cost of using vacuum on the permeate side, or the equally unattractive prospect of compressing the feed and operating at low stage cut. For H_2 , membranes are dominant when the feed is at high pressure. Higher purity or lower feed pressure favor PSA. Very high volume favors cryogenic separation. For CH_4 , membranes compete at low purity and near pipeline (98%) purity, but distillation and absorption are very competitive at large scale and for intermediate CO_2 contamination levels. Membranes are found as adjuncts to most conventional processes, since their use can improve overall economics in cases where membrane strength coincides with conventional process weakness [Baker (2002); Perry and Green (1999)]. It has also been reported that increasing recovery from 90% to 99% will usually double the plant's cost. For this reason, most membrane plants are designed for 80% to 95% product recovery [R. W. Baker and Gottschlich (2000)].

Membranes have three key performance attributes that affect their economic utility for a certain application. The permeability dictates the amount of membrane required, setting the capital cost of a membrane. The selectivity towards the gases to be separated sets the operational cost, directly impacting the recovery of the process and indirectly impacting membrane area and feed gas flow requirements. The third key attribute is the life of the membrane, its maintenance and replacement costs. Thus, there are many combinations of permeability and selectivity which, for a particular separation process will result in the same total cost. Capital cost is approximately inversely proportional to the permeability and to the pressure drop across the membrane. The running cost is inversely proportional to the selectivity and increases rapidly if high purity products are specified [Hichliffe and Porter (2000); Spillman (1989)].

It is reported in Perry and Green (1999), that for most permeation processes, membranes have a characteristic economy of scale cost

$$\phi_1 = r \text{ (area)}^a \quad (7.1)$$

and equipment surrounding and supporting the membrane have an economy of scale cost

$$\phi_2 = s \text{ (size)}^b \quad (7.2)$$

where r and s are empirical constants. For all membrane equipment, it is assumed that $a > b$. There is a trade-off between the amount of membrane area required and the supporting equipment. Either the designer can put in more pumps, thereby achieving higher fluxes and using less membrane; either the device is limited by some other physical factor, such as pressure. There is also a trade-off between adding more membrane area and

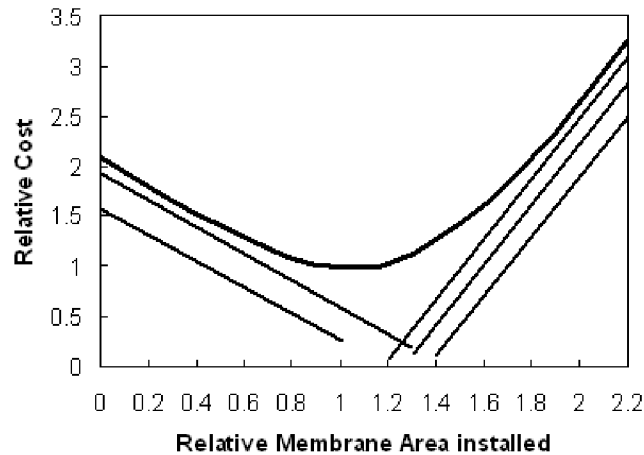


Figure 7.2: Typical simplified capital-cost schematic for membrane equipment showing trade-off for membrane area and mechanical equipment [Perry and Green (1999)].

more ancillary equipment to make the membrane installed more productive. According to the membrane type, the values r and s vary with the kind of membranes and ancillary equipment used, although the exponent a is about the same. The authors present an interesting characteristic schematic of the balance between membrane area and ancillary equipment for a particular plant, shown in Figure (7.2). Lines shown are from families for parallel lines showing limiting costs for membrane and for ancillary equipment. Lines with positive slope represent the total membrane cost. Lines with negative slope refers to the total ancillary equipment cost. The curve is the total capital cost. The minimum cost is at 1.0.

For actual cases studied, the cost of membrane and its immediately related costs (manifolds, housings, etc.) varies with the 0.9 power of area. The cost of ancillary equipment (pumps, pipes, etc.) varies with the 0.4 power of size. Total capital cost represents the sum of the membrane related and the ancillary equipment, shown in Figure (7.2) as a curve with a minimum at the point (1,1). As the curve moves away from the minimum, costs rise approaching a line with slope 0.9 as membrane area increases, representing in the limit the cost of membrane. Moving to the left, the costs approach a line with slope - 0.4, representing in the limit the costs of ancillary equipment. For both membrane and ancillary equipment, there will be a series of parallel lines depending on the values of r and s for the different kinds of equipment chosen for the separation. For example, substituting a ceramic membrane for an organic membrane does not imply that the kind of pumping equipment employed will change. Assuming the ceramic membrane is costlier, using a membrane cost curve shifted upward will change the optimum-cost point, shifting it to the left.

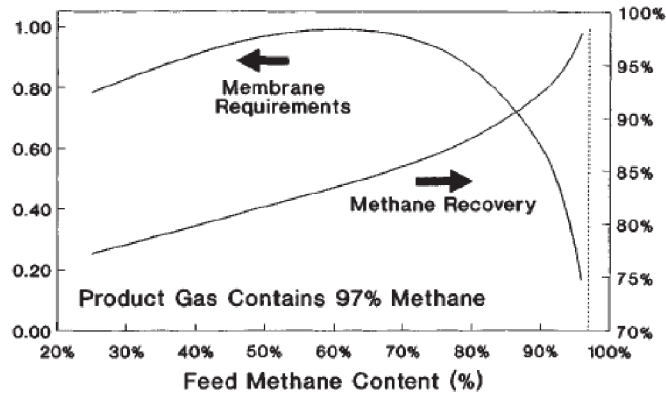


Figure 7.3: Influence of feed purity on total membrane area when the residue gas at fixed purity is the product. Feed gas volume is constant. CO_2/CH_4 cellulose-acetate membrane, $\alpha = 21$ [Perry and Green (1999)].

Another similar curve can be drawn for total operating costs. The three biggest elements in operating costs are usually capital charges, membrane replacement and energy. For most industrial installations, capital charges dominate everything. Membrane replacement is a significant cost factor, but membrane life and reliability are now relatively reasonable. Depending on the local economics and the process, the total operating cost minimum may be shifted a bit to the right or the left of the capital cost minimum, but usually not by a great amount. If membrane life is short, the optimum will move left, while if energy is costly, it will move right.

If compression of either feed or permeate is required, it is highly likely that compression capital and operating costs will dominate the economics of the gas-separation process. When the feed enters the separation process at pressure or/and the residue is the product, it is an advantage for membranes. On contrary the recompression needs may be a significant cost.

Figures (7.3) and (7.4) presents the influence of feed purity on total membrane area when the residue gas at fixed purity is the product, and when the permeate gas at fixed purity is the product, respectively. When the permeate is the product (H_2 or CO_2) the membrane area increase shown is largely the effect of more gas passing through the membrane, since the curve is based on a constant volume of feed gas, not a constant output of H_2 . A distinct behavior is presented when the residue constitutes the product.

According to Baker (2002), the future growth of membrane gas separation will be in the refinery, petrochemical and natural gas industries, with significant increase in the size of the average membrane plant. Membranes resistant to plasticization and able to operate at temperatures of 70-100°C are required in the industrial field.

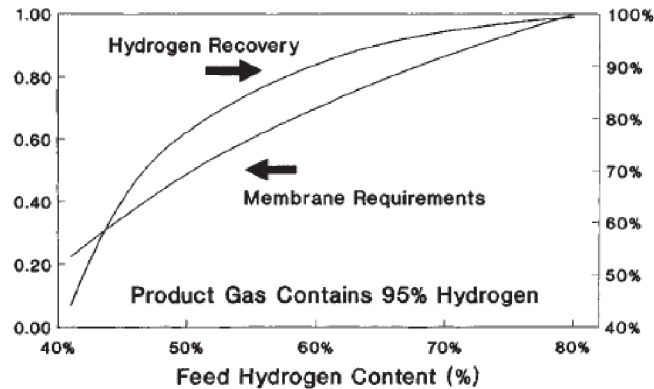


Figure 7.4: influence of feed purity on total membrane area when the permeate gas at fixed purity is the product. Feed gas volume is constant. H_2/CH_4 cellulose-acetate membrane, $\alpha = 45$ [Perry and Green (1999)].

Concerning the adsorptive systems, the amount of adsorbent required and the vessel dimensions are strongly dependent on the nature of the adsorption cycle, the operating conditions, and the adsorbate and adsorbent. This is in contrast with permeation systems since the cost of a membrane process is firstly dominated by the cost of the membrane itself. The energetic costs are also a major economical component that depends on the nature of the cyclic process. For PSA the energy requirement depends on the feed availability at an reasonable high pressure and on the necessity of pressure differences, i.e., the low pressure requirements, as well on the desired product purity.

7.2.2 ANG Processes

Compact, high-density pressure vessel storage for stationary applications using ANG technology improves the social acceptability of necessary gas storage by reducing the ground area and visual impact of storage facilities. Compared with existing facilities, ANG is anticipated to have a volume reduction factor of about 2.5 compared with pressure vessel storage or about 60 compared with low-pressure volumetric (gasholder) storage. By significantly enhancing the capacity of existing pressure vessel stores, it reduces the use of urban land for new facilities to meet expanding demand. Successful exploitation of the technology would lead to increased employment opportunities through manufacturing capacity, project design and installation, and facility operation.

Hence ANG technology is clearly needed. Emission control calls for using clean fuels for vehicles. Although hydrogen is the cleanest fuel that can achieve zero emission through fuel cells, NG will play the major role for many years, before hydrogen energy can be commercialized [Cannon (1994)]. Compared to compressed natural gas (CNG), ANG has the virtue of low storage pressure. As a consequence, savings in both investment and operation costs are expected.

Table 7.1: Estimated costs in Euros for processes implementing the guard-bed partial bypass system.

Design	Guard bed vessel	Heat exchanger	Hot water system	Total
5 m ³ Guard Bed	95.150	88.510	207.080	390.740
10 m ³ Guard Bed	116.900	88.510	207.080	412.490
10 m ³ Guard Bed with 40% recycle	130.260	80.160	168.670	379.090
5 m ³ Guard Bed with 70% recycle	106.880	55.110	110.220	272.210

The potential EU and world-wide market for the technology is very large. For example, a 10% penetration of the diurnal storage grid-support application alone would amount to about 1.5% of the total peak day gas demand in each network, typically at least 3% of the average daily demand. This corresponds to creating an additional 35 million m³ of storage capacity across the EU, with an estimated income to European companies of 1.2 billion Euro [ANGUARD (March 2004)].

A study of estimated installed costs was carried out for two sizes of guard bed, 5 and 10 m³ nominal volumes to examine the effect of employing the recycle process. The guard bed system is comprised of a guard bed vessel and carbon bed, a heat exchanger and a hot water system. There are additional costs known as bulks associated with valves, piping, structural steel, site assembly, foundations and lagging. The overall results of the calculations are shown in Table (7.1), indicating that the use of a recycle loop has a significant effect on lowering costs.

For the 10 m³ guard bed case, only a maximum of 40% of the gas could be by-passed around the guard bed. Once the extra cost of the additional pipe-work and instrumentation has been accounted for, the cost advantage is slight. For the 5 m³ guard bed under the stipulated conditions, the total installed cost of the guard bed system can be reduced by 30% by utilizing the gas by-pass method. If the guard bed size can be reduced further by developing a better guard bed carbon, then this would allow a higher gas bypass ratio, reducing the duty and subsequently the cost of the heat exchanger and hot water system.

7.3 Resume

To conclude this thesis, a brief resume of the work developed during the last four years is presented:

- The adsorption measurements section reports the adsorbent selection and equilibria experimental procedures, the methods used, the results and their analysis. The adsorbent selected was also part of the european project work. The experimental measurements of equilibrium and adsorption kinetics were performed for several

components (C_1 – C_4 , CO_2 , N_2 , THT, TBM). The data was analyzed using the Adsorption Potential Theory and incorporated into the dynamic model of the guard bed; for PSA modeling purposes, however, a more detailed study of the adsorption isotherms was done through the Sips and Toth approaches.

- Permeation measurements were also carried out, where permeances and selectivities similar to those used in the modeling work were obtained experimentally.
- A Pressure Swing Adsorption unit was designed, built. Experiments are reported in order to validate the modeling work and obtain enriched product streams. The laboratory unit is controlled with an in-house developed user-friendly windows interface, with real-time acquisition, visualization and control of the main operating variables, such as temperature, gas flow, pressure, cycle step time intervals and set of switching valves.
- A five-step PSA cycle of ≈ 12 min was implemented in the CO_2/N_2 separation: 1) Pressurization (PR), 2) High pressure adsorption (HPA) step ($P_H = 6$ bar), 3) Cocurrent blowdown (HBD) (up to $P_M = 3.2$ bar), 4) Countercurrent blowdown (LBD, up to $P_L = 0.3$ bar), and 5) Low pressure purge (LPG, at P_L). During HPA and HBD, N_2 product is produced, and during LBD and LPG, the CO_2 product is obtained. In general, depending on the feed composition, a N_2 purity and recovery in the range of 51–99% and 66–69% were obtained, respectively. A CO_2 purity and recovery in the range of 54–92% and 83–99% were obtained, respectively. The performance of the dynamic PSA cycle executed, was compared with the enhanced performance of an hybrid process where a membrane unit was added to the conventional cyclic operation of the PSA process. Results predict an advantage for the use of the integrated membrane/PSA process over the stand-alone PSA, specially in the high feed throughputs region.
- A new dynamic cyclic simulation of a hybrid membrane/pressure swing adsorption (PSA) system, used for binary bulk gas separations, was developed on a mathematical model. Single membrane and PSA models were firstly developed in order to validate and study each unit individually, and finally the integrated process was implemented and analyzed. Two main different hybrid cyclic schemes were developed. Instead of the regular A/B binary mixture feed, the PSA is fed with a mixture which is progressively enriched:
 - in the least permeable/more adsorbed component (called MEMPSA – CASE A process),

- or in the more permeable/more adsorbed component (called MEMPSA – CASE B process).

For each case, simulations were performed to investigate the effects of the most important operating parameters on the performance of the system. Using the different enriched streams from the membrane, the results show that these integration steps enhance the sharpening of the composition wavefronts inside the sorbent bed, giving rise to a decrease of the dispersive forces and higher purity products, enhancing the final process performance.

- Finally, the thesis gave a contribution to the development of ANG process for gas storage applications, performed under the european project ANGUARD and started in 2000, with the duration of 38th months. Since the project was a cooperation of several european industrial and scientific institutions, several tasks were simultaneously undergoing, which, personally gave an enormous motivation to perform the work under the Energy, Environment and Sustainable Development areas.

7.4 Future Work

7.4.1 Membrane/PSA Processes

Undoubtedly, there are several aspects that deserve a continuously attention beyond this thesis. The following recommendations are proposed:

- The equilibrium data of the several gases studied was measured in a high-precision high-pressure magnetic suspension balance, from Rubotherm (GB). Although its tremendous repeatability and accuracy, its operation is limited to pressures in the range UHV - 150 bar and temperatures up to 100°C. It will be difficult to work with an adsorbent with low activity, whereas a degassing procedure at higher temperatures are required.
- Experimental PSA apparatus improvement, specially concerning with temperature and dead volume effects, will add more flexibility to the laboratorial unit.
- The PSA lab-unit is prepared only to operate under controlled pressure conditions in the range of 3–16 bar, and at a stable temperature range of T_{amb} –50°C. These are the main limitations observed. Physically, the PSA vessel is prepared to operate at pressures well above, due either to its wall thickness, either to the available in-line equipment. Nonetheless, temperatures below the ambient one are not possible at the time, since there is no cooling on the apparatus. The availability of only two

digital outputs on the control boards limits the PSA control. This problem should be solved, to execute a real automatic cycle, without needs for human actuation during a experimental run of several cycles.

- A set of more extensive multicomponent permeation measurements are needed, since at the time of the permeation measurements there was no possibility of analyzing multicomponent streams exiting the membrane module. Its also of interest to perform membrane modeling to validate the experimental permeation work.

The possibility of experimentally simulate the use of the exit streams of the membrane module as feed for the PSA unit is a challenge, now possible through the full automatic control of the PSA apparatus. This will reproduce and perform the gas separation using the integrated concept.

- Future work concerning the PSA technology may pass through the coupling of a second adsorbent bed in order to truly perform experimental cyclic operation. Alternative adsorbents can be examined, namely the ANGWARD 6 sample, from Sutcliffe Speakman Carbons Ltd (SSLC, UK), developed after the ANGWARD 5 selection for the project, and a monolith sample also supplied by SSLC which could lead to higher storage capacities and enhancements of ANG technology.
- Besides common performance evaluation of the process, it would be interesting to use the gPROMS optimization package on the hybrid systems developed.
- Concerning the modeling work, several assumptions were made regarding mathematical simplifications. Several parameters, such as heat capacities were assumed independent on temperature; pressure drop on the column was assumed negligible, supported on the preliminary analysis made; radial coordinate in conservation equations were disregarded; from initial permeation simulations made, the temperature effects and pressure drop on each permeator-side were not assumed. Correctly, all of those items should be included in the models. Nonetheless, the aim of the work was to research and prove the feasibility of the innovative hybrid membrane/PSA concept and alternative process for a specific separation of a mixture available at a prescribed operating conditions.

7.4.2 ANG Processes

Future work concerning ANG processes would be the development of guard beds for other applications such as in ANG vehicles. As an alternative to a parallel programme to build a vehicle guard bed, the Consortium has examined vehicle guard bed operational requirements and specifications, and the options of locating the guard bed on-board the

vehicle or integrating it within the refueling station so that the filtering out of the trace components occurs outside the vehicle.

Appendix A

Equipment Description

✓ **High-pressure magnetic suspension balance (MSB)** [Figure (4.1)]

Model: ISOSORP 2000 coupled with a Sartorius microbalance Model BP211

Supplier: RUBOTHERM GMBH Characteristics: for a maximum load of 25 g (total measuring volume, ie. suspension coupling and measuring cell with sample), the balance have a resolution of 0.01 mg, an uncertainty $\leq$ than 0.002% of the measured value, a reproducibility $\leq$ than 0.03 mg, for pressures in the range UHV - 150 bar and temperatures up to 100°C.

✓ **Vacuum Pump (VP)** [Figures (4.2, 4.31)]

Model: A65201

Supplier: BOC EDWARDS

Characteristics: pumping speed 3 m³/h, single-phase 50/60 Hz 110/240 V set to 240 V, operating temperature of - 30°C to 70°C, maximum total pressure in high flux of 1.2×10^{-1} , maximum total pressure of 2×10^{-3} , hydrocarbonated oil.

✓ **Glass Trap**

Model: U-03763-20

Supplier: COLE-PARMER

Characteristics: 1L 304SS dewar flask

✓ **Mass Flow Controllers (MFCs)** [Figures (4.2, 4.31)]

Model: HFC-202

Supplier: TELEDYNE HASTINGS

Characteristics: analog thermal mass flow instruments with flux range of 0.01–30 slpm, accuracy and linearity $\pm 1\%$ FS, repeatability $\pm 0.05\%$ FS, pressure rating of 500 psig, leak integrity $< 1 \times 10^{-9}$ sccs, temperature coefficient $\pm 0.03\%/^{\circ}\text{C}$ (15–45°C) and $\pm 0.05\%/^{\circ}\text{C}$ (0–50°C), STP at 0°C and 760 Torr, input supply ± 15 V at + 50 mA/- 200 mA, flow signal 0–5 V, command 0–5 V with normally closed

valve, 15 pin connector. The instrument is used for different gases through a gas correction factor (GCF) that ensures the original calibration precision. The GCF is necessary when a surrogate calibration gas is used in the adjustment of the mass flow controller instead of the actual process gas to be measured. The GCF is calculated using the ratio of the molar specific heats of the calibration gas and the gas to be measured at the desired temperature. The calibration of all the MFCs was checked in our laboratory. The GCF is then multiplied by the maximum gas flow value to obtain the flow range of the MFC for the specific gas.

MFC I: flux range of 0-10 slpm (STP: 25°C, 760 Torr) calibrated for N₂ at 21.8°C, upstream: atm and 15 barg, downstream: atm and 3 mbarg. Calibration fit: $Flow = 2.0020V + 0.01986$, with V the output voltage.

MFC II: flux range of 0-5 slpm (STP: 0°C, 760 Torr) calibrated for N₂ at 22.3°C, upstream: 35 barg, downstream: 0.2 barg. Calibration fit: $Flow = 0.99170V + 0.01093$, with V the output voltage.

MFC III: flux range of 0-0.1 slpm (STP: 0°C, 760 Torr) calibrated for N₂ at 21.7°C, upstream: 35 barg, downstream: 0.2 barg. Calibration fit: $Flow = 0.01996V - 0.00010$, with V the output voltage.

✓ **Pressure Generator**

Model: 87-6-5

Supplier: HiP

Characteristics: pressure rating of 5000 psi, capacity per stroke 60 ml with teflon packing.

✓ **Refrigerator** [Figure (4.2)]

Model: 3000778

Supplier: SELECTA FRIGEDOR PT

Characteristics: - 20/+ 20°C, 1/5 HP, 285 W of consumption, calorific power of 276 W at - 20°C).

✓ **Baths** [Figure (4.2)]

Model: 6000383

Supplier: SELECTA Ultratherm PT

Characteristics: - 20°C to 200°C, accuracy of 0.1% FS.

✓ **Pt100 Temperature Probes** [Figures (4.2, 4.31)]

Model: Pt100

Supplier: RS Amidata, Spain

Characteristics: 4 wires temperature sensors with platinum resistance, that exhibit a

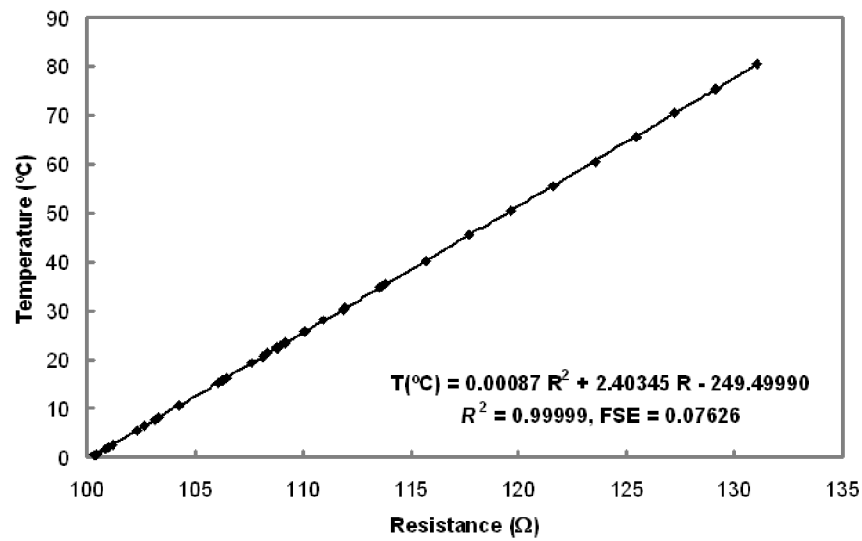


Figure A.1: Calibration fit for the temperature sensors used in the experimental work.

typical resistance of 100Ω at 0°C , typically measure temperatures up to 850°C , Classe B precision $\pm 0.12\Omega$ at 0.3°C . It consists of a thin film of platinum on a plastic film inside a stainless steel involucrum. The relationship between resistance and temperature is relatively linear, but curve fitting is often the most accurate way to make the RTD measurement. The probes were calibrated in the laboratory against a highly accurate Hart Scientific Pt 5613 temperature sensor with an accuracy of $\pm 0.01\text{ K}$. Figure (A.1) shows the calibration fit for the temperature sensor used in several experimental measurements.

✓ **Digital Controllers** [Figures (4.2, 4.31)]

Model: LDS 491030000

Supplier: ERO ELECTRONIC

Characteristics: 100 to 240 VAC~ of supply, 50/60 Hz, 6 VA, sensor input Class 2, main relay of 3 A for output with 250 VAC~ and 50/60 Hz, resistive.

✓ **Acquisition Board I** [Figure (4.2)]

Model: PCI-6023E Low Cost Multifunction I/O Board for PCI

Supplier: National Instruments Corp., UK

Characteristics: analog inputs 16SE/8DI, resolution of 12 bits, sampling rate of 200 kS/s, input range ± 0.05 to $\pm 10\text{ V}$, digital triggers, ambient temperature of 24°C , AI $\pm 10\text{ V}$ differential, associated to software NiDAQ for PC and coupled to a SH6868 shielded cable assembly SCB-68 shielded I/O connector block to the PC of 68 pins with very low noise signal termination.

✓ **Acquisition Board II** [Figure (4.31)]

Model: PCI-6025E

Supplier: National Instruments Corp., UK

Characteristics: analog inputs 16SE/8DI, bus: PCI, PXI, resolution of 12 bits, sampling rate of 200 kS/s, input range ± 0.05 to ± 10 V, two analog outputs at 12 bits resolution and a sampling rate of 10 kS/s, output range of ± 10 V, 32 digital I/O, digital triggers, ambient temperature of 24°C, AI ± 10 V differential, associated to software NiDAQ for PC.

✓ **Platinum resistance temperature detector (RTD) Board** [Figure (4.31)]

Model: SC-2042-RTD

Supplier: National Instruments Corp., UK

Characteristics: temperature acquisition using 8 channel signal conditioning accessory for RTD/thermistor, each input channel has an independent 1 mA current excitation source and screw terminals for 4 wire RTD measurements, the RTD signals are routed to 8 differential inputs of the multifunction DAQ device, ± 5 V of voltage supply, 60 mA of current, operating temperature 0-70°C, with 68 crew terminals coupled to a R1005050 2 m cable and a I/O connector block CB-50LP as a termination board.

✓ **Pressure Transducer (PT)** [Figure (4.2)]

Model: PT P9071-0003

Supplier: Lukas Polaron Schaevitz Sensors, England

Characteristics: absolute pressure range of UHV-5 bar (pressure limit $\geq 5 \times$ FRS pressure or 830 bar, whichever is less; operable temperature range from -40°C to 100°C), input supply voltage of + 15 to + 36 V, and an output of 10 V $\pm 0.3\%$, with a combined nonlinearity, hysteresis and non-repeatability of $< \pm 0.05\%$ FRO, and a combined thermal zero & sensitivity error of $< \pm 0.004\%$ FRO/ $^\circ\text{C}$. The transducer was calibrated by the supplier and checked in FCT/UNL with a excitation supply of + 28 V. An accuracy of $\pm 0.078\%$ FSO Nominal and a linearity including hysteresis of $\pm 0.0227\%$ FSO were determined. No thermal zero and sensitivity shifts were detected over - 20.0°C to + 80°C. Calibration fit: $P(\text{bara}) = 0.5V(\text{volt})$.

✓ **Pressure Transducer (PT)** [Figure (4.2)]

Model: PT P9071-0003

Supplier: Lukas Polaron Schaevitz Sensors, England

Characteristics: pressure range of 0-35 bar, supply voltage of + 28 V, with pressure characteristics at + 20°C: zero pressure output of - 0.043% FSO, FSO of 10 V with + 0.018% Nominal, linearity (including hysteresis) of $\pm 0.0352\%$ FSO; and

temperature characteristics over - 20°C to + 80°C: thermal zero shift of - 0.001% FSO/°C and sensitivity shift of + 0.001% FSO/°C. The transducer was calibrated by the supplier and checked in FCT/UNL with a excitation supply of + 28 V. Calibration fit: $P(bar) = 3.5V(volt)$.

✓ **Pressure Transducer (PT)** [Figure (4.2)]

Model: PT 4090B02A1

Supplier: Kistler Instrumente AG, Switzerland

Characteristics: piezoresistive digitally compensated pressure sensor for pressure measurements up to 200 bar and calibrated by the supplier, input supply voltage range from + 18 to + 30 V, output range from + 0 to + 10 V $\pm 0.3\%$, an overload pressure of 400 bar, end point linearity of $< \pm 0.8\%$ FSO, thermal zero shift of $< \pm 5\%$ FSO and a repeatability of $< \pm 0.1\%$. The maximum error is $\pm 0.16\%$ FS, the compensated temperature range is 50°C to 300°C and the reference temperature is 50°. Amplifier 4618 calibration: range of 3.926 V (10.282 mA) and a zero of -5.986 V. Most transducers are comprised of two main components, one mechanical and one electrical. In Kistler pressure transducers, the mechanical element is the diaphragm, and the electrical element is the quartz crystal or the semiconductor bridge, which give long-term stability, high rigidity and strength, wide measuring range and wide temperature range to make it the ideal sensing element for dynamic pressure transducers.

In our laboratory another calibration of the sensor was performed, for a excitation supply of + 24 V at different temperatures. It was used a direct reading pressure gauge RUSKA Series 6000 Model 6000-350-2500 psi DIFF coupled with a digital multimeter Yokogawa 7552 DIG with 4 – 1/2 digits. The resolution of the measurement was 0.01%, and the uncertainty was 0.008% or 0.04 psi, whichever is greater. Figure (A.2) shows the calibration results obtained in our laboratory. The equation calculated is used as an input in the control/measurement unit of the MSB. The parameters needed as inputs for the weight measurement unit, FA the factor, NP the offset and EX the exponent, are given by the equation $P(bar) = FA[V(volts) - NP]$. It was found two calibration fits temperature dependent. Thus, from the calibration curve obtained from $T < 50^\circ\text{C}$ (10°C, 20°C, 30°C, 40°C and 45°C) result $FA = 1.9682$ and $NP = 0.2392$ for a exponent $EX = -1$. For $T \geq 50^\circ\text{C}$ (50°C, 60°C and 70°C), the results are $FA = 1.9750$ and $NP = -0.2410$ for a exponent $EX = -1$. The original calibration from the supplier was $FA = 1.9750$ and $NP = 0.4200$ for a exponent $EX = -1$.

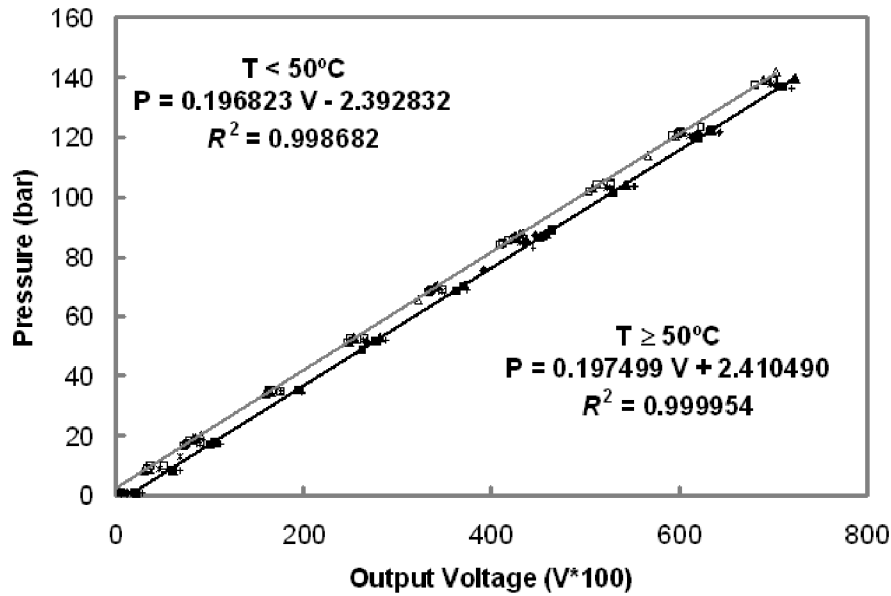


Figure A.2: Calibration fit for the Kistler pressure sensor used in the experimental work.

✓ **Pressure Transducer (PT)** [Figures(4.2)]

Model: PT PAA-215/80549.3

Supplier: Keller AG

Characteristics: pressure range of 0–1 bar, output of 4–20 mA transformed to voltage with a resistance of 0.2486Ω , supply of 8–28 V, zero/span tolerance of 0.5%FS, operating temperature from -20°C to $+80^{\circ}\text{C}$, linearity $\pm 0.2\%$ typ./ $\pm 0.5\%$ max., total error band (including linearity, hysteresis, repeatability, zero/span offsets and temperature effects): $\pm 0.5\%$ typ./ $\pm 1\%$ max. for $+18/+22^{\circ}\text{C}$, $\pm 1\%$ typ./ $\pm 2\%$ max. for $0/+50^{\circ}\text{C}$, $\pm 2.5\%$ typ./ $\pm 4\%$ max. for $+20/+80^{\circ}\text{C}$. The instrument was supplied at 12 V and calibration was checked in the laboratory. The calibration fitting obtained is $P(\text{bar}) = 0.25141V(\text{volt}) - 0.25$.

✓ **Pressure Transducer (PT)** [Figures (4.2, 4.31)]

Model: PT BTE 6035A4

Supplier: Technics

Characteristics: pressure range of 0–35 bar, output with resistance of 4–20 mA transformed to voltage with a resistance of 0.2486Ω , supply voltage of 12–36 V, operating temperature of -40°C to $+100^{\circ}\text{C}$, compensated temperature 0°C to $+70^{\circ}\text{C}$, proof pressure 2x rated pressure, response time of 1 ms (10% to 90%), repeatability of $\pm 0.1\%$ FSO, non-linearity and hysteresis (BSL) of $\pm 0.2\%$ FSO, thermal effects of 0.02 offset% FSO/ $^{\circ}\text{C}$ for $0-70^{\circ}\text{C}$, and of 0.03 offset% FSO/ $^{\circ}\text{C}$ for

- 40–0°C and 70–100°C, zero pressure offset of 4 mA. The instrument was supplied at 12 V and calibration was checked in the laboratory. The calibration fitting obtained for the two transducers used is:

PT I: $P(bar) = 8.76834V(volt) - 8.61371$

PT II: $P(bar) = 8.79928V(volt) - 8.75000$

✓ **Pressure Transducer (PT)** [Figure (4.2)]

Model: PX03D1-3KA5T

Supplier: OMEGADYNE Inc.

Characteristics: pressure range of 0–3000 psia (207 bar) with output signal acquired directly from a OMEGA Display DP41-E-230-GN, error <0.15 psi (0.1 bar). Calibration fit: $P(psia) = -24.00035 + 0.60280V(mV) + 2.81 \times 10^{-7}V^2(mV)$ ($R^2 = 0.99999$, FSE = 0.57505).

✓ **Power Suppliers** [Figures (4.2, 4.31)]

Model: PS 613

Supplier: Velleman

Characteristics: variable voltage of 0–30 V, 2.5 A DC and two fixed supplies of ± 12 V and ± 5 V.

✓ **MFC Power Suppliers** [Figures (4.2, 4.31)]

Supplier: Paralab S.A., PT

Characteristics: manual or automatic operation, MFCs suppliers with variable control voltage for four MFCs, with a supply voltage for the BPR.

✓ **Back-Pressure Regulator (BPR)** [Figures (4.2, 4.31)]

Model: P-702C-FAC-020R

Supplier: Bronkhrost High-tech BV, NL

Characteristics: pressure range of 1–16 bara, controlled absolute pressure of 3–16 bara, output of 5 V, set-point of 5 V, with normally opened valve, inaccuracy of range of $\pm 0.5\%$ Acc. of range 0 to 100 FX at $23 \pm 1^\circ\text{C}$, sensitivity of 0.33233 V/bar, output min. value of 0.01 V, span of 4.985 V, maximum deviation ($>$)0.287% FS, power supply of ± 15 V (+ 15 V at 45 mA, - 15 VDC at 20 mA), repeatability < 0.1% FS, response time < 0.1 s, control stability < $\pm 0.1\%$ FS, temperature sensitivity of 0.1% FS/ $^\circ\text{C}$, leak integrity tested < 2×10^{-9} mbar 1/s He. The calibration was checked in our laboratory and the fitting obtained is $P(bar) = 3.00889V(volt) + 0.96697$ ($R^2 = 0.99999$, FSE = 0.01815).

✓ **Solenoid Valves (SVs)** [Figure (4.31)]

Model: 11500067

Supplier: ASCO Voucomatic

Characteristics: normally closed electrovalves, 230 V at 50 Hz, 10 W with 4 Paralab S.A. PT relay boards (for 4x4 SVs) supplied with 12 V.

✓ **Ball Valves** [Figures (4.2, 4.31)]

Model: SS-43S4

Supplier: Swagelok

Characteristics: 1/4" OD fittings, $C_v = 2.4$, $P \leq 206$ bar, $10^\circ\text{C} \leq T \leq 65^\circ\text{C}$.

✓ **Check Valves** [Figure (4.31)]

Model: SS-4C-TR-1

Supplier: Swagelok

Characteristics: 1/4" OD fittings, PTFE seals, $P_{crack} = 0.06$ bar, $P_{max.} = 206$ bar.

✓ **Several fittings** [Figures (4.2, 4.31)]

Model: Swagelok and Parker types (nuts, unions, reducers, elbows, etc.)

Supplier: Paralab S.A.

Characteristics: 1/4", 3/8" and 1/8" OD fittings.

✓ **Computers (PCs)**

Model: Intel

Characteristics: Pentium 500MB RAM Win 2000 SP4, 20 Gb HD; Pentium M 1.5GHz with 512MB RAM Win XP, 40 Gb HD.

✓ **Gases**

Supplier: Air Liquide and Praxair (Portugal)

Characteristics: Helium (He) type 2 from Air Liquide Alphagaz; Nitrogen (N_2) type 1 from Air Liquide Alphagaz, impurities: $\text{H}_2\text{O} < 3$ ppm, $\text{O}_2 < 2$ ppm, $\text{HC} < 0.5$ ppm; Carbon dioxide (CO_2) N48; Methane (CH_4) N35 (99.95%); Ethane (C_2H_6) N45, 4 m³ at 33 bar, impurities: H_2O , $\text{O}_2 < 3$ ppm mole, $\text{CO}_2 < 1$ ppm mole, $\text{N}_2 < 15$ ppm mole, $\text{H}_2 < 5$ ppm mole, $\text{CH}_4 < 3$ ppm mole, $\text{C}_2\text{H}_4 < 5$ ppm mole, $\text{HC} < 15$ ppm mole; Propane (C_3H_8) N35, 4 m³ at 6.5 bar, impurities: $\text{H}_2\text{O} < 5$ ppm mole, $\text{O}_2 < 15$ ppm mole, $\text{CO}_2 < 5$ ppm mole, N_2 , $\text{H}_2 < 40$ ppm mole, $\text{C}_3\text{H}_6 < 200$ ppm mole, $\text{HC} < 200$ ppm mole; Butane (C_4H_{10}) N35 at 0.75 bar; tert-butylmercaptan (TBM) in He at 25.2 mg/Nm³ (21°C, 1 atm), 7.5 m³ at 150 bar; Tetrahydrothiophene (THT) in He at 23.1 mg/Nm³ (21°C, 1 atm), 7.5 m³ at 150 bar.

✓ **Mass spectrometer (MS)** [Figure (4.31)]

Supplier: Paralab S.A.

Model: Dymaxion quadrupole mass spectrometer DM100 (Serial No. 10206758),

from AMETEK Process Instruments, with a Dycor system 2000 software version 1.63.

Characteristics: Compact quadrupole mass spectrometer capable of distributed control and simultaneous multiplexing of multiple head locations from a single PC. Is composed by a sampling system (connects the outside sample environment to the MS vacuum chamber through a fine capillary), mass spectrometer hardware (ionization through a filament, separation and detection, where sample molecules are converted to ions which are then focused towards the quadrupole to be detected) and the data system (control, acquisition and data storage). The filament produces electrons; as current flows through the filament, its electrically heated to incandescence and emits free electrons, that are accelerated towards the ionizer body by potential difference; the collision of the electron with the sample creates ions to be detected by the quadrupole mass filter. The quadrupole consists of four metal rods, electrically connected, straight and parallel, so positioned that the ion beam shoots down the center of the array. Mass range: 1-100 AMU. Operating pressure range: 10^{-4} Torr to ultrahigh vacuum. Minimum detectable partial pressure: 5×10^{-12} Torr). Resolution adjustable to constant peak width (0.5 AMU at 10% height). Electron energy: 30-150 volts to operate; 200 volts to degas. Emission current: 0.1-10 mA; 50 mA to degas. Ion energy: 1-10 volts. Power: 24 VDC at 3 amp; 100/240 VAC. Stability: mass stability ± 0.1 AMU after 30 min. warm-up; peak height $\pm 2\%$ after 30 min. warm-up. RS-232 Serial communications interface.

Appendix B

Operating Principles of the Magnetic Suspension Balance

The main difficulty when using conventional gravimetric instruments is the direct contact between the measuring cell (sample atmosphere) and the weighing instrument. The balance can be damaged or disturbed by the measuring atmosphere and the measuring atmosphere can be adversely affected by flushing gases and pollution. These limitations considerably reduce the field of application of conventional measuring devices. The advantage of the high-precision MSB consists in the possibility to weigh samples contactlessly under nearly all environments at high accuracy. Instead of hanging directly at the balance, the sample to be investigated is linked to a so-called suspension magnet which consists of a permanent magnet, a sensor core and a device for decoupling the measuring load (sample). The suspension magnet and the connected sample achieve a constant vertical position in the measuring cell. An electromagnet, which is attached to the underfloor weighing hook of a balance, maintains a freely suspended state of the suspension magnet via an electronic control unit. Using this magnetic suspension coupling the measuring force is transmitted contactlessly from the measuring chamber to a microbalance SARTORIUS Model BP211, which is located outside the chamber under ambient atmospheric conditions [Figure (B.1)].

Consequently, this arrangement eliminates almost all restrictions which are inherent to conventional gravimetric measuring instruments. A controlled suspended state is achieved by means of a direct analogous control circle (PID controller and position transducer). This modulates the voltage on the electromagnet in such a way that the suspension magnet is held constantly in a vertical position. A microcontroller driven digital set-point controller, superimposed to the direct PID controller, allows various positions of the suspension magnet to be set up.

The balance can be tared and calibrated automatically. The magnetic suspension balance offers the possibility of lowering the suspension magnet in a controlled way to a

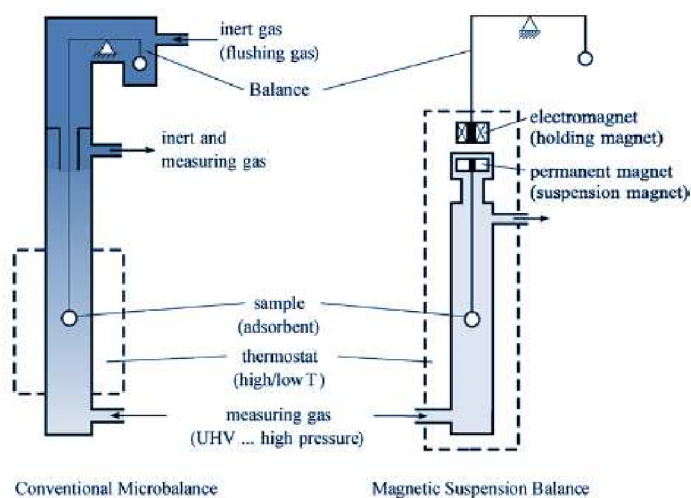


Figure B.1: Gravimetric measurements in controlled environments. Comparison of conventional instrument (left) and magnetic suspension balance (right).

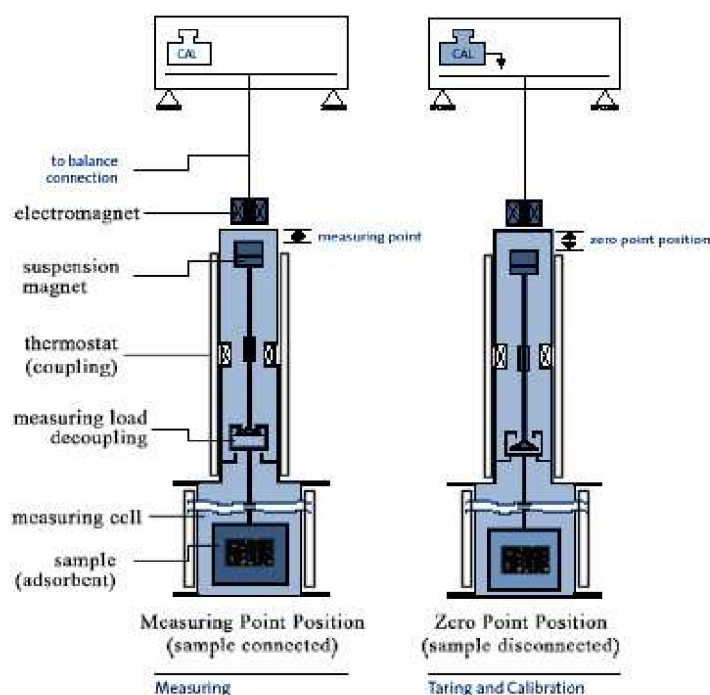


Figure B.2: Measuring position with sample connected to the balance (left) and automatic decoupling (zero point position) of the measuring load in order to tare and calibrate the balance (right).

second stationary position, a few millimeters below the measuring position [Figure (B.2)]. Then, a small carrier to which the sample is connected is set down on a support. Now the sample is decoupled from the balance. The suspension magnet alone is in a freely suspended state and only its weight is now transmitted to the balance. This so-called zero-point position (ZP), which corresponds to an empty balance pan in a normal weighing procedure, allows a taring and calibration of the balance at all times, even when recording measurements under process conditions in the measuring cell (pressure, temperature). This feature enhances the accuracy of the measurements considerably, particularly in the case of long term measurements [Rubotherm (2000)]. For example, it allows the buoyancy change acting on the permanent magnet to be measured separately and the measured data to be corrected even after changing the atmospheric conditions (e.g. increase in pressure). The measuring cell and the coupling area are enclosed by thermostats in order to control the temperature of the measuring gas and the sample. For the measuring temperatures of the studies, the thermostating fluid (silicone oil) is circulated at a certain temperature through double walled tubes.

Figure (4.1) shows the magnetic suspension balance and its components. The volume of the chamber available for the measurements is approximately 84.3 cm³. For a maximum load of 25 g, the balance has a resolution of 0.01 mg, an uncertainty lower than 0.002% of the measured value, a reproducibility smaller than 0.03 mg, for pressures in the range UHV-150 bar and temperatures up to 100°C. Figure (B.2) shows the automatic decoupling of the measuring load in order to tare and calibrate the balance. The suspension magnet and the measuring load decoupling remain more or less untouched by the flow which leads to a clear reduction in noise level caused by high flow rates. Both gas connections can either be used singly or together.

The buoyancy forces were taken into account to correct the influence of gas density and the measuring cell atmosphere on the measured apparent weight of the sample, when calibrating the balance with its built-in calibration device. The displacement of gas by the sample, sample holder, adsorbed phase, and pan was considered. The corrections due to the sample holder and pan were obtained with a blank experiment carried out with the empty sample holder. The buoyancy due to the sample, which results in an apparent loss of weight, was estimated as the product of the skeletal volume of the sample and gas density. The buoyancy effect related to the adsorbed phase was corrected to obtain the absolute adsorption isotherms.

The value of balance display, W , is given by the equation

$$W = M_s + M_L + M_m - (V_s + V_L + V_m)\rho_g, \quad (\text{B.1})$$

with M_s the sample weight (carbon + adsorbed phase), M_L the weight of the load (includes the load cage), M_m the weight of the magnet, V_s , V_L and V_m the volumes of the sample, the load and the magnet, respectively, and ρ_g the gas density at measured P and T . It can be rewritten as

$$W = (M_s + M_L + M_m) \left(1 - \frac{\rho_g}{\rho_{sLm}} \right), \quad (\text{B.2})$$

where ρ_{sLm} is the effective density of the whole measuring system.

If the balance is tared in zero-point (ZP) at a pressure P_o and temperature T_o , then W is defined as

$$W = M_s + M_L - (V_s + V_L + V_m)\rho_g + V_m\rho_g^o, \quad (\text{B.3})$$

where $\rho_g^o \equiv \rho_g(P_o, T_o)$, because the apparent weight of the magnet immersed in the gas at (P_o, T_o) was removed from the balance display value. In the reference experiment, where there is no sample,

$$W = M_L + M_m - (V_L + V_m)\rho_g, \quad (\text{B.4})$$

which shows that the weight displayed in the balance should be a linear function of ρ_g , independent of the type of the gas. By taring the balance in ZP,

$$W = (M_L + V_m\rho_g^o) - (V_L + V_m)\rho_g \quad (\text{B.5})$$

and by fitting a straight line to the pairs (ρ_g, W) , its possible to obtain

$$\begin{cases} a = M_L + V_m\rho_g^o \\ b = V_L + V_m. \end{cases} \quad (\text{B.6})$$

If P_o is sufficiently low so that $V_m\rho_g^o \ll M_L$, then $M_L \approx a$. In an adsorption experiment, after taring the balance at a low pressure P_o , W is given by

$$W = M_s + M_L - (V_s + V_L + V_m)\rho_g + V_m\rho_g^o, \quad (\text{B.7})$$

which knowing a and b from the reference experiment, gives

$$W = M_s + a - (V_s + b)\rho_g, \quad (\text{B.8})$$

with $M_s = M_c + M_a$, where M_c is the carbon weight, M_a is the weight of the adsorbed phase, and $V_s = V_c + V_a$ is the volume occupied by the solid matrix of the adsorbent plus the volume occupied by the adsorbed phase. From this equation,

$$M_a - V_a\rho_g = W - M_c - a + (V_c + b)\rho_g \quad (\text{B.9})$$

or

$$q_{ex} \equiv \frac{M_a - V_a\rho_g}{M_c} = \frac{W - a}{M_c} - 1 + \left(\frac{1}{\rho_c} + \frac{b}{M_c} \right) \rho_g, \quad (\text{B.10})$$

where q_{ex} denotes the well-defined thermodynamic quantity known as excess adsorption [Sircar (1999)], which is the amount of sample adsorbed in excess of the equilibrium gas occupying the same volume, and ρ_c is the density of the sample ($\approx 2.2 \text{ g/cm}^3$ for the ANGWARD samples under study). The most difficult task is knowing the exact value of M_c . The best approximation is taken from the lowest pressure value measured, P_o , where

$$W^o = M_c + a - \left(\frac{M_c}{\rho_c} + b \right) \rho_g^o, \quad (\text{B.11})$$

which gives

$$M_c = \frac{W^o - a + b\rho_g^o}{1 - \rho_g^o/\rho_c}. \quad (\text{B.12})$$

However, if at P_o there is a substantial amount of gas adsorbed, then the mass will have an error. Another approach is based on $(\lim_{P \rightarrow 0} W = M_c + a)$ or $(\lim_{\rho_g \rightarrow 0} W = M_c + a)$.

Either due to carbon surface heterogeneity or microporosity, there are isotherms that deviate from linearity at the lowest pressures, giving rise to a smooth convex curvature with respect to adsorption axis. A number of different equations [J. H. Cole and Rodriguez-Reinoso (1974); N. N. Avgul and Kiselev (1973)] have been proposed to accommodate the deviations of physisorption isotherms from Henry's law. An approach is to adopt a virial treatment that provides a general method of analyzing the low-coverage region of an adsorption isotherm,

$$P = q_{ex} \exp(C_0 + C_1 q_{ex} + C_2 q_{ex}^2 + \dots + C_n q_{ex}^n), \quad (\text{B.13})$$

where $(C_0, \dots, C_n)$ are characteristic constants for a given gas-solid system and temperature [F. Rouquerol and Sing (1999)]. Therefore, the low pressure data can be fit to a virial plot of $\ln(P/q_{ex})$ versus q_{ex} , with a polynomial type equation, and extrapolate to zero to obtain $(M_c + a)$.

System Pre-Treatment

Before each adsorption equilibrium measurement for a given component, or every time the sample cell was changed, a referential blank calibration of the cell (without sample) was performed. This accounts for the buoyancy effects corrections due to the influence of the gas density and the measuring cell atmosphere on the accuracy of a measurement. Several sample cells were used according to the adsorbent size.

The weight and density of the loading cage, without adsorbent sample, were measured at different pressures using nitrogen and methane. At constant temperature, the MSB was tared in ZP position before each weight measurement in the measurement point (MP). Prior to each run, the system was pressurized and depressurized with the gas a couple

Table B.1: Blank calibration of the cells used in the experimental measurements.

Sample Cell	Conditions	M_L (g)	$V_L + V_m$ (cm ³)
Cell 1 (higher mesh)	25.1°C, CH ₄ , N ₂	5.50128	0.66463
Cell 2 (lower mesh)	25.8°C, 50.8°C, N ₂	4.04219	0.48721

of times for complete removal of air inside the balance chamber. Values of a and b were obtained for each sample cell, from the intercept and slope of the linear fitting of the plot gas density versus cell weight, respectively.

Table (B.1) presents the M_L and $(V_L + V_m)$, i.e., a and b values for the two cells used in the experimental measurements. The cells differ in the mesh and were used depending on the adsorbent sample under study.

Figures (B.3) and (B.4) show fittings from where the calibration values were taken for sample cells 1 and 2, respectively.

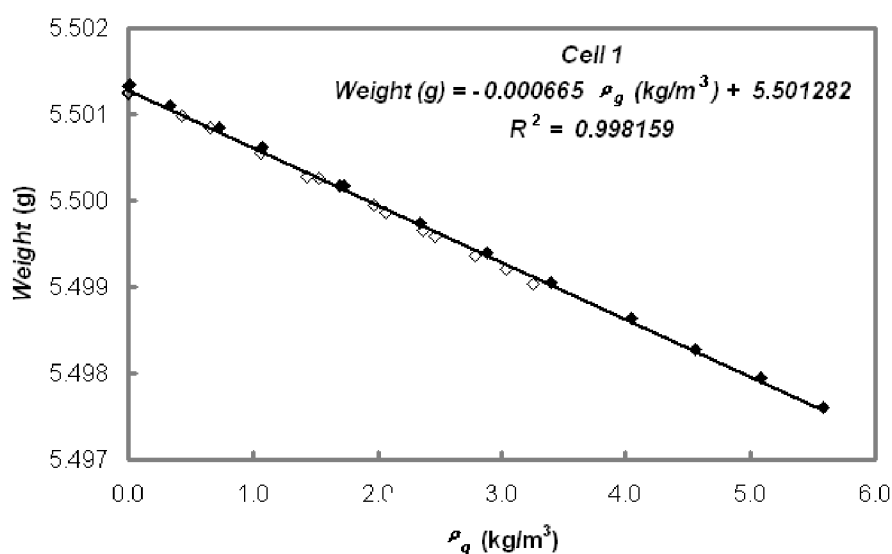


Figure B.3: Referential blank calibration of sample cell 1 used in the MSB measurements. Open and fill symbols represent CH₄ and N₂ data, respectively.

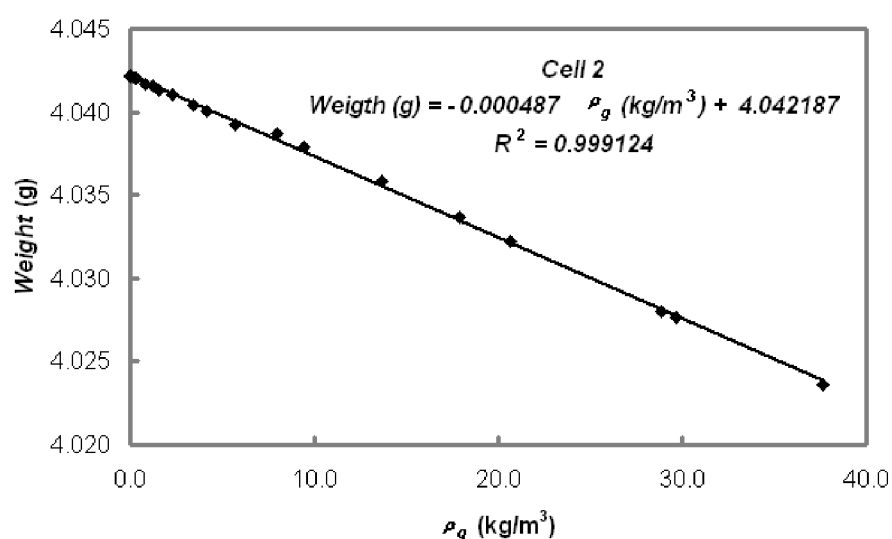


Figure B.4: Referential blank calibration of sample cell 2 used in the MSB measurements. Symbols represent data for N₂.

Appendix C

Adsorbent Characterization

Isotherm Classification

When a solid (adsorbent) is exposed to a gas or vapor (adsorbate), the solid begins to adsorb the gas onto its surface and into its pores, if the solid is porous. Adsorption occurs because of forces acting between the solid and the gas molecules. Two kinds of forces give rise to adsorption: physical (van der Waals) and chemical. These types of adsorption are termed physical adsorption and chemisorption, respectively. In a closed system, the adsorption of a gas onto a solid can be measured by monitoring the decrease in adsorbate pressure within a known volume or by measuring the mass gain of the adsorbent due to the adsorbing gas molecules. Both methods are commonly used and give accurate results [F. Rouquerol and Sing (1999)].

The amount of gas adsorbed in moles per gram of solid, is a function of the adsorbate partial pressure or concentration, temperature of the system, the adsorbate itself, and the adsorbent. Measuring the amount of a compound adsorbed on an adsorbent versus concentration or pressure at a constant temperature results in an adsorption isotherm. Adsorption isotherms are useful for characterizing adsorbents with respect to different adsorbates. The majority of these isotherms fall into five types, as classified by Brunauer classification [Figure (C.1)]. Type I is observed by the physical adsorption of gases onto microporous solids, in which the pore size is not very much greater than the molecular diameter of the sorbate molecule. Types II and III result from the physical adsorption of gases by solids with a wide range of pore sizes. Types IV and V possess a hysteresis loop. Type IV suggests the formation of two surface layers either on a plane surface or on the wall of a pore very much wider than the molecular diameter of the sorbate. Type V is observed if intermolecular attraction effects are large.

Through the equilibrium measurements executed during the thesis, one can conclude that the adsorbents under study exhibit isotherms type I in the International Union of

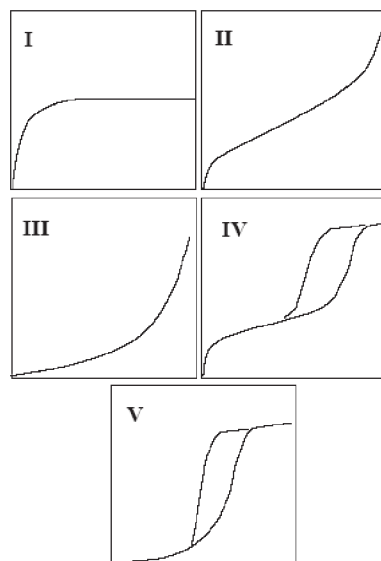


Figure C.1: The five types of adsorption isotherms as classified by Brunauer [F. Rouquerol and Sing (1999), D. M. Ruthven and Kneabel (1994)]. Amount adsorbed versus relative pressure P/P_o , where P_o is the saturation vapor pressure.

Pure and Applied Chemistry (IUPAC) classification, without hysteresis, typical of physical adsorption of gases onto microporous solids.

Carbon Density Determination

The ANGWARD 5 density was given by SSCL, but it was experimentally confirmed, in FCT/UNL, through helium adsorption isotherm analysis. Several adsorption/desorption equilibrium runs in the MSB were performed using *Cell 1* system [see Table (B.1)] at four different temperatures. Helium acts as an inert and does not adsorb into the carbon. Hence, the plot of gas density versus sample weight gives the carbon density. Table (C.1) present the experimental data results.

The carbon weight M_c and the volume V_c average values, through which the carbon density ρ_c is calculated, are given in Table (C.2). M_c and V_c are obtained from the intercept and slope of the fitting, respectively, after subtracting weight and volume of the calibrated measuring system.

Surface Chemistry Characterization of ANGWARDs 4 and 5

The size of individual pores can vary greatly in size and shape for different adsorbents and even within the same adsorbent. Pores are usually characterized in terms of their width, meaning the diameter of a cylindrical pore or the distance between two sides of a

Table C.1: Experimental data obtained from helium adsorption equilibrium measurements.

T = 24.4°C		T = 50.5°C		T = 65.8°C		T = 84.9°C	
Weight (g)	ρ_g (kg/m ³)	Weight (g)	ρ_g (kg/m ³)	Weight (g)	ρ_g (kg/m ³)	Weight (g)	ρ_g (kg/m ³)
8.162	0.001294	8.162	0.001041	8.162	0.000995	8.159	0.000605
8.162	0.210525	8.161	0.180695	8.161	0.177935	8.159	0.168886
8.161	0.414993	8.161	0.391062	8.161	0.351411	8.159	0.290848
8.161	0.565815	8.160	0.585003	8.161	0.493475	8.158	0.406677
8.160	0.808411	8.160	0.747682	8.160	0.729755	8.158	0.547763
8.160	1.086684	8.160	1.017217	8.160	0.954726	8.157	0.911042
8.158	1.956432	8.160	1.015304	8.161	0.600985	8.158	0.742737
8.158	2.481401	8.160	0.686245	8.161	0.250268		
8.156	3.339307	8.161	0.534646	8.162	0.000995		
8.152	5.163729	8.161	0.244707				
8.154	4.326876						
8.157	3.051370						
8.159	1.574199						
8.160	1.058336						
8.161	0.658353						
8.161	0.399628						

Table C.2: ANGUARD 5 density result determined experimentally through helium adsorption equilibrium data ($R^2 = 0.99902$, Standard Error = 0.01711 and RSS = 0.01674).

M_c (g)	2.660
V_c (cm ³)	1.197
ρ_c (g/cm ³)	2.222

slit-shaped pore. Each size range corresponds to different adsorption effects, as observed in an adsorption isotherm.

Activated carbons have microporous (< 2 nm), mesoporous (between 2 - 50 nm) and macroporous (> 50 nm), classification adopted by the IUPAC, and an area of 300-2500 m²/g, in powder and pellets shapes [Kerkhof and Rodrigues (2001)]. Its porosity can be determined by porosimetry, gas adsorption techniques, electronic microscopy, etc. Carbon surface chemistry assumes, traditionally, the existence of a variety of surface complexes formed by combining carbon atoms with other elements (i.e., oxygen, nitrogen, hydrogen, and sulphur). The carbon surfaces have different functional groups as carboxylic acids, phenols, lactones, hydroxils, quinones, among others, depending of the activation method that they were subjected [Figure (C.2)]. Acidic and basic surface sites coexist usually, but the concentration of basic sites decreases with increasing acidic character of the surface.

The accurate analytical description of the specific surface functional groups present on a given carbon material is unfeasible. This inherent difficulty leads to a yet rather

common situation where carbons are employed after empirical trial and error methods. On the other hand, overall surface properties related to the surface chemistry, such as the acid-base character or the redox properties, can be in most cases successfully determined experimentally [M. A. Montes-Morán and Fuente (2003)]. Its identification and quantification can be performed by Boehm titration, mass titration, potentiometry, FTIR (Fourier transformed IR), XPS (X-ray photoelectron spectroscopy) and TPD (temperature programmed desorption), being this later technique the most used. Here, the totality of functional groups are determined through the measurement of the amount of gas desorbed at different temperatures. The samples are heated in a vacuum or in a helium stream with a constant heating rate (often 10 K/min), and the evolved gases, H₂O, CO₂, CO and H₂, are determined, mostly by use of a quadrupole mass spectrometer.

The decomposition temperature (> 400 K) allows the release of CO₂ and CO, allowing the identification of the present groups. Acidic groups (carboxyl groups, lactones, phenol and lactol groups) desorb in the form of CO₂ and basic groups desorb as CO. Nevertheless, the TPD spectrum interpretation can be very subjective, depending on the authors. The peaks shift to higher temperatures with increasing heating rate. The resolution of the peaks associated to a certain activation energy of desorption and identifying each group can be small or peaks can be wide enough to overlap more than one functional group. They are usually very broad, often with pronounced tailing. Thus, the numeric deconvolution of the curves are sometimes very difficult and subjective [Carabineiro (2000), Boehm (2002)]. Nevertheless, they can provide a fair overview of the sample's surface properties.

There is no consensus about the strength as bases of these groups and the extent of their contribution to the overall carbon basicity. Moreover, there is some evidence carbons thus exhibit electrochemical potentials that may be related to functional groups present in the outermost layers of the material and are responsible by the overall basicity of a carbon [J. Angel Menendez and Radovic (1996)].

An attempt to determine the functional groups present in ANGWARD samples was made. TDP was performed, but the decomposition of the peaks revealed an inconclusive result.

Nitrogen adsorption at 77 K allows the determination of total micropore volume. The advantage of N₂ adsorption technique for the characterization of porous solids is that it covers relative pressures from 10⁻⁸ to 1, which results in adsorption in the whole range of porosity. The main disadvantage of N₂ adsorption at 77 K is that when used for the characterization of microporous solids, diffusional problems of the molecules inside the narrow porosity range (size < 0.7 nm) occur. There is also an additional experimental difficulty in the adsorption of subcritical nitrogen because very low relative pressures (10⁻⁸ to 10⁻⁴) are required to extend the range of porosity studied to narrow microporosity. These low

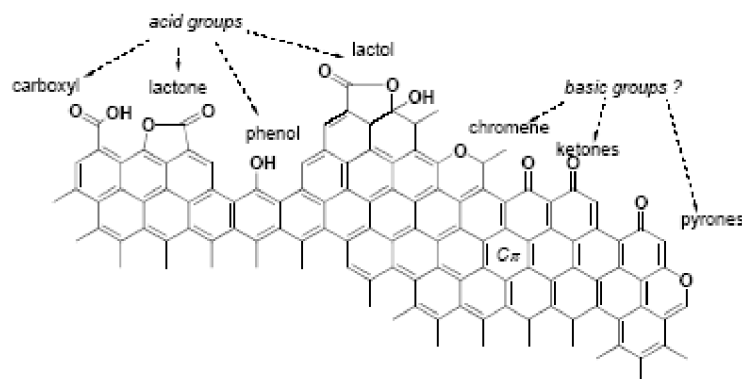


Figure C.2: Acidic and basic functionalities on carbon surfaces [M. A. Montes-Morán and Fuente (2003)].

relative pressures are difficult to reach with conventional adsorption equipments. It has been reported that the CO_2 micropore volume is a good measure of narrow microporosity. CO_2 adsorption at 273 K at subatmospheric pressures is very convenient to analyze this range of porosity. Its physical properties allow to reach very low relative pressures, without the need of complex low pressure adsorption equipment [D. Lozano-Castelló and Linares-Solano (2003), J. Alcaniz-Monge and Linares-Solano (1997), K. Matsuoka and Tomita (2003), Jagiello and Thommes (2003)].

Nitrogen adsorption at 77 K procedure was performed to ANGWARD samples 4 and 5 by Advantica and FCT/UNL. The porosimetry analysis was done by Advantica. The acidity of the carbon surfaces were analyzed in FCT/UNL. The experimental work performed on adsorbent characterization was based on H. Marsh and Rodriguez-Reinoso (1997), Boehm (2002), W. Heck and Boehm (1965), Boehm (1966), y Leon D. and Radovic (1994), Jansen and van Bekkum (1989), E. Papirer and Donnet (1987), J. Angel Menendez and Radovic (1997), C. A. Leon y Leon and Radovic (1992), P. Vinke and Voskamp (1994), M. C. Palma and Lobo (1995) research and simultaneously following the suggestions of F. Silva from FCT/UNL.

• Point of Zero Charge (PZC) Method

This method determines the pH of the carbon surface. A mixture of 0.5 g of well crushed carbon with 50 ml of distillate water was subjected to agitation (200 rpm) for a minimum period of time of 48H, after which the pH of the suspension was determined. The H^+ or OH^- ions from the dissociation of the functional groups on the adsorbent surface are given to the solution until acid-base equilibration is reached. Since the carbon surface has a large variety of acidic and basic functional

Table C.3: PZC results for the ANGULARDs 4 and 5.

	ANGULARD 4	ANGULARD 5
Weight (g)	0.523	0.539
pH^*	8.970	8.440

* pH of destillated water was 5.40.

groups, the value of pH will allow the determination of the acid-base nature of the carbon surface under study.

• Boehm Titration Method

This method identifies the acidic functional groups present in the adsorbent surface. It consists in performing a mixture of 1.0 g of well crushed carbon with 50 ml of basic solutions of different strength (NaOH, Na_2CO_3 and $NaHCO_3$, with concentrations in the range of 0.05 and 0.1 N, subjected to agitation at least for 16H. The idea behind using bases with a wide range of strength was to attempt to neutralize surface functionalities according to their acid strength. NaOH neutralizes phenols, carboxylic and lactone functional groups, Na_2CO_3 neutralizes carboxylic and lactone functional groups, and $NaHCO_3$ neutralize only carboxylic functional groups. The content of each individual group could then be estimated by difference.

Although the validity of the selective neutralization technique has been questioned, its simplicity justifies its extensive use by both industry and researchers. Complications can arise when using Na_2CO_3 and $NaHCO_3$, since these titrants can react to slowly form H_2CO_3 and be combined by side reactions, respectively. An alternative characterization procedure can be performed by combining the chemical analysis to Temperature-Programmed Desorption (TPD) experiments.

The final experiment is the acidic functional groups quantification at the carbon surface by HCL titration. An additional run is also performed with a mixture of 1.0 g of well crushed carbon with 50 ml of HCl at the same concentrations as the basic solutions used. Through this procedure, one can determine the basic functional groups (chromene structures, diketone or quinone groups, and pyrone-like groups) present at the surface of the adsorbent under study.

Experimental Results from the Analysis

• PZC Results

The PZC results are presented in Table (C.3). The carbon surfaces under study revealed a basic nature.

• Boehm Titulation Results

The samples were prepared. A mixture of 1.0 g of well crushed carbon with 50 ml of NaOH at 0.05 N was performed and subjected to a 200 rpm agitation during 48H. The procedure was repeated with Na_2CO_3 , NaHCO_3 and HCL solutions. The basic solutions aferition was made using 10 ml of NaOH with two drops of fenolftaleine, subjected to a 0.1 N HCL titulation. This later procedure was repeated with Na_2CO_3 and NaHCO_3 solutions.

The carbon samples mixtures were then subjected to titration.

- Carbon in basic solution:

The suspension was leveled at rest and a 10 ml of volume was taken. After the addition of two drops of fenolftaleine it was titrated with 0.1 N HCl. The procedure was repeated with Na_2CO_3 and NaHCO_3 solutions.

- Carbon in acidic solution:

The suspension was leveled at rest and a 10 ml of volume was taken. After the addition of two drops of fenolftaleine it was titrated with 0.1 N NaOH.

Three experimental runs were performed for this method:

1. Run 1 with a non-crushed carbon (at the same operational conditions as an typical adsorption process) with all the referred solutions under 24H agitation.
2. Run 2 with a well crushed carbon with all the referred solutions under 48H agitation.
3. Run 3 with a well crushed carbon with just the NaOH 0.01 N solution under 48H agitation.

Tables (C.4) and (C.5) present the results obtained. One can conclude, from the carbon titration with NaOH, that the amount on neutralized functional groups was small (inferior than the sum of the other values). Thus, it is impossible to apply Boehm method to this adsorbents. If acidic groups were present, the more strong base (NaOH) would neutralize the totality of the existing acidic groups in the adsorbent surface. Since this did not occur the adsorbents under study should be mostly clean of acidic groups.

• N_2 Adsorption at 77 K

N_2 at 77 K (liquid nitrogen temperature) adsorption isotherms were performed for 0.067 g of ANGWARD 4 and 0.200 g of ANGWARD 5 in the relative pressure range of

Table C.4: Boehm results from the three runs performed for the ANGULARDs 4 and 5.

		ANGUARD 4				ANGUARD 5			
	Solutions	Aferition conc.(N)	pH of solutions	Weight (g)	Sample conc.(N)	Sample pH	Weight (g)	Sample conc.(N)	Sample pH
Run 1	NaOH	0.0525		1.002	0.0490		1.001	0.0505	
	NaHCO ₃	0.0502		1.002	0.0130		1.000	0.0070	
	Na ₂ CO ₃	0.0504		1.005	0.0320		1.005	0.0260	
	HCl			1.001	0.0250		1.002	0.0285	
Run 2	NaOH	0.0525	12.68	0.984	0.0510	12.73	0.981	0.0525	12.68
	NaHCO ₃	0.0502	9.16	0.925	0.0110	7.65	1.051	0.0120	9.16
	Na ₂ CO ₃	0.0504	12.05	1.004		11.69	1.015	0.269	12.05
	HCl		2.59	0.991		2.13	0.999		2.59
Run 3	NaOH	0.0525	11.69			11.68			11.61
	NaHCO ₃	0.0502							
	Na ₂ CO ₃	0.0504							
	HCl								

Table C.5: Boehm final results for the ANGULARDs 4 and 5.

		ANGUARD 4	ANGUARD 5
	Solutions	Conc. (mmol)	Conc. (mmol)
Run 1	NaOH	0.004	0.002
	NaHCO ₃	0.038	0.043
	Na ₂ CO ₃	0.018	0.024
	HCl	0.022	
Run 2	NaOH	0.002	0.001
	NaHCO ₃	na	na
	Na ₂ CO ₃		na
	HCl	0.025	

$10^{-6} < P/P_o < 0.99$. The isotherms are Brunauer type I, when plotted on a linear-linear scale, as seen in Figure (C.3)]. BET surface areas and total pore volumes at $P/P_o = 0.99$ were taken for each sample using N₂ at 77 K [See Table (4.1)].

• Pore Size Distribution

The Horvath-Kawazoe (HK) [Horvath and Kawazoe (1983)] and the Density Functional Theory (DFT) [N.A. Seaton and Quirke (1989)] methods were used to obtain an estimate of the pore size distributions of samples 4 and 5 [Korili and Gil (2001)].

The HK model outlined is for slit-shaped pores using N₂ isotherms at 77 K, but can be extended to other pore shapes (e.g., cylindrical) and other adsorbates. The model assumes an average potential function between two parallel layers of carbon

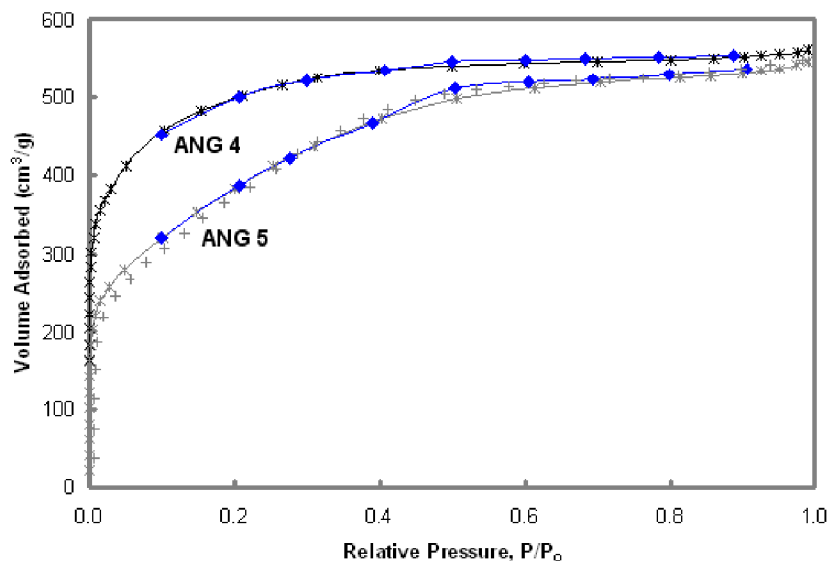


Figure C.3: Sorption nitrogen isotherm at 77 K for ANGULAR samples 4 and 5. Blue represent FCT/UNL data for desorption, black refers to FCT/UNL data for adsorption and gray is the Advantica sorption data.

and then adds the interaction effects of adsorbate molecules within these layers or slit-shaped pores. The HK method is solved for the pore width as a function of P/P_o , i.e., the volume adsorbed at a particular P/P_o value can be related to the pore width calculated for that P/P_o . This is done for every adsorption isotherm point, providing a distribution of pore diameter values [Cal (1995)].

The DFT method is a statistical mechanical attempt to extend the accuracy of pore size distribution analysis in both the mesopore and micropore range. The adsorbent is modeled as a collection of independent, parallel-sided, slit-shaped pores.

Figure (C.4) shows the pore size distribution for the carbons under study, using the HK method, where micropore predominance is visible. The results shows that the pores for ANGULAR samples lie mostly in the micropore region ($< 20 \text{ \AA}$), although sample 5 seems to present a higher pore width proximally to mesopore range. It is visible a broadening of the pore size distribution with increasingly surface area.

Figure (C.5) presents the micropore size distribution from the DFT for the ANGULAR samples 4 and 5. It is visible the existence of small mesopores in sample 5 for pore widths slightly higher than $20 \text{ \AA}$, and micropores with pores sizes inferior to $20 \text{ \AA}$. Figure (C.6) compare the pore size distributions obtained from the HK and DFT methods for both samples. These two distributions are similar enough, although some discrepancies are visible probably due to adsorbent-adsorbate properties (Korili and Gil (2001)). The distributions confirm that carbon samples are predominantly microporous materials, but the maxima in the differential volume

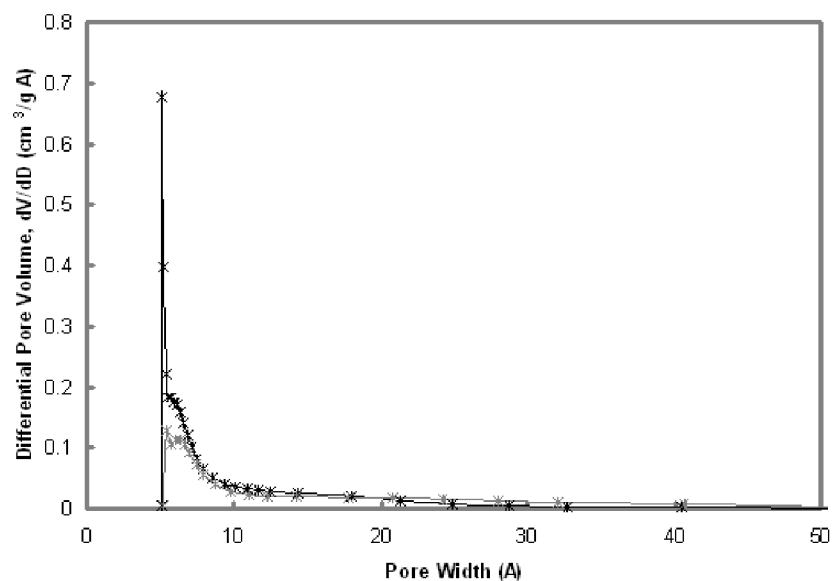


Figure C.4: Micropore Size Distribution for ANGULARDs 4 and 5 using HK Method and N_2 at 77 K. Black represent sample 4 and gray refers to sample 5.

distributions vary slightly. The variation among the distributions indicates a certain lack of consistency among the gas adsorption models.

From Figures (C.3) and (C.4) one can suggest that ANGULARD 4, a coconut shell carbon having greater retention property than the coal based product ANGULARD 5, would be the best adsorbent for removing HCs. Nevertheless, ANGULARD 5 carbon is an extruded form, giving higher density, better mechanical strength and less dusting which is a practical product for use in guard-bed applications. Thus the carbon selected for study was ANGULARD 5 from Sutcliffe Speakman Carbons Ltd (SSCL).

Table (C.6) presents the comparison of ANGULARDs 4 and 5 characteristics obtained from both FCT/UNL and Advantica, which show a very good agreement specially for ANGULARD 5.

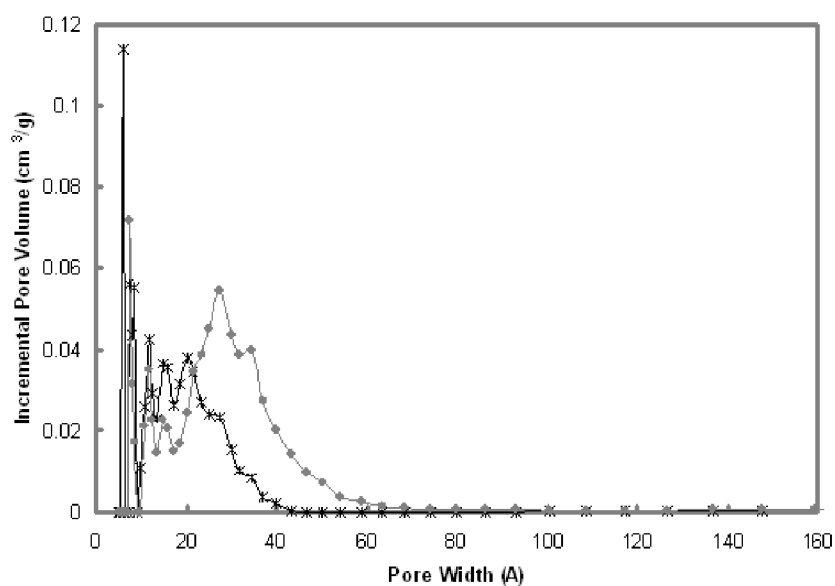


Figure C.5: Micropore Size Distribution for ANGULARDs 4 and 5 using DFT method. Black represent sample 4 and gray refers to sample 5.

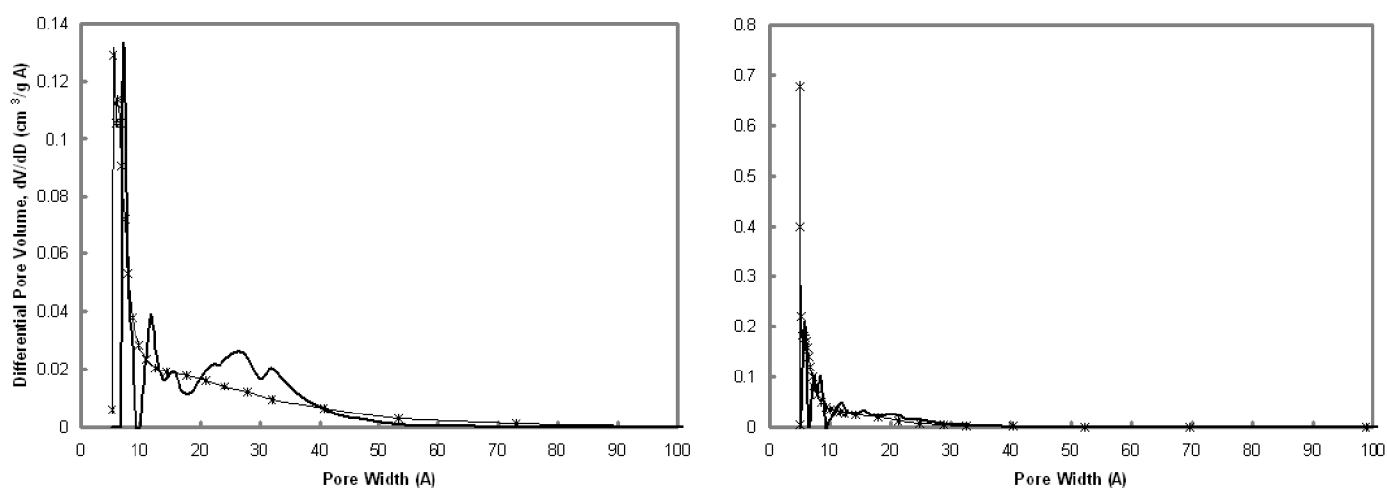


Figure C.6: Micropore Size Distribution for ANGULARDs 4 (right) and 5 (left) obtained from HK and DFT methods. Bold line refers to DFT and crossed line applies the HK method.

Table C.6: Comparison of ANGULARDs 4 and 5 characteristics obtained from FCT/UNL and Advantica. See also Table (4.1).

ANGULARD sample	FCT/UNL	Advantica	FCT/UNL	Advantica
	4		5	
N₂ at 77K				
BET Surface area (m²/g)	1572	1669	1355	1342
DFT Surface area (m²/g)	1311	-	859	-
Total Pore Volume (cm³/g) HK	0.867	0.819	0.846	0.850
Total Pore Volume (cm³/g) DFT	0.732		0.708	
Average Pore Diameter (Å)	22.074	-	24.982	-
D-A W_s (cm³/g)	-	-	0.860	-
Average Pore Diameter (Å)	-	-	25.630	-

Appendix D

Natural Gas

Figures (D.1, D.2) show the typical composition of european natural gases and the AN-GUARD standard NG composition applied in the project. Figure (D.3) presents the odorization values of NG in several european countries. Note that the Basic Safety Requirement in all countries states that the concentration of odorant in natural gas will be such to achieve the alert olfactory degree 2 on the scale of Sales, which corresponds to a gas leak of 1% NG concentration into the air.

Typical composition of European gases.															
	Gas	H ₂	CO ₂	C ₁	C ₂	C ₃	i-C ₄	n-C ₄	i-C ₅	n-C ₅	C ₆	C ₇	C ₈	O ₂	Odorant mg/m ³
UK	Bacton	1	2.040	0.330	93.300	3.240	0.660	0.130	0.040	0.040	0.050	0.030	0.010	0.000	5 TBM/DMS 78/22
	Barrow	2	7.190	0.430	86.040	4.460	1.060	0.250	0.100	0.100	0.060	0.030	0.010	0.000	
	Easington	3	2.140	0.860	93.050	2.960	0.590	0.120	0.035	0.035	0.050	0.030	0.010	0.000	
	St Fergus	4	0.900	2.280	87.440	6.690	2.190	0.220	0.025	0.025	0.010	0.000	0.000	0.000	
	Teeside	5	0.970	2.630	85.270	7.240	2.730	0.460	0.100	0.100	0.030	0.010	0.000	0.000	
	Theddlethorpe	6	2.790	0.780	91.270	3.730	0.890	0.175	0.175	0.050	0.050	0.040	0.040	0.010	
UK average (excl Barrow)			1.768	1.376	90.066	4.772	1.412	0.221	0.221	0.050	0.036	0.022	0.006	0.000	
France	Abu Dhabi	7	0.050	0.000	82.070	15.86	1.890	0.070	0.060	0.000	0.000	0.000	0.000	0.000	20 to 25 THT
	Algerie Montoir	8	0.600	0.000	88.600	8.200	2.000	0.250	0.350	0.000	0.000	0.000	0.000	0.000	
	Norway	9	3.360	1.400	88.720	4.900	1.120	0.140	0.210	0.040	0.000	0.000	0.000	0.000	
	Algerie Fos	10	1.000	0.000	91.200	6.500	1.100	0.100	0.100	0.000	0.000	0.000	0.000	0.000	
	Dutch	11	10.80	1.100	83.500	3.600	0.700	0.100	0.100	0.100	0.000	0.000	0.000	0.000	
	Lacq	12	0.300	0.000	97.300	2.100	0.200	0.050	0.050	0.000	0.000	0.000	0.000	0.000	
	Russia	13	1.800	0.260	96.240	1.170	0.340	90.05	0.080	0.020	0.000	0.040	0.000	0.000	
	Nigeria 1	14	0.400	0.000	88.000	5.500	4.000	1.000	1.000	0.100	0.000	0.000	0.000	0.000	
	Nigeria 2	15	0.400	0.000	85.900	9.000	3.500	0.600	0.600	0.000	0.000	0.000	0.000	0.000	
	France average (excl Dutch)		0.989	0.208	89.754	6.654	1.769	11.53	0.306	0.020	0.000	0.019	0.000	0.000	
Holland	Groningen	16	14.35	0.890	81.309	2.850	0.370	0.070	0.020	0.020	0.050	0.000	0.000	0.000	18 THT
	High CV Industrial	17	3.904	1.325	86.692	6.012	1.607	0.155	0.155	0.040	0.070	0.000	0.000	0.000	
Italy	Pseudo Groningen	18	11.00	4.184	78.990	4.314	1.161	0.095	0.095	0.025	0.110	0.000	0.000	0.000	20 THT or TBM/THT 50/50?
	Domestic	19	0.240	0.030	99.620	0.060	0.030	0.010	0.000	0.000	1.000	0.000	0.000	0.000	
	Russian	20	0.870	0.080	98.260	0.540	0.160	0.030	0.030	0.010	0.010	0.000	0.000	0.000	
	Dutch	21	2.280	0.890	92.690	2.950	0.810	0.110	0.160	0.030	0.050	0.000	0.000	0.000	
	Algerian	22	5.410	0.200	83.800	7.720	1.950	0.280	0.410	0.080	0.070	0.000	0.000	0.000	
	Italy average		2.200	0.300	93.593	2.818	0.738	0.108	0.150	0.030	0.030	0.263	0.000	0.000	
(Continues on next page)															

(Continues on next page)

Figure D.1: Typical Composition of European Gases and the ANGWARD standard NG composition.

Typical composition of European gases (continued).															
	Gas	He	CO ₂	C ₁	C ₂	C ₃	i-C ₄	n-C ₄	i-C ₅	n-C ₅	C ₆	C ₇	C ₈	O ₂	Odorant mg m ⁻³
Spain	Denmark (average)	23	0.325	1.150	88.270	6.250	2.750	0.390	0.590	0.116	0.090	0.069	0.000	0.000	
	Barcelons S-P(72)	24	0.439	0.000	89.123	9.119	1.114	0.088	0.110	0.004	0.003	0.000	0.000	0.000	
	Cartegena S-S-E	25	1.072	0.005	92.356	5.923	0.565	0.036	0.043	0.000	0.000	0.000	0.000	0.000	
	Huelva Red (16)	26	0.527	0.000	88.374	9.425	1.399	0.113	0.150	0.007	0.005	0.000	0.000	0.000	As Italy
	Conex. Francia	27	0.423	0.003	97.426	1.955	0.111	0.085	0.091	0.003	0.003	0.000	0.000	0.000	
	Gasoducto Magreb	28	5.513	0.255	83.656	7.470	2.007	0.301	0.477	0.102	0.120	0.099	0.000	0.000	
	Spain av (excl Magreb)		0.615	0.002	91.820	6.581	0.797	0.081	0.099	0.004	0.003	0.000	0.000	0.000	
	Weser Ens L	29	9.580	2.060	87.610	0.670	0.050	0.010	0.010	0.000	0.000	0.010	0.000	0.000	
Germany	Niederlande L	30	9.850	1.450	84.300	3.430	0.630	0.200	0.220	0.030	0.030	0.060	0.000	0.000	
	Nordsee H	31	1.030	1.270	86.920	8.160	1.940	0.200	0.530	0.000	0.100	0.050	0.000	0.000	
	GUS H	32	0.860	0.100	98.200	0.550	0.190	0.030	0.040	0.000	0.020	0.050	0.000	0.000	10 to 20 THT/TBM 50/50
	Verbund H	33	3.030	1.270	86.750	6.850	1.530	0.200	0.240	0.000	0.080	0.050	0.000	0.000	
	GUS H+Butan/air	34	13.53	0.090	71.340	0.640	0.190	0.000	10.77	0.070	0.070	0.000	0.000	3.390	
	GUS H+Propan/air	35	13.77	0.060	70.880	0.510	11.18	0.000	0.040	0.060	0.060	0.000	0.000	3.490	
	Niederlande L+Butan/air	36	16.57	1.050	68.110	2.970	0.590	0.000	8.480	0.000	0.050	0.040	0.000	2.140	
	Max concentrations		16.57	4.184	99.620	15.86	11.18	90.05	10.77	0.116	0.120	1.000	0.040	0.010	0.000
(Avg.)	UK, France, Italy, Denmark, Spain	Gas 1	1.393	0.471	91.308	5.206	1.179	2.985	0.194	0.026	0.021	0.084	0.006	0.000	
(Avg.)	Groningen	Gas 2	14.35	0.890	81.309	2.850	0.370	0.070	0.070	0.020	0.020	0.050	0.000	0.000	
	ANGUARD Standard		1.0	0.5	88.71	5.0	1.2	3.0	0.2	0.12	0.1	0.04	0.01	0.0	25ppm TBM 25ppm THT

Figure D.2: Typical Composition of European Gases and the ANGWARD standard NG composition.

Country	Odorant	Concentration mg/Nm ³	
		practical	nominal (min-max)
France	THT	25	(15-40)
D	THT	12.5	(10-20)
	TBM + EM	3.8	min
Belgium	THT	20	(17-34)
	Sentinel E	6	(5.4 – 7.1)
Italy	THT	32	(min)
	Sentinel E	8	(min)
DK	THT	10	- 18
Netherlands	THT	18	(10-36)
United Kingdom	BE	(12-16)	
Spain	THT	8	(18-24)
Czech Rep.	THT	(15-30)	

Odorant Nomenclature:				
Sentinel E	THT	Tetrahydrothiophene		
	EM	Ethyl - Mercaptan		
	TBM	Tertiary Butyl Mercaptan	76 %	
	IPM	Isopropyl Mercaptan	16 %	
	NPM	Normal Propyl Mercaptan	8 %	
	BE	Diethylsulfide	+ TBM	+ EM
		72 %	+ 22 %	+ 6 %

Figure D.3: Odorisation of Natural Gas.

Appendix E

MS Composition Analysis and Configuration Codes

MS Composition Analysis

The configuration files built for each mixture to be analyzed are presented. These files provide three trend screens for data acquisition, input, and reporting of concentrations, and allow for the calculation and reporting of normalized concentrations of gaseous CO₂/He/N₂, CO₂/He, CH₄/He and CO₂/N₂ streams [Figure (4.35)]. Each CALC file is not fully automatic. For example, the file CO2N2HeCALC is prepared to analyze a mixture where mass 28 is common to both CO₂ and N₂ components. Here, one has to consider that mass 28 has an amalgam of both N₂ and CO₂. There are two sets of numbers that must be entered manually before any measuring event.

The gases have different ionization efficiencies in the ionizer of the analyzer. Each gas ionizes more/less easily than other gases and the gases that ionize more easily show-up as higher peaks (higher partial pressures/ion currents) than a gas that is harder to ionize.

The primary function of the CALC screen is to acquire the data necessary to perform the concentration calculations. CALC also calculates the sensitivities of the various gases in the mixture. It is the calculation of the sensitivities of the gases that drives CALC. Every gas introduced into the mass spectrometer will exhibit a different affinity to produce ions. This effect is known as Ionization Probability. When the ionization probabilities of two different gases are compared to each other, one can calculate the Sensitivity of the gas by dividing the measured amount of the gas (by using any units that are convenient) by its concentration. By doing this simple exercise, one can quickly see that there are huge differences in how the gases produce ions.

For example, if one introduces into mass spectrometer a known mixture of 50/50 wt% of N₂/CO₂ and observes the mass spectrum, the peak corresponding to CO₂ would appear to be twice as big as that produced by N₂. If one attempt to report the concentrations

of these gases based solely on what the mass spectrum looked like, one would calculate that the mixture was 66.66% CO₂ and 33.33% N₂. Hence, the error in concentrations is due to the differing sensitivities of the gases presented to the mass spectrometer. In order to accurately report the concentrations of the mixture, one must correct for the different sensitivities of N₂ and CO₂. The starting point for this calculation is to make one of the masses a Reference or Normalization mass. In this case, one will select N₂ as the reference mass.

Since we were hypothesizing that CO₂ is twice as large as N₂ based on what the mass spectrum showed us, one would have gathered the following data from the mass spectrum:

$$\begin{cases} \text{CO}_2 = 20000 \text{ data counts} \\ \text{N}_2 = 10000 \text{ data counts} \end{cases} \quad (\text{E.1})$$

Calculating the concentrations directly from this information would give

$$\begin{cases} \text{CO}_2 \text{ concentration} = 20000/30000 = 66.66\% \\ \text{N}_2 \text{ concentration} = 10000/30000 = 33.33\%. \end{cases} \quad (\text{E.2})$$

To correct for the differing sensitivities of the two gases one would first find the sensitivity of each of the gases like

$$\begin{cases} \text{CO}_2 \text{ SENS} = 20000/50\% = 400 \text{ data counts} \\ \text{N}_2 \text{ SENS} = 10000/50\% = 200 \text{ data counts.} \end{cases} \quad (\text{E.3})$$

Since one have decided to use N₂ as the reference, one need to find the correction factor for CO₂. This factor is found by:

$$\text{N}_2 \text{ SENS}/\text{CO}_2 \text{ SENS} = 200/400 = 0.5. \quad (\text{E.4})$$

The correction factor for CO₂ is then 0.5. Once one have the correction factor, one will apply it to any subsequent reading taken for CO₂. Thus, lets correct our original data

$$\begin{cases} \text{CO}_2 \text{ SIGNAL} = 20000 \times 0.5 = 10000 \\ \text{N}_2 \text{ SIGNAL} = 10000. \end{cases} \quad (\text{E.5})$$

Note that there is no correction factor applied to N₂, since this component was chosen as the reference. Concentrations would then be

$$\begin{cases} \text{CO}_2 = 10000/20000 = 50\% \\ \text{N}_2 = 10000/20000 = 50\%. \end{cases} \quad (\text{E.6})$$

Now it is possible to vary the concentrations of these gases from approximately 0.1% to 100% and be able to report the concentration of the mixture accurately. All of the above calculations are performed by CALC file.

The right side of the CALC screen carries a number of operators. The following is a definition of each operator:

- a) 4 is the raw data taken at mass 4,
- b) 28 is the raw data taken at mass 28,
- c) 44 is the raw data taken at mass 44,
- d) CO₂ SENS is the CO₂ sensitivity referenced to N₂,
- e) He SENS is the He sensitivity referenced to N₂, and
- f) It is the total corrected ion signals for all measured components.

The INPUTS screen allows the user to enter the values obtained from the CALC screen. The values that will be entered from the CALC screen are the sensitivities. The INPUTS' definitions are:

- a) CO₂ SENS IN is the channel for entering CO₂ Sensitivity,
- b) He SENS IN is the channel for entering He Sensitivity.

Once numbers have been entered into the INPUTS screen, they are automatically moved to their proper place in the calculation sequence.

The CONCENTRATIONS screen reports the calculated concentrations as calculated by the CALC file. There are no user entries necessary to view concentrations in this screen.

The file is saved and a mixture, with a different composition from the calibration one, is fed to the MS in order to check the correctness of the protocol.

MS Configuration Codes

Mass spectroscopy analysis involves several steps: atomization with conversion of a substantial fraction of atoms formed to a stream of ions (usually singly charged positive ions); ions separation on the basis of their mass-to-charge (m/e) ratio, where m is the ion mass in atomic mass units and e is its charge; and measure of the ion current produced when the ions formed from the sample strike a suitable transducer. Usually m/e is simply the mass of the ion. Although the operation depends on maintaining low and

stable vacuum pressures, and on ensuring that operating conditions of the standards and sample are similar, this technique provides a fingerprint identification for the structural and chemical properties of the individual atoms and molecules converted to ions [[Ametek \(2004\)](#); [Ewing](#); [Gunzler and Williams](#); [Nieman and Skoog \(2003\)](#); [Rouessac and Rouessac](#)].

The pure component mass spectrometer was performed in order to obtain the constant relation of its masses. The experiments were repeated at least three times to check reproductivity. The N₂ spectra show mainly two peaks, for masses 14 and 28. From the total masses observed 93.3% corresponds to Mass 28 and 4.2% to Mass 14. The He spectra shows 96.0% of Mass 4 and 2.0% of Mass 18. The CO₂ spectra presents 78.0% of Mass 44, 5.8% of Mass 28 and 4.1% of Mass 16. The percentage of Mass 28 relative to the Mass 44 is approximately 7.33%.

These constant mass relations for each component are in accordance with the database given by MS suppliers, handbooks or in any MS software.

The MS configuration codes applied in the work are presented as follows:

CO2N2HeCALC.DYC

- REFERENCE: N2 10.1%
- CALIBRATION MIXTURE XCO₂/XN₂/XHe: 45.5 / 10.1 / 44.5%
- CO2N2HECALC SCREEN
Quad: 4
Quad: 28
Quad: 44
 $M_{28} = M_{28}(N_2) + M_{28}(CO_2) = M_{28}(N_2) + 0.073 M_{44}$
 $CO_2 \text{ SENS} = (quad:28 - 0.073 \text{ quad:44})/xN_2 / (quad:44/xCO_2)$
 $It = (quad:28 - 0.073 \text{ quad:44}) + INPUTS.CO_2 \text{ SENS IN} + INPUTS.He \text{ SENS IN}$
- INPUTS SCREEN
 $CO_2 \text{ SENS IN} = CO2N2HeCalc.quad:44 \times D1$
 $He \text{ SENS IN} = CO2N2HeCalc.quad:4 \times D2$
D1 and D2 are calculated with MS admission of the standard calibration mixture after stabilization on the CO2N2HeCALC Screen. Those values are 2.248326 and 0.06171, respectively.

- CONCENTRATION SCREEN

He CONC = INPUTS.He SENS IN $\times$ 100 / CO2N2HeCalc.It

CO2 CONC = INPUTS.CO2 SENS IN $\times$ 100 / CO2N2HeCalc.It

N2 CONC = (quad:28 - 0.073 quad:44) $\times$ 100 / CO2N2HeCalc.It

CH4HeCALC.DYC

- REFERENCE: He 19.9%

- CALIBRATION MIXTURE XCH4/XHe: 80.1 / 19.9%

- CH4HECALC SCREEN

Quad: 4

Quad: 16

CH4 SENS = (quad: 4 / 80.1) / (quad: 16 / 19.9)

It = quad: 4 + INPUTS.CH4 SENS IN

- INPUTS SCREEN

CH4 SENS IN = CH4HeCalc.quad: 16 $\times$ D

D is calculated with MS admission of the standard calibration mixture after stabilization on the CH4HeCALC Screen. The value obtained is 0.2079.

- CONCENTRATION SCREEN

He CONC = CH4HeCalc.quad: 4 $\times$ 100 / CH4HeCalc.It

CH4 CONC = INPUTS.CH4 SENS IN $\times$ 100 / CH4HeCalc.It

N2HeCALC.DYC

- REFERENCE: He 29.9%

- CALIBRATION MIXTURE XN2/XHe: 70.1 / 29.9%

- N2HECALC SCREEN

Quad: 4

Quad: 28

N2 SENS = (quad: 4 / 70.1) / (quad: 28 / 29.9)

It = quad: 4 + INPUTS.N2 SENS IN

- INPUTS SCREEN

N2 SENS IN = N2HeCalc.quad: 28 $\times$ D

D is calculated with MS admission of the standard calibration mixture after stabilization on the N2HeCALC Screen. The value obtained is 0.1263.

- CONCENTRATION SCREEN

He CONC = N2HeCalc.quad: 4 $\times$ 100 / N2HeCalc.It

N2 CONC = INPUTS.N2 SENS IN $\times$ 100 / N2HeCalc.It

CO2HeCALC.DYC

- REFERENCE: He 49.9%

- CALIBRATION MIXTURE XCO2/XHe: 50.1 / 49.9%

- CO2HECALC SCREEN

Quad: 4

Quad: 44

CO2 SENS = (quad: 4 / 49.9) / (quad: 44 / 50.1)

It = quad: 4 + INPUTS.CO2 SENS IN

- INPUTS SCREEN

CO2 SENS IN = CO2HeCalc.quad: 44 $\times$ D

D is calculated with MS admission of the standard calibration mixture after stabilization on the CO2HeCALC Screen. The value obtained is 0.1015.

- CONCENTRATION SCREEN

He CONC = CO2HeCalc.quad: 4 $\times$ 100 / CO2HeCalc.It

CO2 CONC = INPUTS.CO2 SENS IN $\times$ 100 / CO2HeCalc.It

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