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Licenciada em Ciências da Engenharia Química e Bioquímica

**Life Cycle Assessment of Raw White, Dyed and
Pigmented Acrylic Fibres and Proposals for
the Improvement of Environmental Performance**

Dissertação para obtenção do Grau de Mestre em
Engenharia Química e Bioquímica

Orientador: Doutor Paulo Fernando Martins de Magalhães Correia,
Engenheiro de Desenvolvimento, SGL Composites, S.A.

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Aos meus pais, por me incentivarem a ir sempre mais longe.

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Abstract

This master thesis consists on the development of a Life Cycle Assessment (LCA) of raw white (L11), gel-dyed (L25), and pigmented (L28) acrylic fibres. The main goal was to assess the environmental impacts resulting from the production of L11, L25 and L28 fibres, concluding which fibre and which acrylic fibre production stages and activities have the most impact on the environment. Based on the results obtained, suggestions regarding environmental performance improvement are presented.

A cradle-to-gate study was developed, which includes the life cycle stages of raw material production, its transportation to the acrylic fibre plant, and acrylic fibre production, which comprises the stages of: continuous polymerisation (CP), dope preparation (DP), spinning (SP), cut and baling (CB), and solvent recovery (SR). For this study, all data regarding the production of the acrylic fibres was provided by the industrial manufacturer. The product systems were developed in the openLCA software (version 1.10.2) and the impact assessment method was the CML 2001.

It was concluded that the gel-dyed fibre was the one that presented the highest environmental impacts. Continuous polymerisation was the production area which contributed the most to the environmental burdens. In general, acrylonitrile production was the major contributor for the environmental impact categories, followed by steam and dimethylacetamide productions. To make a significant reduction on the impacts, a search for more sustainable sources of acrylonitrile, steam, and dimethylacetamide is proposed in this work. This search would allow the company to move into more sustainable acrylic fibres.

Key-Words: Life Cycle Assessment; cradle-to-gate; acrylic fibre; environmental performance; sustainability.

Resumo

Esta dissertação de mestrado consiste no desenvolvimento de uma Análise de Ciclo de Vida (ACV) de fibra acrílica crua (L11), tinta (L25) e pigmentada (L28). O principal objetivo foi o de estimar os impactos ambientais resultantes da produção das fibras acrílicas L11, L25 e L28, concluindo qual a fibra, etapas de produção de fibra acrílica e atividades que apresentam os maiores impactos no ambiente. Com base nos resultados obtidos, são apresentadas sugestões de melhoria de desempenho ambiental.

Foi desenvolvido um estudo *cradle-to-gate*, que inclui as etapas de ciclo de vida de produção de matérias-primas e utilidades, o transporte das matérias-primas para a fábrica de fibra acrílica e a produção da mesma, que inclui as etapas de: polimerização contínua (CP), preparação de xarope (DP), *spinning* (SP), corte e embalagem (CB) e recuperação de solvente (SR). Neste estudo, toda a informação relativa à produção de fibra acrílica foi fornecida pelo produtor industrial. Os sistemas de produção foram desenvolvidos no *software* openLCA (versão 1.10.2) e o método utilizado foi o CML 2001.

Foi concluído que a fibra tinta foi a que apresentou os maiores impactos ambientais. A área de produção de polimerização contínua foi a que mais contribuiu para os danos ambientais. No geral, a produção de acrilonitrilo foi a atividade mais responsável pelos impactos nas categorias de impacto estudadas, seguida pela produção de vapor e de dimetilacetamida. De forma a tornar possível uma redução significativa dos impactos, é proposta neste trabalho uma procura por fontes mais sustentáveis de acrilonitrilo, vapor, e de dimetilacetamida. Esta procura poderá permitir a que a empresa se mova na direção de fibras acrílicas mais sustentáveis.

Palavras-Chave: Análise de Ciclo de Vida; *cradle-to-gate*; fibra acrílica; desempenho ambiental; sustentabilidade.

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Lists of Abbreviations and Acronyms

20S	20 bar Steam
5S	7 bar Steam
AC	Acetic Acid
ÁdLVT	Águas de Lisboa e Vale do Tejo
AN	Acrylonitrile
ARA	Amsterdam-Rotterdam-Antwerp
AV	Vinyl Acetate
BAT	Best Available Technology
BHET	Bis(2-hydroxyethyl) Terephthalate
CB	Cut and Baling
CCS	Content Claim Standard
CFC-11	Chlorofluorocarbon-11
CFP	Carbon Fibre Precursor
CIF	Cost, Insurance and Freight
COD	Chemical Oxygen Demand
CP	Continuous Polymerisation
CSP	Concentrating Solar Power
CSTR	Continuous Stirred Tank Reactor
CW	Chilled Water
DGT	Diethylene Glycol Terephthalate
DIW	Deionised Water
DMA	Dimethylamine
DMAC	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DMT	Dimethyl Terephthalate
DP	Dope Preparation
EDTA	Ethylenediaminetetraacetic Acid
EI	Environmental Impact Index
ESI	Ecological Sustainability Index
GD	Gel-Dyeing
GHG	Greenhouse Gas
GOTS	Global Organic Textile Standard
GRS	Global Recycled Standard
GVL	γ -Valerolactone
ISCC	International Sustainability and Carbon Certification
ISO	International Standard for Organization
L11	Raw White Fibre

L25	Dyed Fibre
L28	Pigmented Fibre
L3	Acrylic Textile Fibre Polymer
L99	Carbon Fibre Precursor Polymer
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LOI	Limiting Oxygen Index
MEG	Monoethylene Glycol
NREL	National Renewable Energy Laboratory
OCS	Organic Content Standard
PAN	Polyacrylonitrile
PP	Polypropylene
PS	Polymer Storage
PTA	Terephthalic Acid
R&D	Research and Development
RCS	Recycled Claim Standard
REACH	Registration, Evaluation, Authorisation of CHemicals
RH	Relative Humidity
RPI	Recyclability Potential Index
RW	Recovered Water
SETAC	Society of Environmental Toxicology and Chemistry
SP	Spinning
SR	Solvent Recovery
STeP	Sustainable Textile Production
SVHC	Substance of Very High Concern
TF	Tank-Farm
TT	Tow to Top
TW	Cooling Water
UN	United Nations Environment
UT	Utilities
W	Industrial Water

1. Introduction

1.1. Goal and Motivation

The textile and apparel industry are essential for the today's modern world, being fibre manufacturing crucial for these industries. Textile fibre consumption was more than 100 million tonnes in 2019 worldwide ^[1]. Synthetic fibres dominate the textile fibre market, representing more than 60% of textile fibre consumption, and regarding acrylic fibre, its demand has been close to 2 million tonnes ^[2, 3]. Both fibre production and consumption are expected to continue to grow in the upcoming years, due to the continuously increase of world population.

It is known that this industry is responsible for several environmental impacts derived from its activity. To this industry are associated high consumptions of both energy and water, and the release of hazardous waste from the several process production stages, creating environmental concerns. For this reason, textile and fibre manufacturers are increasingly adopting the Life Cycle Assessment (LCA) methodology to assess the environmental impacts of their products, aiming to take action, mitigating these impacts.

The SGL Composites company, being a company interested in reducing its environmental impacts and aiming to move further to sustainable development, sought the development of a LCA study applied to their acrylic fibre production process. The development of this master thesis was the result of this company's goal.

For the reason stated above, the main objective of this master thesis was the development of a cradle-to-gate LCA study applied to the production of the raw white (L11), dyed (L25), and pigmented (L28) acrylic fibres. Through the LCA study, there were also the goals of assessing the environmental impacts of the production of the L11, L25, and L28 fibres, evaluating which fibre presented the major impacts, which production stages and activities were the most responsible for the impacts, and evaluating the benefits of the existing Solvent Recovery (SR) area in the process. Through the study results, a proposal for the environmental performance improvement was developed, with a series of suggestions focusing on the main contributors to the impacts, aiming to reduce the impacts resulting from acrylic fibre production.

1.2. Thesis Structure

The present thesis is structured into six chapters:

- **Chapter 1:** presents an overview of the goals and motivations concerning this master thesis, and also an overview of the thesis structure;
- **Chapter 2:** a theoretical framework is presented, concerning acrylic fibre and other textile fibres, their properties, and their presence in the textile fibre market. A brief introduction of SGL Composites is made, and its acrylic fibre production process is specified. The LCA methodology is introduced and also the subject of textile fibres and sustainability, with special regards to eco-labelling;
- **Chapter 3:** presents the State-of-the-Art concerning the LCA of textile fibres;
- **Chapter 4:** the developed LCA study on raw white, dyed, and pigmented acrylic fibres is presented. The different phases of LCA are included in this chapter;
- **Chapter 5:** presents the several developed suggestions, based on the LCA results, for environmental performance improvement;
- **Chapter 6:** the final drawn conclusions and proposals for future work are presented in this final chapter.

2. Theoretical Framework

2.1. Textile Fibres

A textile fibre is described, according to the European Regulation N° 1007/2011, as a “unit of matter characterized by its flexibility, fineness and high ratio of length to maximum transverse dimension, which render it suitable for textile applications” [4].

The manufacturing of fibres to textiles is one of the ancient crafts in history. Clothing had mainly the purpose of human protection from cold, rain or heat. Nowadays, clothing represents a basic human need, being also relevant for fashion. Up until the 17th century, textile manufacturing was based on a domestic production. The used fibres were from a natural origin, being predominantly used the cotton and wool fibres. With the Industrial Revolution came the mechanisation of production processes, allowing the development of new and faster methods for fibre manufacture [5, 6].

In the 19th century, the first man-made fibres were developed. C.F. Schönbein, in 1846, accidentally discovered cellulose nitrate. It was concluded that, through the action of a mixture of sulphuric and nitric acids, cotton can be transformed into a soluble plastic substance [6, 7]. Later in 1884, Hillaire de Chardonnet extruded this substance into fine filaments. Cellulose nitrate, contrary to cellulose, was soluble in a mixed alcohol/ether solvent and, thus, spinnable. Based on a similar process, the commercial production of viscose rayon fibre started based on cellulose sodium xanthate, the intermediate product, and, at the end of the century, started the production of cellulose acetate fibre. These fibres are named as regenerated cellulose fibres, except for cellulose acetate, which is no longer considered in this group, since acetate is the polymer formula to produce the acetate fibre, a cellulose ester, and not cellulose.

In 1938, W.H. Carothers and his group produced the first entirely synthetic fibre successfully, in the USA. This fibre was named nylon 66 and it was produced from adipic acid and hexamethylene diamine. To form the fibre, the filaments were pulled out from the melt. In Germany, polycaprolactam was discovered by Paul Schlack, usually called as nylon 6, which production started at the beginning of the Second World War, in 1939. Other synthetic fibres were then discovered. In 1949 it was discovered polyacrylonitrile, in 1950 polyvinyl alcohol, in 1953 poly(ethylene terephthalate), in 1957 polypropylene (PP), in 1962 aromatic polyamide and, in 1972, aromatic polyester fibres [7].

Summing up, the fibres can be classified into three main fibre groups: natural, regenerated, and synthetic. Synthetic and regenerated fibres are usually known as man-made fibres. Inorganic fibres, like carbon and glass fibres, are man-made fibres too, but not textile ones [6].

Natural fibres are the ones that occur in nature and can be divided into vegetable/cellulosic or animal/protein fibres. Animal-based fibres can be classified into wool, hair (e.g. mohair, cashmere, and angora), and silk. Vegetal fibres can be classified as seed (e.g. cotton), hemp and jute, bast (e.g. flax), and leaf (e.g. sisal).

For clarification, regenerated fibres are the ones which are made from natural polymers, and although not being possible to use them in their early form, they can be regenerated, as the name says, to create useful fibres. Viscose, an example of this type of fibre, is regenerated from wood pulp. Synthetic fibres, like acrylic and polyester, are obtained through polymerisation in industrial processes. A natural mineral fibre is known, asbestos, but it is no longer used, since to its considered carcinogenicity.

In figure 2.1, a diagram of the categories of the most important fibres, with some examples within each category, is shown.

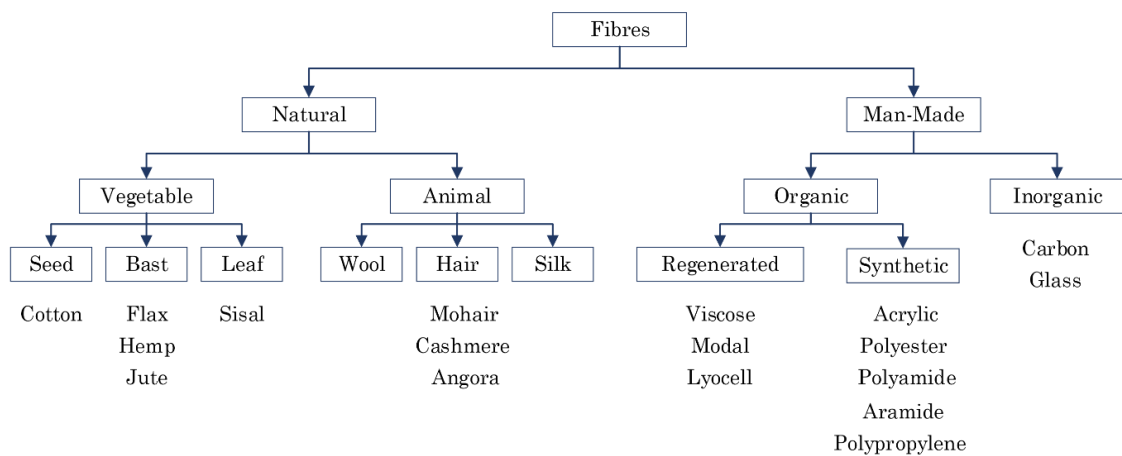


Figure 2.1 - Fibre types and categories.

A more detailed description of acrylic fibres is presented afterwards, as well as a description of its main competitors in the textile fibre sector: cotton, wool, viscose, and polyester [5, 8].

2.1.1. Acrylic Fibres

Acrylic fibre is usually defined as a fibre containing at least 85% w/w of acrylonitrile (AN) monomer. The produced polymer is polyacrylonitrile (PAN). The main comonomers used are neutral esters, which include vinyl acetate (AV) and methyl acrylate. These comonomers improve the solubility of the polymer in the solvent and fibre flexibility and morphology. If the polymer contains 15 to 50% w/w of comonomer and at least 35% w/w of acrylonitrile, it is considered as a modified acrylic fibre, being named as modacrylic fibre [9].

The French chemist Moreau was the first person to synthesise acrylonitrile and polyacrylonitrile. Moreau reported two methods for synthesising AN in 1893 and, a year later, reported the method for AN polymerisation into PAN. The polymer did not receive much attention in the beginning since no known solvents existed, and, also, due to the polymer decomposition before the reaching of its melting point. Herbert Rein from I.G. Farbenindustrie, before the Second World War, was able to perform fibre spinning from a polymer solution in aqueous solutions of quaternary ammonium compounds, such as benzyl peritoneum chloride, or of metal salts, such as sodium thiocyanate, lithium bromide, and aluminium perchlorate. The initial interest for acrylonitrile polymers was not for textile purposes, but for their use in synthetic rubber. The first acrylonitrile-butadiene rubber was produced by I.G. Farbenindustrie in 1937 [10, 11].

In 1944, DuPont produced the Orlon fibre, the first commercial acrylic fibre. DuPont's process used *N,N*-dimethylformamide (DMF) as the solvent, being the process based on dry-spinning. Later, Chemstrand, the future Monsanto Fibres and Intermediates Company, produced the Acrilan fibre, Süddeutsche Chemiefaser the Dolan fibre, and Bayer the Dralon fibre. Chemstrand's process used wet-spinning, where a steam-annealing step was added to overcome abrasion difficulties, and coherence of the fibres was improved by the presence of AV. To sum up, dry-spinning processes usually use DMF as the solvent and methyl acrylate as the comonomer, allowing the modification of fibre morphology and increase of the dyeability, and wet-spinning processes most frequently use dimethylacetamide (DMAc) as the solvent and vinyl acetate as the comonomer. Another possible way for the late method is using as the solvent a solution of aqueous sodium thiocyanate and as the comonomer methyl acrylate. Dimethylformamide is also a common solvent in wet-spinning processes. These are the most used spinning methods in the industry, and it is mostly the spinning process which distinguishes the different existing technologies for acrylic fibre production. The

majority of acrylic fibres are produced by wet-spinning. To overcome the existing difficulties in dyeing, cationic dyes were developed [6, 10, 12].

The polymerisation may occur in slurry or in solution. In slurry polymerisation, water-soluble peroxy bisulphate redox systems are used to initiate the polymerisation. By purifying and demonomerising the polymer entirely, a compact polymer granulate is produced. This polymer granulate may be dried after washing and filtering. Regarding solution polymerisation, polymer solutions are obtained as result of the copolymerisation of acrylonitrile, which can be spun without further processes after the residual polymers elimination [13].

The powder polymer is dissolved in a solvent. The resulting solution is designated by dope. The contained polymer in the prepared solution is transformed into a fibre by either dry or wet-spinning, by being pressed through the spinneret's small holes. Hot air or a hot inert gas is used in dry-spinning. In wet-spinning, a coagulation bath of water and solvent is used.

In summary, acrylic fibre production technology is mature and mainly consists in three processes: polymerisation of acrylonitrile with a comonomer, such as vinyl acetate or methyl acrylate, to form PAN in the presence of a catalyst, dope preparation, and the formation of fibres through spinning. Many additives are usually incorporated to, for example, improve protection against ultra-violet radiation and microorganisms. Good resistance to most types of chemical attack and toleration to high temperatures up to 150 °C are also characteristics of acrylic fibres [6].

This type of fibre is usually used for clothing and household furnishings and is commonly used in blends with wool due to its properties. This fibre has also a more technical application in outdoor fabrics due to its high resistance to light, weather conditions and mould.

A more detailed description of the acrylic fibre production process at SGL Composites company is presented in chapter 2.5.

2.1.2. Cotton

Cotton fibres are the most common natural fibres and nature's most abundant polymer, where about 90% of its composition is cellulose. The noncellulosic part of cotton is made of proteins, waxes, inorganics and pectins. Dependent on the growing conditions and cotton variety are the structure and composition of cellulose and noncellulosics. [14].

This fibre is considered to be the biggest fibre source for clothing, being also used for industrial products. Cotton's main producers are China, the United States, and India. These countries together, among Pakistan, Uzbekistan, Turkey, and Brazil, are responsible for 80% of the world's cotton production [6].

After the harvesting of cotton, the seed cotton is transported to the ginning plant. This process consists of a mechanical process, in which the separation of the fibres from seeds and other plant matter, such as dirt and leaves, occurs. The processes involved in ginning are conditioning, for adjusting the moisture content, cleaning, seed-fibre separation, and packaging. Until this process, cotton has a low commercial added value [6].

Ginned cotton is spun to transform the fibre into yarn and can be subjected to finishing processes such as dyeing and bleaching.

Cotton seeds are usually pre-treated with fungicides, insecticides, and plant growth regulators to avoid diseases and pests. Pesticides are also applied during the growing periods to the cotton crops [14].

2.1.3. Wool

Wool is a natural protein fibre essentially composed by keratin. This fibre can have its origin in different breeds of sheep, such as Merino and Sussex [6].

Sheep breeding has been an important activity throughout most Europe, Asia, and the Americas. The majority of wool harvest from New Zealand, Australia, Argentina, and South Africa is exported to textile manufacturers in the northern hemisphere. After the declining of wool manufacturing in these countries in 1960, other importers have emerged, such as China, Iran, Japan, and Russia [15].

To harvest the wool, powered hand clippers to shear the live sheep wool are often used. Each fleece is examined during shearing to remove faults relating to contamination, length, and colour. The main contaminants are woolgrease, dirt, and suint. Woolgrease consists of a wax formed by action of the sebaceous glands in the sheep skin. Suint is formed by the sudoriferous glands. Woolscouring is the process that is applied to clean these contaminants through detergents. The extracted grease is turned into lanolin, a by-product with commercial value [15, 16].

Wool can be contaminated by pasture weeds, producing seeds and burrs that become entangled in the growing fleece. If it is severe, this contamination cannot be treated conventionally, being required an acid process that embrittles vegetable matter, named

carbonising, adding costs in wool processing and categorising. Woolgrowers often use pesticides and agricultural sprays to assure that wool does not contain unwanted residues.

After the scouring, combing of wool and spinning follows in a spinning mill. Some finishing processes are also applied to wool, being similar to those referred for the other fibres mentioned above.

2.1.4. Viscose

First patented in 1893 by Cross and Bevan, viscose, or viscose rayon, is a regenerated cellulose fibre. It was discovered that, through the reaction of an alkali and carbon disulphide with raw cellulose from wood, or cotton, cellulose xanthate could be produced. Stearn, in collaboration with Cross, in 1898, developed the spinning method for viscose. After the acquisition of the viscose process patents by Courtauld & Co, viscose was first commercialised in 1904 [6].

Pulp production is the process of breaking down the structure of wood to free the cellulose fibres in a sulphite pulp [13, 17]. To produce viscose, the pulp is initially subjected to an aqueous solution of sodium hydroxide, swelling the fibres, and causing the conversion of cellulose to sodium cellulose, or alkali cellulose. After that, to obtain a precise ratio of alkali to cellulose, the swollen mass is pressed. Then it can be shredded, providing proper surface areas, allowing a uniform reaction. To depolymerise the cellulose, the obtained alkali cellulose is aged under controlled time and temperature conditions. This can be achieved through oxidation to the desired degree of polymerisation, previous to the reaction with carbon disulphide to produce sodium cellulose xanthate. A solution of viscose is obtained, after the xanthate is dissolved in dilute sodium hydroxide. The obtained solution is filtered, deaerated, and ripened to the desired coagulation point suitable for spinning. After the solution is extruded through the spinneret holes into a spin-bath of sulphuric acid, zinc sulphate, sodium sulphate, and water, the filaments are formed. After this process, the filaments are washed to remove the acid, desulphurised and bleached before the final washing and the application of the finishing process.

2.1.5. Polyester

Polyester fibres, or poly(ethylene terephthalate) (PET) fibres, are the dominating fibres in the synthetic fibres group. In its main polymeric chain are ester groups. Polyester, besides its presence in the textile industry, it is also utilised for the manufacturing of plastic bottles and liquid crystal displays, for example. An important advantage of polyester is the possibility of its relatively simple recycling. Another advantage of this fibre is the fact that it is inexpensive, versatile, and easily manufactured from fossil sources, with a high range of physical properties [6, 18].

W. H. Carothers developed the first work on polyester manufacturing at DuPont, around 1930. Still, only after the Second World War, Whinfield and Dickson synthesised PET from terephthalic acid and its purified dimethyl ester, through the reaction with ethylene glycol. PET was first commercialised in the early 1950s by DuPont and by Imperial Chemical Industries [18].

This type of fibre can be produced through two methods: the dimethyl terephthalate (DMT) or the terephthalic acid (PTA). The first method is based on the reaction of DMT with monoethylene glycol (MEG) in the presence of a catalyst, usually a metal oxide, in which the diethylene glycol terephthalate (DEGT) monomer is produced. Then, DEGT is subjected to a polycondensation polymerisation in the presence of a catalyst, usually a metal acetate, to produce the PET polymer. The second method consists of the reaction of PTA with ethylene glycol, with metal oxides as catalysts, to obtain bis(2-hydroxyethyl) terephthalate (BHET). PET oligomers are produced after the BHET production. Following that, the product mixture is transferred directly to the polymerisation vessel for the next step to obtain the PET polymer [6, 18].

In the melt-spinning process are fed the polyester polymers. The polymer is melted in the hopper feeder and then sent to the melt extruder. To improve the fibre properties, the obtained filaments are subjected to a drawing process and to finishing treatments as well [18].

2.2. Textile Fibre Properties

All these fibres have different properties which have an influence on production techniques, such as spinning, and have a direct impact on how these fibres behave during its use. Table 2.1 presents some typical property values for the above mentioned fibres. These fibre properties allow a distinction between them [19, 20, 21].

Table 2.1 – Textile fibre properties [19, 20, 21].

Fibre	Fibre Length	Diameter (µm)	Moisture Regain at 65% RH (%)	Elongation Strain to Failure (%)	Dry Tenacity (N/tex)	Flammability (Limiting Oxygen Index)
Acrylic	Filament	—	1.5-2.5	25-45	0.2-0.5	18
Cotton	10-50 mm	10-27	8,5	7	0.3-0.5	17-19
Wool	25-355 mm	15-40	13.6	35	0.1-0.2	25-27
Viscose	Filament	4-60	11	25	0.1-0.3	16-18.7
Polyester	Filament	15	0,4	15	0.3-0.9	22

Table 2.1 shows that synthetic fibres have a more similar value for moisture regain at 65% of relative humidity (RH), meaning that these fibres, acrylic and polyester, are hydrophobic, absorbing almost no water compared to the other fibres. Fibre elongation partially reflects the extent of stretching easiness, meaning that the higher is the value of elongation strain to failure, the higher is the flexibility of the fibre. This way, wool and acrylic fibre are the most flexible fibres. Tenacity refers to the maximum amount of stress that a fibre is able to support before its breaking, and tex is a common unit in the textile industry, equal to the fibre weight in grams of 1000 meters of material. High tenacity fibres are usually preferred to allow the reduction of the strength deficiency of rotor spun yarns, fibrous rotor deposits resultant of the aggressive action of the opening roller, and end-breakages. Polyester seems to be the most tenacious fibre and wool and viscose the least tenacious fibres. Regarding to fibre flammability, or limiting oxygen index (LOI), it is related to the amount of oxygen required to support combustion. Considering that the oxygen content of Earth's atmosphere is approximately 21% v/v, fibres that have an LOI value lower than 21% v/v, such as acrylic and cotton, burn more easily comparing to those with LOI values above this percentage [21, 22].

2.3. Textile Fibre Market

Global fibre production was around 107 million tonnes in 2018 and it has more than doubled in the last 20 years [23]. Nonetheless, fibre production has experienced the slowest growth in three years, 1%, due to the worsening world economic state [24]. Figure 2.2 shows the world textile fibre consumption from 1981 to 2019 [1].

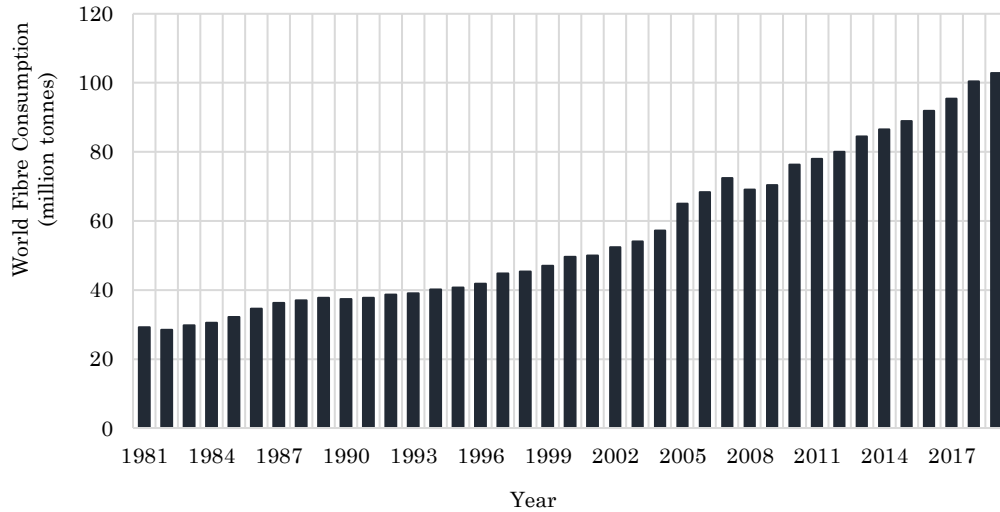


Figure 2.2 – World textile fibre consumption from 1981 to 2019 [1].

Synthetic fibres have been dominating the fibre market since the mid 1990s, having surpassed the cotton market. Polyester itself has a market share of around 52% of total global fibre production and dominates synthetic fibre consumption [23]. The production of cotton has increased in the past five years, especially in the United States, China, Turkey, India, and Central Asia, being the second largest volume textile fibre [25]. Cellulosic fibres are an increasingly important fibre category and are essentially composed by viscose, lyocell and modal. This fibre category had a growth of almost 3% in 2018, while synthetic fibres had a growth of 2%. Regarding wool, this fibre has a market share of around 1% and its production has been declining [24]. The world consumption of natural and man-made fibres, split by type of fibre, in 2019, is presented in figure 2.3 [2].

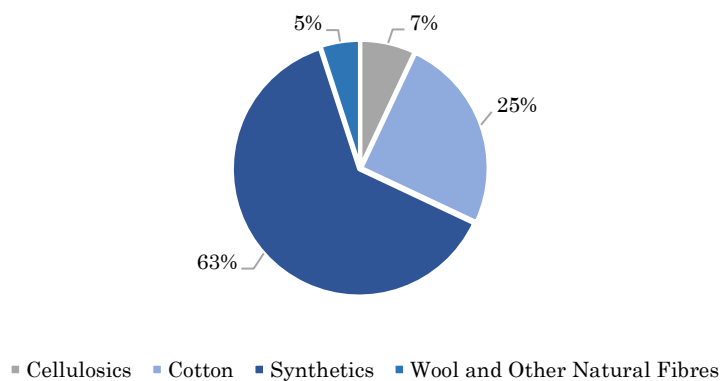


Figure 2.3 - World consumption of natural and man-made fibres in 2019 [2].

In 2019, and in 2018 as well, China was the largest synthetic fibre producer. China along with India and other countries from Asia-Pacific account for 95% of the total global consumption, production capacity, and production of synthetic fibres [25]. The production share of synthetic fibres in 2017 is presented in figure 2.4 [26].

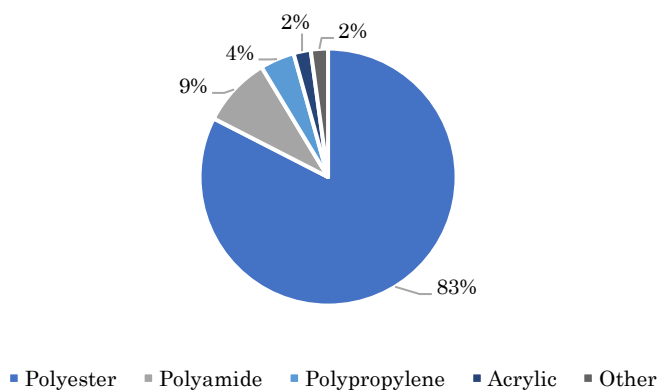


Figure 2.4 - Production share of synthetic fibres in 2017 [26].

Regarding acrylic fibre, the global demand for this fibre was around 1.8 million tonnes in 2018 [3]. The region that holds the highest market share is Asia-Pacific, accounting for around 50% of the total global market, followed by the Middle East and Africa, and Europe. Asia-Pacific owes its position due to the growing acrylic fibre manufacturers for the possible reason that there are fewer legislations by environmental regulation bodies. The Middle East and Africa region is the second largest market due to the presence of acrylonitrile raw material producers. Europe has fewer manufacturers comparatively to the two regions referred above [27].

China is the largest producer of acrylic fibre and holds more than 30% share in the global market for acrylic fibre production, although the world largest producer, Aksa, is based in Turkey ^[28]. Despite the large production capacity of acrylic fibres in China, the country still imports some of its requirements from the global marketplace ^[29].

Some of the major manufacturers of this fibre are Aksa Akrilik Kimya Sanayii AS, the largest producer with a capacity of around 315 000 tons per year, Dralon GmbH, Formosa Plastics Group, Thai Acrylic Fibre Co. Ltd., China Petrochemical Corporation, Aditya Birla Management Corporation Pvt Ltd., and Toray Industries Inc. ^[27]. These companies account for almost 50% of the world acrylic fibre market ^[28].

The major markets for acrylic fibres are the textile and apparel industries ^[28]. Due to its properties, the demand for this type of fibre is essentially for blending with other fibres to obtain the required characteristics and enhance the stability, strength, and absorbency of the final product. Acrylic fibres are lightweight and improve yarn softness, warmth, and durability. The stretch from acrylic makes the yarn easier to work with as well. For example, the blending of acrylic fibre with wool improves the final product's elasticity, resilience and durability, and the blending with cotton improves warmth, durability, and softness. Furthermore, the limited availability and high cost of natural fibres increase the demand for blended fabrics, augmenting the acrylic fibre market's growth ^[30].

The cost of acrylic fibre is highly dependent on the volatile cost of acrylonitrile ^[29]. This volatility is due to the fluctuations in crude oil prices, which negatively affect the prices of petroleum fraction products, affecting in its turn the production cost of acrylonitrile. This makes a significant impact on the demand for acrylic fibre. Furthermore, even when the price of acrylonitrile is lower, the price of acrylic fibre is still higher than the polyester fibre. For this reason, over the past years, acrylic fibres have been facing a competition with low-cost fibres, such as polyester. Besides its lower cost, polyester is produced from a highly available raw material and it is recyclable ^[31].

2.4. SGL Composites, S.A.

The SGL Composites company, previously known as FISIFE, is a producer of acrylic fibres located in Lavradio, Barreiro, Portugal. The company was founded in 1973, as a joint venture between CUF (*Companhia União Fabril*) and the Mitsubishi group [32]. The plant technology is the Monsanto's one and this company exports 99% of its total production [33].



Figure 2.5 - Location of SGL Composites [34].

Due to the difficult times that Portugal was facing, related to the political situation and with an aggravation by the first oil crisis, which increased the acrylonitrile price, the production of acrylic fibres only started in 1976, with a capacity of 12 500 tonnes/year. These events had an impact on the viability of the investment, due to, for example, the nationalisation of CUF and, as a consequence, the assets began to be managed by Quimigal company. The participation of the Japanese partners was kept intact until 1997, the year when CUF was reprivatised. In 1980, the capacity was increased to 23 000 tonnes/year.

In the beginning, the produced fibre market was only the Portuguese textile industry, which needed to import great amounts of acrylic fibre before the FISIFE start-up. At that time, the biggest European producers of acrylic fibre were Bayer, Montefibre and Courtaulds.

The first positive results emerged in 1984 after an increase to 45 000 tonnes/year of the plant capacity, allowing FISIFE to become an international competitor and to enter the Lisbon Stock Market. The tariff protection that the company had was suppressed in 1987, opposite to what it was agreed between the European Union and the Portuguese Government. Also, in 1986, the whole textile industry was in crisis due to the

abolishment of European frontiers relating textile products, resulting in a reduction of plant capacity.

In 1988, FISIFE began to focus on the external market, investing as well in R&D, allowing the company to become more independent and autonomous regarding the Mitsubishi know-how. However, due to the strong market competition and to the need for finding new markets outside Europe, the next decade was marked by low rentability.

After the privatisation of FISIFE, the company acquired Acordis in 2000, an acrylic fibre plant in Barcelona. This plant had the advantage of providing markets with other textile specialities not yet developed in Portugal, like dyed fibres. However, the increase of maintenance costs and oil prices in international markets, and the present textile industry crisis led to the plant closure in 2004. In 2005, to make up for the great losses of FISIFE, CUF started an operation to increase capital and to facilitate its alienation, to make FISIFE feasible and constituted Negofor, to which CUF transferred its actions in FISIFE (86%). To avoid the closure of FISIFE, three members of the board acquired, individually, a share in Negofor through a Management Buy Out (MBO).

In 2007, EDP communicated that the Barreiro's thermal power plant was going to be shut down in 2009 due to environmental concerns. FISIFE depended on this plant for steam production. As a result, FISIGEN was founded in 2010 to assure the steam supply in better environmental and operational conditions, consisting in a natural gas cogeneration plant with a capacity of 24MW, where FISIFE has a share of 49% and EDP 51%.

FISIFE began to develop the carbon fibre precursor (CFP) after realising it as the future of the industry. Associated with this technical textile, CFP, are market annual growth rates of more than 10% and a frequent shortage of supply of CFP in the industry. It was known that the technology detained by FISIFE, licensed by Mitsubishi Rayon, Monsanto, is the one that shows the best results for the precursor production, justifying FISIFE's interest and ability to produce the precursor. This process was successful in 2009 and, in 2010, the first carbon fibre was produced in the second pilot line, allowing FISIFE to test the fibre formulation.

FISIFE's success was noticed by the SGL Group, the major carbon fibre producer in Europe. It resulted in FISIFE's acquisition by the group in 2012. Due to this, FISIFE left the Lisbon Stock Market. Because of the acquisition, some of FISIFE's textile fibres production lines were converted and expanded for the production of CFP. This also allowed SGL to expand its network for raw material supplies for the production of carbon fibres [35].

In 2018, FISIPE was renamed as SGL Composites, due to rebranding processes in the SGL Group, which was also renamed as SGL Carbon.

2.5. Production Process for Acrylic Fibres

The information contained in this subsection was kindly supplied through personal communications and visits to the production areas of SGL Composites company, as well as from the company's website and the Description Manual of the plant [36, 37].

At SGL Composites, different types of acrylic fibres are produced: raw white, gel-dyed, pigmented, and technical fibres, which include fibres for reinforcement of materials for the civil construction sector. These fibres are commercialised in three forms: tow, staple and top. The tow fibre is in the form of a continuous filament and it is an uncut fibre. If the fibre is cut, it is then designated by staple. The top fibre is a stretch broken tow.

The technology used by the company, as previously mentioned, is the Monsanto's technology. The production process consists of different areas: Continuous Polymerisation (CP), Polymer Storage (PS), Dope Preparation (DP), Spinning (SP), Cut and Baling (CB), Tow to Top (TT), Solvent Recovery (SR), Utilities (UT), Gel-Dyeing (GD) and Tank-Farm (TF).

Acrylonitrile polymerisation occurs in CP area, being the dope prepared in DP, followed by the acrylic fibre extrusion in SP area. Then, the fibre is subjected to a final treatment and packed in its final form in CB area, or it firstly goes to TT area to be obtained the top fibre. The other areas are auxiliary areas of the main fibre production areas.

The generic diagram flow of the existing process is shown in figure 2.6.

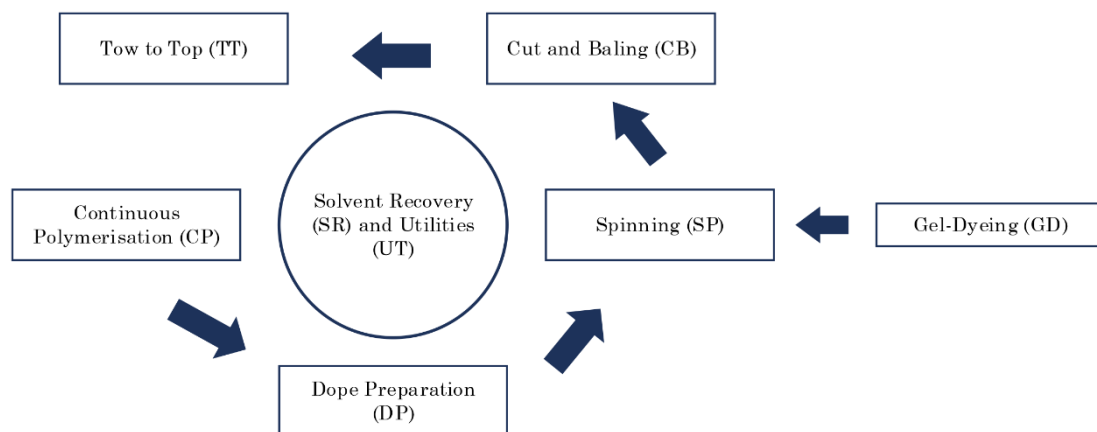


Figure 2.6 – Diagram flow of the acrylic fibres process production.

2.5.1. Continuous Polymerisation

A polymerisation reaction occurs in four CSTR reactors between the comonomers acrylonitrile (AN) and vinyl acetate (AV), in an aqueous medium, forming polyacrylonitrile (PAN). Each of these reactors is equipped with a cooling jacket. For the reaction catalysis, a redox system is used.

The non-reacted acrylonitrile is separated from the aqueous suspension in a slurry stripping column. The suspension is sent to a vacuum rotating filter, where the polymer is filtered and washed. The resulting filtered and washing-water is sent to a monomer stripping column, where the remaining monomers are removed. The wet polymer is removed from the filter and goes to a pelletiser, where pellets are formed. These pellets fall into an oscillating transporter screen, which distributes the pellets uniformly into the dryer screen. After the pellets are dried, they are sent to the weighing silos and are subjected to a milling process in a hammer mill. Then, the polymer powder goes to the storage silos, at the PS area.

An inhibitor is added to avoid the proceeding of the reaction after the reactor's overflow. To assure the intended size of the pellets, a solution of a surfactant agent is added in the suspension tank or directly in the rotating filter.

2.5.2. Polymer Storage

This area is destined to store the polymer in storage silos. It can be stored polymer within and without specification. The transport of the polymer from this area to area DP is managed through a polymer transfer plan which consists of a combination of diverse silos.

2.5.3. Dope Preparation

In the DP area, the dope for the production of acrylic fibre is prepared. This can be done through a dissolution of the polymer powder in the dimethylacetamide (DMAc) solvent. This solvent is usually referred to as CR at the plant. Before the dissolution in the solvent, the polymer is stored in a buffer silo. Once the dope is formed, it goes through press filters to remove non-dissolved polymer particles and impurities.

Bright dope and direct dope are produced, being the latter used for the production of whitened fibre. The difference between these dopes relies on the residence time. The

direct dope is sent immediately to SP area after filtration, minimising its yellowing. In this way, it is possible to produce a whiter fibre. To minimise the yellowing of the dope in contact with air, the deaeration tanks, as well as the other tanks, work in an inert gas atmosphere.

The dope, polymer and DMAc from purge operations and washes from the whole process are recovered, being produced another dope, the regenerated one, to be incorporated in dark fibre production.

In this area, the carbon black pigment, other pigment dispersions, and suspensions of titanium dioxide are prepared, being the latter a delustrant agent. These preparations are injected in the feed of the bright dope to the spinning machines. The pigment dispersions, including the carbon black, are prepared in discontinuous through grinding. The pigmented fibre is named L28.

2.5.4. Spinning

In the spinning area, the dope obtained in DP is transformed in acrylic fibre, or spun tow, through the extrusion of the solution of acrylic polymer and solvent. This process is designated by wet-spinning. The bright dope is distributed into the spinning machines, being previously heated.

The dope goes through the spinnerets, which consists of dozens of thousands of orifices, before coagulating. The spinnerets are immersed in a double coagulation bath, which contains an aqueous solution of solvent DMAc in recirculation. The excess of the coagulation solution is sent to SR area. Dope coagulation originates a filament bundle, whose grouping forms a tow. The several tows formed are removed from the coagulation vat by the first rolls, to be subjected to several washing steps with cold and hot recovered water (RW), to remove the solvent, and stretched. This is achieved by the speed difference between the rolls. It also occurs a neutralisation operation with sodium bicarbonate to neutralise the acid dragged in the tows.

In some spinning machines, the fibre can be dyed in the gel-dyeing vat, through an application of a cationic dye mixture, prepared to obtain the intended colour. This fibre is designated by L25. If the produced fibre has no colour, it is named raw white and designated by L11.

After the tows are washed, they are subjected to a finish application in a bath that contains an aqueous emulsion of finish products. Then, the tows are dried in a set of

steam-heated drying rolls. The water evaporated from the strips is removed by an exhaustion system.

The obtained fibres are crimped, allowing the posterior handling of the spun tow without entanglement. In the end, the spun tow goes into a distributor that places the fibre on zigzag in a metallic container to go to the CB area.

2.5.5. Cut and Baling

The spun tow obtained in the spinning area is subjected to annealing in an autoclave, to improve its physical properties and to remove fibre internal tension. After this process, the fibre can be turned into tow or staple fibre. Tow fibre can be baled or sent to TT area to form top fibre. Staple fibre is submitted again to crimping, then to cooling, cut and baling. If this fibre is retractable, it will be subjected to stretching before crimping.

After pressing, the obtained fibres are covered with polypropylene covers and fixed by steel wires or polypropylene straps, labelled and, after quality control, stored in the warehouse.

2.5.6. Tow to Top

Tow fibre from area CB is subjected to a continuous stretch breaking operation. After the stretch breaking process, there is a crimping operation and, depending on the intended product, continuous annealing might also be applied. Regular top, 100% retractable top or high-volume top can be obtained in the TT area.

2.5.7. Solvent Recovery

This area has as goals: the separation of the solvent from the water coming from the SP area (SR process), solvent production (SM process), and removal of accumulated solids in the process. Both solvent and water are reused in the DP and SP areas, respectively.

In the solvent recovery process, the stream to be treated is mainly the one which, besides solvent and water, has other contaminants, such as solids, which include degraded polymer and insoluble salts, and solvent hydrolysis resultant products, *i.e.*, dimethylamine (DMA) and acetic acid (AC), which comes from the SP area. To recover DMAc, there are four distillation columns, with four different effects. These columns are placed in series with successive head pressure reduction, allowing the use of head

vapours from each column as the only heat source for the next column. The resulting products are removed in stripping columns, reutilised in the SM process. The system for solids and contaminants removal is made by treating the purges from the vaporised tank feed to the first effect column.

In the solvent manufacture process, dimethylacetamide is produced through the reaction between dimethylamine and acetic acid. This process also aims the removal of solvent impurities, which include ammonia, trimethylamine, monomethylamine derivatives and solids.

2.5.8. Utilities

UT area supplies to the process several utilities: cooling (TW), chilled (CW), industrial (W) and deionised (DIW) water, compressed air, nitrogen, steam (pressure of 7 and 20 bar, or 5S and 20S steam), and electricity.

The industrial water comes from a groundwater well located in the plant vicinity and it supplies the whole plant through a water tank. This water tank supplies two different water lines: the line that feeds the different production areas, especially for the UT area for the production of the different types of water, and the water line that feeds the fire network.

The production of TW, in the refrigeration towers, is based on a direct contact between an upward stream of air, which heats up and gets humidified, and a downward water stream which will be cooled down either by loss of sensible heat or by the necessary heat transfer for vaporisation. This water and air circulation inside the towers is forced, and a small amount of pressure drop is introduced to increase the contact time between the upward air and downward water.

For CW production, the refrigeration system is based on the practical implementation of Carnot's ideal cycle, on a strand of Rankine's cycle of steam compression. The refrigeration is achieved in an evaporator and ammonia is the refrigerant. In this case, it is vaporised, and the heat is rejected in a condenser, resulting in the refrigerant's condensation.

The production of DIW is achieved by reverse osmosis. There are three units for deionisation, being obtained three deionised waters (DIW1, DIW2 and DIW3). DIW1 and DIW3 have got the same purity. DIW3 is used only on FISIGEN. DIW2 is the purest type

of deionised water and it is only used in CP area. DIW2 is subjected to an additional electrodeionisation process, besides the reverse osmosis.

The production of compressed air is achieved by electric compressors. Nitrogen is not produced in the plant, being supplied in the liquid form. Before feeding the plant, nitrogen is vaporised.

All the required steam is produced in FISIGEN, through a cogeneration process with natural gas. The hot gases that result from the combustion go through a gas turbine, where the generated movement is transformed into electricity. Afterwards, the hot gases go through a boiler where the steam is produced. Electricity is supplied to the plant by EDP.

The industrial and domestic effluents are sent to the collector of Águas de Lisboa e Vale do Tejo (ÁdLVT).

2.5.9. Gel-Dyeing

In this area, usually called by the “colour kitchen”, the dyes are stored and weighted individually. To prevent the formation of deposits in piping and equipment, it is added a dispersant to every colour preparation. The dyes are supplied in solution with acetic acid.

2.5.10. Tank-Farm

Every continuous flow raw material needed to the process is stored in this area, such as acrylonitrile, vinyl acetate and dimethylacetamide.

2.6. The Life Cycle Assessment Methodology

According to the standard ISO 14040 [38], the Life Cycle Assessment (LCA) is a methodology which allows the assessing of the environmental aspects and potential impacts associated with a product. This assessment can be done by gathering an inventory of inputs and outputs of a product system, evaluating the potential environmental burdens associated with those inputs and outputs, and by interpreting the results of the inventory analysis and impact assessment phases.

LCA is a relevant tool from a sustainability perspective as environmental issues are increasingly playing a bigger role in decision-making processes. It is also a decision-making tool which addresses the need for the selection and optimisation of available technological solutions. The success of LCA is due to its high applicability, for all product systems from which data can be generated and to which it is possible to compare the results with competing, or even improved, systems [39].

LCA studies may include the whole product's life cycle, starting from raw material extraction in the nature, through transportation, production, use, reuse, recycling, and disposal. Studies can be based on a cradle-to-grave, cradle-to-gate, gate-to-gate, or cradle-to-cradle approach [38].

This tool can be used to: identify improvement opportunities of environmental aspects of a product's life cycle, to assist in the decision-making at different levels (governmental and non-governmental organisations, industry, consumers). LCA is a powerful tool on assisting in a product or process design and strategic planning, to select relevant indicators of environmental performance, and to assist in the marketing area (environmental claims or product environmental declarations) [38].

2.6.1. History of LCA

In the 1960s, the first approach to LCA was made in the United States, focusing on the consumption of raw materials, energy efficiency and on an attempt to minimise waste disposal. Harold Smith reported his initial work on LCA, in 1963, at the World Energy Conference. His work was based on the calculation of energy needs for chemical products and for their intermediates [40].

The Coca-Cola Company, in 1969, developed a study by analysing different beverage containers, aiming to identify the container which had the lowest environmental impact. The study aimed to quantify the raw materials and fuel employed in the process, and in

the quantification of environmental loadings related to manufacturing. This company was an example and not much later, other companies in the country and in Europe, started developing similar life cycle inventory analyses.

The studies were only possible due to the existence of public information sources, such as “Resource and Environmental Profile Analysis”, in the United States, and “Ecobalance”, in Europe. During the oil crisis, in the 1970s, the studies were more focused on energy rather than waste. This approach changed in the early 1980s, since environmental concerns were getting more noticed. In the 1990s, LCA began to be more than an inventory analysis and moved towards impact assessment. Three organisations participated in the development and standardisation of LCA: United Nations Environment (UN), Society of Environmental Toxicology and Chemistry (SETAC), and International Standard for Organization (ISO). In 1997, ISO developed its first standards for LCA, resulting in the ISO 14000 series. Since 2002, these organisations have the purpose of spreading awareness and encourage the use of LCA worldwide [40,41].

2.6.2. Principles of LCA

As defined by the international standards, LCA consists of four phases [40]:

1. Goal and scope definition;
2. Life cycle inventory (LCI) analysis;
3. Life cycle impact assessment (LCIA);
4. Life cycle interpretation.

Life cycle assessment can be defined as an iterative process, where all the phases are related to each other (figure 2.7) [38].

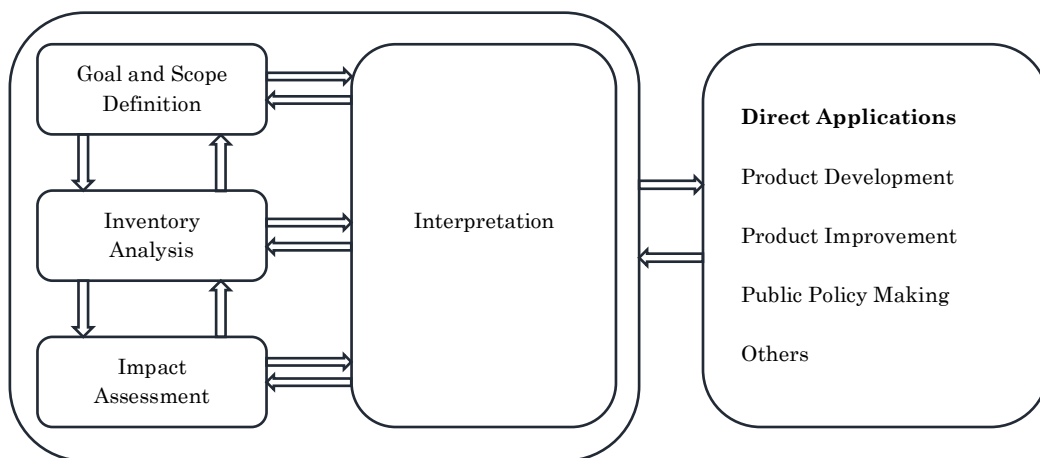


Figure 2.7 - Methodological framework of LCA, according to ISO 14040 [38].

2.6.2.1. Goal and Scope Definition

In the first phase, the study to be conducted is described and the objectives and scope of the study are defined. In the scope definition, details of the product to be studied and its functions are described. It is also important to define the product system boundaries, functional unit, life cycle stages to be included in the study, categories of impact to be considered, allocation procedures, LCIA methodology, cut-off criteria, sources of data and the LCA software to be used. The assumptions to be employed and limitations of the study should be stated at this stage ^[40].

According to ISO 14040, the functional unit is the “quantified performance of a product system for use as a reference unit in a LCA study”. The system boundary to be defined is the “interface between the product system and the environment or other product systems” ^[38].

The inputs are material or energy which enter a unit process. These materials may be raw materials and products. The outputs are material or energy which leave a unit process, where materials, in this case, may be raw materials, intermediate products, final products, and wastes. A unit process is the “smallest portion of a product system for which data are collected when performing an LCA”, while a product system is the “set of materially and energetically connected unit processes which performs one or more defined functions”. The “partitioning of the input and output flows of a unit process to the product system” is allocation ^[38].

The “specification of the amount of material or energy flow, or the level of environmental significance associated with unit processes, or the product system, to be excluded from a LCA study”, is defined as the cut-off criteria ^[38].

2.6.2.2. Life Cycle Inventory (LCI) Analysis

Life Cycle Inventory consists on the collecting and quantification of inputs and outputs for a product throughout its life cycle. In this phase, associated with the system definition, it should be included the graphical presentation, in the form of a flow diagram, of the processes within the defined system boundary ^[40].

The data collection is referred to relevant inputs and outputs of the life cycle of a product. The quantification of raw material and energy requirements, emissions to land and solid wastes, atmospheric and waterborne emissions, and other releases to the environment, are significant to the LCI.

In LCI, there are four steps to be followed. The first step of a LCI is the development of the flow diagram of the processes, followed by the development of a data collection methodology (second step), collection of the relevant data (third step), and evaluation and reporting of results (fourth step).

2.6.2.3. Life Cycle Impact Assessment (LCIA)

LCIA intends to understand and assess the magnitude and significance of the potential environmental impacts for a product. The effects of the consumed resources and released emissions into the environment are identified and detailed. The quantification of the effects on the environment and human health due to the activities identified in LCI are also evaluated [40].

To conduct the LCIA, the following steps should be considered:

- *Selection and definition of impact categories*: selection of relevant impact categories, such as global warming potential;
- *Classification*: assignment of LCI results to the relevant impact categories;
- *Characterisation*: quantitative modelling of life cycle impacts associated with used resources and emissions to the environment;
- *Normalisation (optional)*: adjustment of the expression of the characterised impact results to a common reference, allowing the comparison of each impact category;
- *Grouping (optional)*: relating different impact indicators in terms of factors, such as location;
- *Weighting (optional)*: cumulative expression of the results as a single environmental indicator;
- *Evaluating and reporting LCIA results*: evaluation of the LCIA results, aiming to a better understanding of their reliability.

There are two LCIA approaches. One is the midpoint approach, which is problem-oriented, known as the classical impact assessment method, translating category impacts into real phenomenon-based environmental subjects, such as climate change. The other approach is the endpoint, which is damage-oriented, and it expresses environmental impacts into major issues of concern, such as ecosystem quality.

Several LCIA methods allow the quantification of the life cycle impacts, such as CML, Eco-indicator 99, ReCiPe, Impact 2002+, TRACI, among others. These methods are available in several LCA softwares, such as SimaPro, openLCA, GaBi, and Umberto [40].

2.6.2.4. Life Cycle Interpretation

This is the last step in a LCA study. It is important to identify the significant issues to evaluate sensitivity, consistency, completeness check, and to withdraw conclusions, limitations, and recommendations ^[39].

The key parameters and improvement options can be identified through sensitivity studies and uncertainty propagation. A critical analysis allows the evaluation of the influence of the chosen boundaries and hypotheses. The environmental impacts can be compared with economic or social impacts ^[41].

2.6.3. Attributional, Consequential and Cut-off LCA Studies

To conduct a LCA study it is important to opt between an attributional or consequential LCA approach ^[40]. The attributional approach mostly describes the effects of changes within the life cycle and the impact of those changes, according to a set of possible decisions. In this approach, the used values are average values based on current trends and normal business practices. The identification of opportunities that allow the reduction of direct impacts, resulting from several life cycle stages of a product, is possible. Concerning the consequential approach, it predicts the consequences, if changes are made to the established processes. The indirect effects of these changes, along with the direct ones, are addressed. The studies are dependent on economic models, such as the demand for inputs and elasticity of prices, and due to this, the accuracy of the results is not well known. There is a new and recent approach, which may be considered as a “variation” of the first method, that is based on the recycled content, or cut-off, and consists of the “underlying philosophy that a producer is fully responsible for the disposal of its wastes, and that he does not receive any credit for the provision of any recyclable materials” ^[42].

2.7. Textile Fibres and Sustainability

The World Commission on Environment and Development defines sustainability as “the development that meets the needs of the present without compromising the ability of future generations to meet their own needs” [43]. Recently, environmental protection, ecological sustainability, and sustainable development, have gained greater attention. Industries are being increasingly challenged to move towards sustainable development, including the textile industry. Applying the sustainability concept to the textile industry, a sustainable fibre is typically manufactured from raw materials, energy and other materials obtained from renewable resources [44].

Sustainable development can be defined as a long-term strategy that includes environmental, social, and economic pillars. If the industry compromises to prevent pollution through proactive actions, if society becomes aware of this common responsibility towards the environment, and if environmental protection becomes an integrated search for solutions, sustainable development will be succeeded. The cooperation involving the three pillars results in an implementation of sustainable development in areas like technology, education, legislation and policy, enhancing quality of life, keeping natural resources within the ecological capacity of the planet, preserving its diversity and vitality, and creates a global alliance with the aim of preserving the environment [44].

Textile industry is usually known for the several resultant environmental impacts derived from its activity, such as the pollution of air, water, and soil due to the use of hazardous compounds in the production processes. Added to this, a significant amount of energy, water and other resources are consumed during the fibres production processes. Processes like fibre manufacturing, spinning, dyeing, and finishing require high amounts of water, energy, chemicals, dyes, and auxiliaries. Besides this, the large amount of waste, resulting from the several processes, creates environmental concerns. In a textile product’s life cycle, every single stage may have some environmental and social impact. At some point, what seems to be positive may have some negative consequences at its later stages of the lifetime in the supply chain [45]. Textile industry is being implementing solutions for several of these impacts and looking for new options to solve the other impacts not yet solved. This will improve the sustainability of these important industrial sector.

Recently, LCA has been increasingly applied by textile companies to assess the environmental impacts of their products. Examples of these companies are the fibre manufacturers Lenzing, Dupont and Advansa. Also, organisations like the European

Commission and Modint have also dedicated efforts to assess the environmental burdens of the products coming from the textile sector ^[46]. The companies aim to identify their environmental impacts and provide actions to minimise them. Additionally, for preventing environmental damage, there is the need for the textile sector to follow environmental standards and regulations ^[45]. Consumers are also becoming aware of the environmental concerns and began demanding more eco-friendly and more efficient manufacturing methods, having shown rising interest in more sustainable textile products.

The LCA methodology, according to ISO 14044, may be used as an impartial process that allows making environmental decisions, definition of key impact areas, evaluation of potential environmental threats, and ensures the certification and eco-labelling of textiles. The assessment of production processes may be developed from raw material extraction to waste materials. To determine whether the product presents the required conditions, the obtained results and data are compared with the criteria of the predetermined environmental standards and labels ^[45].

2.7.1. Eco-labelling and Certification

Different international organisations, such as ISO, World Trade Organisation, European Commission, and the United Nations, through the Environmental Programme, created the eco-certification rules. Environmental labels have been presenting different certification systems and several requirements. Some of these are based on LCA studies and consider the environmental impacts across the product chain, such as ISO and EU eco-label. Other labels focus on user safety, like the OEKO-TEX® standard, and some may certify raw material quality. In addition, labels reflecting social and ethical aspects are getting more importance, such as the *Fair Trade* and the *No Sweat* labels. Labels where both environmental and social dimensions of the companies' activities are investigated, are underlining the difference between social and ecological labels. Examples of these labels are the Global Organic Textile Standard, the Global Recycle Standard, and the Sustainable Textile Production ^[45].

As main goals, environmental and social labelling have to provide information to consumers about the environmental and social impacts of the manufacturing, consumption, and end-of-life phases of the products. Also, these labels encourage governments, producers, and other organisations to raise the environmental standards of products and services. It is hoped that more changes towards more environmentally friendly consumption patterns will emerge with these labels.

The ISO classification is the best known in environmental labelling, having published a series of standards, the ISO 14020 series. This series applies specifically to eco-labelling, namely: ISO 14020, 14021, 14024, and 14025. This series presents three types of labelling schemes which describe the environmental advantages that a product should present [45, 47]:

- *Type I*: environmental label, multiple criteria based, voluntary, and third-party verified. A licence which authorises the use of environmental labels on products is awarded and indicates the overall environmental preferability of a product within a product category, based on life cycle considerations. Criteria for products is well defined (ISO 14024);
- *Type II*: self-declared environmental claim and single-attribute label developed by the manufacturer, with no independent third-party certification. Unlike the other two types, Type II does not present a high reliability, and there are neither criteria nor labelling schemes (ISO 14021);
- *Type III*: eco-label based on quantified environmental data of a product under pre-determined parameters or categories. It is awarded by a qualified third-party based on a full LCA (ISO 14025).

Environmental and social labels can be classified into three different categories, based on LCA [45]:

- *Single-attribute*: one stage of the product's life cycle is mainly addressed, being the raw material and product use stages the most common ones, e.g.: OEKO-TEX® Standard 100;
- *Multi-attribute*: every stage of the product's life cycle is practically covered. It offers a more fragmented vision of the life cycle, by acting on different stages separately. ISO Type I labels are similar to these;
- *Life cycle-oriented*: an entire life cycle assessment is provided. The LCA methodology is based on the ISO 14040 series of standards, or at least on a formal life cycle approach. It is also recommended that criteria applying to life cycle stages are considered as early as the design phase, e.g.: SMaRT programme.

For a company in the textile sector, it is uncommon and expensive to control or own the fibre manufacturing process, starting from raw materials to the final product. Thus, companies need to cooperate with direct suppliers to assure the needed integrity and transparency across the supply chain to the system of verification. To avoid double testing and spread of the financial expenses of certification across all the production stages involved, a modular system of certification was proposed by the OEKO-TEX®

Association, and, for OEKO-TEX® Standard 100 (chemically safe textiles), textile products may be tested and certified at any production stage. Certificates can be issued for the following: raw materials, fibres, filaments; yarns, raw and finished; textile fabrics, raw and finished (dyed, printed, finished); ready-made products; and for textile and non-textile accessories ^[45].

Table 2.2 presents the main characteristics and aim of the most common certifications and labels for both textile and clothing products.

Manufacturers have an important role on the minimisation of environmental impacts of the textile supply chain. Because of this, they should be aware of LCA studies. These studies help them identifying which activities to focus attention on, allowing them to reduce the resulting environmental impacts. One way to achieve this is by using the “best available technologies” (BAT), which reduce the environmental effects through the overall quality increase, while reducing costs, as well as the implementation of an efficient process control. Other measures are the selection of machinery with higher reliability and service life, and energy efficiency. The precise measurement and control of materials and energy consumption, as well as of waste and emissions, the good maintenance of process machinery, and the use of closed loop production systems, such as the recycling and reuse of process water and solvents, are also examples. Setting up energy use, levels of waste production and emissions objectives is also important ^[6].

Table 2.2 - Labels for textile and clothing products [45, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59].

Label	Life Cycle Assessment			Emphasis On			Aim
	Single-Attribute	Multi-Attributes	Life Cycle-Oriented	Ecological Criteria	Social Criteria	Both	
OEKO-TEX® Standard 100	✓			✓			Test the presence of harmful substances.
Global Organic Textile Standard (GOTS)		✓				✓	Ensure the organic status of textiles.
EU Ecolabel		✓		✓			Indicate overall environmental preferability.
Sustainable Textile Production (STeP)		✓				✓	Support to companies to help them implement environmentally friendly production processes.
bluesign® Standard		✓				✓	Ensure that products are manufactured with a responsible use of resources and the lowest possible impact on people and on the environment.
Content Claim Standard (CCS)	✓						Verification of a specific input material in a final product.
Organic Content Standard (OCS)	✓			✓			Track the presence of organic raw materials.
Recycled Claim Standard (RCS)	✓			✓			Track and trace recycled input materials (product contains at least 5% of recycled material).
Global Recycled Standard (GRS)	✓					✓	Track and trace recycled input materials (product contains at least 20% of recycled material).
SMaRT Consensus Sustainable Product Standards			✓			✓	Establishes life cycle environmental performance requirements for sustainable products.
Cradle to Cradle			✓			✓	Assessment of the environmental and social performance of the products across critical sustainability categories, e.g. material health.
Fairtrade Standard for Cotton	✓				✓		Verification of fairly traded raw materials.

3. State-of-the-Art on the LCA of Textile Fibres

The LCA methodology has been implemented in the textile industry by researchers, companies, and other organisations, to study the resulting impacts from the industry on the environment. Nonetheless, not many recent LCA studies on textile products can be found in literature, especially regarding acrylic fibre. Also, no open-source LCI databases, which allow further research studies, are available. Some of the studies found in literature are LCI studies, where no environmental impacts are assessed, but only the inventory of the product systems. Also, nondisclosure of company-related information and databases are common due to confidentiality issues. Most of the existing studies are based on data provided by suppliers from the textile and clothing supply chain [40]. In addition, the majority of textile LCA studies consider the functional unit in terms of clothing garments, such as “one t-shirt” of a specific fibre, which does not allow the comparison with studies where the functional unit is in terms of fibre weight as, for example, in cradle-to-gate fibre LCA studies. For comparison purposes, functional units must be consistent [40].

For the reasons stated above, both the research that has been made, and the State-of-the-Art presented hereafter, focus on studies in which their results can be compared to those obtained in the present work. LCI studies allow the comparison between the inputs and outputs of the processes. In the studies in which more than the fibre production phase was considered (for example, in cradle-to-grave studies), the results from each life cycle phase are presented individually, allowing the comparison of the production phases with the present work.

Regarding acrylic fibre, Yacout et al. [60], have analysed the impacts of its production in Egypt, on a cradle-to-gate study. The study also presents the purpose of obtaining information to assist decision-makers in improving relevant environmental protection measures. The functional unit was 1 kg of acrylic fibre. It was concluded that 82% of the impacts is on fossil fuel depletion, due to the high-demanding energy process of acrylonitrile production. Regarding human health, it accounts for 15.9% of the impact, and ecosystem quality accounts for 2.1%. The lowest impact was on carcinogen potential. No impacts were detected for ozone layer and mineral depletion, radiation potential, land use, or on the human respiratory system. Process emissions include particulate matter and volatile organic substances from dyeing, printing, and from chemicals handling. The manufacturing of acrylic fibre is the major responsible for the impacts, mostly due to the high-energy consumption during the process.

Thai Acrylic Fibre Co. Ltd. ^[61], a company belonging to the Aditya Birla Group, has developed a cradle-to-gate LCA study on the production of 1 tonne of acrylic fibre, or, more specifically, on the production of the three-denier regular Birlacril bright and semidull staple acrylic fibre. Both the study and LCI profile were based on actual plant data. It was found that acrylonitrile, electricity, and steam consumption are the main hot spots in the fibre production. The polymerisation and the spinning are the major responsible processes for the high impacts on global warming potential. Both processes are also responsible for a high primary energy demand and blue water consumption, especially polymerisation. The company concluded that it should be carried out an improvement in both steam and electricity consumption in the processes of polymerisation, solvent recovery, and wet-spinning, and that the scenario of usage of acrylonitrile produced through the propane ammoxidation route should be evaluated.

La Rosa et al. ^[62] developed a cradle-to-gate LCA study on the production of both 1 tonne of fibre and 1 tonne of cotton, jute and kenaf textiles. In the functional unit regarding 1 tonne of textile, all the steps starting from cultivation to yarn production, which included cleaning and sorting, spinning, pre-treatment, dyeing, finishing, washing, and drying, were considered in the LCA study. The conclusions were that spinning, cleaning, and sorting, contribute the most to energy consumption, where spinning (the process of converting fibres into yarn) presents the highest energy consumption. It was found that, for cotton industry, water consumption is the major concern, and that acidification and eutrophication are also very intense. A comparison between traditional and organic cotton cropping led to the conclusion that a shift towards organic cotton should be made to reduce the high impacts related to cotton fibres. This is justified by the fact that water and energy consumption is lower for organic cotton. Nonetheless, organic cropping presents a reduced cropping yield and the evaluated impacts for organic cotton, although similar, are still higher, to the estimated impacts for kenaf and jute fibres.

Textile Exchange ^[63] conducted a cradle-to-gate study on organic cotton fibre, in which the functional unit was the production of 1 tonne of lint cotton at the gin gate. The goal was to create an updated and well-documented LCI for organic cotton fibre, representative of the worldwide global production. The results from the study indicate that organically grown cotton presents as potential impact savings, over the conventional one, the savings of 46% on global warming, 70% on acidification, 26% on eutrophication, 91% on blue water consumption and 62% on primary energy demand. Field emissions due to agriculture present the most significant impact. An important factor, land occupation, was not included in the report. This indicator is indirectly proportional to the yield, which means that a low yield results in a higher land occupation, consequently

meaning that the final results could be significantly different from the ones that were presented in this bibliographic reference.

Barber and Pellow ^[64] developed in their study a detailed inventory of resource inputs for the New Zealand Merino wool and assessed its total energy use profile comparatively to other textiles. The functional unit used for the study was the production of 1 tonne of dry wool top. All on-farm inputs were included, but further processing such as spinning, which would make it comparable with the other fibres, and knitting and weaving, to produce the fabric, were excluded from the analysis. It was concluded that to produce wool top at a Chinese spinning mill, 52% of the total energy required was due to on-farm production, while wool processing accounts for 45%, of which almost 90% is due to wool scouring. Transport represents 3% of the total energy use. Fertiliser is the second largest input. It was also found, according to the authors, that wool production compared to man-made fibres production, consumes significantly less energy, wool consuming 38% and 27% of the energy and resources needed to produce polyester and acrylic fibres, respectively.

Shen and Patel ^[65] performed a cradle-to-gate LCA study on five staple fibre products, including Lenzing viscose Asia and Lenzing viscose Austria. The functional unit used for all fibres was the production of 1 tonne of staple fibre. It was found that, compared to viscose Asia, viscose Austria offered environmental benefits in all impact categories, except for water and land use. Viscose Austria was one of the fibres that presented the lowest impacts. Viscose Asia presented the highest impacts compared to the other regenerated fibres. The most significant concerns associated with this fibre were on global warming, acidification, abiotic depletion, and photochemical oxidation. The main difference between viscose Asia and viscose Austria is in the integration of the pulp and fibre plants. The Austrian viscose fibre plant is integrated with a pulp mill, while pulp and fibre production are separate for viscose Asia, being the Austrian plant the best available technology. Comparing the regenerated fibres with conventional cotton and PET, cotton was recognised as the least preferred fibre due to its high ecotoxicity impacts, water and land use, eutrophication, and low land use efficiencies. Cooling water represents the highest water use for cellulose fibre production, accounting for about 90% to 95% of total water consumption. Viscose Austria requires more process and cooling water than viscose Asia. The environmental concerns of PET are mostly on global warming, abiotic depletion, and acidification. The benefits of viscose Austria are mainly due to the low fossil energy needs in pulp and fibre production, resulting of both process integration and use of renewable energy. Viscose Austria presents a better environmental profile than PET and cotton.

Van der Velden et al. [46] carried out a cradle-to-grave LCA benchmarking study on textiles made of acrylic, cotton, and polyester. The cradle-to-gate processes from raw material extraction to the manufactured greige fabric were included. The first gate considered in the study, is related to the exit of the greige fabric from the material processing plant. The second gate deals to the entry of the textile into the product manufacturing plant. The considered functional unit was the production of 1 kg of greige textile. It was concluded that the impact of spinning is relatively high, and that a LCA study on textiles can only be accurate when a specification on yarn thickness is made. It is mentioned that emissions from the process production phases are highly dependent on the fact that whether modern best practices of green production are used, and that the emissions are also dependent on both the specific colours used and finishing processes. For a yarn of 70 dtex, the results show that acrylic and PET textiles present the best environmental scores, and that, among all the studied fibres, acrylic textiles present the best environmental profile. The worst environmental performance is related to cotton textile products. It was found that, at a higher yarn size, the environmental burden is reduced, due to the energy use decrease in spinning and, also, in weaving. The study rejects the use phase as the most significant life cycle stage for textile products and attributes it to the manufacturing process. It also states that the majority of the publicly available LCA and process data are outdated and not transparent, especially concerning system boundaries.

Laursen et al. [13] have developed a screening of environmental key-features based on inputs and outputs of the production processes for cotton, wool, viscose, polyester, and acrylic fibres. The functional unit was the production of 1 kg of fibre product. Energy and water consumption, emissions, produced wastes, as well as the application of fertilisers and pesticides on natural fibres, are presented in this bibliographic reference. The study concluded, for example, that the acrylic fibre production is a high-energy demanding process, that the production of polyester generates high levels of greenhouse gas (GHG) emissions and that its wastewaters emit volatile monomers, that the fertilisers and pesticides used on natural fibres have significant impacts, and that viscose production is energy demanding and emits high amounts of GHG, especially when compared to the production of cotton. The study also states a series of recommendations to apply on the production of the selected fibres.

Thomas et al. [66] have developed a cradle-to-grave LCA study focused on the carbon footprint of clothing in the UK, in which acrylic, polyester, cotton, viscose and wool fibres and yarn were considered. The considered functional unit was “the entire life cycle of all garments, both new and existing, in use in the UK in 2009”. It was concluded that, due

to the methane emissions from sheep and manure, and to the nitrous oxide emissions from fertilisers, wool was responsible for the highest emissions. After wool, nylon, acrylic and polyester were the major responsible ones. Regarding the electricity required for yarn production, cotton, wool, and silk present the highest values. The major hot spots were washing, drying and fabric production.

Beton et al. ^[67] conducted a cradle-to-grave LCA study which included acrylic, cotton, wool, viscose, and polyester fibres, in order to estimate and compare the potential environmental impacts of the textile products consumed in the EU-27. The functional unit of 1 kg of finished woven fabric was used. The study led to the conclusion that the production and the use phases present significant contributions to the environmental impacts, contributing, respectively, from 16% to 96% and from 4% to 84% to the overall impacts. Cotton appears to be the major contributor amongst all fibres, due to the nature of its production and to its large share in the textile market. Furthermore, the environmental impacts per kg of fibre are higher for cotton than for the other fibres. The main impacts from cotton production are attributed to the use of high amounts of pesticides and fertilisers. The second most significant contribution is from polyester. Regarding acrylic fibre, LCI data had only been found for the fibre manufacturing and dyeing stages, and concerning the other life cycle stages, LCI data had to be mainly extrapolated from polyester fabric manufacturing. It was stated that there is still a scarcity of data related to acrylic fibre, despite its significant presence in the textile market. Improvement options are presented for all the life cycle of the fibres.

Muthu et al. ^[68] developed a cradle-to-gate LCA study on acrylic, wool, conventional and organic cotton, polyester, and viscose fibres, in order to quantify their environmental impact and to obtain an Environmental Impact Index (EI) and an Ecological Sustainability Index (ESI). According to the authors, not much research has been developed to assess the fibres in terms of their ecological sustainability. The selected functional unit was the production of 1 kg of textile fibre. For this study, use of renewable resources, energy consumption, fibre recyclability and biodegradability, among other factors, were considered. Considering the EI and ESI values, organic cotton had the lowest impact on the environment and acrylic was the fibre with the greatest impact, being organic cotton the most sustainable fibre and acrylic the least. Organic cotton is obtained from a renewable resource, also consuming less energy, and emitting lesser carbon dioxide, being also biodegradable, subsequently creating less damage to ecosystem quality, human health, and resources, opposite to acrylic and to the other synthetic fibres, such as polyester. Natural fibres, due to these factors, scored better than the synthetic ones. Nonetheless, conventional cotton presents a high amount of water

consumption, and of fertilisers and pesticides, a significant consumption of energy and also emits a significant amount of carbon dioxide in its manufacturing. In the case of organic cotton, it is stated that it consumes the same amount of energy and water as conventional cotton, but it emits less carbon dioxide and does not require fertilisers and pesticides to enhance its growth. Wool, in general, had a better score than cotton, including for recyclability. Regarding viscose, although it requires less water than conventional cotton, that it uses renewable resources, and although that it is biodegradable, factors such as damage to ecosystem quality, resources, and to human health, are more present during its manufacturing process. However, the results are based on index scores and on a scoring system which were developed by using secondary data for LCI. Additionally, the LCIA results lay on specific hypotheses and made assumptions.

Muthu et al. ^[69] carried out a LCA study for the development of a Recyclability Potential Index (RPI) of textile fibres, including acrylic, cotton, wool, viscose, and polyester. Both the environmental and economic gains from the recycling process were highly considered. The functional unit of 1 kg of virgin textile fibre was selected. Results show that polyester outperforms all the considered fibres in the study. Acrylic outperforms cotton, wool, and viscose. Wool presented the lowest Economic Gain Index. It was stated that economy is a key deciding factor, being able to promote or demote recycling.

Summing up, the process of manufacturing fibres has significant impacts on the environment, where spinning represents one of the most crucial stages on fibre production. Regarding acrylic fibre, it was verified that there are still few LCA studies on this type of fibres, especially in comparison with the other textile fibres. In the case of LCA studies regarding acrylic garments, they are usually in terms of a blend with another fibre. Tables 3.1 to 3.4 present an overview of the mentioned studies.

Table 3.1 - Overview of the state-of-the-art studies.

Study	Cradle to Gate Environmental Impact Assessment of Acrylic Fibre Manufacturing	Life Cycle Assessment of Acrylic Fibre and Garment in Thailand	Comparative Life Cycle Assessment of Cotton and Other Natural Fibres for Textile Applications	The Life Cycle Assessment of Organic Cotton Fibre	LCA: New Zealand Merino Wool Total Energy Use	Life Cycle Assessment of Man-Made Cellulose Fibres
Reference	Yacout et al. [60]	Thai Acrylic Fibre Co. Ltd. [61]	La Rosa et al. [62]	Textile Exchange [63]	Barber and Pellow [64]	Shen and Patel [65]
Location	Egypt	Thailand	—	India, China, Turkey, Tanzania, USA	New Zealand	Austria and Asia
Goals	Analysis of the acrylic fibre manufacturing impacts. Obtaining information for assisting decision makers on improving relevant environmental protection measures.	Quantification of environmental impacts and hot spot analysis, assisting in the development of a LCA Report for communication to stakeholders.	Evaluation of the environmental impacts of cotton cropping and fibre production for textiles. Comparison between traditional and organic cotton cropping, and between cotton and jute, hemp and kenaf.	Build an updated and well-documented LCI for organic cotton, representative of the worldwide global production. Conduct a LCIA of organic cotton to allow the identification of environmental hot spots.	Development of a detailed inventory of resource inputs for the New Zealand merino wool and assessment of the total energy use profile comparatively to other textiles.	LCA of the man-made cellulose fibres Lenzing viscose Asia, Lenzing viscose Austria, Lenzing modal, tencel Austria, and tencel Austria 2012.
Functional Unit	1 kg acrylic fibre	1 tonne of acrylic fibre	1 tonne of fibre/textile (cotton, jute and kenaf)	1 tonne of organic lint cotton	1 tonne of dry wool top	1 tonne of staple fibre
Life Cycle Stages	Raw material production and fibre production process.	Raw material production, polymerisation, dope making, wet-spinning, after-treatment, and packaging.	Cultivation, harvesting, ginning and yarn production (including for the textile the cleaning and sorting, spinning, pre-treatment, dyeing, finishing, washing and drying phases).	Cultivation, transport of the seed cotton to the gin, ginning and packaging.	Fertiliser, chemical and fuel production and formulation, farming, wool shearing, scouring and combing, and shipment to China.	Extraction of raw materials and fuels, transportation, wood, pulp and fibre production (including alkalisation, pre-aging, xanthogen, dissolving, ageing, spinning and desulf, bleaching, finishing and drying for viscose).
Method	Eco-indicator 99	CML	CED, ILCD 2011 Midpoint+, CML-IA baseline	CML 2001	—	CML 2000 baseline, CED, Eco-indicator 99
Impact Categories	Global warming potential, acidification potential, eutrophication potential, carcinogen potential, ecotoxicity potential, respiratory inorganic formation potential, respiratory organic formation potential, radiation potential, ozone layer depletion, mineral depletion, land use and fossil fuel depletion.	Abiotic depletion, acidification potential, eutrophication potential, global warming potential, human toxicity potential, photochemical ozone creation potential, terrestrial ecotoxicity potential, primary energy demand and blue water consumption.	Cumulative energy demand, water resource depletion, acidification, eutrophication, abiotic depletion, abiotic depletion, global warming, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, land occupation, non-renewable energy, and mineral extraction	Global warming potential, eutrophication potential, acidification potential, primary energy demand (non-renewable), water use and water consumption	—	Non-renewable energy use, renewable energy use, cumulative energy demand, water use, land use, global warming potential, abiotic depletion, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification, and eutrophication.

Table 3.2 - Overview of the state-of-the-art studies (continuation of table 3.1).

Study	Cradle to Gate Environmental Impact Assessment of Acrylic Fibre Manufacturing	Life Cycle Assessment of Acrylic Fibre and Garment in Thailand	Comparative Life Cycle Assessment of Cotton and Other Natural Fibres for Textile Applications	The Life Cycle Assessment of Organic Cotton Fibre	LCA: New Zealand Merino Wool Total Energy Use	Life Cycle Assessment of Man-Made Cellulose Fibres
Hot Spots	82% of the impacts was on fossil fuel depletion, 15.9% on human health, and 2.1% on ecosystem quality. No impacts were detected on radiation potential, ozone layer depletion, land use, mineral depletion, or human respiratory system.	Acrylonitrile, electricity, and steam consumption were the major hot spots.	Cotton production had a high consumption of energy, due to cultivation and yarn production. Manufacturing caused the highest impacts. Cleaning, sorting and spinning provided the highest contribution in energy consumption. Water consumption was the major concern.	Field emissions due to agriculture presented the most significant impact. Opposite to conventional cotton, fertilisers, pesticides, and insecticides did not represent a significant problem.	On-farm production accounted for 52% of the total energy required to produce wool top. Wool processing accounted for 45%, of which almost 90% was due to wool scouring.	Relatively inefficient coal-based heat and power production in Asia was responsible for the major impacts in viscose Asia. The water use for cellulose fibre production was dominated by cooling water. This water accounted for about 90-95% of total water consumption.
Conclusions	The manufacturing of acrylic fibre was the major responsible for the impacts, mainly due to the high-energy consumption.	Polymerisation and spinning were the main responsible processes for the high impacts on global warming potential, primary energy demand and blue water consumption.	Shift towards organic cotton cropping to reduce the high environmental impact associated with cotton fibres, as the amount of water and energy consumption was lower than that for the traditional cropping.	Organically grown cotton had as potential impact savings over the conventional one: 46% reduction on global warming potential, 70% on acidification potential, 26% on eutrophication potential, 91% on blue water consumption, and 62% on primary energy demand.	Wool production used less energy than man-made fibres, consuming 38% and 27% of the energy and resources need to manufacture polyester and acrylic fibres, respectively.	Viscose Austria had environmental benefits in almost all categories compared to viscose Asia. Cotton is the least preferred fibre due to its high ecotoxicity impacts, eutrophication, water use, land use, and low land use efficiencies. Environmental concerns of PET are mainly focused on global warming, abiotic depletion, and acidification.
Limitations	Neither packaging nor transportation were included in the study. Average electricity production data in Africa was used. Data and impacts for specific fibre production phases were not specified.	Local LCA, being the region known for having less legislations by environmental regulation bodies.	Average data from the database ecoinvent were used for the estimation of the impacts of cultivation and yarn production. Results from LCIA literature were used for the impact of organic cotton cropping and production, and for the comparison with hemp cropping and fibre manufacturing.	The study does not compare the impact of organic cotton production between the countries or within the considered regions. Land occupation was not included in the report. Default values were needed as primary data.	Spinning and winding were not included in the assessment due to the lack of suitable data. The study only evaluated one impact category (energy use).	In Eco-indicator 99 all forms of land use were assumed to occur within Europe, therefore the environmental impacts were also assumed to occur in Europe. Marine aquatic ecotoxicity was excluded due to data uncertainties in the characterisation factors. The inventory data for cotton and PET were obtained from literature sources.

Table 3.3 - Overview of the state-of-the-art studies (continuation).

Study	LCA benchmarking study on textiles made of cotton, polyester, nylon, acryl, or elastane	Environmental Assessment of Textiles	A Carbon Footprint for UK Clothing and Opportunities for Savings	Environmental Improvement Potential of textiles - IMPRO Textiles	Quantification of Environmental Impact and Ecological Sustainability for Textile Fibres	Recyclability Potential Index (RPI): The Concept and Quantification of RPI for Textile Fibres
Reference	van der Velden et al. [46]	Laursen et al. [13]	Thomas et al. [66]	Beton et al. [67]	Muthu et al. [68]	Muthu et al. [69]
Location	—	—	United Kingdom	EU-27	—	—
Goals	Provide an improved and updated insight into the environmental burdens of the textiles, and as a function of the thickness of the yarn, in the range of 50–500 dtex.	Screening of environmental key-features based on inputs and outputs for the manufacturing of textile products made of cotton, wool, viscose, polyester, and acrylic fibres.	Provide an overview of the carbon impacts of the UK clothing through its life cycle, identifying the most significant contributions to the carbon footprint and quantifying opportunities for its reduction.	Identification of the consumption of textile products, estimation, and comparison of the potential environmental impacts of the textile products, identification of the main environmental improvement options and estimation of their potential.	Development of a model to quantify the environmental impacts made by textile fibres and position them in terms of ecological sustainability. Derive Environmental Impact and Ecological Sustainability Indexes.	Proposition of a concept and quantification of the Recyclability Potential Index of textile fibres, considering environmental and economic gains from the recycling process.
Functional Unit	1 kg of (greige) textile	1 kg of fibre product	Entire life cycle of all garments, both new and existing, in use in the UK in 2009	1 kg of finished woven fabric	1 kg of textile fibre	1 kg of textile fibre
Life Cycle Stages	Raw material extraction, transportation, manufacturing of fibre and fabric (including spinning, texturing, weaving, knitting, pre-treatment, thermofixing, dyeing and finishing), use and end-of-life.	Production of raw materials, refining of the product, production of end products, consumption, recycling, and disposal of waste.	Extraction of raw materials, processing of materials, production of fibre, yarn and fabric, treatment of fabric, production and packaging of garments, transportation, storage at a regional distribution centre and at retail outlets and use and end-of-life.	Raw material production and processing, pre-treatment (only for natural fibres), sizing, spinning, desizing, warping, fabric formation, finishing, printing and dyeing, and the end-of-life treatment of stitching (a finishing sub-process) and warping.	Raw material extraction and fibre production process.	Virgin fibre production and respective end-of-life (landfilling, recycling, and incineration).
Method	Eco-costs 2012, CED, ReCiPe	—	Carbon Footprint	ReCiPe	Eco-indicator 99	Ecological Footprint, IPCC 2007 GWP 100a, Eco-indicator 99
Impact Categories	Eco-costs, carbon footprint, cumulative energy demand and ReCiPe scores	—	Carbon footprint.	Climate change, ozone depletion, photochemical oxidant and particulate matter formation, ionising radiation, terrestrial acidification, human toxicity, terrestrial, freshwater and marine ecotoxicity, metal, fossil and water depletion, freshwater and marine eutrophication, agricultural and urban land occupation, natural land transformation, human health, ecosystem diversity, resource availability.	Damage to ecosystem quality, human health, and to resources.	Ecological footprint, carbon footprint and ecological damage in terms of human health.

Table 3.4 - Overview of the state-of-the-art studies (continuation of table 3.3).

Study	LCA benchmarking study on textiles made of cotton, polyester, nylon, acryl, or elastane	Environmental Assessment of Textiles	A Carbon Footprint for UK Clothing and Opportunities for Savings	Environmental Improvement Potential of textiles - IMPRO Textiles	Quantification of Environmental Impact and Ecological Sustainability for Textile Fibres	Recyclability Potential Index (RPI): The Concept and Quantification of RPI for Textile Fibres
Hot Spots	The impact of spinning and weaving was high, being weaving the most significant life cycle stage followed by the manufacturing of the base material.	Energy and water consumption, use of fertilisers, pesticides, herbicides and insecticides on natural fibres, and emissions and waste streams analysis.	Washing, drying and fabric production were identified as the major hot spots.	The production and processing phases were predominant for indicators like eutrophication, agricultural land occupation and natural land transformation.	Factors like resort to renewable resources, amount of energy consumed, fibre recyclability and biodegradability were highly considered.	Economy was one of the major deciding factors, which may promote or demote recycling.
Conclusions	LCA on textiles may only be accurate when yarn thickness is specified. Energy consumption per kg of yarn was inversely proportional to the yarn size in dtex. Acrylic and PET had the least impact on the environment. Cotton had the highest environmental burden in all four single indicators.	Production of acrylic fibre is high-energy demanding. Polyester manufacture generates high levels of GHG emissions, and its wastewaters emit volatile monomers. Fertilisers and pesticides have significant impacts. Production of viscose is energy-intensive and emits high amounts of GHG when compared to cotton production.	Wool was responsible for the highest carbon emissions, due to the methane emissions from sheep and manure, along with nitrous oxide emissions from fertilisers. After wool, nylon, acrylic and polyester were the major responsible ones.	The production and the use phases made significant contributions to the environmental impacts. Distribution and recycling/disposal at the end-of-life phase were both of minor importance. Cotton was the main contributor due to its large share in the textiles market and to the nature of its production.	Natural fibres scored better than the synthetic fibres. Organic cotton had the least environmental impact and it was the most sustainable fibre, unlike acrylic that was the least preferred fibre in terms of environmental impact and ecological sustainability.	Polyester outperformed all of the fibres under consideration. Acrylic outperformed cotton, wool, and viscose. Wool had the lowest Economic Gain Index value.
Limitations	Sewing and assembling, distribution, marketing and sales of the textiles were excluded. Transportation was only included in the first step of material production. Most of the chosen datasets for the calculations were from sources of European origin.	Several life cycle steps and processes were only briefly described with little or no data. No impact categories were evaluated. The screening was based on existing available environmental data mainly from other studies.	Significant amount of data was retrieved from literature. Factors like transportation of consumers to and from the point of retail purchase, packaging used at all life cycle stages, fabric softeners, other material inputs used during washing, and water use for ironing, were not included in the assessment.	Based on a high amount of literature data. Some production processes of specific fibres were extrapolated to different fibres when no fibre-specific data were available. Most of the life cycle phases take place in different locations around Europe and the world.	The results were on the basis of index scores given to each fibre and on the basis of a scoring system that was developed using secondary data for LCI, being both quite arbitrary. LCIA results rest on certain hypotheses and assumptions.	The model is subjective. Technological challenges of sorting and recycling facilities, different recycling policies, availability of different fibres for recycling, rate and efficiency of recycling, and quality of recycled materials compared to virgin materials were not included in this model due to lack of data.

4. Life Cycle Assessment of Raw White, Dyed and Pigmented Acrylic Fibres

The methodology applied in this LCA study follows the ISO 14040 standard series. Therefore, this study comprises the four different phases of LCA.

4.1. Goal and Scope Definition

The main goal of this study is to assess the environmental impacts of the production of raw white, dyed, and pigmented acrylic fibres (L11, L25, and L28 fibres, respectively, as designated by SGL Composites). Therefore, three different fibre production scenarios were considered and modelled. Fibre aspect and specifications for the three fibres in study are presented in figure 4.1 and table 4.1, respectively. Within the main aim of this work, the benefits of the existing solvent recovery process will be evaluated. The present study points out for the three fibres which one presents more environmental burdens, and also which production stages and activities cause more concerns. The identification and proposal of environmental improving actions for acrylic fibre production will also be addressed.



Figure 4.1 - Samples of the fibres in study (from left to right: raw white, dyed and pigmented).

Table 4.1 - Specifications of the fibres.

Fibre	Code Name	Colour	Cut Type	Thickness (dtex)
Raw White	L11	—	Tow	3.3
Dyed	L25	White	Tow	3.3
Pigmented	L28	Tan	Staple	2.2

The fibres were selected because these are the most relevant ones in terms of the company's sales, in each of the three fibre categories. This information was provided by the Sales Department.

Through this study, the manufacturer will know which activities must be selected to focus attention on, aiming to reduce the resulting environmental impacts, moving

towards a more sustainable process and to an increasing environmental awareness. The results also make possible for customers to know more about the environmental performance of the acrylic fibres on a cradle-to-gate perspective.

The selected functional unit was 1 tonne of finished acrylic fibre. The selection took into account the considered functional units in other textile fibre LCA studies, such as the previously mentioned in the State-of-the-Art, where it was verified that this was the most common functional unit used in this field of study, in terms of fibre. In this way, it will be possible to compare this study with the majority of the textile fibre LCA studies, due to the fact that, for comparing studies, functional units must be consistent [40].

For this study, the attributional LCA approach was followed due to the established goals and to the fact that the inventory values used are not based on trends. This is contrary to the consequential approach, in which besides the fact that the values used in the consequential approach are based on economic models, the results' accuracy is still not well known [40]. Furthermore, the selected attributional approach allows the identification of opportunities to reduce the impacts arising from the several life cycle stages.

A cut-off criteria of 0.1% was applied, meaning that only processes which contribute with more than 0.1% to the environmental load are presented in the results. According to PRé Consultants, the relevant environmental issues are still displayed with this cut-off value [70].

A cradle-to-gate approach was followed in this study. Therefore, the included life cycle stages were the production of the different raw materials and commodities, the transport of the raw materials to the acrylic fibre production plant (SGL Composites), and all the production stages, previously described in chapter 2.5, involved in the manufacture of the products being studied: continuous polymerisation, dope preparation, spinning, cut and baling and solvent recovery. The TT area was not included in the modelling since the selected fibres to be studied are in the form of tow for L11 and L25 fibres, and in the staple form for L28 fibre, as presented in table 4.1, and not in the top form. Figure 4.2 illustrates the system boundaries of the present study. No allocation procedures had to be made.

All inventory data comes from reports and documentation provided by SGL Composites, related to the months of February, March, and April 2020. For modelling, the ecoinvent v.3.4 database was used (gently supplied by the co-supervisor).

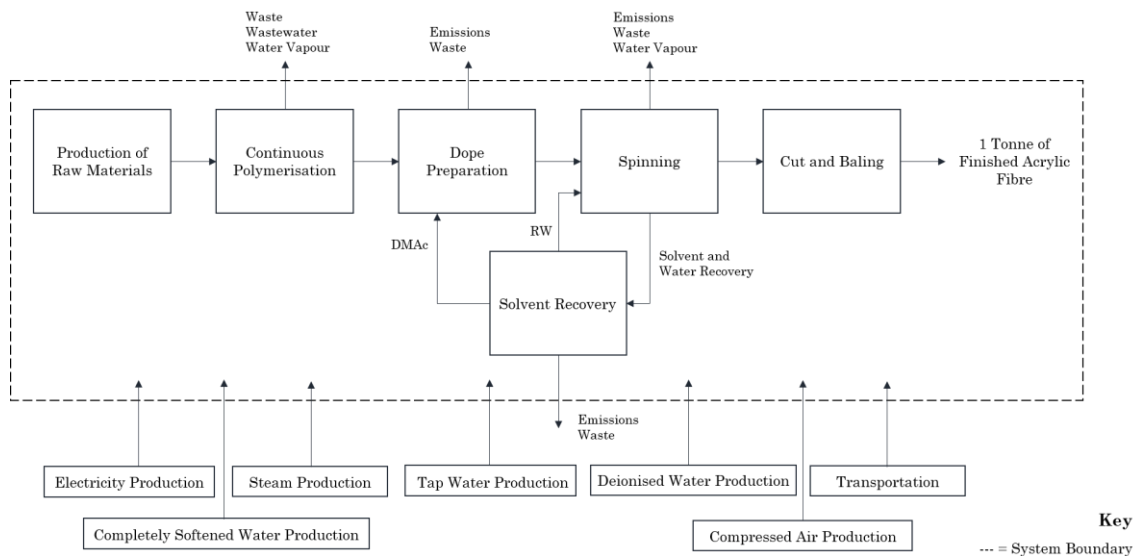


Figure 4.2 - System boundaries.

During the modelling of the production processes, some assumptions had to be made. Those were the following:

- i. Both DIW1 and DIW2 were considered in the database as “deionised water”, TW as “tap water”, and CW and W as “completely softened water”. The criteria for selecting water quality in the modelling may seem exigent for TW, CW, and W, that is, water production systems with a higher quality than that existing in the industry were selected. However, this was limited by the water production systems in the ecoinvent database.
- ii. A distinction between the 5S and 20S steam was not available in the database. As a result, steam inputs were considered to be “steam, in chemical industry”;
- iii. For the electricity, cogeneration was considered, by natural gas, at a capacity of 1 MWe. This was the closest scenario available in the database to the electricity production on site. FISIGEN has, in reality, a capacity of 24.3 MWe [71];
- iv. Sodium bicarbonate was not available in the database, so it was considered to be ammonium bicarbonate;
- v. Due to the fact that both dyes and pigments were not available in the database, for the dyes similar molecules (anthraquinone for the two dyes and benzimidazole for the fluorescent brightener) were considered and, for the pigments, the total quantity was considered to be carbon black;
- vi. Some waste values, such as dope waste and non-processed fibre, had to be estimated through reported total plant waste values;

- vii. When not known, the closest harbour to the material's plant was considered in the transportation process;
- viii. In the case of the acrylonitrile train transportation from Russia to Latvia, a document from the main state-owned railway company in Latvia informed that the most common type of traction of the trains is electric in this country; thus, this type of transportation was assumed in the modelling phase ^[72];
- ix. The baling process was not included in the modelling, due to the fact that the packaging components were not available in the database. Also, it was not possible to quantify, in weight, each component separately;
- x. Due to their inexistence in the database, the following compounds were excluded from the study: ammonium persulphate, oxalic acid, hydrogen sulphite, anti-foams, detergents, dyeing speed retardant, softeners, cohesive agents and other additives, and monomethylacetamide.

Due to the existence of the Solvent Recovery (SR) area, two avoided burdens were considered in the mass balances: dimethylacetamide and deionised water production. This area allows the recycling of DMAc and the recovery of deionised water, decreasing the overall environmental impact of the products.

The selected impact assessment method was CML 2001. This method was developed by the Institute of Environmental Sciences of Leiden University, at The Netherlands. It restricts quantitative modelling to early stages in the cause-effect chain, limiting uncertainties. The obtained results are grouped in midpoint categories ^[73]. By having midpoint results, this offers more detailed information about the impacts on the environment caused by the production of the acrylic fibres. Furthermore, this method was selected since its results are more transparent and understandable, comparing to other LCIA methods ^[74]. Due to the complexity of the fibres' process production and to the plant's location, the following impact categories were considered: abiotic depletion, acidification, eutrophication, freshwater aquatic ecotoxicity 100a, freshwater sediment ecotoxicity 100a, global warming 100a, human toxicity 100a, marine aquatic ecotoxicity 100a, marine sediment ecotoxicity 100a, ozone layer depletion 40a, photochemical oxidation and terrestrial ecotoxicity 100a.

The software used for the development of this study was the openLCA v.1.10.2 (version for Windows 64 bit), from GreenDelta (Berlin, Germany) ^[75]. It presents the advantage of being an open-source software with free and purchasable databases.

4.2. Life Cycle Inventory Analysis

For the development of this study, it was necessary to collect all data regarding the production process inputs and outputs for the L11, L25, and L28 fibres. This information was kindly supplied by SGL Composites and measured, calculated, or estimated by the company, for each unitary process and for each fibre.

As previously described, the continuous polymerisation (CP), dope preparation (DP), spinning (SP) and cut and baling (CB) areas are involved in the production of acrylic fibres. The solvent recovery (SR) area is considered as an auxiliary one which main aims are the recovery of the solvent dimethylacetamide (DMAc) and water, later on designated as recovered water (RW). Solvent from the SP area and two thirds from the total of deionised (DIW) and recovered water fed to the SP area are fed to the SR area. The recovered solvent is fed to the DP area and the recovered water to the SP area, which means that, during the modelling of the processes, the recycling of DMAc and recovery of water had to be considered. This recycling, regarding the solvent, presents its benefits, such as the advantage of avoiding to buy higher quantities of DMAc, and also reducing the environmental impacts related to DMAc production. As it was previously mentioned, the TT area was not included in the modelling since the selected fibres' final form is not the top form.

For the production of polyacrylonitrile (PAN), acrylonitrile and vinyl acetate are the two main required raw materials. Following the production of PAN in the CP area, the dissolution of the polymer powder in the solvent, in the DP area, is performed. The obtained dope goes to the SP area to be extruded into acrylic fibre. In the CB area, the spun tow has its physical properties improved, as well as its fibre internal tension balanced among the filaments. In this area, the fibre will be baled as tow or cut into staple form. For L25 fibre, the dyestuff is added in the SP area. Regarding L28 fibre, the pigment dispersion is added in the DP area.

Some of the provided data had to be adjusted due to the functional unit. Data related to the SP and CB areas did not need any adjustments. Data from DP area had to be adjusted to match the needed dope in the SP area. After knowing how much polymer is needed for each fibre, data related to the CP area was adjusted to the needed polymer amount. Knowing how much solvent and water goes to the SR area, adjustments to this area were then made.

To be included in the study, waste values regarding the DP and SP areas, in terms of dope waste and non-processed fibre, respectively, had to be estimated. This was possible through the company's total waste report of April 2020. By having these waste values,

as well as the production values for both the L3 and P2 polymer, and the production values for the L11, L25 and L28 fibres, it was possible to estimate approximately how much of that waste corresponded to acrylic textile fibre waste. The L3 polymer is produced for the textile fibres and the P2 for the carbon fibre precursor (CFP). In the modelling, the wastes were classified as “process-specific burdens, residual material landfill” in the database.

Regarding the input values of commodities, it was not possible to differentiate the values between the three fibres, except for the DIW's in the SP area. These values were retrieved from reports regarding the plant specific consumptions, from April 2020 for all areas, except for the CP area, which was from March 2020, and for the SR area, which was from February 2020. The difference in DIW's values for the SP area is because its value varies depending on the fibre being produced. For this case, the values were retrieved from the table of operating conditions. Concerning the inputs and outputs of raw materials, the values came from the operating conditions tables of each area and from information present in the company's databases.

Processes dealing with the production of raw materials, such as acrylonitrile, commodities, and transportation, were included in the analysis through the selection of the available processes in the ecoinvent database. The scenarios available in the database that were closer to the real conditions of production and transportation were selected for all the processes included in this study.

As previously mentioned, some assumptions had to be made regarding the dyestuffs and the pigments. The chemicals used in the production of the acrylic fibres were not available in the ecoinvent database, and, for their impact on the environment to be considered and to make a clear distinction among the three fibres, similar compounds had to be considered in the study. Regarding the production of L25 fibre, anthraquinone is considered as the raw material to produce cationic dyes in the GaBi database [76]. Therefore, this compound was considered adequate as the total dye quantity used in the process. The fluorescent brightener is a benzimidazole derivative [77]. Hence, this chemical replaced the fluorescent brightener. Regarding the pigments used in L28 fibre, the total quantity was considered to be replaced by carbon black, the available pigment in the database. During the development of this study, it was found that other databases had the necessary dyes and pigments, such as the GaBi database (extension XV of Textile Finishing) regarding the dyestuffs and other finishing compounds, and the Evah Pigments Database for the pigments [78, 79]. The access to these databases was not possible due to their costs. This can be an issue to be improved in future works.

The transport of all included raw materials was considered. Information regarding the suppliers and transportation of the raw materials was kindly provided by SGL Composites. To build the LCA model, the distance between the origin of raw materials and SGL Composites had to be estimated. The Google Maps tool was used to calculate the distance made by every type of transport. When the transport was made by a ship, the distance had to be estimated in nautical miles, through the Sea Distances website (an online tool for calculating distances between sea harbours) [80, 81]. The nautical miles were then converted into kilometres. Most of the raw materials are transported by tanker trucks.

Information regarding the location of the shipping harbour in Mexico, concerning the shipping of the dyes and the fluorescent brightener, and the shipping harbour in India, regarding the shipping of the surfactant, was unknown, therefore, additional assumptions were made. For these assumptions, the considered factors were the harbours distance to the producer of the raw materials and the distance between the harbours and the following destination. As these distances were intended to be the minimum as possible, the considered harbours were the Tuxpan port, in Mexico, and the Mumbai port, in India. For these estimations, the Google Maps tool for calculating the distance between the raw materials plants and the harbours was used, as well as the Sea Distances website for calculating the distance between the harbours and the following destinations.

As it was previously mentioned, due to their inexistence in the ecoinvent database, some compounds that are involved in the production of acrylic fibre were not considered. Inventory data regarding these compounds had been previously estimated and provided by SGL Composites.

4.3. Life Cycle Impact Assessment

The environmental impacts of the production of raw white, dyed, and pigmented fibres were quantified through the CML 2001 method. A brief description of the assessed impact categories is hereby presented. Each of the categories refer to ^[82]:

- **Abiotic depletion:** depletion of natural resources, including energy resources (expressed in kg antimony equivalent);
- **Acidification:** impacts on soil, groundwater, surface waters, ecosystems, biological organisms and materials due to the acidifying pollutants (expressed in kg sulphur dioxide equivalent);
- **Eutrophication:** all potential impacts of excessively high environmental levels of macronutrients, where nitrogen and phosphorus are the most important chemical elements (expressed in phosphate equivalent);
- **Freshwater aquatic ecotoxicity 100a:** impacts of toxic substances on freshwater aquatic ecosystems, in a 100-year time horizon (expressed in kg 1.4-dichlorobenzene equivalent);
- **Freshwater sediment ecotoxicity 100a:** impacts of toxic substances on the sediment of freshwater ecosystems, in a 100-year time horizon (expressed in kg 1.4-dichlorobenzene equivalent);
- **Global warming 100a:** impact of human emissions on the radiative forcing of the atmosphere, in a 100-year time horizon (expressed in kg carbon dioxide equivalent);
- **Human toxicity 100a:** impacts on human health of toxic substances present in the environment, in a 100-year time horizon (expressed in kg 1.4-dichlorobenzene equivalent);
- **Marine aquatic ecotoxicity 100a:** impacts of toxic substances on marine aquatic ecosystems, in a 100-year time horizon (expressed in kg 1.4-dichlorobenzene equivalent);
- **Marine sediment ecotoxicity 100a:** impacts of toxic substances on the sediment of sea water ecosystems, in a 100-year time horizon (expressed in kg 1.4-dichlorobenzene equivalent);
- **Ozone layer depletion 40a:** thinning of the stratospheric ozone layer as a result of anthropogenic emissions, in a 40-year time horizon (expressed in kg CFC-11 equivalent);
- **Photochemical oxidation:** formation of reactive chemical compounds, such as ozone by the action of sunlight on certain primary air pollutants (expressed in kg ethylene equivalent);

- **Terrestrial ecotoxicity 100a:** impacts of toxic substances on terrestrial ecosystems, in a 100-year time horizon (expressed in kg 1.4-dichlorobenzene equivalent).

The overall impact assessment results regarding the production of the three acrylic fibres in study are presented in table 4.2.

Table 4.2 - Overall impact assessment results according to the CML 2001 method. All values are referred to the functional unit of 1 tonne of finished acrylic fibre. The red, yellow, and green cells represent the highest, mid, and lowest relative values in the impact category results, respectively.

Impact Category	Unit	Results		
		L11	L25	L28
Abiotic Depletion	kg Sb eq.	58.63	58.60	59.21
Acidification	kg SO ₂ eq.	23.03	31.13	22.96
Eutrophication	kg PO ₄ ³⁻ eq.	10.50	10.68	10.56
Freshwater Aquatic Ecotoxicity 100a	kg 1.4-DB eq.	781	796	753
Freshwater Sediment Ecotoxicity 100a	kg 1.4-DB eq.	1626	1667	1565
Global Warming 100a	kg CO ₂ eq.	5473	5439	5413
Human Toxicity 100a	kg 1.4-DB eq.	1448	2250	1278
Marine Aquatic Ecotoxicity 100a	kg 1.4-DB eq.	3610	3604	3453
Marine Sediment Ecotoxicity 100a	kg 1.4-DB eq.	3785	3793	3620
Ozone Layer Depletion 40a	kg CFC-11 eq.	5.12E-04	5.23E-04	5.20E-04
Photochemical Oxidation	kg C ₂ H ₄ eq.	1.19	1.51	1.23
Terrestrial Ecotoxicity 100a	kg 1.4-DB eq.	1.63	1.57	1.53

Through table 4.2, it can be concluded that, in general, the dyed fibre, L25, presented higher environmental impacts than the raw white and pigmented fibres, L11 and L28, respectively. From the twelve selected impact categories, the dyed fibre presented the higher impacts in eight of them. Despite the possibility of the dyed fibre being considered the most environmentally concerning fibre among the three fibres, in general, the difference between the values of the impact results was not very high. Human toxicity, acidification potential and photochemical oxidation were the impact categories for which the difference between the impact results for the L11 and L28 fibres comparing to the L25 fibre, in percentage, was more notorious.

For a better understanding of the impact results and of what processes contributed to them, figures 4.3 to 4.26 show the contribution from the production of raw materials and other activities to the environmental impacts concerning each impact category and fibre. An overview on the contribution of each production area to the environmental impacts is also shown.

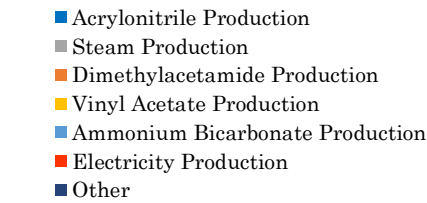
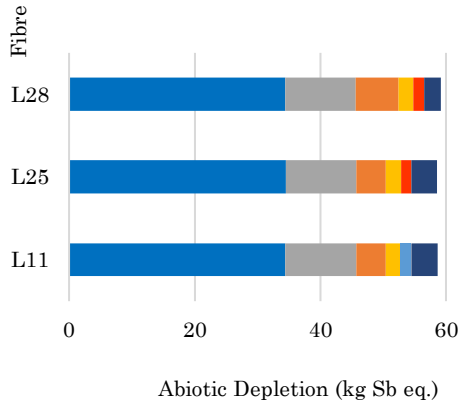


Figure 4.3 - Abiotic depletion for 1 tonne of finished acrylic fibre.

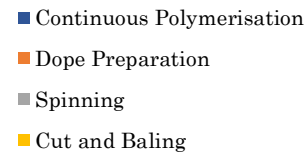
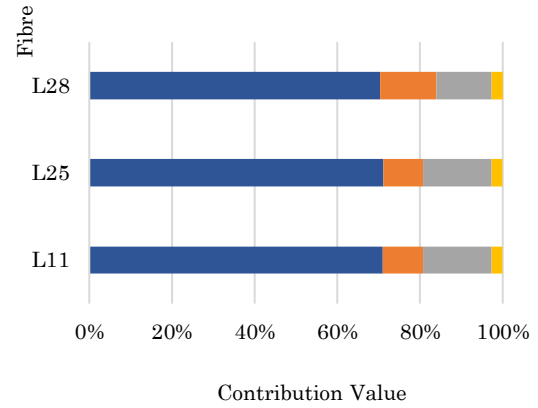


Figure 4.4 - Contribution to the impacts by production area, regarding abiotic depletion.

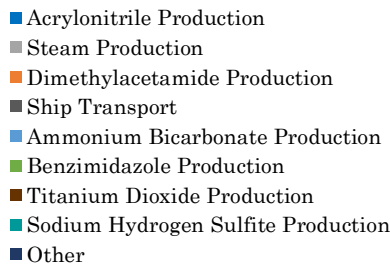
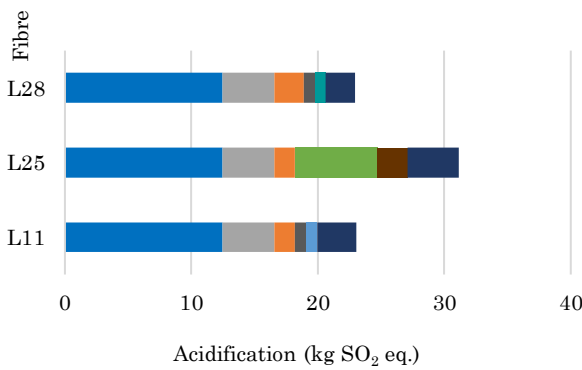


Figure 4.5 – Acidification for 1 tonne of finished acrylic fibre.

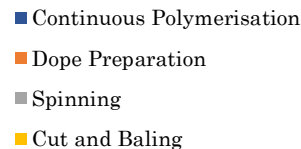
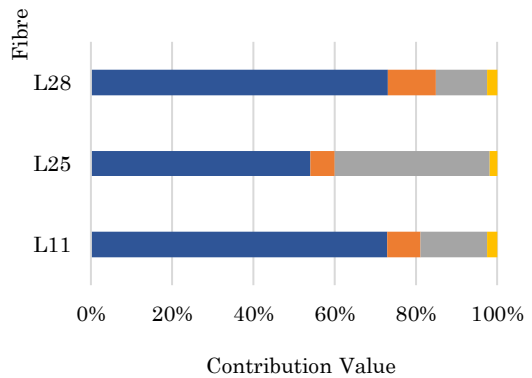


Figure 4.6 - Contribution to the impacts by production area, regarding acidification.

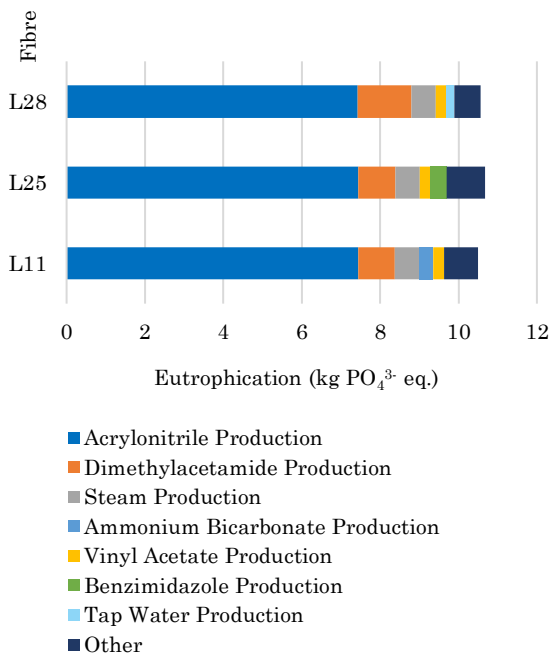


Figure 4.7 – Eutrophication for 1 tonne of finished acrylic fibre.

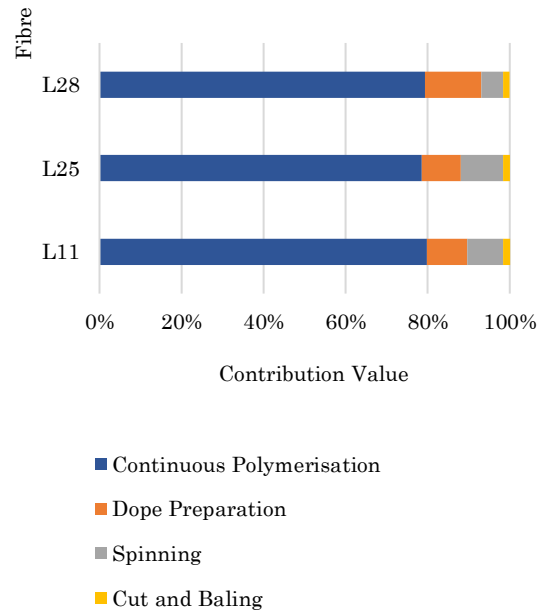


Figure 4.8 - Contribution to the impacts by production area, regarding eutrophication.

Regarding abiotic depletion, the production of acrylonitrile, steam and dimethylacetamide had the highest contribution to the environmental impacts. This is valid for the three fibres. The production of acrylonitrile accounted for more than a half of the impacts for all the fibres. Concerning steam production, this activity accounted for around 20% of the impacts for all the fibres as well. The production of acrylic fibre is a highly intensive energy consuming process and the same issue is valid for the production of raw materials, especially for acrylonitrile production [13]. The most significant estimated depletion on abiotic resources was the one regarding natural gas, crude oil, and hard coal. Continuous polymerisation was the production area which had more responsibility on the environmental impacts. While the spinning area had more responsibility on the impacts than the dope preparation area for L11 and L25 fibres, the opposite was verified for L28 fibre.

In the case of acidification, for L25 fibre, acrylonitrile production accounted for 40% of the impacts and benzimidazole production (the chemical used in the modelling instead of the fluorescent brightener) for 21%, while for L11 and L28 fibres acrylonitrile production was responsible for more than half of the environmental impacts and steam production approximately 18%. The third biggest contributor for L11 and L28 was dimethylacetamide production, while for L28, it was the steam production. Dimethylacetamide production was only the fifth biggest contributor for the pigmented fibre, while titanium dioxide production was the fourth. It was estimated that sulphur

dioxide, nitrogen oxides, and ammonia are the highest released acidifying pollutants due to acrylic fibre production. Once again, CP area accounted for most of the environmental impacts, although, in the case of the dyed fibre, SP area accounted for 38% of the impacts. This means that the additional compounds added to this area, for L25 fibre, which are essentially the dyestuff compounds, present a significant impact on acidification potential, compared to the other fibres.

For eutrophication, acrylonitrile production accounted for approximately 70% of the environmental impacts for the three fibres. The next big contributors were dimethylacetamide and steam production. Solvent production had a slightest higher contribution in the case of L28 fibre. It was estimated that sources of eutrophication compounds in the production of acrylic fibre are mostly COD emissions to water and the emission of ammonium and nitrogen oxides to the air. These compounds will be the most responsible for nutrient enrichment and elevated biomass production in aquatic and terrestrial ecosystems. These situations may cause an undesirable shift in species composition and cause surface waters to become unacceptable as a source of drinking water. Also, the increased biomass production in aquatic systems may lead to depressed oxygen levels, due to the additional consumption of oxygen in biomass decomposition [82]. Continuous polymerisation area was responsible for around 80% of the impacts. The additional compounds added to both L25 and L28 fibres, in the SP and DP areas, respectively, had an impact on the contribution of the two areas, as SP had a higher contribution for L25 fibre and DP area for L28 fibre.

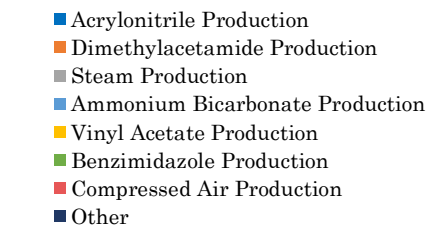
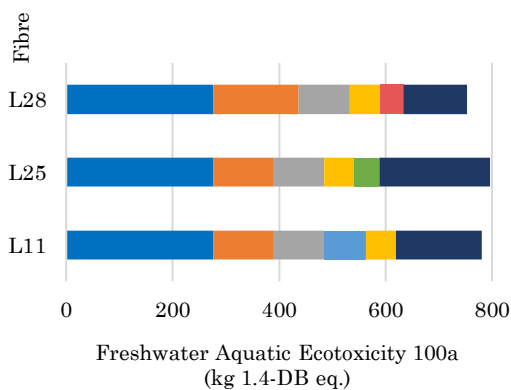


Figure 4.9 - Freshwater aquatic ecotoxicity 100a for 1 tonne of finished acrylic fibre.

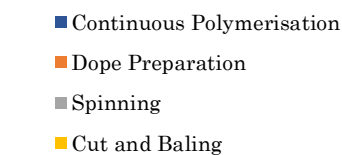
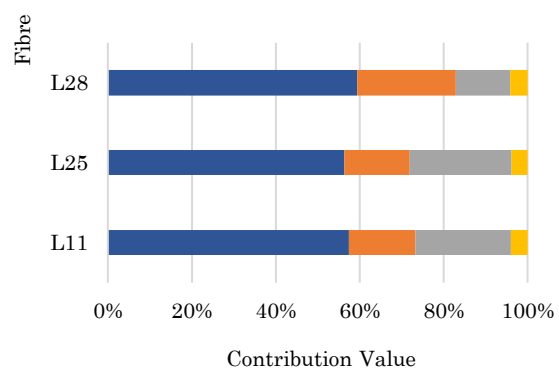
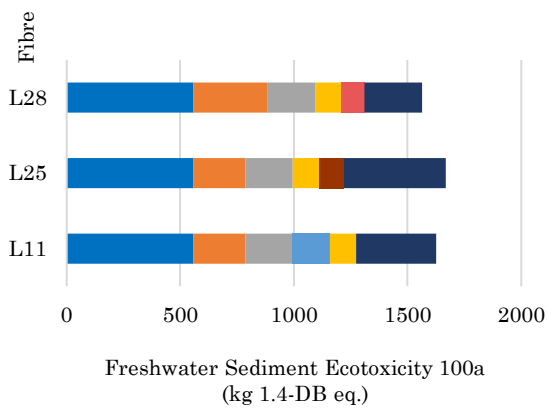
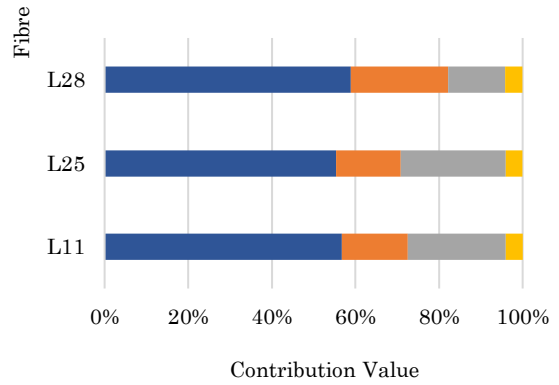


Figure 4.10 - Contribution to the impacts by production area, regarding freshwater aquatic ecotoxicity 100a.



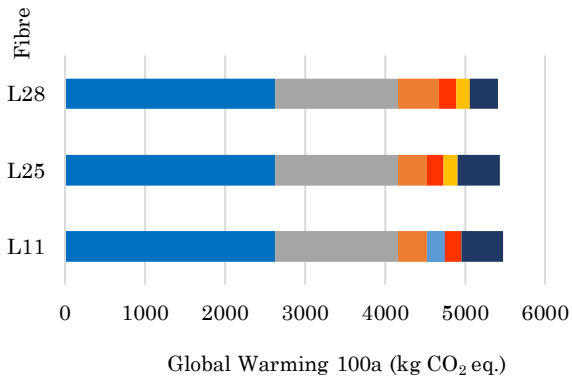
- Acrylonitrile Production
- Dimethylacetamide Production
- Steam Production
- Ammonium Bicarbonate Production
- Vinyl Acetate Production
- Titanium Dioxide Production
- Compressed Air Production
- Other

Figure 4.11 - Freshwater sediment ecotoxicity 100a for 1 tonne of finished acrylic fibre.



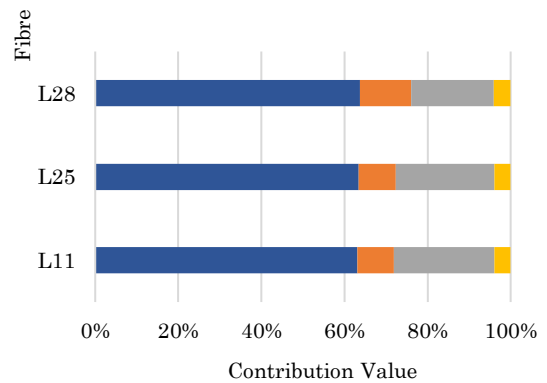
- Continuous Polymerisation
- Dope Preparation
- Spinning
- Cut and Baling

Figure 4.12 - Contribution to the impacts by production area, regarding freshwater sediment ecotoxicity 100a.



- Acrylonitrile Production
- Steam Production
- Dimethylacetamide Production
- Ammonium Bicarbonate Production
- Electricity Production
- Vinyl Acetate Production
- Other

Figure 4.13 - Global warming 100a for 1 tonne of finished acrylic fibre.



- Continuous Polymerisation
- Dope Preparation
- Spinning
- Cut and Baling

Figure 4.14 - Contribution to the impacts by production area, regarding global warming 100a.

As for freshwater ecotoxicity, for both the aquatic and sediment categories (figures 4.9 to 4.12), acrylonitrile production showed a significant contribution for all fibres. Dimethylacetamide and steam production were the next biggest contributors. The contributions from all activities were very similar for these two impact categories. In the case of acrylonitrile, its production contributed from 34% to 37% to the environmental impacts, for both categories. Vinyl acetate production was the fourth biggest contributor regarding freshwater sediment ecotoxicity, except for L11 fibre, where ammonia bicarbonate production took the fourth position. Comparing to the previously mentioned impact categories, where five contributors accounted for almost the total of the environmental impacts, in the case of freshwater aquatic and sediment ecotoxicities, other activities shared a small, but still significant contribution. Compressed air production, train transportation and tap water production altogether accounted for approximately 18% of the impacts, regarding L11 and L28 fibres. For L25 fibre, this contribution value was due to benzimidazole, titanium dioxide, and compressed air production. Comparing the two impact categories, it may be assumed that acrylic fibre production raises more concerns on the sediments of freshwater ecosystems, due to the potential release of toxic substances. The substances that are mostly emitted to these ecosystems are zinc, copper, and nickel. Regarding the contribution of each production area, again, for both impact categories, the contributions were similar. Clearly, the addition of the auxiliaries, the dyestuff and the pigment dispersion has an impact on environmental burden contribution for each production area.

Regarding global warming, around half of the emitted carbon dioxide equivalent is due to acrylonitrile production and 28% is due to steam production. Dimethylacetamide production presented a smaller contribution, around 7% for L11 and L25 fibres, and 10% for L28 fibre. As it was previously mentioned, acrylonitrile and acrylic fibre production are high energy consuming processes, which is clearly reflected in this impact category. The global warming results were similar for the three fibres. Per tonne of finished acrylic fibre, approximately 5.4 tonnes of CO_{2,eq.} are released to the atmosphere. Comparing the contribution of each production area to the environmental impacts, CP area accounts for more than 60% of the impacts and SP area presents a contribution of 24% for both L11 and L25 fibres, and 20% for L28 fibre. Compared to DP area, the spinning area presents a more significant contribution in this case for all fibres. Through this, it is possible to conclude that CP and SP areas are both energy intensive, especially when compared to DP area.

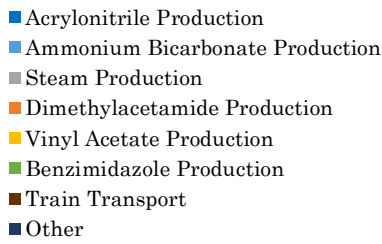
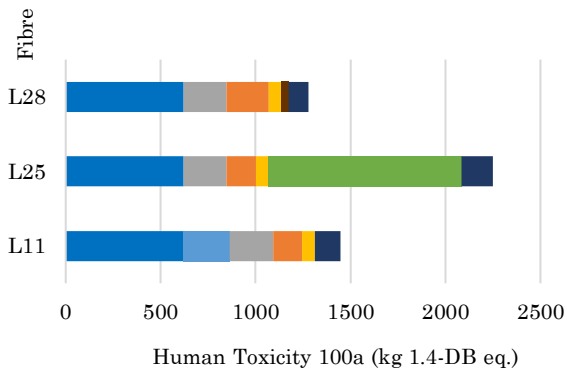


Figure 4.15 – Human toxicity 100a for 1 tonne of finished acrylic fibre.

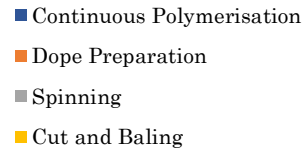
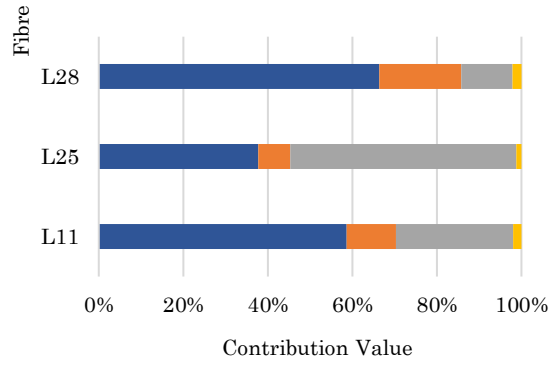


Figure 4.16 - Contribution to the impacts by production area, regarding human toxicity 100a.

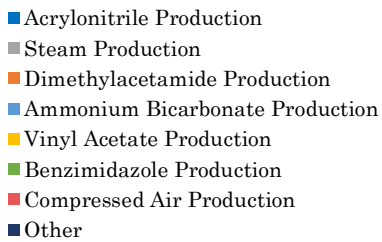
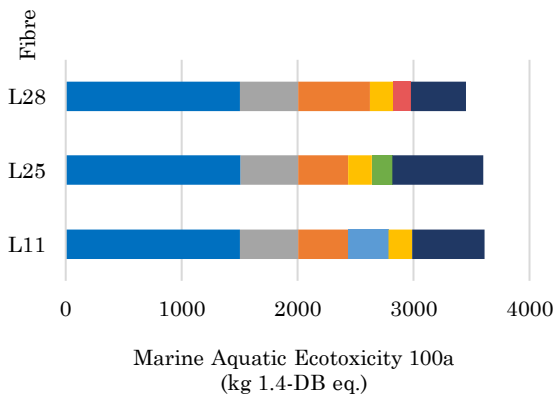


Figure 4.17 - Marine aquatic ecotoxicity 100a for 1 tonne of finished acrylic fibre.

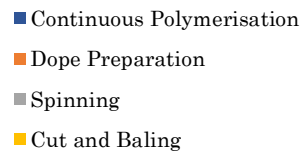
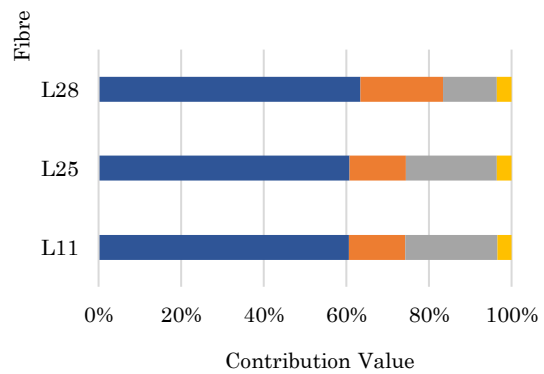


Figure 4.18 - Contribution to the impacts by production area, regarding marine aquatic ecotoxicity 100a.

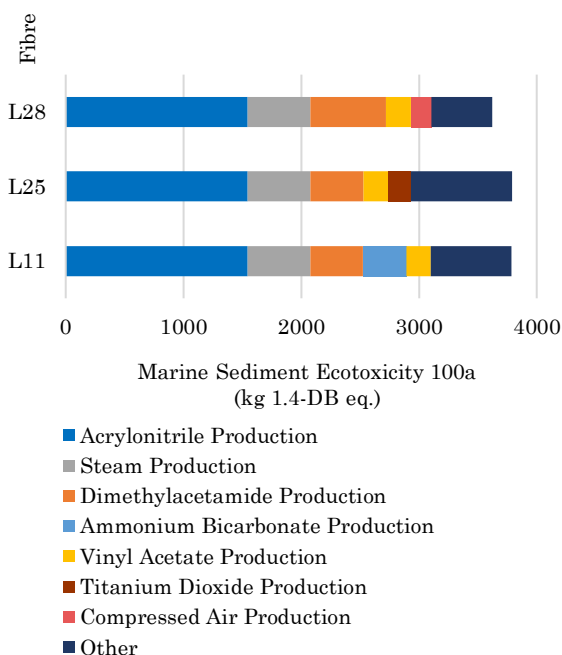


Figure 4.19 - Marine sediment ecotoxicity 100a for 1 tonne of finished acrylic fibre.

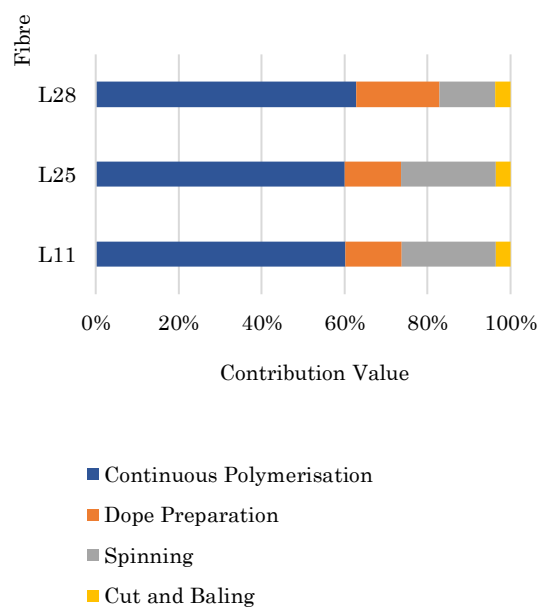


Figure 4.20 - Contribution to the impacts by production area, regarding marine sediment ecotoxicity 100a.

For human toxicity, benzimidazole production appears to be, in this case, the activity with the biggest contribution for the environmental burdens, with a contribution of 45% for the dyed fibre. Regarding the other two fibres, acrylonitrile production is still the activity which contributes the most, 43% for L11, and 49% for L28 fibres. For L25 fibre, acrylonitrile production accounts for 28% of the impacts. In the case of the raw white fibre, ammonium bicarbonate (considered in the modelling instead of sodium bicarbonate) and steam production had a similar contribution, 17% and 16%, respectively, while dimethylacetamide production had 11%. Regarding L28 fibre, steam and dimethylacetamide production contributed similarly to the impacts, respectively, 18% and 17%. Benzimidazole, one of the dyeing compounds, has a significant impact on human toxicity. Ammonium bicarbonate, which is used in a higher quantity in L11 fibre, has also a significant impact compared to other compounds and activities. Regarding the pigment dispersion in L28 fibre, dimethylacetamide did not account with a such high contribution as the other compounds, and the pigment itself had a contribution of only 0.58%. In this category, the dyed fibre is the one with more environmental concerns. Toxic substances potentially emitted due to acrylic fibre production that present risks to human health are mainly benzene, ethylene oxide, and nickel. The impact of benzimidazole in L25 fibre is again showed by the contribution of SP area, 53%, which

is higher than the one from CP area. For the other fibres, CP area represented the major contribution.

Concerning marine ecotoxicity, for both the aquatic and sediment categories, the contributions to the environmental impacts from the several activities were very similar. Acrylonitrile production was the major contributor, accounting for 41% and 40% of the impacts, respectively, for aquatic and sediment ecotoxicity, for L11 and L25 fibres. For L28 fibre, it accounted for 44%. For L11 and L25 fibres, steam and dimethylacetamide production were the next biggest contributors, by this order, contributing with 14% and 12% to the environmental impacts, for both marine aquatic and sediment ecotoxicities. For L28 fibre, the reverse was verified, being dimethylacetamide production the second biggest contributor, with 18%, and steam production the third, with 14%. In this fibre, a higher quantity of solvent is employed due to the pigment dispersion, which may have caused these results. Again, similarly to the freshwater ecotoxicity categories, comparing to other previously mentioned impact categories, where five contributors accounted for almost the total of the environmental impacts, other activities shared a small, but still significant contribution. These activities were compressed air production, train transportation, and tap water production for L11 fibre, all together contributing with 12% for the two impact categories. For L25 fibre and concerning marine aquatic ecotoxicity, these activities were titanium dioxide production, compressed air production, train transportation and, also, tap water production. All together, these activities accounted for 18% of the environmental impacts. Concerning marine sediment ecotoxicity, the activities were benzimidazole production, compressed air production, train transportation, and tap water production, together accounting for 17% of the environmental burdens. Regarding L28 fibre, these activities were essentially the train transportation and tap water production, representing a total of 8% of the environmental impacts, for both marine and sediment ecotoxicity. Barite, zinc, and copper were estimated as the most potentially released toxic substances on marine ecosystems, due to acrylic fibre production. CP area was responsible for more than 60% of the environmental impacts for both impact categories, and for the three fibres. While for L11 and L25 fibres, SP area accounted for 22% to 23% of the environmental impacts, for L28 fibre, DP area accounted for 20%. As it was verified for the freshwater ecotoxicity categories, acrylic fibre production raises more concerns regarding the sediments of seawater ecosystems.

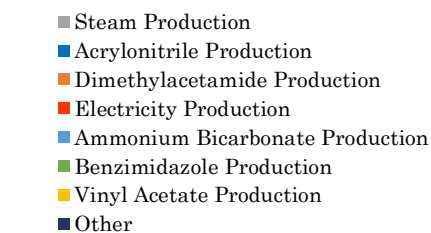
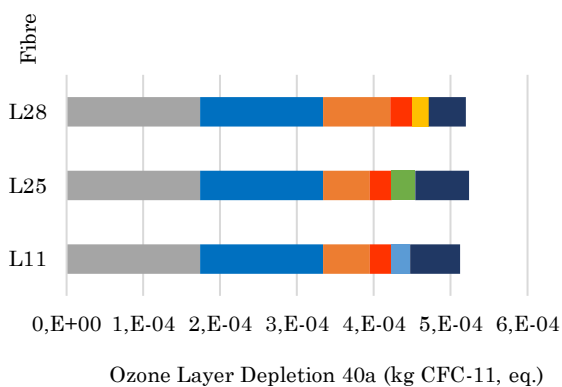


Figure 4.21 - Ozone layer depletion 40a for 1 tonne of finished acrylic fibre.

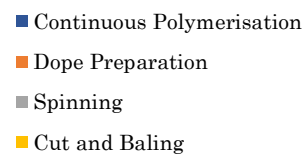
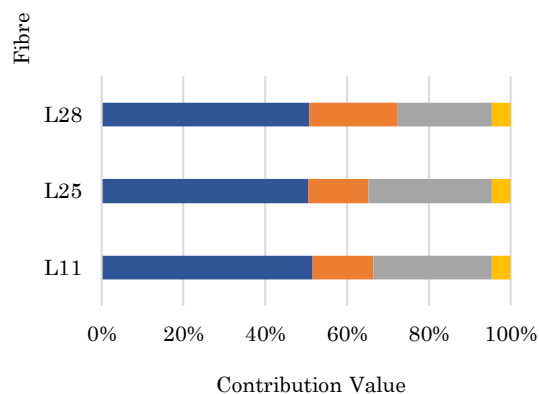


Figure 4.22 - Contribution to the impacts by production area, regarding ozone layer depletion 40a.

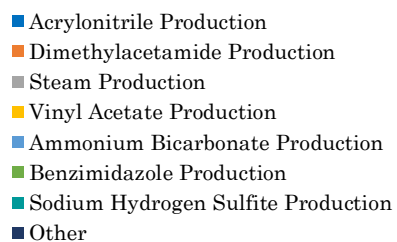
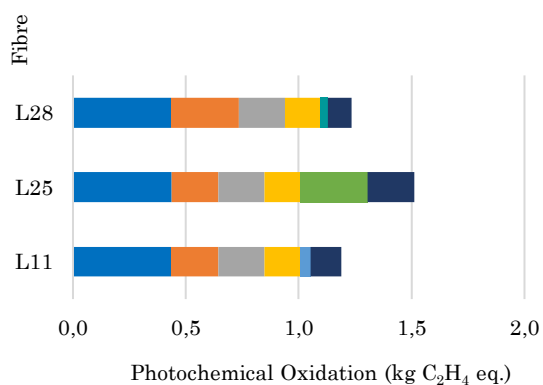


Figure 4.23 - Photochemical oxidation for 1 tonne of finished acrylic fibre.

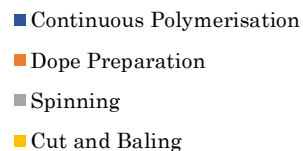
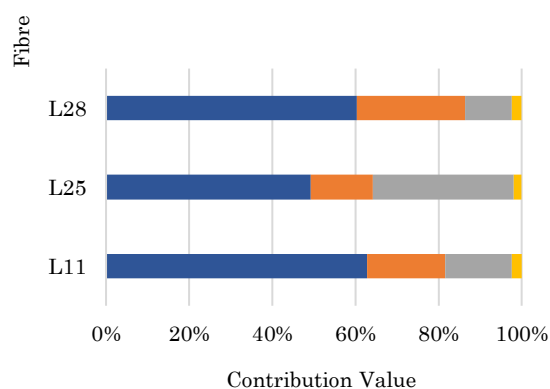


Figure 4.24 - Contribution to the impacts by production area, regarding photochemical oxidation.

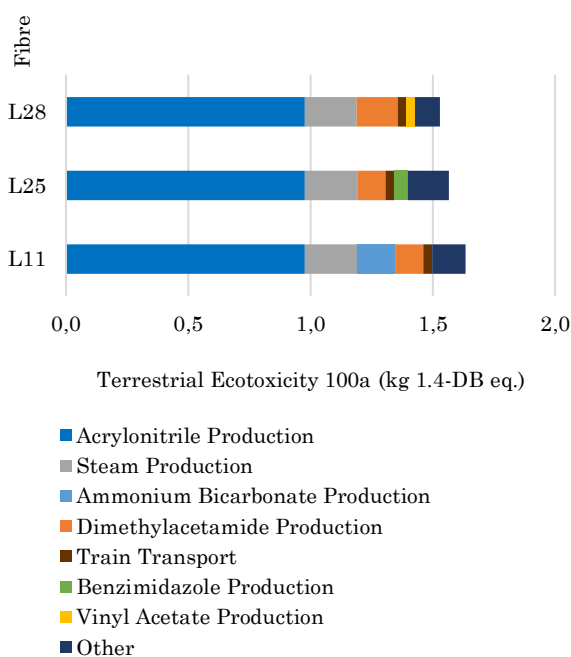


Figure 4.25 - Terrestrial ecotoxicity 100a for 1 tonne of finished acrylic fibre.

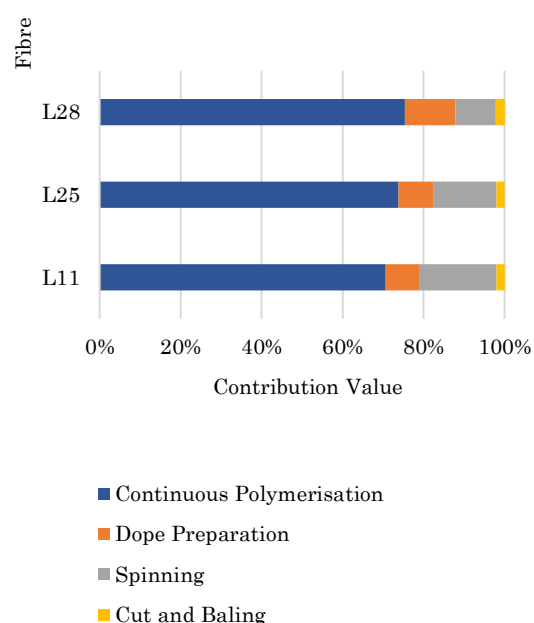


Figure 4.26 - Contribution to the impacts by production area, regarding terrestrial ecotoxicity 100a.

Regarding ozone layer depletion, steam and acrylonitrile production shared a similar contribution, being both the major contributors to the environmental impacts for the three fibres. Still, steam production had a bigger contribution than acrylonitrile production. Together, the two activities contributed with more than 60% of the impacts. CP area accounted for around half of the environmental impacts. For L11 and L25 fibres, the SP area was responsible for approximately the double of the impacts compared to DP area. For L28 fibre, the two areas presented a similar contribution. Through the results of this impact category, it is possible to conclude that acrylic fibre production does not have a significant impact on ozone layer depletion.

For photochemical oxidation, acrylonitrile production was the major responsible for the impacts. For both L11 and L28 fibres, dimethylacetamide and steam production were the next biggest contributors, while for L25 fibre benzimidazole and dimethylacetamide production were the next contributors. Also, while for the raw white and the pigmented fibres acrylonitrile production contributed with 37% and 35%, respectively, to the environmental impacts, for the dyed fibre, it contributed with 29%. Due to acrylic fibre production, mainly methane, sulphur dioxide, and carbon monoxide are emitted to the atmosphere. These compounds contribute to the formation of reactive compounds which cause harm on human health and ecosystems. For L11 and the L28 fibres, the CP area was responsible for more than 60% of the environmental impacts, and the DP area

presented more environmental concerns than the SP area. For the dyed fibre, CP area was responsible for 49% of the impacts and the SP area contributed approximately with the double of the impacts, compared to the DP area.

Finally, for the last studied impact category, terrestrial ecotoxicity, acrylonitrile production was responsible for 60% to 64% of the total environmental impacts. Steam production was the second biggest contributor for all the fibres, accounting for around 13% to 14% of the impacts. While dimethylacetamide production was the third biggest contributor for L25 and L28 fibres, for L11 fibre was ammonium bicarbonate production the third contributor. The main toxic substances causing harm on terrestrial ecosystems that were estimated to be emitted to the environment were vanadium, barium, and nickel. Barium is essentially emitted to the soil, while vanadium and nickel are emitted to the air. CP area was responsible for more than 70% of the environmental burdens. SP area was responsible for approximately 19% and 17% of the impacts for L11 and L25 fibres. For L28 fibre, SP area was responsible for 10% of the impacts, being DP area responsible for 12%. Compared to the other toxicity related categories, terrestrial ecotoxicity did not have a significant expression.

Although the solvent recovery (SR) area is not one of the essential areas to the production of acrylic fibres, its presence in the plant allows the continuous recycling of the solvent. This has strong benefits on an environmental perspective because it is not necessary for the producer to purchase a higher amount of dimethylacetamide, and, also, the associated environmental burdens dealing with its production are avoided. Thus, a reduction on the environmental impacts of acrylic fibres is achieved. To understand the magnitude of the environmental impact reduction, the impact savings resulting from the SR area activity are shown in figure 4.27, for each considered impact category.

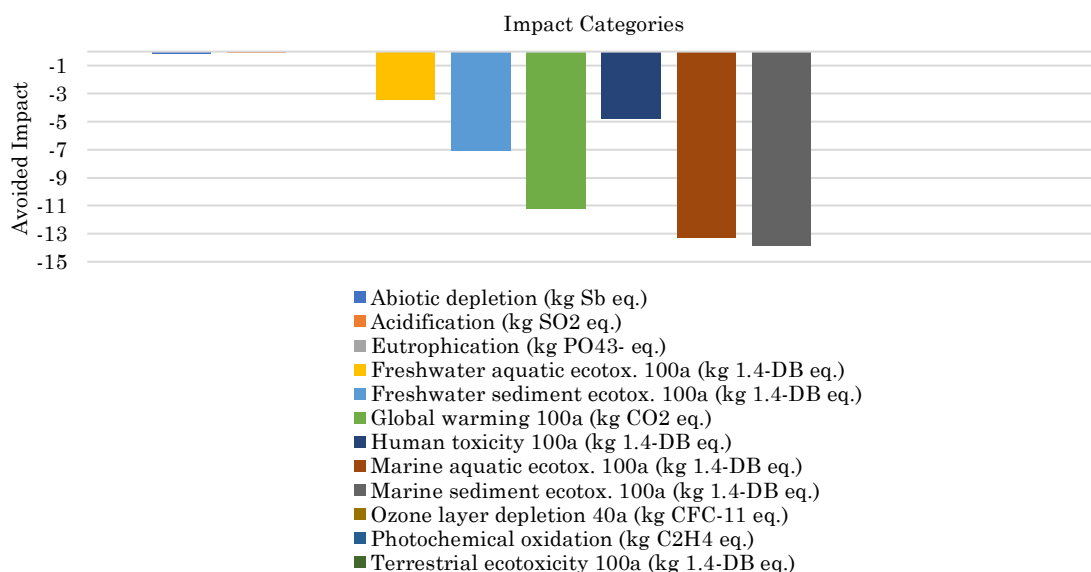


Figure 4.27 - Impact savings resulting from SR area per 1 tonne of finished acrylic fibre.

The higher impact savings from the SR area (figure 4.27), in absolute value, were verified for marine sediment ecotoxicity, marine aquatic ecotoxicity, and global warming. These were also the impact categories with the highest contribution dealing with solvent production. Regarding the impact savings, in percentage, the higher savings were verified for both freshwater ecotoxicity categories, with more than 0.4% of reduction, for the three fibres, and for photochemical oxidation, with more than 0.5% of reduction for the raw white and the pigmented fibres, and more than 0.4% for the dyed fibre.

Summing up, acrylonitrile production was the major contributor to the environmental impacts caused by acrylic fibre production. This was also the main reason for the association of continuous polymerisation area to mostly of the environmental impacts as well. In general, steam and dimethylacetamide production were the following biggest contributors. For the dyed fibre (L25) benzimidazole production has also shown a significant contribution to some of the impact categories, especially to human toxicity. It was also verified that the addition of auxiliary compounds, the dyestuffs and the pigment dispersion contributed to the environmental impacts related to each production area. While the spinning area usually presented more impacts for the raw white (L11) and the dyed fibres (L25) than the dope preparation area, for the pigmented fibre the opposite was verified in almost all impact categories. The addition of auxiliary compounds in the SP area, as well as of the dyestuffs in this area for L25 fibre, and of the higher solvent quantity in the DP area for L28 fibre (due to the addition of the pigment dispersion), have influenced these contribution results. Regarding the cut and baling area, the

maximum contribution that this area presented was approximately 5% on ozone layer depletion.

A comparison of the results obtained in this study with some of the literature mentioned on the State-of-the-Art chapter is presented hereby. When not specifically mentioned, the comparison is being made with the average value of the three fibres.

Comparing to the LCA study of acrylic fibre developed by Yacout et al. ^[60], although the selected impact method was different from the one considered in the present study, the values for global warming and for acidification obtained by Yacout et al. ^[60] were similar to those obtained in the present work. Their estimated value for global warming, through the impact assessment method Eco-indicator 99, was the release of 5.4 kg CO_{2,eq.} per kg of fibre, while for acidification was of 0.013 kg of SO_{2,eq.} per kg of fibre. Through the method CML 2001, it was estimated in this study the same value for global warming for L25 and L28 fibres, while for the raw white fibre the release of 5.5 kg of CO_{2,eq.} per kg of fibre was estimated. Regarding acidification, the obtained results in this study were slightly higher. In average, it was estimated the release of 0.026 kg SO_{2,eq.} per kg of fibre. Yacout et al. ^[60] also underlined the fact of the process being energy intensive, and its effect on the depletion of fossil resources. It was also stated the fact that the process has significant impacts regarding toxicity. These subjects were also discussed in this life cycle assessment. Additionally, no impacts were detected regarding ozone layer depletion, similarly to what was observed in the present work.

In the Thai Acrylic Fibre Co. Ltd LCA study ^[61], the raw material production was the major contributor to the environmental impacts, and the continuous polymerisation area was associated with the majority of the impacts followed by the spinning area. The observations on the present work were the same as for the Thai Acrylic Fibre Co. Ltd. LCA study ^[61]. Again, like in this LCA, the activities which contributed the most to the impacts were acrylonitrile and steam production. Also, regarding their acrylonitrile production contribution to the global warming impact category, it was stated as being approximately 42%, while in the LCA study here shown, it was approximately of 48% for all fibres. An important remark must be made on Thai Acrylic Fibre's study: the version of the CML method used is not clear. Despite this, it can be concluded that by comparing the two studies, the overall environmental impact results of the manufacturing of acrylic fibre is lower in this present work than in the Thai Acrylic Fibre's study, except for the eutrophication and human toxicity categories. For acidification, it was estimated the release of 32.7 kg SO_{2,eq.} per tonne of fibre, while in average, in this study, this value was

estimated as 25.7 kg SO_{2,eq.} per tonne of fibre. Regarding eutrophication results, 3.2 kg PO₄³⁻_{eq.} per tonne of fibre was the estimated by Thai Acrylic Fibre's study, being 30% lower than the one estimated in this LCA study. For global warming, Thai Acrylic Fibre has estimated the release of 9429 kg of CO_{2,eq.} per tonne of fibre, a value 1.7 times higher than the one obtained in this study. The selected time horizons for the human and terrestrial ecotoxicity categories were different than the ones selected in this study. As for photochemical oxidation, the result from the Thai Acrylic Fibre's study was 50% higher than the one obtained in the present LCA study.

Van der Velden et al. [46] studied the carbon footprint of acrylic fibre through the ReCiPe impact method. Considering the steps of polymer pellet production, extruder spinning, texturing and heat setting, the carbon footprint was approximately equal to 5.4 kg CO_{2,eq.} per kg of fibre for acrylic fibre, matching the obtained results in this study regarding global warming. It was also reported that the carbon footprint for cotton and polyester was approximately 12 and 5 kg CO_{2,eq.} per kg of fibre, respectively. This means that, according to the study developed by van der Velden et al. [46], acrylic fibre has a slightly higher carbon footprint than polyester, but cotton has a carbon footprint 2.2 times higher than acrylic fibre.

Beton et al. [67] through the ReCiPe midpoint method assessed the environmental impacts of acrylic, cotton, wool, viscose, and polyester fibres. Considering only the steps of raw material production and processing, pre-treatment, sizing, and spinning for all the fibres, wool was the fibre with a higher value for climate change, with approximately 14 kg CO_{2,eq.} per kg of fibre. Acrylic was the next fibre, with a release of 12 kg CO_{2,eq.} per kg of fibre, followed by viscose, polyester, and cotton, with the values of 10.3, 7.5, and 5.5 kg CO_{2,eq.} per kg of fibre, respectively. Comparing to the results obtained in the present work, Beton et al. [67] reported a value of more than the double of CO₂ emissions for acrylic fibre. Concerning human toxicity, wool was again in this study the fibre with the highest environmental impact, followed by viscose, cotton, acrylic, and polyester. For the freshwater ecotoxicity, cotton was the fibre with the highest environmental impact, followed by acrylic, viscose, wool, and polyester. In terms of environmental impacts due to the production phase, in general, it was reported by Beton et al. [67] that acrylic fibre presents less impacts than cotton, polyester, and viscose. Cotton, according to Beton et al. [67], was the fibre with the highest environmental impacts amongst all fibres, followed by polyester.

Thomas et al. [66] reported a much higher value for acrylic fibre footprint, 26 tonnes CO_{2,eq.} per tonne of fibre, a value 4.8 times higher than the one calculated in the present work. Regarding the other fibres, wool presented the highest value of 29 tonnes CO_{2,eq.}

per tonne of fibre, followed by viscose (21 tonnes CO_{2,eq.} per tonne of fibre), cotton (10 tonnes CO_{2,eq.} per tonne of fibre), and polyester (8 tonnes CO_{2,eq.} per tonne of fibre).

La Rosa et al. [62] used the CML-IA baseline impact method to assess the environmental impacts of cotton. To compare with the values obtained in this study, the impact results from cotton textile were considered, which includes, besides the cultivation, harvesting, and ginning phases, the cleaning and sorting, spinning, pre-treatment, dyeing, finishing, washing, and drying phases. Regarding global warming 100a, it was reported a release of 23.4 kg CO_{2,eq.} per tonne of fibre. A value of 165 kg SO_{2,eq.} per tonne of fibre was reported for acidification. For eutrophication, a value of 70.8 kg PO_{4³⁻,eq.} per tonne of fibre was reported, which is approximately 6.7 times higher than the one reported here for acrylic fibre. The reported values for freshwater aquatic ecotoxicity and for marine aquatic ecotoxicity were significantly higher, approximately 62 and 11 times higher, respectively. Regarding human toxicity and terrestrial ecotoxicity, the reported values were, respectively, 5.8 and 1752 times higher. This means that, according to the study developed by La Rosa et al. [62], cotton represents significant ecotoxicity risks and much more significant ones than acrylic fibre, especially regarding terrestrial ecotoxicity. As for ozone layer depletion and photochemical oxidation, the reported values were 193 and 3.7 times higher.

Shen and Patel [65] have assessed, through the CML 2000 method, the environmental impacts of viscose Asia and Austria, polyester, and cotton. Regarding abiotic depletion, the obtained result of this present study for acrylic fibre was the highest, followed by polyester with 45 kg Sb_{,eq.} per tonne of fibre, where viscose Austria presented the lowest result of 14 kg Sb_{,eq.} per tonne of fibre. For acidification, viscose Asia presented a value of 45 kg SO_{2,eq.} per tonne of fibre, followed by cotton with 41 kg SO_{2,eq.} per tonne of fibre, polyester with 21 kg SO_{2,eq.} per tonne of fibre, and viscose Austria with 14 kg SO_{2,eq.} per tonne of fibre. This means that acrylic fibre presents less environmental impacts on acidification than viscose Asia and cotton. Comparing to the values for eutrophication, only cotton presented higher environmental impacts, being approximately 2.1 times higher. For freshwater aquatic ecotoxicity, cotton was again the fibre that presented more environmental impacts than the ones obtained for acrylic fibre in this study, being 22.3 times higher, while polyester presented the lowest environmental impacts. As for human toxicity and terrestrial toxicity, cotton presented again the highest environmental impacts, while viscose Austria the lowest for human ecotoxicity, and acrylic fibre for terrestrial ecotoxicity. Viscose Austria presented less impacts on ozone layer depletion and the same for photochemical oxidation. For ozone layer depletion, acrylic fibre presented the highest impacts, while viscose Asia showed the highest

impacts on photochemical oxidation, followed by acrylic fibre. Finally, for global warming, while viscose Austria was carbon neutral, acrylic fibre, compared to the results of Shen and Patel [65], presented the highest environmental impacts in this category, followed by polyester with a value of 4.1 tonnes CO_{2,eq.} per tonne of fibre.

As it is not always clear which fibre is more environmentally friendly and greener, depending on process operation conditions, LCA modelling, assumptions, among other factors, two conclusions can be withdrawn: (i) the production process of acrylic fibre may be optimised and (ii) more research on this issue is still necessary. As this thesis focus on acrylic fibre, it was verified that acrylonitrile, steam, and dimethylacetamide production played a significant role in the environmental impacts of the raw white, dyed, and pigmented acrylic fibres. Due to this, some research was made to better understand how the environmental impacts of the production of these fibres could be reduced, improving the environmental performance of SGL Composites, moving the company further to a more sustainable production process. The discussion of this subject is presented in the following chapter.

5. Proposals for the Improvement of Environmental Performance

To get a significant improvement of the environmental performance, actions regarding the critical activities that cause the most harm to the environment must be taken. These activities are mainly the productions of acrylonitrile, steam, and dimethylacetamide. Considering that acrylonitrile production represented the major environmental concern regarding acrylic fibre production, by reducing the associated environmental impacts to the production of this raw material, a consequent reduction in the fibre production impacts would be achieved.

A route for SGL Composites to accomplish a significant impact reduction would be through the selection of more environmentally friendly suppliers for acrylonitrile, steam, and dimethylacetamide mostly. Nonetheless, a search for other eco-friendly substitute raw materials and best practices should always be carried out. The possible alternatives that might be implemented in the acrylic fibres production process are hereby presented, including suggestions for the fibre dyeing and recycling.

5.1. Acrylonitrile

Conventional acrylonitrile, based on fossil resources, is usually produced through the SOHIO process, by ammoxidation, using propylene, ammonia, and air as feedstocks. Propylene ammoxidation also produces acetonitrile, carbon oxides, and hydrogen cyanide as by-products. An alternative process has emerged over the last 20 years, which decreases the production costs in about 20%, compared to the propylene ammoxidation process. This process is propane ammoxidation, decreasing the need to produce propylene, which is a highly energy consuming process ^[83]. Despite the economic advantage and the reported lower carbon footprint for propane ammoxidation, this process is still based on fossil resources ^[84]. Due to this fact, some innovative and more sustainable production processes for acrylonitrile have emerged, regarding its production from renewable feedstocks.

One of the bio-based processes to produce acrylonitrile is the glycerol process, mainly consisting of the dehydration of glycerol, producing acrolein, followed by acrolein ammoxidation to produce acrylonitrile. Glycerol is a highly generated by-product during biodiesel production, and it cannot be used as fuel, neither in cosmetic nor pharmacy industries because it does not have the necessary purity for this means. Due to the existing glycerol surplus and to its low price, this raw material is expected to become

important for future biorefineries. There are three known different routes for production of acrylonitrile from glycerol, which are: (i) one step-process from glycerol; (ii) two step-process from glycerol via acrolein; (iii) and the three step-process from glycerol via acrolein, depuration of acrolein, and acrolein to acrylonitrile [85]. The obtained yields of acrylonitrile for each of these processes were, respectively, 48.5 % with one reactor [86], 40% with two reactors in tandem [87], and 60% with two reactors in series and intermediate purification of acrolein [88]. The reaction pathway is the same for these three methods for acrylonitrile production, starting by the formation of acrolein by glycerol dehydration, then by acrolein ammoxidation to acrylonitrile. Even though these processes seem promising, they still have its drawbacks. These drawbacks are mainly the short life of the dehydration catalyst, the poisoning of the acrolein catalyst by unreacted glycerol, and the fact that after an efficient dehydrogenation step, acrolein becomes the precursor for acrylonitrile, but it is not the most preferable one, reducing the yield of acrylonitrile. The process of glycerol ammoxidation still presents a lower energy and material efficiency, a higher land use, and higher raw material and investment costs compared to propane ammoxidation. For example, for glycerol ammoxidation, the total cost is 2806 €/tonne of produced acrylonitrile, while for propane ammoxidation is 1890 €/tonne [83]. Furthermore, the major concern related to the glycerol pathway is the fact that it is derived from a food source, making it more difficult to be accepted by government regulations and by the community.

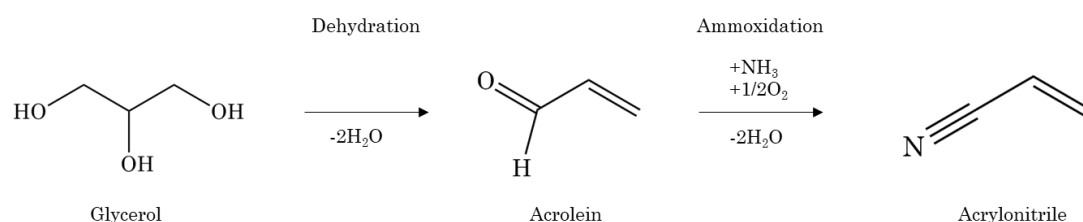


Figure 5.1 - Reaction to produce acrylonitrile from glycerol.

The production of acrylonitrile from glutamic acid is another alternative, where, in this case, the raw material is not a source of food. Glutamic acid is obtained from biomass waste streams, such as the soluble fraction waste stream produced during the bioethanol production from corn and wheat. To produce acrylonitrile, Sanders et al. [89] suggested that two steps are necessary, which are the oxidative decarboxylation from glutamic acid to 3-cyanopropanoic acid and the decarbonylation-elimination of 3-cyanopropanoic acid to produce acrylonitrile. Through this process, a 100% conversion of glutamic acid at a 90% selectivity to 3-cyanopropanoic acid was obtained. The same authors suggested an

alternative method to obtain the 3-cyanopropanoic acid through the oxidative decarboxylation with an enzyme, most specifically, the vanadium chloroperoxidase enzyme [90]. Through this new process, a 100% conversion of glutamic acid at a 100% selectivity to 3-cyanopropanoic acid was obtained. The second process is more eco-friendly and economic. Another group of researchers, Miranda et al. [91], investigated this pathway for acrylonitrile production using different conditions from the ones used by Sanders et al. [89], obtaining a yield of 23%. The used catalyst was palladium(II) chloride, while Sanders et al. [89] used sodium bromide as catalyst. The main verified difficulties in the bio-based glutamic acid process were the polymerisation of acrylonitrile occurrence as side reaction in the attempts of increasing the yield [85].

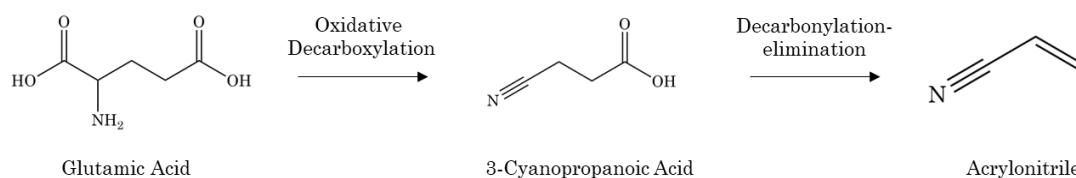


Figure 5.2 - Reaction to produce acrylonitrile from glutamic acid.

Lactic acid, obtained by fermentation of biomass, is also a route for the production of bio-based acrylonitrile [92]. Through this pathway, no reduction or oxidation steps are necessary. Water is the only by-product if ammonia is used as the nitrogen source. Mack et al. [92] developed a process in which occurs a direct amidation of lactic acid with ammonia in the presence of water. The formation of lactamide may be catalysed by electrophilic zeolites. Following the amidation step, lactamide is dehydrated to acrylonitrile with the assistance of acetic anhydride, which can be regenerated. It was verified an increase on the conversion and a repression on the side reactions due to ammonia excess. A yield of 62% on acrylonitrile may be achieved [92].

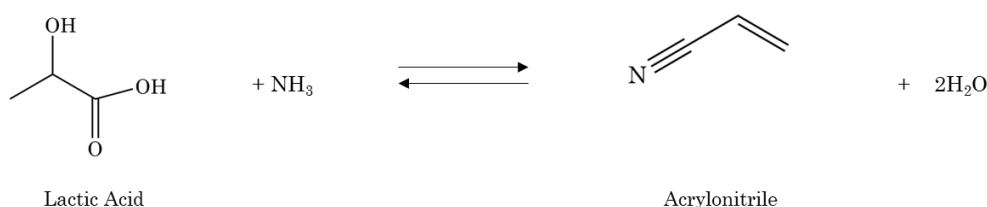


Figure 5.3 - Reaction to produce acrylonitrile from lactic acid.

Oxygenated intermediates, obtained through the fermentation of sugars, such as agricultural wastes and cellulosic materials, are an alternative to produce bio-acrylonitrile. A team of researchers from the National Renewable Energy Laboratory (NREL), in the United States, developed a process for the production of acrylonitrile through a nitrilation process, in which 3-hydroxypropionic acid produced from sugar fermentation is the raw material [93]. In this process, ethyl 3-hydroxypropanoate, a derivate from 3-hydroxypropionic acid, through dehydration and nitrilation with ammonia, produces bio-acrylonitrile [84]. The used catalyst is titanium dioxide and this process may achieve a molar yield of more than 90% of acrylonitrile. Another investigated process by the researchers is the nitrilation using ethyl acrylate, instead of ethyl 3-hydroxypropanoate, being ethyl acrylate separated from the ethyl 3-hydroxypropanoate in the process by reactive distillation. This pathway, using ethyl acrylate as the substrate to produce acrylonitrile, presents an even higher yield. The decreased carbon deposition on the catalyst, due to the reduced quantity of water present in the process is responsible for the higher yield. This nitrilation process to bio-acrylonitrile presents benefits in terms of green chemistry compared to the conventional ammoxidation process. In nitrilation, the process control is relatively simple and runaway reactions are avoided, due to the endothermic reaction, in opposition to ammoxidation, which is exothermic. Also, the used catalyst is 30% cheaper, and toxicity is minimised, as hydrogen cyanide is not produced, which is a toxic reaction by-product. A 14.1% improvement on GHG emissions was already estimated compared to propylene ammoxidation [84].

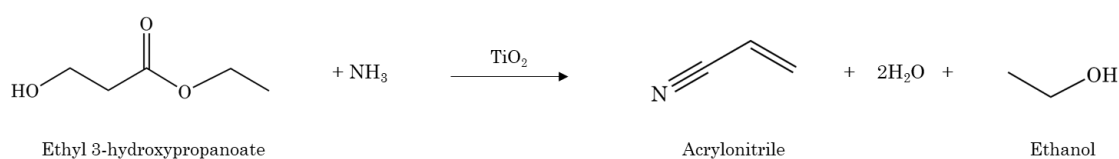


Figure 5.4 - Reaction to produce acrylonitrile from ethyl 3-hydroxypropanoate.

The Southern Research Institute, in the United States, has also developed a process to produce bio-based acrylonitrile, through the conversion of sugars from non-food biomass, such as glucose [94]. The biomass sugars are converted to oxygenates, which through the action of a catalyst, are converted to an intermediate. This intermediate is then converted to acrylonitrile. This is a multi-step catalytic process. In the hydrocracking step, the intermediate glycerol is produced, then follows dehydration which produces the intermediate acrolein, and, in the final step, the ammoxidation reaction will produce

acrylonitrile ^[95]. The advantages of this process are, for example, the absence of hydrogen cyanide as a by-product, and the use of advantageous catalysts which produce, for example, propylene glycol, a valuable product in the market. Additionally, a LCA of this process was developed. A result of 0.29 kg CO_{2,eq.} per kg of acrylonitrile through this bio-based process was reported, while through the petroleum-based process 6.05 kg CO_{2,eq.} per kg of acrylonitrile are emitted, meaning that the bio-based process presents less environmental impacts ^[96]. Southern Research expects to begin building their first plant by the end of 2021, which will allow the product commercialisation. This plant will have a production capacity of 5 000 to 10 000 tonnes per year of acrylonitrile ^[96].

While the previously described processes are not already available on a commercial scale and not ready to be commercialised, being all still at a research level, there is already one bio-based acrylonitrile option available in the market. This option is Econitrile[®], the sustainable acrylonitrile produced by AnQore ^[97]. AnQore is a commodity chemicals manufacturer of acrylonitrile, among other products, based in Geleen, the Netherlands ^[98]. Econitrile[®] production is based on a certified mass balance method and on certified sustainable raw materials, being produced from both propylene and ammonia which do not have a fossil origin ^[97]. The production of propylene is based on agricultural waste streams and the ammonia source is based on biogas. Additionally, it is expected that propylene production from circular plastic streams will start soon by Sabic, supplying it to the process production of Econitrile[®]. The plant that is used to produce conventional acrylonitrile is used for Econitrile[®] production. Econitrile[®] presents the same properties as the conventional product. The suppliers of propylene and ammonia, and AnQore, are certified by ISCC PLUS. This certification supports the development of the circular economy and of both reuse and recycling, being recognised by global initiatives. A mass balancing approach is used to determine the sustainable share and amount of the sustainable outgoing product being certified, based on the already certified input material ^[99]. This way, it is possible for the following process in the value chain to be certified by ISCC PLUS as well, and so on, creating a more sustainable value chain. A LCA analysis was developed with the University of Maastricht and it was estimated that the Econitrile[®]'s carbon footprint is 60% lower than the one from conventional acrylonitrile, as stated in the Econitrile[®] website ^[97]. According to AnQore, who showed the kind availability for the realisation of a meeting to get to know more about Econitrile[®], the product may even be considered as carbon neutral. Regarding its cost, it may be considered as the double of the cost of conventional acrylonitrile. Considering that, in average, the acrylonitrile price in October 2020 was about 1689 USD/tonne, regarding the CIF ARA price, this would make Econitrile[®] cost

about 3378 USD/tonne ^[100]. This means that cost, insurance, and freight (CIF) charges are included in this price, considering the load or discharge at one of the ports of Amsterdam, Rotterdam, or Antwerp (ARA) ^[101].

As Econitrile[®] is the only available sustainable source for acrylonitrile in the market, it is only possible to start mitigating the environmental impacts from acrylonitrile production in a short time through this product. Since acrylonitrile production represented in most of the impact categories about half of the total environmental impacts, the use of Econitrile[®] could approximately reduce the impacts by a half, due to its carbon-neutrality. This means that it would significantly reduce the existing environmental impacts resulting from acrylic fibre production. Furthermore, the possibility of being certified by ISCC PLUS would increase the fibres' value in the textile market, also allowing the SGL Composites' clients to get certified if intended, working on the creation of a more sustainable value chain. The main constraint will be the higher cost of Econitrile[®].

5.2. Steam

There are essentially two currently more environmentally sustainable processes for steam production. These two processes are based on the technology of concentrating solar power (CSP) in which there is a steam generation, and on steam generation from biomass combustion.

CSP is a power generation technology, based on renewable energy, in which the sun's rays are concentrated through the use of mirrors, or lenses, usually to heat a fluid, producing steam. Similarly to conventional power plants, a turbine is then driven by the produced steam, generating power ^[102]. There are four different types of this technology: solar parabolic dishes, parabolic trough collectors, solar power tower and linear Fresnel reflectors ^[103]. Parabolic trough collectors is the most established technology. It is possible for CSP plants to be equipped with a heat storage system, which allows the plant to generate electricity even after sunset or in cloudy days. This fact makes CSP more advantageous compared to solar photovoltaics, due to the increase in the capacity factor ^[102]. In Spain, there are already more than 35 parabolic trough power plants ^[103]. Although CSP technology is not currently present in Portugal, there are already plans to bring this technology, especially the one related to parabolic trough systems, to the Southern Portugal, due to the verified high direct normal irradiance levels, and higher

land availability and flatter terrain, compared to the rest of the country ^[104]. In this specific technology, there is a direct steam generation, in which the steam is obtained by the heating of water by a super-hot liquid through a heat exchanger ^[103]. In a LCA study of a parabolic trough CSP plant, the estimated GHG emissions were about 0.026 kg CO_{2,eq.} per kWh (in the study it is not clear whether it is electrical or thermal kWh) ^[105].

In biomass power plants, energy is produced through biomass combustion. Forestry residues can be included as feedstock, for example. All the produced carbon dioxide during the process is absorbed back into the forests and by other natural biomass, not contributing to global warming and mitigating climate change ^[106]. The biomass needs to be subjected to mechanical pre-treatment processes and to be upgraded to improve its characteristics. This improvement will facilitate its handling, transport, and combustion processes ^[107]. The pre-treatment processes are drying, pelletisation and briquetting, and torrefaction for woody biomass, in which it is obtained char. Woody biomass, following torrefaction, is commonly pelletised, then presenting similar properties to coal. Bio-oil, biogas, and solid charcoal are produced through pyrolysis, a thermochemical process which occurs in the absence of oxygen. Bio-oil presents the double of the energy density of wood pellets, while woody biomass presents a value for energy and bulk density 25-30% higher compared to conventional pellets. For the power generation, the technology of fluidised bed combustion presents high efficiencies and low emissions for the biomass combustion. A combined heat and power generation, or cogeneration, allows the efficient conversion of waste heat into steam. In Portugal, there are two biomass plants with steam generators, which are the plants of Fundão and Viseu. These plants present a yearly consumption of biomass of 138 386 tonnes ^[108]. The biomass is supplied in different formats, being essentially from pine and eucalyptus. There is a steam production of 60 tonnes per hour ^[108]. Assuring good quality feedstock at affordable prices for the process may be a challenge, as the biomass supply availability is not constant, being this a key issue for biomass power plants. In the LCA study of Tagliaferri et al. ^[109], assessing the environmental impacts of a biomass cogeneration plant in the UK, it was estimated a saving of almost 0.7 kg CO_{2,eq.} per kWh produced (in the study it is not clear whether it is electrical or thermal kWh).

Regarding carbon dioxide emissions, comparing to power generation through hard coal combustion, values from LCA studies in the range of 0.8 to 1.2 kg of CO_{2,eq.} per kWh produced are reported, presenting significantly higher impacts than the previously mentioned pathways for power generation. Concerning power generation through a

combined cycle by natural gas, values from 0.35 to 0.41 kg CO_{2,eq.} per kWh produced are reported (in these studies it is not clear whether it is electrical or thermal kWh) [110].

Although the alternatives for steam production present benefits from a sustainability perspective, the investment costs for both the alternatives are relatively high. Regarding parabolic trough power plants, through the reported project costs, for example, for the Andasol plant in Spain, with a capacity of 50 MW and a storage capacity of 7.5 hours, it was estimated a total investment cost of 364 million USD [102]. Regarding biomass power plants, for a plant also of 50 MW, the total investment cost is approximately 205 million USD [111]. Due to this fact, it is not expected for SGL Composites to make such an investment only for steam production. These suggestions are here presented to show the eventual possibility of changing the steam source to a more sustainable one, reducing the resulting acrylic fibre production impacts, as the reported emissions of carbon dioxide equivalent were significantly lower for the presented alternatives, compared to the ones reported for the more conventional power plants. As biomass power plants are already present in Portugal and have environmental impact savings, this is the most feasible alternative among the two.

5.3. Dimethylacetamide

N,N-Dimethylacetamide, or DMAc, has been identified as a Substance of Very High Concern (SVHC), mostly due to its associated reproductive toxicity [112]. Being considered as SVHC, DMAc is one of the chemical candidates to the European bans on solvents, regarding the REACH chemical legislation [113]. For this reason, since a long time the industry, including SGL Composites, is making efforts to reduce the use of dimethylacetamide, to improve its recovery rate, or even to replace it. It has been estimated that more than 90% of the total quantified releases of this solvent to the environment are due to the production and use of fibres, namely acrylic and elastane fibres [114].

Dimethylacetamide is a dipolar aprotic solvent, with a high solving power for high molecular-weight polymers, being miscible with several organic and inorganic compounds. DMAc high boiling point, about 166 °C, makes possible for reactions to be carried out at high temperatures, without the need of operating under pressure, unlike other organic solvents [112]. Its polar nature also allows DMAc to perform as a combined reaction catalyst and solvent. It is important that the potential substitutes of DMAc present similar or potentially similar inherent properties to this solvent.

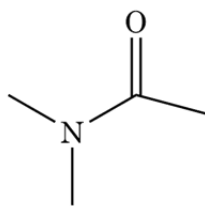


Figure 5.5 – Dimethylacetamide molecular structure.

Dimethyl sulfoxide, or DMSO, has been suggested as being one potential substitute for dimethylacetamide ^[114]. It is usually referred to as being the safest and most competitive alternative among the conventional polar aprotic solvents, being well established in the market. DMSO presents a stronger polar bonding than DMAc and a higher boiling point (189 °C). It is commonly produced from methanol and hydrogen sulphide. In studies regarding solvent selection for this solvent category, DMSO was always preferable than DMAc, being DMAc use undesirable, presenting major issues, and being its substitution requested ^[113]. Nonetheless, DMSO substitution is still advisable, because several chemicals and impurities may induce thermal instability, being potentially reactive. Additionally, some compounds, such as strong bases (*e.g.* sodium hydride), may accelerate the exothermic decomposition of DMSO at lower temperatures. Regarding health risks, DMSO presents a low concern for the human health and for the environment, being of low acute toxicity and not having reproductive toxic effects ^[115]. A patent (US 9,296,889B2) from 2016 by Montefibre to produce acrylic fibres using DMSO as the solvent was found ^[116]. It is stated in this patent that the use of DMSO allows the formation of high polymer concentrated solutions, no corrosion phenomena occurs from its use, DMSO is easily recovered and recycled, and that it presents a low toxicity.

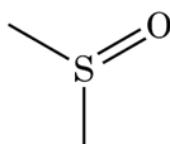


Figure 5.6 - Dimethyl sulfoxide molecular structure.

Since no dimethylacetamide LCA studies were found, it was assessed the available dimethylacetamide production process from the ecoinvent database to compare with the obtained impact results for DMSO production, also assessed from the database, to have a clearer comparison. The impact method used for both the assessments was CML 2001, with a cut-off of 0.1%. Regarding global warming 100a, dimethylacetamide production

emits 3.19 kg CO_{2,eq.} per kg of produced solvent, while DMSO production emits 1.34 kg CO_{2,eq.} per kg of produced solvent, a value approximately 2.4 times lower. Concerning human toxicity 100a, a critical aspect of DMAc, the impact result for dimethylacetamide was 1.36 kg 1,4-DB_{eq.} per kg of produced solvent. For DMSO, this value was about 2.1 times lower, of 0.64 kg 1,4-DB_{eq.} per kg of produced solvent, confirming its lower toxicity concerns.

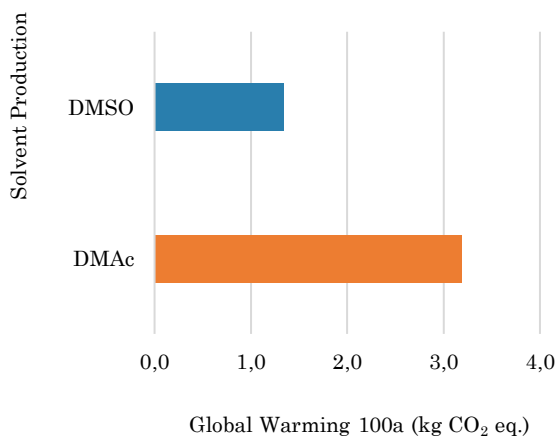


Figure 5.7 - Global warming 100a for 1 kg of produced solvent.

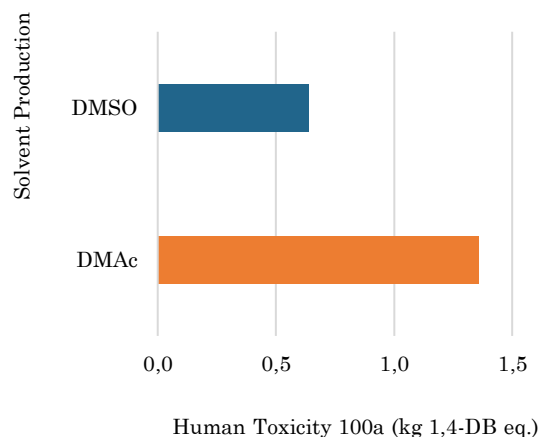


Figure 5.8 – Human toxicity 100a for 1 kg of produced solvent.

Regarding greener, more sustainable, and alternative solvents, there are two solvents which have been suggested as potential substitutes for dimethylacetamide: cyrene and γ -valerolactone, or GVL [117]. Both solvents are derived from renewable sources.

Cyrene, or dihydrolevoglucosenone, is a cyclic ketone produced from cellulose. Cellulose is converted to levoglucosenone, which is then hydrogenated to cyrene [117]. This reaction may be conducted in an auxiliary solvent-free environment, giving also economic advantages to the process. Its boiling point has been already determined, being approximately 203 °C, although a more precise analysis is still being necessary [118]. Cyrene, compared to other dipolar aprotic solvents, is the most similar with dimethylacetamide concerning the polar interactions, and the most similar to DMSO regarding a dispersion perspective [117]. Being a bio-based solvent, lower environmental impacts are expected. No LCA studies regarding cyrene were found. It is already being commercialised by the Circa Group [119]. Concerning toxicity studies, cyrene is not considered to be acutely toxic and it is not considered to be a concern for both human health and the environment [120]. Although seeming a promising solvent, cyrene applications are still being investigated and it is still required further technical investigations, especially to ensure its stability and to ensure that its degradation during the production processes is avoided.

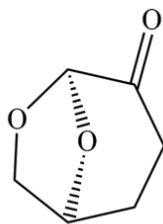


Figure 5.9 - Cyrene molecular structure.

γ -Valerolactone, or GVL, may be produced through the hydration of hydroxymethylfurfural to levulinic acid from cellulose, or through the hydrogenation of furfural to furfuryl alcohol, being then hydrolysed to levulinic acid, after the acid hydrolysis of the biomass into glucose and other sugars [121]. Levulinic acid is then hydrogenated and dehydrated to GVL. GVL presents a boiling point of approximately 207 °C, it does not decompose at room temperature, and it is considered to be stable and non-toxic, not presenting any risks to both the human health and environment [117]. It has a high polarity, presenting a similar polarity to dimethylacetamide [121]. A patent from 1955 regarding the production of acrylonitrile polymers, already mentioning the use of GVL as a possible solvent, was found [122]. No LCA studies were also found for this green solvent to compare with dimethylacetamide production. Currently, the high production costs of GVL limit its industrial applications [117].

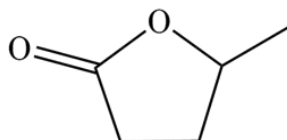


Figure 5.10 - γ -Valerolactone molecular structure.

Comparing the two bio-based solvents, GVL has been more investigated and applied to different possible applications. Cyrene is more recent, and more research must be developed to understand its applicability. Nonetheless, both solvents require further research to better study their applicability in the processing of acrylic fibres. The cyrene production process is simpler, but there are more concerns regarding its stability than with GVL stability. A concern that both production processes still present deals with the process of hydrogenation, that requires H₂, which is still produced from steam reforming, a process based on fossil feedstock [117]. It is hoped that soon the sustainable hydrogen industry provides a solution for this matter. The production of GVL presents higher costs when compared to cyrene, but it is stated that the production cost for both of them is

about 3 USD per kilogram, comparable to other high-end dipolar aprotic solvents, but about the double price of the conventional dimethylacetamide [117].

Although cyrene and GVL seem promising alternative solvents for the dimethylacetamide substitution, this substitution, especially at an industrial scale, may only be possible in a few more years. This way, to reduce the toxicity related impacts with dimethylacetamide production, DMSO seems to be a suitable alternative for the production of acrylic fibres.

5.4. Fibre Dyeing

Since the dyed fibre was the one which presented the higher impact results (despite the fact that the impacts may have been overestimated, taking into account the chemicals that had to be considered), an improvement on the dyeing process would also be important to mitigate the impacts resulting from acrylic fibre production.

The use of enzymes to improve acrylic fibre dyeability has been reported. The polymer's hydrophobic nature makes the dyeing process more difficult. Other concern regarding acrylic fibre, is the usual irreversible yellowing of the fibre, resulting of the occurring hydrolysis at the surface of the fibres, which may be improved through selective enzymatic hydrolysis [123]. It was verified that the surface modification of polyacrylonitrile (PAN) by a nitrile hydratase and amidase, makes the fibre more hydrophilic, improving the fibre articles wear comfort, improves the fastness of some finishes, and enhances the adsorption of the dye [124]. The nitrile groups are hydrolysed into carboxylic groups, or into amides, at the fibre surface, which allow the adsorption of more dye into the fibre. Other benefits from the incorporation of enzymes in the process, are the enhanced catalytic efficiency through the use of nitrilases, improvements on energy savings, and the fact that the use of nitrile hydratase and amidase allows the reduction of the release of ammonia from PAN [123, 124]. The use of these enzymes is most recommended for wet-spinning, and the industrial recovery of the enzymes, as well as the elimination, would require pH/temperature shifts and size exclusion chromatography processes [125, 126].

The use of dye controllers is also important [67]. The controllers analyse the process conditions and alter the parameters to optimise the dyeing conditions, such as pH, colour, salt, and chemical levels, based on liquor ratio and temperature. They also have the ability to control the amount of water used in the dyeing process, consequently controlling the amount of produced effluents. This aspect is significant, because the

amount of waste chemicals in the effluents is dependent on the dye liquor ratio. It is also possible to use low liquor ratio dyeing machines, although more impact savings are related to the controllers. The estimated savings were 28% for the dyeing machines and 70% for the controllers, regarding water use, according to Beton et al. [67]. Concerning chemical use, it was estimated a saving of 59% for the controllers.

A remark that should be made is that the gel-dyeing technology, or in-line dyeing, is a more eco-friendly process than off-line dyeing [127]. Off-line dyeing means that the dyeing of the raw white fibre is performed at the next stage of the supply chain, not at the fibre production plant. Gel-dyeing uses less energy, water, and chemicals during the dyeing of the fibres. Additionally, a more efficient consumption of the dyes is verified, consequently discharging less harmful chemicals to the environment [128]. According to a LCA study about the 'Thai Acrylic Fibre' Radianza® gel-dyed fibre production, it was reported that, by using this fibre to make one garment, up to 30 litres of water could be saved, it consumes approximately less 25 MJ of energy, and regarding global warming potential it creates less 1.45 kg CO_{2,eq.} [129].

5.5. Fibre Recycling

The recovery of waste fibre and its recycling within the acrylic fibre production process would minimise waste generation and add value to the final product, acrylic fibre. Besides the environmental benefits through the recovery of waste fibre and its reuse, which otherwise would end up in a landfill, this recycling process would also allow the certification of the eco-label Recycled Claim Standard (RCS) [55]. This eco-label may be requested to certify any product containing 5-20 wt.% of recycled material. Each production process has to be certified.

Aksa, the major producer of acrylic fibre worldwide, started in 2019 on a commercial scale the production of Acrycycle®, a recycled acrylic fibre completely constituted by pre-consumer material [130]. Raytent, a project from an Italian textile producer, is dedicated to the recycling of acrylic fabric from the awning industry, in which 10% of the fabric is discarded for each made tent [131]. Their produced acrylic yarn is constituted by 50% of recycled fibre and it is stated that its quality is not compromised. Shimi Research Center, in India, recycles acrylic fibre waste into the polymer powder, polyacrylonitrile [132]. The polymer can be used again as raw material to produce acrylic fibre and no changes in the fibre properties are reported. Its production technology patent was found, in which it is stated that the production costs are reduced, and that the intrinsic viscosity of the recycled PAN powder was approximately equal to 1.40 ± 0.02 , which matches the value

for the original PAN polymer [133]. For its determination, a 0.2% w/v solution of polymer in 0.2 M lithium bromide/DMF at 25 °C was used. The first stage of the process is the dissolution of waste acrylic fibre in a solvent, such as DMAc, in a 1-25% concentration at a temperature lower than 90° C. Then follows a filtration process to remove non-dissolved compounds and other impurities. The precipitation of the polymer occurs in an aliphatic primary, secondary, or tertiary alcohol, such as methanol, ethanol, or n-propanol, in a 1:1 to 1:10 v/v ratio of polymer solution to alcohol. Following precipitation, vacuum filtration is performed to remove the solvent and the precipitating agents, and the polymer is dispersed in deionised water (1:5 to 1:20 w/v) to remove the existing residual solvent. Then filtration occurs to be obtained the purified polymer. The wet precipitate is directly dried or pelletised before the drying process. Finally, to obtain fine PAN powder, the dried polymer is pulverised and sieved. All the used solvents are recovered and reused.

In addition to the all presented suggestions for the environmental performance improvement of acrylic fibre production, two other aspects may also be improved that could also reduce the impacts. Concerning the production itself, an optimisation of commodities consumption, especially regarding steam consumption, should always be sought. Another aspect is the seeking of raw material suppliers which are closer to the plant compared to some current ones, such as the acrylonitrile supplier, reducing the impacts regarding raw material transportation.

A cost-benefit analysis would have been important to better understand the applicability of all the suggested proposals for environmental performance improvement. This analysis was not possible to develop in this study due to time limitations. Nonetheless, the development of a cost-benefit analysis is suggested for future works.

6. Conclusions and Proposals for Future Work

6.1. Conclusions

The LCA methodology allowed the assessment of the impacts resulting from the production of raw white (L11), dyed (L25), and pigmented (L28) acrylic fibres. After the goal and scope definition, the life cycle inventory (LCI) of this cradle-to-gate study was possible through all the process data provided by SGL Composites. Following the LCI, the life cycle impact assessment allowed to analyse the most critical aspects on the production of these fibres on an environmental perspective.

The dyed fibre presents the most environmental concerns since it had the highest environmental impacts in eight out of twelve impact categories. Despite this fact, it was not verified a significant difference in the environmental impacts between the three fibres. This difference was higher regarding human toxicity, acidification, and photochemical oxidation. Concerning the human toxicity, it was clear that the dyed fibre was the one with the most concerns. As in the majority of LCA studies, some assumptions and simplifications were assumed in the LCA model constructed in the present work. Some of them were related to the absence of auxiliary chemicals, dyestuffs, and pigments from the ecoinvent database. Although the results obtained are in line with the data reported in the literature, the extent to which the results were affected by these assumptions and simplifications may be studied in future works.

Acrylonitrile production was the major contributor to the environmental impacts. It represented, roughly, half of the estimated impacts. The biggest contributors following acrylonitrile production were the steam and dimethylacetamide productions. Benzimidazole production, concerning the dyestuff of the dyed fibre, also presented some significant impacts for this fibre, especially in terms of human toxicity, being the major contributor in this impact category for the dyed fibre.

The production area of continuous polymerisation (CP) accounted for most of the impacts, mostly due to its association with acrylonitrile. This is mostly because it is in the CP area that this raw material is introduced in the overall process. The spinning area (SP) was also associated with a significant contribution to the impacts, especially concerning the raw white and dyed fibres. It was verified that the addition of the auxiliary compounds, the dyestuffs, and of the pigment dispersion, had an impact on the contribution of each production area. Being SP the area where most of these chemicals are introduced for L11 and L25 fibres, its higher contribution compared to the dope preparation area (DP) makes sense. A higher contribution of the DP area, in which the

pigment dispersion is added, for example, was verified for the pigmented fibre. The cut and baling area (CB) did not represent a significant contribution for any of the impact categories. The existing solvent recovery area (SR) reduces the environmental impacts resulting from acrylic fibre production, presenting impact savings.

To effectively reduce the impacts from the production of these fibres, actions regarding acrylonitrile, steam and dimethylacetamide should be taken and prioritised, due to the fact that their production was what mostly contributed to the environmental impacts. For this reason, the suggested proposals and developed research concerned mainly acrylonitrile, steam, and dimethylacetamide. Proposals regarding fibre dyeing were also presented, especially because the dyed fibre had the highest environmental impacts. The matter of fibre recycling was also presented for impact minimisation and for the possible RCS eco-label certification.

Regarding acrylonitrile, its production from glycerol, glutamic acid, lactic acid, and biomass is still on a research level. One option for a more sustainable acrylonitrile is already on the market, Econitrile®. This product is produced from both sustainable propylene and ammonia and it is considered to be a carbon neutral product. This means that, through Econitrile®, there is the possibility of reducing up to half of the impacts, considering that acrylonitrile production generally represented half of the estimated impacts.

For steam, its source from the CSP technology, or from biomass, are currently the most sustainable alternatives. These suggestions were only presented as possible sources for steam, as the investment costs for steam production through these two pathways are significantly high.

Concerning the solvent, dimethylacetamide (DMAc), dimethyl sulfoxide is currently one of the best substitution alternatives, due to its reduced toxicity compared to DMAc. The bio-based alternative solvents cyrene and γ -valerolactone present the highest potential to replace dimethylacetamide in its applications, although their own use for fibre production is still being currently researched.

The suggestions regarding fibre dyeing by the use of enzymes and dye controllers aim to reduce the hazardous chemical usage and the amount of produced effluents, reducing the environmental impacts. Through fibre recycling, based on its reprocessing in the acrylic fibre production process, the generation of waste fibre would be minimised, and the environmental impacts would be reduced.

The assessment and identification of the environmental impacts resulting from acrylic fibre production at the SGL Composites plant, allows the company to act towards its mitigation and contributing for the introduction in the market of more sustainable acrylic fibres.

6.2. Proposals for Future Work

Although the developed work in this master thesis already presents significant advances regarding the company's sustainability goals, further work could still be developed in the future. Through the future work, this study could still be improved and complemented. Some suggestions for future work are as follows:

- i. The development of a LCA study using other databases which include the necessary dyes, pigments, textile finishing products, and other chemicals that were not available in the used database and let to its replacement by other chemicals. Alternative databases suggested are the GaBi database (extension XV of Textile Finishing) regarding the dyestuffs and other finishing compounds, and the Evah Pigments Database for the pigments;
- ii. Study the extent to which the results were affected by the made assumptions and simplifications in this work, through an uncertainty study;
- iii. The inclusion of acrylic fibre baling in the LCA study;
- iv. The development of comparative LCA studies especially regarding the comparison between this LCA study and the impact assessment of changing the source of acrylonitrile, steam, and dimethylacetamide;
- v. A LCA study in which it would be included the process of waste fibre recycling could also be developed, allowing the evaluation of the impact savings from this process. This study would also be important regarding an eventual RCS certification;
- vi. The estimation on how much the value of acrylic fibre would be increased due to the changing of the acrylonitrile source for Econitrile®, for example, and considering the recycling of waste fibre. This estimation would be interesting to develop due to the fact that both the possible ISCC PLUS and the RCS certifications, resulting from using Econitrile® and recycling waste fibre in the process, would have an impact on the acrylic fibre cost;
- vii. For the particular case of the in-line dyed acrylic fibre, a comparison with the conventional raw white off-line dyeing process could also be undergone to evaluate the actual benefits of in-line dyeing *vs.* off-line dyeing.

- viii. A cost-benefit analysis should be developed to study all the suggested proposals for environmental performance improvement.

7. References

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