

Solvent-based dye removal in polyester recycling

A process evaluation and modelling study

by

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Preface

This master thesis was presented to us during a meeting with our supervisor Christian Hultberg. He is one of the co-founders of the company Rewin Textiles AB, and during this discussion, he mentioned the issue of decolourising fabrics in polyester recycling. This caught our attention and led us to choose this problem as our master thesis topic. Therefore, we want to thank him for bringing us on this project and for all the support he has given us.

To deepen our knowledge within the area of fabrics and textile recycling, we have discussed the issue with additional sources. Thus, we would like to thank Anders Arkell for broadening our knowledge of Rewin and for giving us valuable insights on potential solutions. We also want to thank Anna Edsberger from RISE for her helpful inputs and giving us the confidence in our methodology. Additionally, we are thankful for the help from Joakim Karthäuser at SiOX machines and Lotta Turner from Lund University about supercritical carbon dioxide systems. Lastly, for the aid in Aspen Plus modelling, we would like to thank both Ola Wallberg and Edvin Bågenholm-Ruuth from Lund University.

This thesis concludes our academic journey at Lund University as students of the environmental engineering program. We are grateful for this time and for all the support we have been given from our friends and families. Therefore, our final thanks go to them, we could not have done it without you.

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Abstract

The transition towards sustainable textile approaches, such as textile recycling, requires improved methods for handling dyes. Currently, no real industrially implemented processes exist that remove dyes without damaging them and this thesis investigates this issue together with Rewin Textiles AB. This company recycles polyester through depolymerisation and therefore, the implementation of a pre-treatment step using a solvent for dye-extraction purposes is evaluated. Five solvents are assessed: DMSO, benzyl alcohol, Cyrene, supercritical carbon dioxide, and ethylene carbonate with tetramethylurea. DMSO exhibits the most favourable overall trend, taking into consideration toxicity, process practicality, extraction efficiency and cost.

Rewin aims at recycling 5000 kg/h polyester and according to experimental values found, 25,000 kg/h DMSO is needed to extract 87 % of dyes after one cycle of 30 minutes at 100 °C. This constitutes the basis of the recommended flowsheet, which instead includes three cycles implemented through a counter-current batch process. After dye extraction, polyester is cleaned with water, whilst the dye is separated from DMSO through precipitation. To improve the precipitation behaviour of dyes, Aspen Plus was used to model a single evaporator representing a three-stage evaporator, achieving a 90 % removal rate of DMSO at 0.16 bar and 130 °C. Following, 660 kg/h of water is mixed in the DMSO-dye solution to trigger the dye to precipitate, which is then filtered out. Lastly, DMSO and water are recovered through distillation. The solvent cost is 351 million SEK per year with a recirculation rate of 95 %, which represents a higher cost than what can be saved through the process.

Overall, the thesis showed that a solvent-based pre-treatment step is a promising process to separate dyes from polyester. However, due to many assumptions and limitations, the presented results should be taken with precautions, and further research is needed.

Keywords: Polyester recycling; Disperse dyes; Dye extraction; Solvent-based decolourisation; Hansen Solubility parameters; Process modelling; Aspen Plus

Sammanfattning

Övergången till en hållbar textilindustri, såsom textilåtervinning, kräver förbättrade metoder för hantering av färgämnen. För närvarande finns inga generella, industriellt implementerade processer som avlägsnar färgämnen utan att skada dem, och examensarbetet undersöker detta tillsammans med Rewin Textiles AB. Företaget återvinner polyester genom depolymerisering och därför utvärderas implementeringen av ett förbehandlingssteg med ett lösningsmedel för extraktion av färgämnen. Fem lösningsmedel undersöks: DMSO, bensylalkohol, Cyrene, superkritisk koldioxid och etylenkarbonat med tetrametylurea. DMSO uppvisar den bästa övergripande trenden, med hänsyn till toxicitet, praktisk genomförbarhet, extraktionseffektivitet och kostnad.

Rewin strävar efter att återvinna 5000 kg/h polyester och enligt experimentella värden behövs 25,000 kg/h DMSO för att extrahera 87 % av färgämnena efter en cykel på 30 minuter vid 100 °C. Detta utgör grunden för det rekommenderade flödesschemat, som i stället inkluderar tre cykler implementerade med en motströms batchprocess. Efter extraktionen av färgämnen, rengörs polyestern med vatten, medan färgämnet separeras från DMSO genom utfällning. För att förenkla utfällningen hos färgämnena användes Aspen Plus för att modellera en enskild indunstare som representerar en trestegsindustare, som åstadkommer en borttagning på 90 % av DMSO vid 0.16 bar och 130 °C. Därefter blandas 660 kg/h vatten i blandningen av DMSO och färgämne för att få färgämnet att fällas ut, som sedan filtreras bort. Slutligen återvinns DMSO och vatten genom destillation. Kostnaden för lösningsmedlet är 351 miljoner kronor per år med en återcirkulering på 95 %, vilket representerar en högre kostnad än vad som kan sparas genom processen.

Slutligen visade examensarbetet att ett förbehandlingssteg som använder lösningsmedel är en möjlig process för att separera färgämnen från polyester. På grund av antaganden och begränsningar bör dock de presenterade resultaten tas med försiktighet, och ytterligare forskning behövs.

Nyckelord: Polyesteråtervinning; Dispersionsfärger; Färgextraktion; Lösningsmedelsbaserad avfärgning; Hansens löslighetsparametrar; Processmodellering; Aspen Plus

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List of abbreviations

δ_D	Dispersion solubility
δ_H	Hydrogen bonding solubility
δ_P	Polar solubility
δ_T	Total solubility parameter (Hildebrand solubility)
BA	Benzyl alcohol
BHET	Bis(hydroxyethyl) terephthalate
CED	Internal cohesive density
Cyrene	Dihydrolevoglucosenone
DCM	Dichloromethane
DEG	Di ethylene glycol
[D]_{f,eq}	Equilibrium dye molality on the fibre (mol*kg ⁻¹)
[D]_{s,eq}	Equilibrium dye concentration in the bulk solution (mol*dm ⁻³)
DMT	Dimethyl terephthalate
DMSO	Dimethyl sulfoxide
DR60	Disperse Red 60
EC	Ethylene carbonate
EG	Ethylene glycol
E_v	Molar energy of vaporisation
HSP	Hansen solubility parameter
HTHP	High temperature high pressure
K	Equilibrium sorption constant
MEG	Mono ethylene glycol
MLR	Material-to-liquid ratio
MSE	Multi-stage evaporators
NRTL	Non-Random Two-Liquid
PET	Polyethylene terephthalate

R_a	Radius of interaction
R_o	Radius of solubility
RED	Relative energy difference
scCO₂	Supercritical carbon dioxide
TEG	Tri ethylene glycol
T_g	Glass temperature
TMU	Tetramethylurea
TPA	Terephthalic acid
UNIFAC	Universal Quasichemical Functional-group Activity Coefficients
V_m	Molar volume
wt%	weight percentage

1 Introduction

Textiles have been used for a very long time, with the earliest known example being woollen fabrics discovered in southern Turkey dating back to around 6000 B.C. [1]. Since then, numerous types of textiles have been uncovered along with many weaving techniques, most of which originated in Asia and the Middle East. The earlier production of textile was mainly done through manual labour, with difficult and time-consuming dyeing processes. However, with new inventions such as the loom and the much later spinning wheel, productivity increased drastically. Especially once the industrial revolution took place with innovations such as the Spinning Jenny, mechanical production rapidly expanded, leading to a skyrocketing mass production of textiles. Today, with synthetic materials dominating the market and the making of a T-shirt taking 1-5 minutes on a large industrial line, textiles hold a large share of the global market [2].

The production of textiles today causes 6 to 8 % of the global carbon dioxide emissions, with most of the synthetic materials being made from petrochemical sources [3]. Due to fast-fashion companies and the constant emergence of new fashion trends on social media, these emissions are projected to increase. Along with the rapid manufacturing, a lot of textile waste is continuously accumulating and being discarded. Additionally, during the dyeing process of textiles, about 10-15 % of dyes end up in wastewaters. These dyes are often extremely persistent and may contain heavy metals, acids, alkalis and other toxic organic compounds, which can cause great damage to aquatic life [4]. Further issues with textile production are that it is an extremely water- and energy-intensive industry and many dyes are carcinogenic, toxic and non-biodegradable.

In Sweden, a consumer purchases between 13 to 15 kg of new clothing and home textiles every year [5]. Various studies have shown that there is about $\frac{1}{3}$ of clothes in a wardrobe that are unused and once these garments get discarded, they are often thrown away in the residual waste and incinerated, despite being undamaged. On average, a Swede discards 7-9 kg of textiles each year. As part of the Waste Framework Directive, the European Union has implemented that as of January 1st, 2025, textiles must be separately collected to facilitate their reuse and recycling [6]. Whilst reuse is the optimal option in minimising the environmental effects caused by the textile industry, recycling is needed for the garments that are torn and damaged. Currently, only about 1 % of textile waste in the EU is recycled. However, a recent study showed that if 10 % of textiles are recycled, the EU could save approximately 440,000 tonnes of CO₂ equivalents a year, which is comparable to removing 90,000 cars from the roads [7].

There exists a variety of different recycling methods of textiles, both mechanical and chemical [8]. Most of them show very promising results in the creation of new textiles, with high conversion rates and good quality. However, they all face a major limitation, which is the removal of dyes. Dyes are considered to be an impurity and common methods for removing them destroys the dye molecule, which makes it lose its ability to show colour. As the EU wants to move towards a more circular approach at all levels, it is necessary to find a solution of removing dyes without destroying their molecular structure and potentially explore the recycling of dyes as well.

1.1 Dye removal today for polyester

Currently, dye removal processes today mostly aim at recovering the textile fibre to virgin conditions, while the dye molecules are often damaged or destroyed [9]. There are two types of dye removal approaches, where the first one is called dye destruction. This results in the destruction of dye particles to smaller fragments, therefore destroying the part of the dye molecule that is responsible for the colour [10]. Techniques such as oxidation, oxidising the dye molecule and thus destroying the part that is responsible of colour, or reduction, breaking the dye molecule into smaller parts, can be used for this purpose. However, these methods can also cause substrate degradation, which would therefore reduce the quality of the recycled fibre.

The other option of removing of dye is dye extraction, which relies on detaching the dye from the substrate without altering the dye's molecular structure [10]. This can for example be done by using a solvent to release the dye from the textile structure. This approach reduces the risk of textile degradation, as it usually only swells the fibre and release the dye from entrapment in the fibre. For example, DyeRecycle is a London-based company which performs solvent-based extraction to recover both dye and textile intact [11].

However, a more common dye removal process is rather an indirect removal process [9]. During textile recycling, the process breaks down the textile fibres into smaller constituents, such as monomers or oligomers, which weakens the bond between the dye and the fibre. This leads to the desorption of the dye from the polyester. Nevertheless, this process can cause dye damage or dye destruction, leading to hazardous waste accumulation.

1.2 Project description

This thesis is investigating alternative dye removal techniques that do not damage the structure of both the dye and the fibre. Therefore, dye-extraction techniques are preferred over dye-destruction ones. The project is carried out along with Rewin Textiles AB (Rewin), a company focusing on the recycling of polyester textiles using chemical recycling through glycosylation with the help of a catalyst. Therefore, the focus is to study dye-extraction techniques that remove dyes from polyester fabrics. Today, Rewin removes the dyes after the catalytic reaction, which is where the depolymerisation of the polyester occurs. The dye-removal happens due to the breaking down of polymers to oligomers and monomers, which results in the dye desorption explained earlier and Rewin believes that the dye is destroyed or damaged by the catalytic reaction. This creates impurities in the product stream, which may reduce the quality of the product or the lifetime of the catalysts. Therefore, and for other reasons listed in the report, identifying techniques that can extract dyes before depolymerisation is essential for improving their process.

Due to the relatively weak bonds between dyes and polyester fibres, a simple solvent-extraction technique could function as an effective pre-treatment process for Rewin. Therefore, this thesis investigates several possible solvents that can be appropriate to the Rewin process in terms of sustainability, economic viability and practicality. Previous studies on solvent-based dye-extraction techniques have shown limitations, due to an inefficient dye-removal process, high solvent-to-material ratios or the use of a toxic solvent, such as DMF [10]. Additionally, many studies focused more on identifying solvents that has a high dye solubility, rather than weakening the bonds between dye and fibre, which is essential to achieve an efficient dye-removal process.

1.3 Aim

The aim of this thesis is to evaluate different solvents for removing dyes from polyester fabrics, which is done through an extensive literature review. Furthermore, an objective is to expand the understanding of the decision process of which solvent to choose depending on multiple factors such as environmental impact, cost and chemical relationship between the solvent, the fibre and the dye. Additionally, the study aims to create an overall process flowsheet to then perform a more detailed modelling for the solvent that shows the highest potential. This will be performed in Aspen Plus V14, which is a tool that allows the user to model chemical processes. A simple techno-economic analysis is also performed to further assess the feasibility of the selected solvents. The study is limited to existing literature and focuses on the upscaling of their results into an industrial scale as well as matching their processes with Rewin Textile AB's input to their process. The research questions for this study are as follows:

1. Which solvents and operating conditions yield the most efficient and sustainable dye removal performance from polyester textiles?
2. How do environmental impact, toxicity, and economic cost influence the selection of solvents for dye removal in large-scale textile recycling?
3. What separation methods and process conditions enable effective recovery and reuse of the solvents used for dye removal in polyester recycling?

1.4 Scope

The study provides a literature-based evaluation rather than an experimentally validated process design. It is limited to polyester fibres and disperse dyes, which are the most common dyes used when dyeing polyester. Furthermore, solvent-based dye removal methods are thoroughly studied, with a focus on dye removal efficiency, environmental impact, economic feasibility, and chemical compatibility. All the parameters in the Aspen Plus modelling comes from either experimental data provided by the found sources from the literature study, through other sources or by estimation. The modelling of polyester in Aspen Plus is as a solid without any relationship with either the dye or solvent for simplicity. Furthermore, the solubility between dyes and solvents is based on calculations and plots performed by Aspen Plus. Lastly, the economic assessment is simplified and does not include a detailed estimation of all the necessary costs for such a pre-treatment.

This thesis has used AI tools to support the structuring of the report and for language revision of the text. All text has been reviewed to ensure academic integrity.

1.5 Disposition

The report is structured into five sections, with the introduction as the first one. Then, the background chapter describes textiles, dyes and textile-recycling processes. The methodology presents criteria for solvent selection, findings from the literature review, and identified separation techniques for recovering solvents and dyes. It also outlines the overall process flowsheet and introduces the Aspen Plus framework used to simulate and upscale the selected process. The results and discussion combine analysis of solvent performance, environmental and economic evaluation, and detailed proposed flowsheets for industrial implementation. The report concludes with key findings, limitations, and suggestions for future research.

2 Background

Firstly, the background introduces textile and fibres with focus on polyester. This section covers the production of polyester, followed by a thorough explanation of its chemical structure and properties. Secondly, dyes are presented, including their history, classification and properties, to then go more specifically into the dye that colours polyester fabric and its processes. Finally, various textile recycling methods are presented, to lastly focus on the Rewin Textile process.

2.1 Textiles and fibres

Textiles and fibres are the foundation of dyeing, because without the substrate, the application of colour would have no purpose. In this section, textiles and different types of fibres are explained. This is done to provide a broader knowledge of fibres, in this case polyester, and its mechanical and physical properties.

2.1.1 Classification of fibres

A wide variety of fibres are available on the market, and in this section, the most common types are discussed. A regular way of classifying fibres is by their origin, if they are either natural or man-made [12]. Based on this distinction, a classification tree of the types of fibres that exist can be established, Figure 1.

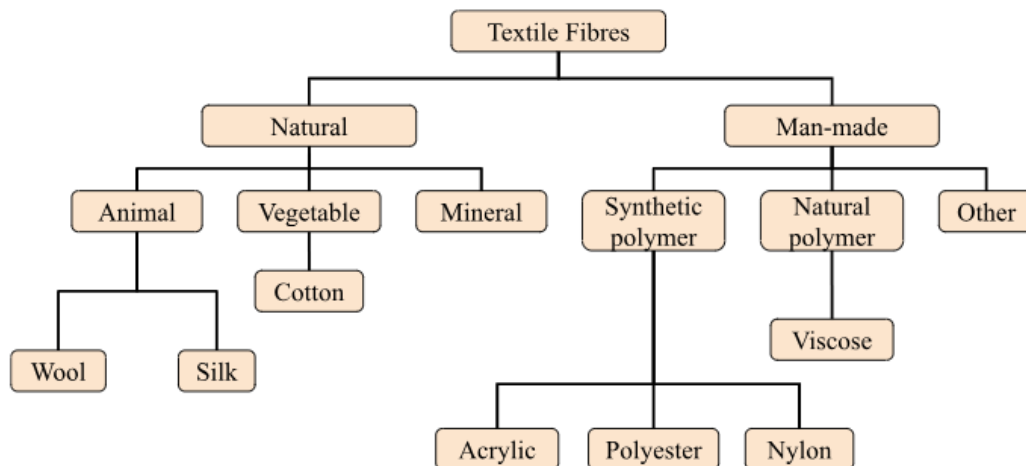


Figure 1: Classification tree of common fibres. Adapted from [12].

Cotton

Cotton fibre is the second most common type of fibre in the global market after polyester, accounting for 20 % in 2023 [13]. It is a natural fibre and is almost entirely made of cellulose, from seeds of a cotton plant [12]. The cotton has a twisted ribbon-like structure, and its chemical structure has both crystalline and amorphous regions. The semi-crystalline structure gives cotton both strength and softness in the fibre. Furthermore, it has a high moisture absorption capacity, making the textile especially pleasant in warmer climates. However, the fabric wrinkles easily and can also hold onto water longer, which can lead to some issues when blended with synthetic materials.

Wool

Another natural fibre is wool, which, unlike cellulosic fibres, is a protein-based fibre that comes from the fleece of sheep and other animals [12]. The surface of the fibre is covered by overlapping scales and the internal structure is made up of keratin as the building block. It is the keratin that provides the fibre its natural crimp and elasticity, giving it a resilience to being stretched out [14]. Moreover, wool can absorb much moisture without giving the feeling of being wet and the crimp can trap air which leads to a great thermal insulation [12]. The market fibre shares for wool in 2023 was 1 % [13].

Silk

Silk is also a natural protein fibre, which is produced from the excretion of silkworms and collected as a continuous filament [12]. The chemical structure is highly crystalline, which gives the silk an extraordinary tensile strength, especially in relation to its fineness in the filament. Even though silk is seen as a smooth and luxurious fabric, it can lose strength when wet and is sensitive to abrasion, meaning that it is not able to withstand wear and repeated use. Thus, it is only used in limited apparels, as seen in the market fibre share of 0.1 % [13].

Viscose

Viscose is made of chemical processing of natural cellulose and often comes from wood pulp [12]. The cellulose is regenerated into filaments, and the resulting viscose can exhibit many properties similar to those of cotton. Furthermore, it also has silk-like appearance, as the fibres are moderately weak and have poor abrasion resistance. Viscose is often mixed with other stronger fibres to improve its performance, and it holds the majority of man-made cellulosic materials, accounting for 5 % of the fibre market [13].

Polyester

Synthetic fibres, such as polyester, have a low production cost due to the abundance of the raw material, crude oil [15]. This facilitates a fast and large-scale production of the man-made textile material. Further, polyester has many versatile properties such as being lightweight, durable and resistant to wrinkles and shrinking. These properties together with the low production costs makes the material desirable for many fast-fashion companies, that build their business models on being cheap and providing new clothes rapidly. In 2023, polyester holds the highest market share out of any fibre at 57 % [13].

Nylon

Nylon is a synthetic polyamide fibre and has great strength and elasticity [16]. Additionally, it can withstand abrasion and is lightweight with a smooth surface, where one of its major uses has been for hosiery. However, as the absorbency is low, the textile is not suitable for warmer climates. It has a market fibre share of 5 % [13].

Acrylic

Acrylic is a synthetic fibre made of polyacrylonitrile that is designed to mimic the properties of wool, due to it being warm, soft and lightweight [12]. As acrylic fibre can withstand both sunlight and many chemicals, it has a good outdoor durability. Its low moisture regain allows it to dry quickly, but it is less breathable than natural fibres. In 2023 acrylic accounted for 1 % of the market fibre share [13].

2.1.2 Polyester

As mentioned in the introduction, the focus of this report is on polyester due to Rewin's process. According to a report from 2024, polyester holds the highest market share out of any fibre with the increase from 67 million tonnes in 2022 to 75 million tonnes in 2023, and prognoses suggests that it is only going to increase [13].

Polyester was first introduced in 1941 when chemists Whinfield and Dickson were able to create filament out of polyethylene terephthalate, otherwise known as PET, which today stands for the largest type of polyester [17]. PET is most known to be used in plastic bottles, but $\frac{2}{3}$ of manufactured PET is actually used for polyester textile production. From this point onwards in the report, PET used for textiles is referred to as polyester. Polyester can be manufactured through two different methods, either the dimethyl terephthalate method or the terephthalic acid method [16].

DMT method

Dimethyl terephthalate (DMT) and mono ethylene glycol (MEG) react together in a transesterification process with the presence of a catalyst to create the monomer bis(hydroxyethyl) terephthalate (BHET) [16]. Transesterification refers to the reaction of an ester, DMT, with an alcohol, MEG, where the ester's alcohol group is displaced and replaced by the new alcohol into a new ester [18]. Then, polycondensation polymerisation of the BHET is done at 265-285 °C to achieve the long polyester chains [16]. Polycondensation polymerisation is a stepwise reaction, which can also be chain growth, where monomers react to form longer polymer chains and releases a small molecule, which in this case is an alcohol. The transesterification is seen in Figure 2 a) and the polycondensation is seen in Figure 2 c) below. This process was widely used during the earlier years of polyester production but is much less used today, as the process requires a lot of energy and produces methanol as a byproduct.

TPA method

The most common method of producing polyester is through the terephthalic acid (TPA) method [16]. This involves TPA and MEG in an esterification reaction with a metal oxide catalyst at a temperature of 250-290 °C. Esterification here means the reaction of a carboxylic acid, TPA, and alcohol, MEG, to produce an ester. The reaction yields the monomer BHET, as well as water as a byproduct. To drive the reaction forward, the water needs to be removed. The second step is a polycondensation polymerisation of the BHET monomer to produce the polymer chains, whilst removing ethylene glycol (EG) in the process. BHET is seen as the building block for polyester. This process continues until the desired polymer weight and chain length is reached for the polyester [19]. The TPA method reaction chain can be seen in Figure 2 b) which shows the esterification and the polycondensation is seen in Figure 2 c), same as for the DMT method.

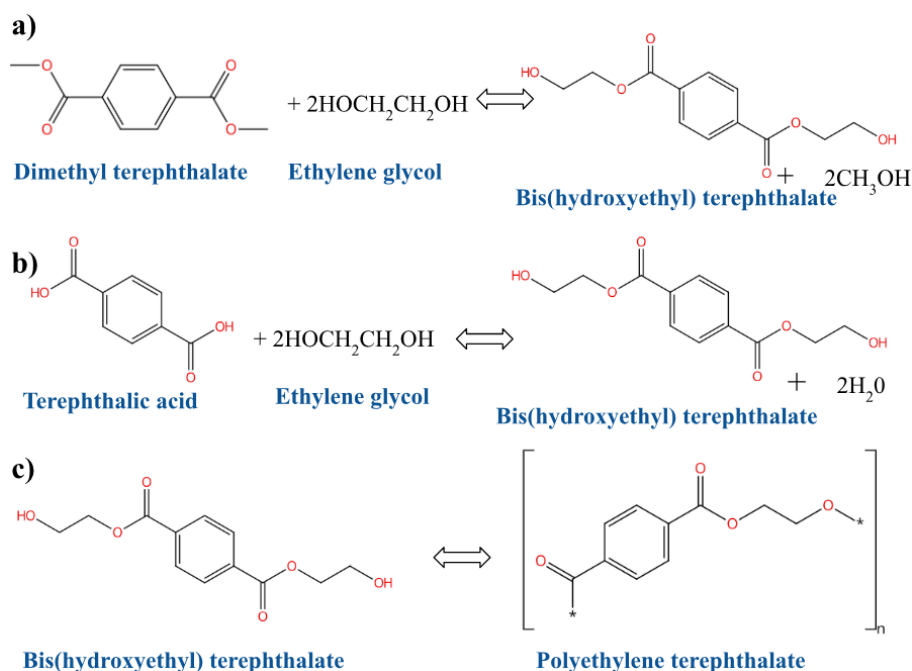


Figure 2: Production of PET. a) DMT method, b) TPA method, c) Polycondensation. Adapted from [20].

The final step of polyester polymer creation is to extract it, which can be done either as a polymer chip or as a molten polymer mix [19]. If the process occurs in a batch process, extrusion of the polyester chain with an inert gas that cools down the polymer into chips or granules happens. However, if the process is a continuous polymerisation process, the polymer is already molten and immediately sent to a spinneret unit, which is a common tool used for creating long fibres out of polymers.

Polyester can be re-moulded and re-melted, as it is a thermoplastic polymer [12]. This ability is utilised in the production of threads from a batch process as the polyester is in the form of a chip or granule. The chip is heated at 280-290 °C to a liquid state and then extruded through a melt extruder, turning it into filaments, which is then fed into the spinneret. As the polyester exits the spinneret, it is typically stretched by a pulling mechanism, which increases its tensile strength and stiffness. The polyester filament is then immediately solidified as it is cooled down by the ambient air [16].

Lastly, the filament from the spinneret has a low crystallinity and is thus not desirable as a textile fabric [19]. To increase crystallinity, the filament is stretched mechanically to 3-5 times its length into a yarn. This is called drawing, and it gives the polymer chain a higher tensile strength and dimensional stability. To further stabilise the yarn, it is exposed to a controlled heat under tension. The yarn is then finished and can be turned into a fabric through either woven or knitting techniques.

2.1.3 Properties of polyester

As previously mentioned in 2.1.1, polyester holds the largest market share of any fibre, and this is partially due to its cheap production but also for its properties. Polyesters can be very diverse and hold properties comparable to natural fibres, depending on the production of the polymer chain. The polymer can also be modelled to achieve specific desirable traits in the fabric [12].

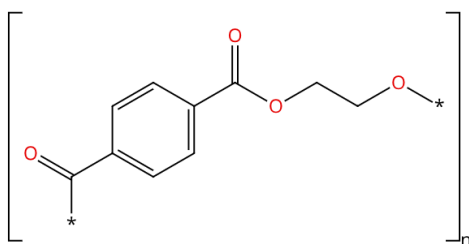


Figure 3: Polyester structure [21].

The structure of polyester contains both TPA and ethylene glycol (EG), linked with ester bonds in a repeating manner, Figure 3 [12]. The benzene ring in TPA causes the chain to be rigid and hinders the free rotation, whilst the esters make the polymer more polar. The polarity enables intermolecular dipolar interactions. These properties ensure that polyester is a stiff chain, whilst being capable of packing into ordered structures.

Polyester has both crystalline and amorphous regions and is thus called semi-crystalline [19, 12]. The strong crystallinity of the polymer chain is achieved through the drawing motion of the polymer, especially being oriented in the fibre axis. This creates a regular, parallel packed formation in some regions which allows for intermolecular forces that lock chains together. The intermolecular forces are both van der Waals and dipole-dipole. The crystalline regions give the fabric fibre a higher density, high tensile strength and modulus, high melting point and resistance to solvents and deformation. However, an excessive crystallinity can reduce flexibility and dyeability, as this influences the diffusion of the dye into the fibre.

Nevertheless, due to steric hindrance from the benzene rings, all regions cannot be crystalline and therefore there are some disordered non-crystalline regions in the fibres [19]. This causes a lower density, a looser chain packaging and more chain mobility of the polymer. These characteristics provide flexibility and elongation to the fibre and lowers the glass transition temperature (T_G). T_G is the temperature at which the material goes from being rigid like glass to elastic like rubber [12]. T_G influences the dyeability as the temperature above it allows for dye to diffuse into the fibre in the amorphous regions, whilst below the temperature, the regions are rather frozen in place, which does not allow for the dye to diffuse into the fabric.

In the last step of polyester production, which is the drawing of the fibre, the manufacturer can decide which characteristics they want to achieve with the fabric, depending on the end-use. Since the focus of this research is on textile for wear, the end-use needs to suit that. Polyester fibres used for apparel wear hold a crystallinity of about 35-45 %, to balance between the needs for good abrasion resistance as well as flexibility and dyeability [19]. Polyester fabrics also hold good elasticity and resilience to resist wrinkling and keep its shape, due to the rigidity of the aromatic rings and the amorphous regions.

Furthermore, due to the benzene rings and the strong dipole interactions between the ester groups, the T_G is around 70 °C and the melting point is at 250-260 °C [19]. Also, the crystallinity prevents degradation during melting, which ensures that mechanical recycling can be performed. PET polymers have a hydrophobic backbone, and the crystalline structure does not allow for water molecules to enter, leading to polyester not being able to absorb almost any water [12]. The compact structure also influences the dyeing capability of polyester as they block the dye. It is only the amorphous regions that allow for dye through diffusion, but it needs high temperatures to increase the molecular mobility and to overcome T_G , as mentioned previously.

2.2 General aspects of dyes

Now that textiles and fibres have been introduced, dyes can be presented. To first provide a general knowledge of dyes, the history and categorisation of dyes are discussed to then give a closer overview of the most common dye class for polyester: disperse dyes.

2.2.1 History of dyes

Dyes and pigments have been essential to human expression since prehistoric times, back when colour was derived from either minerals, plants or animals [22]. Archaeological findings dating back 30,000 years, such as the animal paintings in the Chauvet cave, are a demonstration of how humans used natural colourants to express creativity. Later, in ancient Egypt times dyeing became a more frequent practice with the appearance of the first natural dyes such as henna. Many dyes and pigments emerged, finding uses in cosmetics, on textiles, and writing materials, and even giving rise to the earliest synthetic pigment, Egyptian blue. Figure 4 depicts the shade of blue of this pigment, which was manufactured in a similar way to glass.



Figure 4: Statue in Egyptian blue [23].

In Antiquity, textile dyeing was seen as an art as well as a symbol of status [22]. For example, Tyrian purple was only used for Roman royalty due to its rarity and complicated production process. Other dyes such as saffron, weld and kermes were also cherished across Europe. Another major centre for dyes and pigments was Asia, where both India and China were prominent actors in colourant emergences.

Relatively few dyes were discovered during the Medieval times, but due to development of the transport sector, more knowledge of dyes could be brought from Asia to Europe which has led to advancements in both the products and the dyeing processes [22]. Dyes like Brazil wood and Indigo were brought from Asia. Indigo quickly replaced the lesser woad dye, which was known to be environmentally damaging and due to its negative impact on nature, its ban has led to one of the first environmental laws.

The industrial revolution marked a critical turning point in the history of dyes: the creation of the first synthetic organic dye “Mauveine” [22]. It was in 1856 that William Henry Perkin sought to synthesise quinine but instead accidentally discovered Mauveine. Quinine, which was used to treat Malaria, was very expensive to produce and Perkins mentor, chemist Hofmann, wanted to synthesise it instead of extracting it from cinchona trees. He noted that one ingredient of coal tar, Naphthalidine, was chemically very similar to Quinine. When Perkins attempted to synthesise Quinine from coal tar, an intense purple colour emerged instead, hence its name

Mauveine. This marked the beginning of the synthetic dye industry, which developed rapidly by the emergence of synthetic dyes with a wide range of colour, such as azo dyes, which were more stable and economical than the natural dyes. Hoechst, BASF and Bayer were companies that became pioneers in the synthetic dye manufacturing and the development of reactive dyes in the early 20th century, made a big breakthrough in the dyeing of cellulosic fibres.

In the 20th/21st century, the dyeing industry has gone from Europe, more specifically Germany, to countries in Asia such as China and India [22]. The excessive dyeing which has risen from all these discoveries, has drawn a lot of attention on the environmental and health concerns of synthetic dyes. The synthetic chemistry is still dominant for textile dyeing due to its relatively low cost and reproducibility. However, worries about wastewater pollution, toxicity and sustainability has inspired a possible development of the textile industry by using cleaner technologies and textile recycling.

2.2.2 Structure of dyes

Dyes are organic molecules dissolved in a medium [24]. They are either soluble in water and/or in an organic solvent, while pigments are soluble in neither and are most of the time inorganic. Thus, pigments are essentially unaffected by the application media, which is not the case of dyes. Another distinction between the two lies in the affinity the dye must have to the substrate which is not required for pigments.

The organic dye molecule is composed of three main components: the chromogen, the chromophore and the auxochrome [24]. The chromogen is a chemical compound that is either already coloured or can be coloured by the addition of a chromophore. Both the auxochrome and the chromophore are part of the chromogen. The chromophore is an unsaturated covalent group capable of absorbing in the ultraviolet (UV) and visible region. Therefore, the compound appears coloured as light is absorbed in the visible region. The chromophore determines the fundamental colour range, while the auxochrome acts more in the details by altering the hue and/or the intensity of the colour. If an auxochrome is attached to a chromophore, it generally increases both the wavelength and the intensity of the absorption. Common auxochromes are for example NH₂ and OH groups. Figure 5 is a representation of 4-Hydroxyazobenzene where the chromogen, chromophore and auxochrome are illustrated.

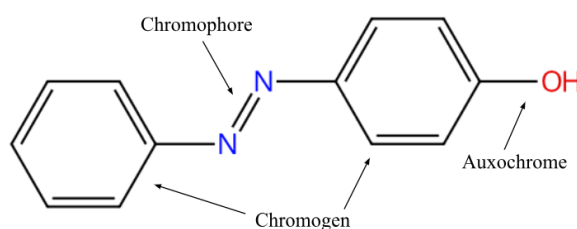


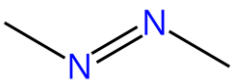
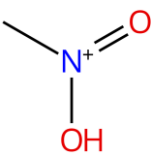
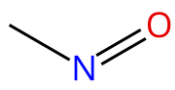
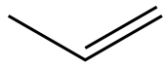
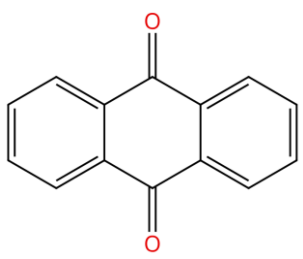
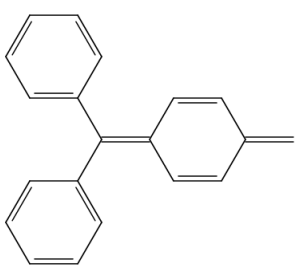
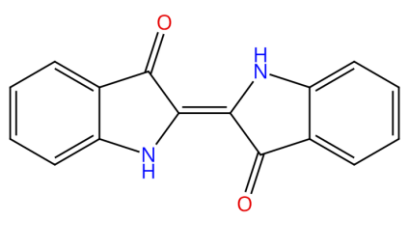
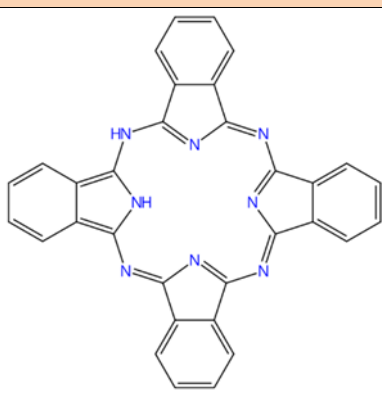
Figure 5: The 4-Hydroxyazobenzene molecule with its chromogen, chromophore and auxochrome presented. Adapted from [12].

To impart any colour, a chromophore needs to be part of a conjugated system [24]. A conjugated system means that a double bond automatically follows a single bond like in aromatic rings for example, Figure 5. The more conjugated the system is, the higher the wavelength that can be absorbed, usually leading to a greater intensity of the colour. Therefore, both the conjugation of the system as well as the auxochrome are important factors to control in order to achieve the

desired colour. However, the chromophore remains the essential group in the exhibition of colour for a molecule.

There are two types of auxochromes, colligators and non-colligators. Colligators are electron-withdrawing groups that mediate the dye-textile interactions and non-colligators are electron-donating groups that modify colours [24]. Furthermore, a chromophore is usually an electron-withdrawing group and an auxochrome an electron-donating one, therefore a non-colligator. This leads to a donation of electrons from the auxochrome to the chromophore through the conjugated system, which in turn leads to a longer wavelength absorbed. This is the reason to the higher intensity of colour exhibited with a non-colligator auxochrome. However, if the auxochrome is a colligator then it is also an electron-withdrawing group, resulting in no increased intensity of the hue. Instead, it leads to an increased solubility of the dye as well as binding interaction with the substrate. The following table, Table 1, displays the most recurrent chromophoric groups as well as their molecular structure.

Table 1: Chromophoric groups with their molecular structures [21].

Azo group	Nitro group	Nitroso group
		
Methine group	Anthraquinone group	Triarylmethane group
		
Indigo group	Phthalocyanine	
		

2.2.3 Properties of dyes

The performance of dyes on polyester fabrics depends on the interaction of the dye with the fibre as well as the conditions of dyeing and processing. Therefore, properties such as light fastness, wash fastness, substantivity and affinity and thermal stability are paramount to understand the durability and uniformity of the colour on the fabric.

Light fastness

Light fastness is the capacity of a dye or a colorant to resist fading or decolourisation when exposed to light, especially when exposed to UV radiation [25]. UV radiation is made of high-energy photons which can break the chemical bonds in the dye, causing it to fade over time. Some dyes have a higher ability to withstand UV radiation, and the grading scale of this property goes from 1 to 8. 1 standing for an unsatisfactory performance and 8 for an excellent one [12]. For example, a larger and more compact dye in its structure will have a greater potential to resist fading as it reduces the risk that light energy can break bonds. Furthermore, the light fastness also depends on the structure of the substrate, where a more closely packed fibre-knit is less exposed to UV radiation. Continuously, a dye can have a great light fastness on one material and an unsatisfactory one on another substrate, which demonstrates the importance of a good dye-fibre attachment. Other factors such as environmental conditions, impurities and application parameters are highly relevant for this property.

Wash fastness

Wash fastness is the ability of a dyed substrate to retain its original colour and quality after repeated washing [12]. It also includes the capacity of a dyed fabric to not bleed dye while washing which could potentially transfer colour to surrounding materials [25]. The wash fastness depends on several factors such as dye-fibre attachment, washing conditions, the solubility and size of the dye and dye chemistry [12]. For example, some dyes bond to the fabric through covalent bonds, which are strong chemical bonds, therefore resulting in a strong wash fastness. The rating system for wash fastness goes from 1 to 5, where 1 displays poor wash fastness properties and 5 exhibits a great one [25].

Substantivity and affinity

Substantivity and affinity could be perceived as synonyms, however, there is a slight difference in their definitions. Affinity refers to how strongly two substances are drawn to each other [26]. In dye chemistry, the affinity of a dye with a fibre is based on chemical attractions such as hydrogen π -bonds and covalent bonds and on mechanical factors such as the entrapment of the dye within the porous structure of the textile [12]. Substantivity, on the other hand, highlights that the attraction between a dye and a substrate is also dependant on the application conditions, which can vary. To summarise, affinity expresses the tendency of a dye to bind to a fibre, while substantivity focuses on the actual amount of dye absorbed under specific application conditions.

Thermal stability or sublimation fastness

The sublimation temperature is the temperature at which a compound goes directly from solid to vapor without going through the liquid phase [27]. A dye must have a sublimation temperature that is greater than the temperature that it will go through during the dyeing process or parts of the dye will be lost as gas fumes [12]. This can result in a lighter shade than expected, which is undesirable. Therefore, an elevated sublimation temperature is advantageous which can be obtained with greater molecular weights or stronger intermolecular binding forces of the dyes.

2.2.4 Classification of dyes depending on application method

Dyes can be grouped into different classes depending on their chemical structure and uses. This section of the report provides a basic overview of each dye category depending on its application method so that the reader gains a broader understanding of the subject. As this report is focusing on separating dyes from polyester textiles to increase the efficiency of the polyester-recycling processes at Rewin, the focus later in the report is on disperse dyes.

Direct dyes

Direct dyes are a water-soluble dye, which are majorly used on cotton and other cellulosic fabrics [12]. They do not need a mordant or a fixating agent in order to bind to the fabric, which makes them simple to use and of a relatively low cost. They also come in a large range of hues and their light fastness capacities can go from low to excellent. However, the wash fastness of such dyes is low.

Vat dyes

Vat dyes are water-insoluble dyes, which are also majorly used on cellulosic materials [12]. Vat dyes comprise of at least two carbonyl groups, which when reduced under alkaline conditions, enables the conversion of the dye to be water-soluble. This is how it gets absorbed by the cellulose fibre. Continuously, the dye is converted back to its original insoluble shape due to oxidation of the dye within the fibre making it extremely resistant, giving it its excellent wash and light fastness.

Reactive dyes

Reactive dyes are water-soluble dyes majorly used on cellulosic substrates but also on polyamide materials and protein fibres [12]. These dyes are special because the chromophores contain groups capable of forming covalent bonds between the dye and the fibre making the dye an integral part of the fabric. This results in an excellent light and wash fastness. Furthermore, reactive dyes have a very wide range of shades including very vibrant shades compared to other cellulosic dyes. Due to their excellent wash fastness, reactive dyes slowly replace direct dyes.

Acid dyes

Acid dyes are mostly applied on protein fibres or synthetic fibres such as nylon [12]. As the dye is anionic, it dissolves in water, after which an acid is added to the bath to lower the pH to a range of 2 to 6. The fibre, which has positively charged sites due to the addition of the acid, attracts the negatively charged dye resulting in the electrostatic bonding of the dye with the fibre, on top of the affinity that the dye has for the fibre. Depending on which type of acid dye, the wash and light fastness can vary, giving rise to different application possibilities.

Disperse dyes

Disperse dyes are non-ionic dyes and for most cases insoluble in water and applied to hydrophobic and synthetic substrates such as polyester, nylon, cellulose acetate and acrylic fibres [12]. However, its largest application is on polyester. Since the dye is insoluble in water, dispersing agents and continuous agitation are necessary to hold the dye in suspension in the dye bath. Continuously, the high temperatures help the fabric to swell, enabling the dye to bond to the fibres. The fastness properties of disperse dyes vary on the fibre but are generally good. Furthermore, disperse dyes are classified by their sublimation temperature which goes from A to D with A having the lowest sublimation temperature. A higher molecular weight usually corresponds to a high sublimation temperature.

Basic dyes

Basic dyes are water-soluble and non-ionic dyes which are mostly used on acrylic, paper and nylon fibres but can occasionally be used on polyester [12]. Contrary to acid dyes, basic dyes dissolve in water to create cations which are then attracted to fibres having negatively charged sites. No base is needed as the fibres have pre-existing negative sites and, on the contrary, an acid bath is used to enhance the uptake of the cations by the negatively charged sites. Basic dyes have poor to average light and wash fastness and are known for their intense colours [28].

2.2.5 Classification of disperse dyes depending on chemical structure

As mentioned before, dyes can also be classified depending on their chemical structure and chromophores. The same chromophores can be available for different types of dyes, and this section aims at introducing some of the predominant ones for disperse dyes. For disperse dyes, the biggest chromophoric groups are the following: azo dyes and anthraquinone dyes. Table 1 visualises these chromophoric groups.

Azo dyes

Azo dyes are the most common dyes as they represent 65 % to 75 % of all commercial dyes [29]. They include one or more azo groups ($-N=N-$), where each nitrogen is bonded to a conjugated structure, usually aromatic rings [24].

If there is only one azo structure present in the molecule, then it is called a monoazo dye and these represent 50 % of all disperse dyes, which makes them the biggest chemical class of dyes within disperse dyes [12]. These dyes are relatively simple to synthesise through a two-step process: diazotisation and azo coupling [24]. First, a primary aromatic amine is diazotised into a diazonium salt, a reactive intermediate. This intermediate is then coupled with an electron-rich nucleophile which results in a monoazo dye. Monoazo dyes are mostly used to reveal colours that are yellow to the red-brown region as well as black. However, they are also known to not have the best sublimation fastness. Figure 6 is an example of a monoazo disperse dye.

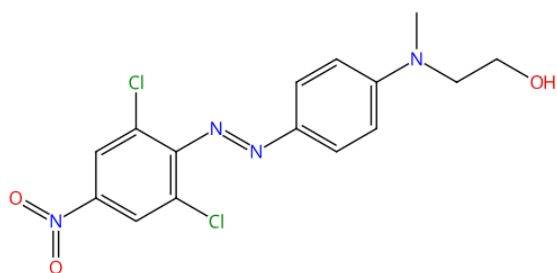


Figure 6: Disperse Orange 5 [21].

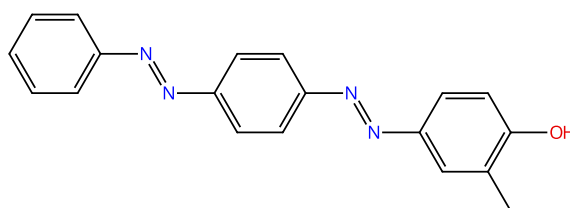


Figure 7: Disperse Yellow 23 [21].

If there are two azo structures in the molecule, then it is called a diazo dye and these account for 10 % of disperse dyes [12]. Their synthesis is similar to monoazo dyes but with an additional diazotisation and coupling step to introduce a second azo group. The molecular weight of diazo dyes is usually higher than the monoazo dyes, giving them better sublimation fastness and light fastness properties than many monoazo dyes. These dyes are commonly used for yellow and orange shades with Figure 7 displaying an example of a yellow disperse diazo dye [30]. However, diazo dyes are usually less bright than monoazo dyes [31].

Azo dyes are popular because of their simple structure which makes them easy to synthesise and allows for a wide variety of substituents, leading to an almost unlimited number of colours

[24]. Depending on the substituents, azo dye can be classified as carbocyclic, if there are aromatic amines on both ends of the azo group(s), or heterocyclic, if it has one or more heterocyclic groups. Heterocyclic groups are rings including heteroatoms.

Anthraquinone dyes

Anthraquinone dyes are the second largest chemical class of dyes within disperse dyes and accounts for 25 % of it [12]. Furthermore, compared to azo dyes, which are bound to be synthetic, anthraquinones can be found in nature, although most commercial dyes are synthetic [24]. The base of an anthraquinone dye is of course the anthraquinone structure, which is a fused aromatic system containing a quinone unit, and it can have numerous diverse substitutions. The synthesis of anthraquinone intermediates and derivatives is usually made by adding substituents to the anthraquinone nucleus or by direct synthesis of the whole anthraquinone ring. Therefore, their structure is more complicated than azo dyes making them more elaborated to synthesise and therefore more expensive [12].

Due to the superior molecular weight and rigid structure of anthraquinone dyes, they have greater fastness properties than azo dyes even though some anthraquinones have a very poor light-fastness due to its low resistance to fading while in contact with nitrous oxide [24]. Anthraquinone dyes are used to exhibit brighter shades in the red to blue-purple region [12, 30]. Figure 8 illustrates an example of an anthraquinone dye called Disperse Red 60.

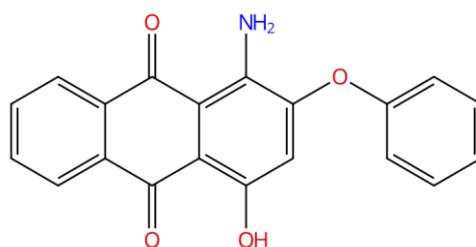


Figure 8: Disperse Red 60 [21].

2.2.6 Disperse dyes

Disperse dyes represent the second biggest class of dyes and have a market value of \$8.51 billion in 2024 [12, 32]. It is also predicted to grow at 5.5 % between the years 2025 and 2032 which is majorly due to the increase of polyester in the textile industry.

As stated before, disperse dyes are mostly used for polyester fabrics but can be used for other synthetic substrates as well [12]. As a matter of fact, disperse dyes were first invented in 1923 for cellulose acetate, as it was the first hydrophobic fibre. Therefore, in order to effectively dye cellulose acetate, a water-insoluble dye was necessary. Subsequently, it was discovered that this dye could be used on a variety of substrates. For a fabric to be dyed with disperse dyes, it should possess a crystalline structure, a melting temperature above 150 °C and be hydrophobic [33].

Disperse dyes are generally sold as powder, which only has a dye content of 15 to 40 % [12]. This is because disperse dyes are insoluble in water and need to be mixed with other components. The resulting dye powder is milled together with a dispersing agent and a bit of water. This leads to an increase of their surface area which aids its pseudo-dissolution in the bath, which followingly, increases the dye's uptake by the fibre. After the milling, the mixture is

dried and combined with diluents to give the sought-after concentration of the dye powder. The role of the dispersing agent is to hinder the clumping back of the dye particles after milling and to keep them in dispersion in the dye bath. Therefore, the choice of dispersing agent is paramount to get an optimal stability of the dye particles in the dye bath and a maximum uptake rate of the dye by the fibre.

An important thing to consider is the possible thermal degradation of disperse dyes. A recent study showed that especially monoazo dyes are susceptible to degradation under higher temperatures [34]. The degradation of monoazo dyes can possibly lead to the formation of aromatic amines, which are highly carcinogenic. It was found that disperse dyes with electron-withdrawing substituents start to thermally degrade at 120 °C, which is due to the azo linkage on one side being weaker than the other leading to breakage. Whilst if the azo dye has one or more electron-donating groups, the dye is much more stable and can withstand higher temperature, starting degradation at 180-200 °C. However, there is not yet any research on either diazo or anthraquinone dyes.

On top of that, these dyes have a low molecular weight compared to other dyes, leading to an increased volatility of the particles [31]. Therefore, if the temperature is too high, the particles can sublime as the sublimation temperature has been reached and end up as gas fumes.

Like many other dyes, disperse dyes are not biodegradable [12]. Their existence can therefore persist in textile effluent and damage local ecosystems. Furthermore, from a health perspective, some disperse dyes such as Disperse Blue 106 and 124 are known to generate allergic reactions [35]. These aspects highlight the importance of developing more sustainable approaches for handling disperse dyes and dyes in general.

2.3 Disperse dye on polyester

Both polyester and disperse dye have now been introduced and it is therefore important to explain how the dyeing process of polyester fabrics takes place, starting with an explanation of the kinetics and thermodynamics behind dyeing.

2.3.1 Thermodynamics and kinetics behind dyeing

What is pursued with dyeing is to achieve a uniform shade across a substrate which also matches the desired colour [12]. To understand how this is accomplished, it is necessary to be conscious of both the thermodynamics, which determine the equilibrium state, and the kinetics, which affects the rate and mechanism by which the equilibrium is reached.

Thermodynamics

Thermodynamics for dyeing describes how much dye is taken up by the fibre once the equilibrium is reached [12]. In order to understand the thermodynamics behind dyeing, several essential notions need to be described.

In Section 2.2.3, the dye properties affinity and substantivity are explained. These two characteristics are fundamental for the thermodynamic process of dyeing as a stronger affinity and substantivity of the dye for the substrate usually means a higher dye uptake [12].

The sorption of the dye to the substrate is an exothermic process, meaning that heat is released during the reaction [12]. According to Le Chatelier's principle, this also means that if the temperature is increased in the system, the equilibrium shifts back to absorbing heat [36]. This

corresponds to the reverse process, which is when the dye leaves the fibre. Therefore, dye sorption benefits from lower temperatures and dye desorption from higher temperatures.

The sorption of the dye onto the fibre can be graphically modelled by various sorption isotherms, where the quantity of product at equilibrium is plotted against the reactants [12]. Three models are commonly used: the Nernst isotherm, the Freundlich isotherm and the Langmuir isotherm, Figure 9.

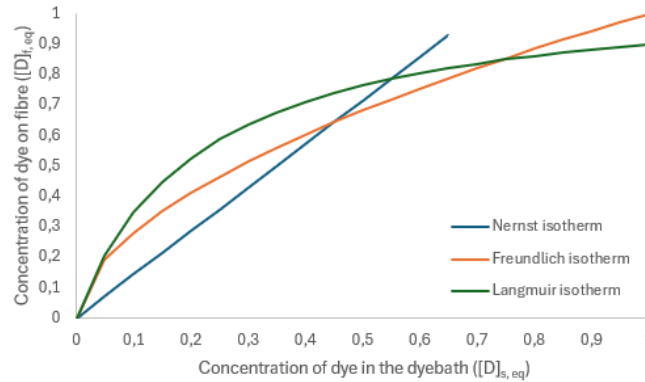


Figure 9: The Nernst, Freundlich and Langmuir isotherms for dyeing.

The Nernst isotherm is the one used to graphically model the sorption of disperse dyes on polyester [12]. It assumes a linear relationship between the equilibrium dye concentration in the fibre ($[D]_{f,eq}$) and in the solution ($[D]_{s,eq}$). This means that the fibre is assumed to behave like a solvent for the dye molecules and that the fibre takes up the dye continuously until saturation is reached. The parameter K is a constant describing how the dye partitions between the fibre and the solution, Equation 1.

Equation 1

$$[D]_{f,eq} = K \cdot [D]_{s,eq}$$

$[D]_{f,eq}$ = Equilibrium dye molality on the fibre ($\text{mol} \cdot \text{kg}^{-1}$)

K = Equilibrium sorption constant (–)

$[D]_{s,eq}$ = Equilibrium dye concentration in the bulk solution ($\text{mol} \cdot \text{dm}^{-3}$)

Kinetics

Kinetics control how fast the equilibrium is reached, and the dyeing process generally require three consecutive steps, Figure 10 [12]:

- The transport of the dye molecule from the bulk phase to the fibre.
- The adsorption of the dye molecule onto the fibre surface.
- The diffusion of the dye molecule into the interior of the fibre.

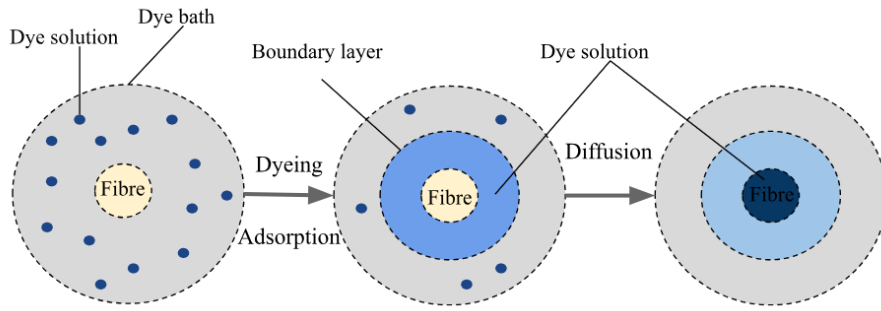


Figure 10: Kinetics of the dyeing process. Adapted from [37].

In a dye bath, a pump is responsible for agitation, which carries the dye molecules closer to the fibre through convective diffusion [12]. Approaching the fibre, the liquid flow slows down and a thin boundary layer forms where molecular diffusion is the only type of transport. With stronger agitation, the thickness of the boundary layer is reduced, speeding up the dye transfer to the fibre. However, with less agitation, the boundary layer gets thicker, which slows down dye uptake.

When the dye molecule reaches the fibre surface, it is adsorbed by the fibres which can either be physically or chemically [12]. Physical adsorption is when it is physical forces that causes the attraction between two objects like with van der Waals bonds for example. On the other hand, chemical adsorption is when there is the formation of a chemical bond between two objects like covalent or ionic bonds for example. Chemical adsorption tends to be much stronger than physical adsorption. Although the adsorption step can be either physical or chemical, it is in both cases very fast to reach quasi-equilibrium and is never the rate-limiting step.

However, the last step, the diffusion of the dye from the fibre surface to inside the fibre, is usually the rate limiting step [12]. Two different models can be used to describe this process: the pore-volume model and the free volume model. The pore-volume model assumes that the fibres have small capillaries, which are filled with water, in which the dye can diffuse through and later adsorb to the fibre surface. The free-volume model presumes that the dye diffuses through temporary openings, which are created by the movement of polymer chains in the amorphous regions. As previously mentioned, crystalline regions of polymers are assumed to be unreachable for the dye. The movement of polymer chains increases as temperature increases, especially when it is above T_G . This phenomenon is called swelling and the more the substrates swells, the larger these free-volume openings are, making the inner fibres more accessible for dyeing. The free-volume is usually applied on textiles containing polymer chains such as polyester whereas the pore-volume model is used for cellulosic fabrics such as cotton.

2.3.2 Polyester and disperse dye interaction

The interaction between polyester fibres and disperse dyes is essential to understanding its dyeing process. Since polyester is a hydrophobic and semi-crystalline molecule, its structure largely determines how disperse dyes are taken up. While Section 2.3.1 outlines the thermodynamics and kinetic aspect of dyeing, this section focuses on the bonds and mechanisms that control the affinity between disperse dyes and polyester.

Disperse dyes do not carry an ionic charge, meaning that it interacts with the fibres of textiles through physical forces rather than ionic bonds [33]. The physical bonds between disperse dyes and polyester are van der Waals forces, dipole-dipole interactions and hydrogen bonds. Van der

Waals forces are the dominating interactions, and these arise from the dense packaging of hydrophobic aromatic rings of the disperse dyes with the aromatic backbone of polyester. These forces are relatively weak, but they are the key driver of the compatibility between disperse dyes and polyester. Furthermore, dipole-dipole interaction occurs between the polar groups of the dye ($-\text{NO}_2$, $-\text{CN}$, $-\text{CO}-$) and the polar ester groups ($-\text{COO}-$) in polyester. Dipole-dipole forces have a stronger force than van der Waals, but they are less abundant. Lastly, if the dye contains $-\text{NH}_2$, $-\text{OH}$ or $-\text{NH}-$ groups, they can also form hydrogen bonds with the carbonyl oxygen in the polyester's ester. This force is the strongest, but the rarest.

However, in the dyeing process these three weak bonds are not enough for dye fixation, which is why polyester must rely on physical entrapment of the disperse dye in order to retain colour [33]. Physical entrapment firstly depends on the diffusion of the dye into the amorphous region of polyesters. After the dyeing process is completed, the temperature is lowered below T_G , which reduces the polymer chain mobility. This closes the previously formed openings, leading to the entrapment of the dye within the polymer structure.

2.3.3 Dyeing processes on polyester

Various dyeing methods exist, of which the three most common are exhaust dyeing, continuous and printing [12]. Exhaust dyeing is a batch process where the fabric is plunged in a dye bath, and the dye is adsorbed to the fibre surface and then diffused into the fibres. Continuous dyeing is when the fabric passes through a production line system where the dye is continuously applied, dried, fixed, and washed in one process. Lastly, printing is when the dye is applied locally to create patterns. This can be done with inkjet printing, print paste on rollers or by screens.

For polyesters there are two main methods of exhaust dyeing, where the first one is with carriers [12, 30]. For this method, the dye bath is at atmospheric pressure and with a temperature around $100\text{ }^\circ\text{C}$. The reason to why the temperature is not higher is because of the addition of carriers in the solvent. Carriers are small organic molecules that decrease the T_G of polyesters. Even if this technique is effective, it comes with certain disadvantages. Carriers can be toxic, difficult to remove and negatively affect light fastness which makes this alternative less environmentally friendly. The high cost, along with the other named limitations, are the reasons to why it is less commonly used today.

The second, and preferred choice for dyeing of polyester, is the high temperature and high pressure method (HTHP) [12]. Pressure is here used to reach the necessary temperature, enabling a penetration of the dye within the substrate without carriers. This method leads to a higher dye yield due to shorter cycles and better light-fastness properties, while avoiding the environmental and technical difficulties of carriers. However, the harsh conditions require the use of specialised equipment which can be expensive.

Another dyeing process for polyesters is a continuous dyeing technique called dry-heat fixation or the thermosol method [30]. The fabric is first padded with an aqueous solution of the dye, then dried and baked at $180\text{--}230\text{ }^\circ\text{C}$ for less than a minute. As this sequence is comparatively rapid, it allows for a rapid dye sorption without the need for pressurised equipment or carriers.

2.4 Textile recycling

Now that the report has detailed how polyester fabrics are dyed with disperse dyes, the focus shifts to polyester recycling. This next section explores the different possible processes in textile recycling as well as the ones implemented at Rewin Textiles AB (Rewin).

2.4.1 Mechanical and chemical recycling

As previously mentioned in the introduction, the textile industry accounts for about 6 to 8 % of the global carbon dioxide emissions, which gravely affects climate change [3]. To minimise these, recycling of textile can be done in order to utilise the already existing resources instead of discarding them. Other ways to minimise the effects of the textile industry is to reuse the clothes by selling them second-hand or to refurbish clothes that are distressed.

Textile waste can be separated into three categories, and these are industrial, pre- and post-consumer textile waste [38]. Industrial textile waste refers to various fabrics such as old conveyor belts, safety gear, used wipes and carpets. Pre-consumer waste generally refers to waste generated before the textile reaches the customer, such as textile scraps from cutting fabrics. Post-consumer waste is the waste generated from consumers after use.

Textile waste can be used for energy recovery, which is how textile waste has mostly been dealt with until now [39]. However, textile waste has mainly ended up in landfills in most countries. As a measure to combat this, EU adopted a new Directive in 2023, which is supposed to facilitate waste sorting as it states that textile can no longer be thrown in the residual waste [6]. Therefore, textile waste can instead be recycled and used for open-loop recycling or closed-loop recycling. Open-loop recycling refers to the process of old clothes that are turned into insulation materials like in mattresses for example [8]. However, the better option is through closed-loop recycling as you can better preserve the material's value and recycle it multiple times. Open-loop fibres cannot be recycled a second time, whilst closed-loop fibres can be recycled again, which is why closed-loop recycling should be the main route for textile recycling.

There are a number of different levels of recycling, Figure 11, where fabric recycling means recycling the fabric as it is without shredding it to small pieces [40]. Fibre recycling on the other hand is the process of shredding the garment and breaking it down mechanically to its fibre and then turn it into a yarn or thread again. Lastly, monomer, oligomer or polymer recycling involves breaking down the fibre into its constituents chemically.

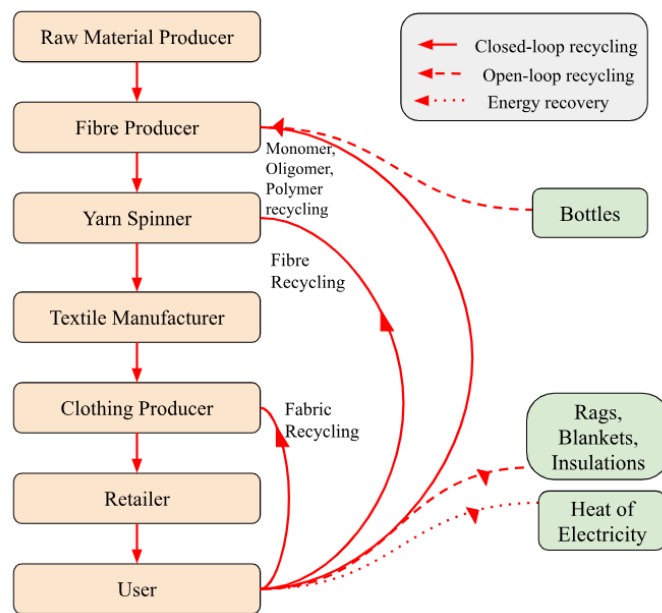


Figure 11: Showing possible routes for textile reuse and recycling. Adapted from [40].

There are two types of procedures in textile recycling: chemical and mechanical recycling [39]. Both recycling methods require the same primary steps, which is the sorting of textiles according to their material fraction, meaning the separation of one fibre from another. The sorting of textiles can either be through manual work, which is the most common method, or through molecular characterisation of the fibre content [8]. However, as many clothes today contain a mixture of fibres, it is complicated to separate these, which instead puts pressure on the recycling process to handle fibre blends. Chemical recycling can tackle this problem as the process can be designed to only recycle one fibre while leaving another fibre nearly unaffected. In contrast, mechanical recycling cannot handle blended fabrics at all and requires almost 100 % pure fibres.

After the sorting of textiles, mechanical recycling and chemical recycling requires shredding of the fibres [39]. Shredding turns fabrics into smaller components which facilitates the removal of buttons or zippers. For mechanical recycling, shredding also ensures that the smaller pieces are more uniform before entering the recycling process. Moreover, chemical recycling is more effective if the fibres are more accessible, meaning that the shredding causes more fibre surface to be exposed which facilitates the work of solvents, enzymes or depolymerisations agents [8]. The next steps of textile recycling differ for chemical and mechanical, thus these are explained separately, starting with mechanical recycling.

Mechanical recycling

Mechanical recycling methods are usually classified according to the defined value of the end-product, where the quality of the end-product is the deciding factor [39]. The highest quality that is achievable is textile-to-textile recycling, or as previously called the closed-loop recycling. This method involves carding of the shredded fabric, which aligns them, separates and ensures that the fibres are clean. Then, the fibres are spun into a new thread which can be used to produce new and recycled textiles. However, in this process about 40 % of the fibres are lost. To account for the loss and increase quality, virgin fibres can be added, which however, increases the environmental impact.

Mechanical recycling is also used for open-loop recycling, and this method of recycling gives the lowest quality of end-product [39]. This method gives nonwoven materials; hence the products are usually used for stuffing or insulation in mattresses. These nonwoven materials can be produced through a needle punching technique or by moulding the fibres and applying a heat treatment, so they melt together and become uniform. The latter process mentioned is often used for polyester fibres that do not have an enough high quality for chemical recycling.

Chemical recycling

Chemical recycling can also be carried out using several different methods, but they all generally follow the same pattern. After the shredding of the textile, the fibres are subjected to specific chemicals that transform them into monomers or oligomers [8]. Continuously, a purification step is performed, and the old fibres are converted into new fibres or polymers that can be used to produce new fabrics. What is especially good about chemical recycling against mechanical recycling, apart from being able to handle blended materials, is that the processes give a higher quality of the fibres [39]. A common pathway for chemical recycling is depolymerisation, which is explained below, but there are more processes existing such as enzymatic hydrolysis.

Depolymerisation is the process of breaking down polymers into monomers, with the report focusing on polyester fabrics and thus PET polymers [8]. Depolymerisation for closed-loop recycling of polyesters can be done by using glycol (glycolysis), methanol (methanolysis) or water with added heat and pressure (hydrolysis). The end-products after depolymerisation are the building blocks of polyester, although the specific product depends on the method of depolymerisation used, Figure 12. For glycolysis, the end-product is BHET which is the intermediate product in the TPA process. BHET can be purified to create a high-quality polyester with similar properties as virgin polyester [41]. Methanolysis instead generates DMT, the reactant in the DMT method of polyester. However, this process creates impurities that can negatively affect the quality of the new polyester, and it is also more expensive and energy intensive. Lastly, hydrolysis depolymerises the polyester into TPA, but this process is more expensive, and energy intensive compared to glycolysis. With the aid of catalysts, it is possible to target the specific polyester fibre whilst allowing for another fibre in the blend, such as cotton, to be untouched.

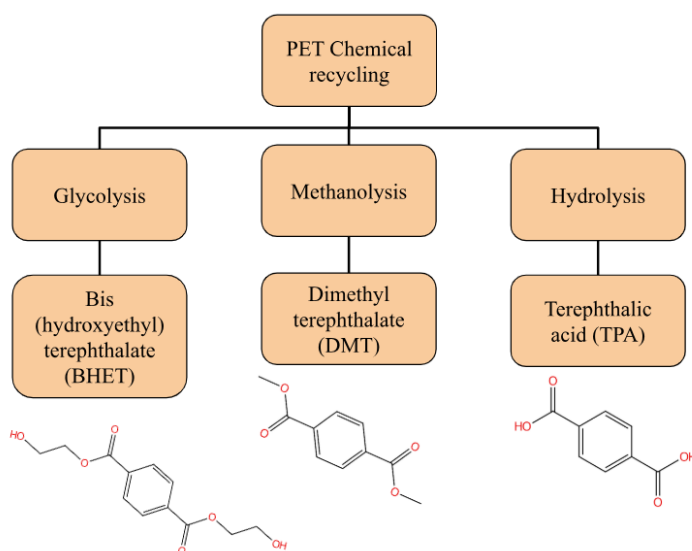


Figure 12: Chemical depolymerisation pathways for closed-loop recycling of polyester. Adapted from [41].

2.4.2 Rewin Textiles AB

Rewin Textiles AB is a company that focuses on the recycling of polyester textile and aims to overcome the challenge of handling mixed fibres, polyester and cotton, and materials, zippers and buttons, efficiently with a high purity recycled output [42, 43]. The process developed by Rewin enables fibre-to-fibre recycling in which the material can be turned into high-quality textile and thus closing the loop for the textile industry. Furthermore, the process does not damage the cotton in the blend, which can be sent to other companies that recycle cotton.

The process is a chemical recycling method, where the depolymerisation is performed with glycol with the presence of a catalyst [43]. As mentioned in 2.4.1, using glycol as the depolymerisation method is the most energy-efficient and least costly method. The process then ends up with BHET, the intermediate product for the TPA method of production of polyester. For a reference to the patented Rewin process, Figure 13.

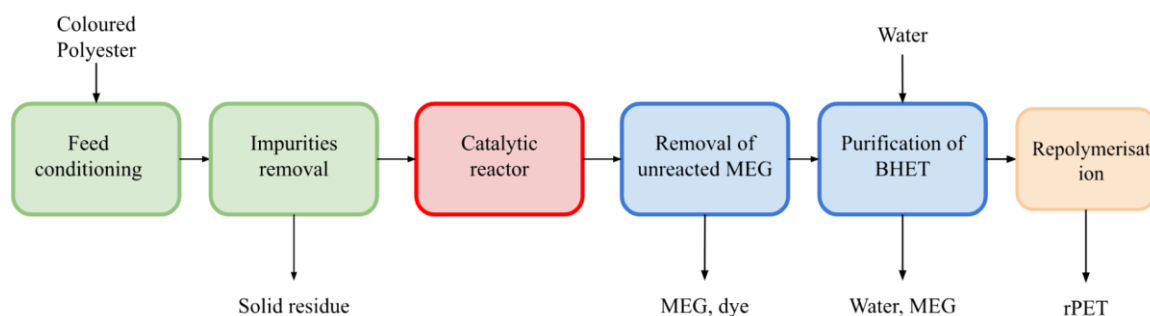


Figure 13: Polyester recycling process for Rewin Textile AB. Adapted from [43].

The first step is called feed conditioning, where mixed fibres are combined with MEG and then heated to 190-260 °C [43]. This temperature overcomes the T_G for polyester, thus making the amorphous regions more flexible and the polyester chains start to depolymerise into monomers and oligomers of polyester in MEG. In this step, the materials that are not polyester, such as cotton, buttons and zippers, are separated by filtration.

Secondly, the solution containing MEG and dissolved polyester is sent to a reactor where the polyester undergoes glycolysis with excess of MEG [43]. Glycolysis refers to the transesterification between the ester groups in the polymer and a diol, MEG, which produces BHET. This step is performed with the help of a heterogeneous catalyst. The catalyst is usually attached to the filter fibres and apart from aiding the reaction it also filters out residues. BHET and remaining oligomers precipitate as the solution is cooled down and thus separate from MEG, which in turn can be purified and reused in the process. Lastly, BHET and remaining oligomers are dissolved in water and recrystallised. These are then filtered to achieve high purity which can be re-polymerised to produce high quality polyester products.

3 Materials and methods

Now that textiles, dyes and the dyeing of textiles have been introduced, the following section focuses on the central topic of this report, namely the removal of dyes. Sections 3.1 - 3.4 provide the context and basis for this topic, including the placement of the dye removal step within the Rewin process chain and the criteria used for selecting a suitable solvent. Then, a literature review is presented along with its results on possible solvents for dye extraction. Continuously, additional information about separation techniques is introduced, with focus on separating dyes from solvents once the polyester has been treated. These sections therefore constitute the material forming the basis for the subsequent work.

Section 3.5 describes the applied methodology, including the development of the process flow-sheet, along with an introduction about the software used, Aspen Plus V14. The data used in the process model are also presented and an economic review of the chosen solvents is performed as part of the methodological approach.

3.1 Dye removal process placement

The aim of this report is to efficiently add a dye removal step in the process chain of Rewin Textiles AB. Based on insights from professors at LTH and reviewed literature, there are two possible placements of the dye-extraction step: before the feed-conditioning step or at the catalytic reactor, shown as the black boxes in Figure 14.

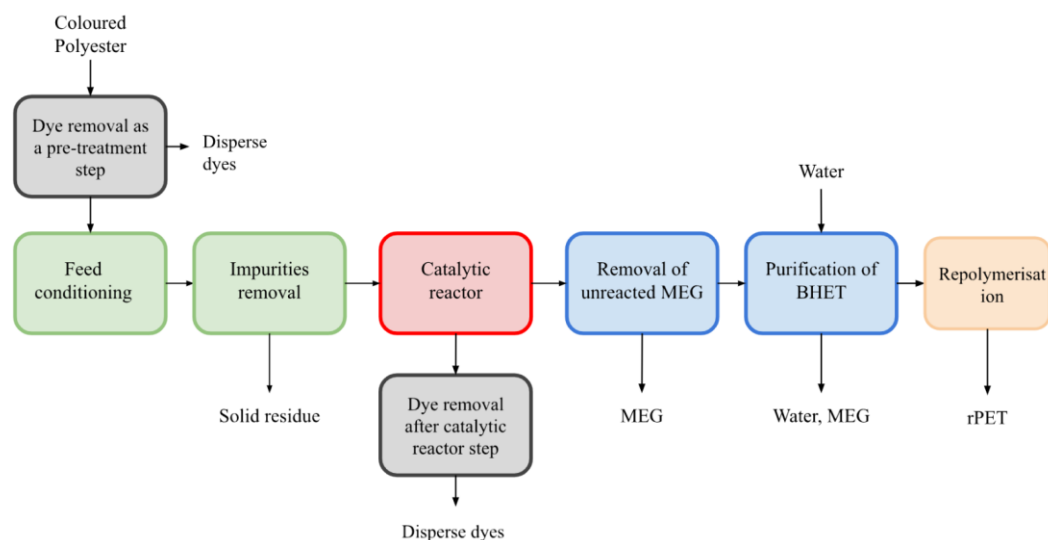


Figure 14: Dye removal placement possibilities at Rewin Textiles.

3.1.1 Dye removal step placed before the feed-conditioning

Placing the dye separation before the feed-conditioning step, would classify it as a pre-treatment step to the already existing process chain. Its position ensures the elimination of dye particles before entering the depolymerisation step as these could interfere with either the catalysts in the reactor bed or with the depolymerisation reactions. Furthermore, by introducing this step early, it could lead to an increased purity and quality of the resulting polymer due to less contaminants present in the system.

As explained in 2.3.2, the bonds between disperse dyes and polyester are mostly van der Waals bonds, which are relatively weak bonds. Furthermore, a significant portion of the dye is trapped inside the polyester structure which is densely packed. A solution to extract the dye from the substrate is to place the dyed fabric in a solvent at a temperature above T_G [9]. Above T_G , polyester starts to swell, which reduces the density of the polymer structure. As the van der Waals interactions follow a $1/r^6$ dependence, the increase of distance between dye and polyester that comes from the decreased density, weakens the bonds tremendously. This destabilisation of the dye molecule leads to an increase of their chemical potential, which can be seen as their escaping tendency. As the dyes are initially stable within the polymer matrix, their desire to escape is low and therefore their chemical potential is low as well. However, as the polymer swells, the density decreases and the van der Waals bonds weaken, which leads to the chemical potential of the dyes to increase. Thus, dye extraction becomes thermodynamically favourable when the dyes possess a higher chemical potential in the fibre than in the surrounding solvent. Consequently, the dyes spontaneously diffuse out from the fibres.

To extract the most trapped dyes within the substrate structure, multiple extraction cycles are recommended with a solvent-assisted dye removal step [10]. The reason is that the dye-removal system reaches equilibrium rapidly, meaning that longer durations do not proportionally mean better extraction. This behaviour can be explained by the Nernst isotherm explained earlier in 2.3.1, which says that once equilibrium is reached, further desorption is limited.

3.1.2 Dye-removal step placed at the catalytic reactor

An alternative to the pre-treatment dye removal is to perform the dye-separation step within the catalytic reactor, where the depolymerisation of polyester occurs. Compared to the pre-treatment step, the dye molecule is not physically extracted by a solvent but is instead released from the substrate due to chain cleavage during depolymerisation [44]. As bonds are cleaved and the polymers are reduced to monomers and oligomers during the depolymerisation process, the van der Waals bonds are extremely weakened, and the physical entrapment is null leading to the release of the dye particles from the monomers. Therefore, the dye extraction is here not a separate step but rather a consequence of the depolymerisation process. Thus, the resulting mixture of this process contains monomers, oligomers and polymers, which are dissolved in the MEG solvents as well as solubilised dye molecules.

If no pre-treatment dye removal step is installed, a separation step needs to be added to isolate the dyes from the rest of the mixture. This can be done through various separation methods like with a specific catalyst or recrystallisation for example [45, 46]. The catalytic reactor already possesses a catalyst, and this one is able to reduce the dye molecules to smaller fragments [42]. However, an excessive loading of dyes could instead interfere with the catalysts and poison or deactivate them. This could lead to decreased depolymerisation efficiency and product quality.

Integrating the dye-removal step after the catalytic reactor reduces the number of units compared to the pre-treatment option, but it also introduces certain drawbacks. The biggest inconvenience is the interaction of the dye with the catalysts, which may lead to its deactivation. Furthermore, the catalyst in the reactor reduces some dyes but the extent and mechanisms of this process remain unclear, making the modelling and simulation possibilities complicated. Lastly, the pre-treatment option is much more documented, providing more data and information for analysis of the dye removal step. For these reasons, this report focuses on a pre-treatment step as the preferred method to remove dyes from polyester textiles.

3.2 Solvent selection

The pre-treatment option is chosen as a dye-removal step for the Rewin recycling process and therefore, an appropriate solvent needs to be selected to efficiently and sustainably extract disperse dyes from polyester. To understand the mechanism behind dye extraction, the solubilities of solvents and criteria for solvent selection must be explained.

3.2.1 Solubility of solvents

The term solubility describes how well a substance, the solute, can disperse or dissolve within another substance, the solvent, to form a homogeneous phase [47]. It largely depends on the balance between the intermolecular forces: the cohesive forces holding the substances together and the adhesive forces which are acting between the solvent and the solute [48]. Dissolution of the solute in the solvent occurs when the cost of energy for separating the solute-solute and solvent-solvent interactions is compensated by favourable solute-solvent interactions. To quantify these energetic relationships, solubility parameters have been developed to predict the solubilities of different solutes in solvents.

Solubility parameters were first introduced by Hildebrand who defined the total solubility parameter (δ_T) as the square root of the internal cohesive density (CED), which is the molar energy of vaporisation (E_v) divided by the molar volume (V_m), Equation 2 [49]:

Equation 2

$$\delta_T = \left(\frac{E_v}{V_m} \right)^{1/2}$$

Two substances with comparable δ_T are expected to show strong interactions and solubility of the system, according to the empirical rule “like dissolves like” [49]. The Hildebrand approach is mostly used for systems with non-polar or weakly polar substances as the single parameter is not enough to describe the complexity of polar and hydrogen-bonding interactions. It is Hansen that extended Hildebrand’s theory to overcome this limitation. Here, the total cohesive energy is split into three parameters: dispersion solubility (δ_D), polar solubility (δ_P) and hydrogen bonding solubility (δ_H). δ_D characterises the contribution of the non-polar interactions called London dispersion forces, and they dominate in non-polar systems such as hydrocarbons. Two substances with similar δ_D indicate that they have similarities in their non-polar character, suggesting that they can interact favourably through their van der Waals bonds. Continuously, δ_P represents the cohesive energy arising from dipole-dipole interactions, which basically gives indications on the polarity of the substance. Lastly, δ_H quantifies the hydrogen-bonding interactions, which describes how strongly a molecule can accept or donate hydrogen bonds. Hydrogen bonds are when a hydrogen atom bound to electronegative atom is attracted by lone-pair electrons on other molecules. The Hansen solubility parameters (HSP) represent then each substance as a point in the three-dimensional “Hansen space”, Equation 3. Figure 15 shows a clearer representation of the Hansen space.

Equation 3

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

Accordingly, the solubility interaction between two substances can be represented by the distance R_a of their points in the Hansen space, Equation 4.

Equation 4

$$R_a = \sqrt{4 \cdot (\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2}$$

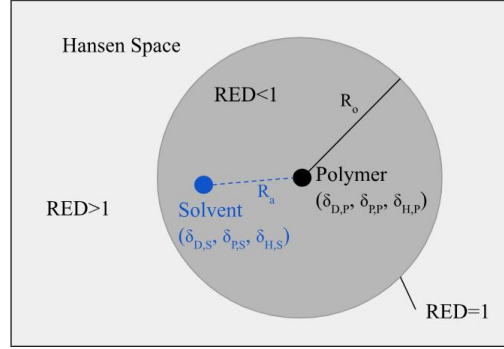


Figure 15: Hansen space with all its parameters. Adapted from [50].

As seen in Figure 15, a smaller R_a suggests that the species are close in the Hansen space, demonstrating stronger interactions and thus a strong affinity and solubility [49]. Furthermore, when analysing R_a , it is often compared to R_o , which represents the radius of the solubility sphere of a solute in the Hansen space. The sphere displays the region in which the solvent needs to be in to be considered as good for the solute. The relative energy difference (RED) is the result of the fraction of the two parameters, where RED larger than 1 means that the solute is not soluble in the solvent and RED less than 1 means that the solute is, Equation 5.

Equation 5

$$RED = \frac{R_a}{R_o}$$

In the context of polyester dye removal, the Hildebrand or Hansen solubility parameters are essential to predict the performance of the chosen solvent in relation to the solute, in this case polyester. By comparing the solubility parameters of solvents with those of dyes and the polyester, it is possible to identify efficient and sustainable solvents for dye removal.

3.2.2 Criteria for solvent selection

To obtain the best possible solvent for dye extraction, several criteria need to be fulfilled. Firstly, the solvent must efficiently swell the fabric at the decided temperature above T_G [9]. According to Mu et al., a polyester fabric is efficiently swollen when the solubility parameter of the solvent is close to the one of the fabrics rather than of the dye. If one would focus on similar solubility parameters between the dye and the solvent, the dye may remain stable within the polyester, which would not favour dye removal.

The solubility parameters of the solvent should then be close to the one of the fibres, but they cannot be too close as this could possibly result in the dissolution or degradation of the polymer, which is an unwanted side effect for a pre-treatment step [49]. According to Charles M. Hansen, there are six different steps in the scale of the solubility of a polymer in a solvent. These are: Soluble, almost soluble, strongly swollen and slight solubility, swollen, little swelling and no visible effect. For the dye removal of polyester, the right category is “swollen”.

Other requirements include the safety precautions such as a low toxicity [9]. Furthermore, the operational practicality of the solvent is fundamental as the solvent should lead to efficient swelling of the substrate at moderate temperatures and have a reasonable liquor ratio to improve process feasibility. Lastly, the solvent should be chosen considering its sustainability, as it should be easily recyclable and have a low environmental impact.

3.3 Solvent options

To optimise the dye-removal stage, the role of solvents in disperse dye extraction from polyester fabrics must be evaluated together with the criteria previously mentioned. Therefore, this section performs a literature review on previous studies and their attempt to remove dyes from fabrics with a solvent-assisted approach.

The literature study is conducted using the LUBsearch database, which was renamed to Finn during the course of the thesis work. A combination of keywords, including *dye extraction*, *dye removal*, *solvent*, *disperse dyes* and *polyester*, were used to identify relevant scientific articles. An initial screening of the search results was performed to assess their relevance to the scope of this study. Publications focusing on solvents known to be hazardous were excluded, as were studies and reports that did not align with the objective of evaluating solvent-assisted dye removal as a potential pre-treatment step.

Based on this screening, the solvents presented in this section were identified as effective for dye removal from polyester, as they efficiently swell the substrate without affecting its structure or molecular weight.

3.3.1 DMSO

Dimethyl sulfoxide (DMSO) is a highly polar and water-miscible solvent with a wide range of industrial, chemical and medical applications [51]. In chemical processes, it serves as an efficient reaction medium, and in medicine it acts as a vehicle for carrying medicines through the skin. Furthermore, it has a relatively low toxicity compared to bleaching agents, but DMSO is known to penetrate the skin, which means that it needs to be handled with care [52]. The cost for DMSO is 35 SEK per kg and has a boiling point of 189 °C [53, 21]. Figure 16 shows the structure of DMSO.

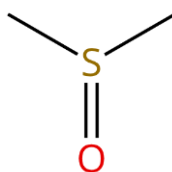


Figure 16: DMSO [21].

Sharma et al. conducted experiments on dye removal from 100 % polyester, 100 % cotton and different poly-cotton blends with DMSO as the solvent [52]. The fractionated textile waste was milled to a small size before being submerged in DMSO with a material-to-liquor ratio (MLR) of 1:18 at varied temperatures of 90, 130 and 150 °C. The researchers allowed the fabric to sit in 500 ml flasks containing the solvent for 1 hour and then washed away the remaining DMSO from the fibres. Their results show that with increased temperature, especially at 130 and 150 °C, the diffusion of DMSO into the polyester matrix happened more rapidly which led to a higher desorption of the dye compared to the experiment at 90 °C. Furthermore, the study showed that for polyester, three cycles in DMSO at 130 °C led to an optimal removal of dye.

In the case of cotton, there could not be seen as much of a decrease in dye removal from the fabric [52]. This is explained by the stronger bonds between cotton and reactive dyes, the dye bound to the cotton in the experiment. These are strong covalent bonds and cannot be cleaved by DMSO, even though the solvent showed to swell the cellulosic fibres. For the blended textiles, the results were consistent with those from pure polyester and pure cotton. This means that with a higher percentage of polyester in the mix, a greater decolourisation was seen. However, with only 20 % polyester in the mix, there was not as much colour removed. Lastly, the researchers observed no damage to either the removed dye molecules or the fibres.

Mu and Yang also tested DMSO as a solvent on polyester and cotton fibres [9]. Their experiments were conducted with a MLR of 1:5 at 80-100 °C for 30 min. Results showed that a higher temperature during solvent extraction was more efficient in removing dyes, in accordance with Sharma et al [52]. The specific dye these researchers tested on was Disperse Blue 56, which is an anthraquinone, and they used their own dyed fabric rather than textile waste. At 100 °C, about 87 % of the disperse dyes on polyester were removed after one cycle. However, the researchers chose not to do any more dye removal cycles with DMSO but focused on other solvents instead [9].

Additionally, in this article the dye used on cotton was direct dye and DMSO showed to significantly remove this dye from the fabric [9]. This is because the bonds between direct dye and the cellulosic fibre are van der Waals and hydrogen bonds and not covalent bonds, thus facilitating the detachment of the dye from the fibre. Lastly, the researchers showed result of no structure damage of the tested fibres. Additionally, Mu and Yang also tried to dye virgin polyester and cotton with the recovered dye, and it was showed to be successful, indicating no damage on the dye molecule after the extraction with DMSO.

3.3.2 Cyrene

Dihydrolevoglucosenone, commonly known by its trade name Cyrene, is a polar biobased solvent derived from cellulosic waste [21, 10]. Although it was first synthesised in 1974, it took almost 40 years for a company to commercialise it, due to growing interest in a biobased replacement for traditional solvents. Cyrene is a non-toxic and biodegradable solvent that has a lower carbon footprint than traditional solvents such as DMF and DMSO [10]. Cyrene has a boiling point of 203 °C, is miscible with water and has strong solvation abilities [54]. However, Cyrene is more viscous than traditional solvents so it typically needs to have a co-solvent such as water, otherwise rigorous mixing would suffice. It is also recognised that Cyrene may cause eye irritation [55]. Figure 17 displays its molecular structure.

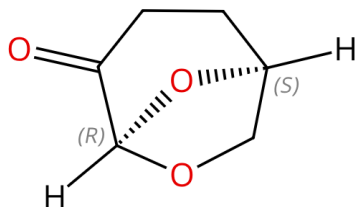


Figure 17: Cyrene [10].

Fernando et al. believed that a similarity between dispersion solubility parameters (δ_D) between polyester and the solvent would lead to a stronger swelling capacity [10]. Therefore, the researchers saw an opportunity in using Cyrene as a sustainable solvent for dye removal. The experiment tested two anthraquinone dyes, Disperse Red 60 and Disperse Blue 56. They dyed

polyester at both 98 and 130 °C, to test the efficacy of dye removal on dyes dyed at different temperatures. Additionally, the researchers tried three different Cyrene:water ratios, 75:25, 50:50 and 25:75 to find which mixture of solvent is optimal. They conducted all the dye removal experiments at 98 °C.

The report concluded similar findings as with DMSO in 3.3.1, that three 30-minutes cycles work best for dye removal in polyester fabrics [10]. Fernando et al. also saw that the best ratio was 75:25 and that it could achieve 96 % dye removal for the low temperature dyed fabric whilst it could achieve 75 % dye removal for the high temperature dyed fabric. Furthermore, the 50:50 ratio showed some decent results as well, as this mixture could remove 70-71 % of the dyes for both the high and low temperature dyed fabrics. An MLR of 1:10 was found to be optimal for this experiment.

A drawback with using Cyrene is that the solvent can also dissolve polyester at temperatures above 140 °C, so it is crucial that the dye removal step does not exceed this limit [10]. Lastly, the production of Cyrene is quite costly as it is not as widely used as other solvents, and the price to purchase one kg of Cyrene is 420 SEK [56].

3.3.3 Benzyl alcohol

Benzyl alcohol (BA) is the simplest aromatic alcohol and exists naturally in essential oils [57]. Its simple structure results in its many industrial uses. Chemically, it is a biodegradable solvent that is slightly polar because of its hydroxyl group [58]. It is only slightly soluble in water but is miscible with many organic solvents and has a high boiling point of 205.4°C [57]. However, according to the Swedish Chemicals Agency's tool PRIO-guide, BA is classified as a level 2 priority risk-reduction substance [59]. This means that its usage should include risk-reduction measures, which is due to its allergenic properties. Figure 18 displays the molecular structure of BA.

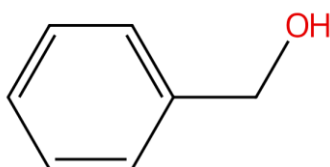


Figure 18: Benzyl alcohol [21].

Mu et al. investigated how BA could be used as a solvent to efficiently extract dyes from polyester textiles during fibre-to-fibre recycling, where their approach can be applied to glycolysis [58]. Firstly, the polyester fabrics were dyed at 130 °C with 2 wt% (weight percentage) Disperse Blue 79, which is a high-energy monoazo dye. Then, the pieces were placed in BA at 100-130 °C for 5 minutes and this step was repeated three times. For the lab conditions in the report, the MLR was 1:2 but advised to be 1:4 for industrial implementation. Furthermore, drops of acetic acid were added to prevent any damage to the dyes by creating a slightly acidic environment. The study showed that BA was effective in dye removal as it removed 95 % of all dyes after one cycle and 99.8 % after three cycles at a temperature of 130 °C.

The authors think that the reason to why BA is so efficient at extracting dyes from polyester is due to polar solubility parameter (δ_P) being similar to the one of polyester [58]. Furthermore, 99.1 % of the polyester weight was retained, demonstrating the solvents non-destructive behaviour towards polyester. Even the dyes did not suffer from structural changes from the extraction. Additionally, Mu et al. considers the cost of this process to be 20 % of the cost for the traditional

polyester production, assuming a recovered dye selling price of 100 SEK/kg and the cost of BA is 20 SEK per kg [60]. Moreover, the writers believe that due to the strong affinity a high-energy dye has to polyester, lower-energy dyes should be even easier to separate in the recycling process [58].

3.3.4 Supercritical carbon dioxide with co-solvent

Supercritical carbon dioxide (scCO₂) has lately emerged as an efficient non-toxic, non-flammable and non-polar solvent for polymer processing [61, 62]. This is partly due to its advantageous properties such as low viscosity and high diffusivity while still having a liquid-like density. These characteristics facilitate polymer impregnation and therefore efficient swelling of the polyester. The supercritical state of carbon dioxide is when it is kept above its critical temperature and pressure, which are at 30.85 °C and 7.38 MPa. The price for carbon dioxide is at a price of 12 SEK per kg but the equipment in order to obtain supercritical conditions is a costly investment [63].

Huang et al. studied how scCO₂ could be used as a solvent to extract dyes from polyester [61]. The polyester fabrics were cut into small pieces and were then dyed in a 130 °C bath with disperse dyes. The disperse dyes used in the article were Disperse Red 74 and Disperse Yellow 23 which respectively are a monoazo dye and a diazo dye. Subsequently, the polyester samples were subjected to the scCO₂-treatment at a temperature of 80 to 120 °C and a pressure of 8 to 10 MPa. Within the pressurised system, DMF was also added with a MLR of 1:10-1:50. Several co-solvents were examined but DMF gave the best results. A co-solvent is needed because sCO₂ is efficient at swelling fabric but relies on another solvent to extract the dye molecules from the substrate due to the extremely low solubility of dyes in sCO₂. However, DMF is a phase-out substance due to its toxicity on the reproductive system [59].

The report showed that at 8 MPa, 90 °C and with a 1:20 MLR, a single cycle of 20 minutes resulted in an 86 % removal rate [61]. Furthermore, by doing three 20-minute cycles for the yellow dye and two 20-minute cycles for the red dye, almost everything was completely extracted. The yellow dye was found to have a higher activation energy for the desorption process than what the red dye has, explaining the extra cycle required. Continuously, the process preserved the structure of both the substrate and the dye, where the latter was shown to be able to be precipitated from the solvent by the addition of water and reused, while the scCO₂ could be recycled through depressurisation. Moreover, the report reveals that the subsequent yield of BHET was improved from 64 to 69 % due to the decolourisation step.

Another report, written by Ren et al., also inspected the role of scCO₂ with a co-solvent in the decolourisation of polyester [64]. The disperse dyes examined were the anthraquinone Disperse Red 60 and the monoazo Disperse Blue 301 and were dyed to a polyester sample at 25 MPa and 120 °C. The results demonstrate that the decolourisation was highly dependent on the solubility parameter of the co-solvent and when it is similar to the one of the dyes instead of polyester, the removal efficiency exceeded 95 % for the two dyes. These results were found when the co-solvent had 2 % volume, 1:500 bath ratio, 120 °C, 25 MPa and 3 hours of processing. The most studied co-solvent in the article is BA, and it showed reasonable results of 93 % removal for the red dye and 95 % removal for the blue dye. The study further explained that both the dyes and the substrate were structurally preserved during the treatment and concluded that a scCO₂/co-solvent system is a highly promising decolourisation strategy for polyester.

3.3.5 Combination of ethylene carbonate and tetramethylurea

Ethylene carbonate (EC) is a highly polar organic solvent and is produced through the reaction of carbon dioxide with ethylene oxide [65]. Continuously, its boiling point is at 248 °C and due to the low volatility of the substance, it is relatively safe to handle and biodegradable [21]. However, it can cause eye irritation and cause damage to organs if swallowed [55]. The price for EC per kg is 50 SEK and the general structure is illustrated in Figure 19 [66].

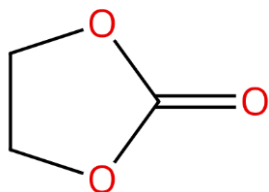


Figure 19: Ethylene carbonate [21].

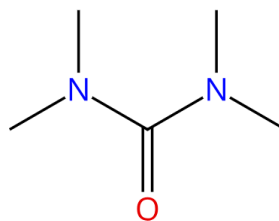


Figure 20: Tetramethylurea [21].

Tetramethylurea (TMU) is also a polar compound, and it is hydrogen-bonding [67]. On the contrary to EC, TMU has a lower boiling point at 176.5 °C [21]. This compound is considered to be toxic due to its cancerogenic and reproductive hazard properties, meaning that there is more pressure on handling this solvent with care [67]. Nevertheless, it is not listed in the PRIO-guide [59]. TMU is more expensive than EC, coming in at 325 SEK per kg and the structure of TMU is seen in Figure 20 [68].

While EC can effectively cause swelling of the polymer fibres, it is comparatively inefficient at keeping the dye dissolved [9, 69]. In contrast, TMU is less efficient at swelling the fibres, but it does exhibit a strong ability to stabilise aromatic compounds, such as dyes [70]. The different abilities were something that Mu and Yang observed in their research, where they found that using EC individually for the dye removal of polyester only led to about 70 % of colour reduction after one cycle at 90 °C [9]. But experiments with a combination of both EC and TMU at a 7:3 mass ratio (EC:TMU) led to an 88 % decrease after one cycle at the same temperature. This mixture of solvent is critical because it can balance solvent-polymer interactions to swell polyester without damaging the polymer backbone, whilst the solvent-dye interaction maintains the structure of the dye.

Mu and Yang conducted their experiments at a liquor ratio of 1:5 and they only tested on an anthraquinone dye, Disperse Blue 56 [9]. Their findings were that a solvent mixture of 7:3 was the most efficient at removing dyes, and these results were found in the same article as the second DMSO article presented in this thesis. The researchers concluded that EC:TMU was more efficient than DMSO, and thus they selected EC:TMU to study how many 30-minutes treatment cycles were needed to achieve 99 % dye removal from polyester. They conducted their experiment both at 90 and 120 °C. At 90 °C, no further dye removal occurred after the third cycle, whilst for 120 °C the process only needed 2 cycles to achieve a 100 % dye removal.

3.4 Separation of dye from solvents

For the prior part of the method, Section 3.3, the focus was solely on the separation of dye from polyester. For this part of the method, the focus is instead on the separation of the dye from the solvent. First, several separation techniques are presented, including those used in the final flowsheet. Then, one complete separation process that is discussed in one of the articles from the literature study is presented. Lastly, separation of dye from scCO₂ is discussed.

3.4.1 General separation techniques

Once the dye has been separated from the polyester fibre, it enters the bulk of the solvent where it is dissolved and thus becomes a solute [36]. The solvent and solute together create a homogeneous mixture, that needs to be separated according to the principle of homogeneous separation. The principle says that another phase needs to be created within the system in order to force the separation. One of the most common ways is to utilise the difference in boiling point or volatility between the solvent and the solute, but other solutions can be to introduce an agent that allows for precipitation or crystallisation of the dye so it can be filtered out or adsorbed onto another media.

Evaporation

Evaporation refers to the process of vaporising a solvent, resulting in a concentrated residual solid of the dye [71]. Hence, the purpose of evaporation is to collect the solute and to boil off the solvent. The process takes place over a controlled heating source and with pressure reduction, to boil the volatile solvent away from the non-volatile dye. It is possible to recover the vapor by condensing it into a liquid again. Therefore, the solvent can be reused to separate dye from polyester fibres again. The setup of an evaporation process can either be single-stage or multistage, depending on how pure the products need to be.

Distillation

Distillation relies on the difference in boiling points between two liquids, where the liquid with a higher boiling point ends up at the bottom of the column and the lower boiling point at the top of the column [36]. In the process, a tower equipped with multiple trays is carefully heated so that the low-boiling liquid vaporises at each stage and rises through the column. The vapor is then condensed at the top into a highly pure liquid. The high-boiling liquid on the other hand, moves down in the column, which is then collected as a liquid. Additionally, a common characteristic for a distillation process is the repeated vaporisation and condensation of the two components, which ensures an even purer fraction of the separated compounds.

Precipitation

Precipitation, or chemical precipitation, is the process of adding an anti-solvent to a liquid mixture, causing a dissolved solute to become solid again [72]. The purpose of this process is to reduce the solubility of the mixture, so that the dye is not soluble in the mixture anymore. The anti-solvent that is applied needs to be miscible with the solvent but poorly soluble with the dye, where water is a common choice. Therefore, precipitation follows the “like-solves-like” principle, where water causes the similarity in solubility between the solvent and dye to differ largely instead, leading to separation. To promote precipitation, cooling the solution helps. Otherwise, some mixing is needed to ensure that the water reaches all dissolved particles.

Crystallisation is very similar to precipitation and can be seen as a sub-category of it [72]. The difference between the two is that with crystallisation the solid outcome is in a crystalline and structured order, whilst for precipitation it can also be amorphous. If the dye has a more crystalline structure, it is usually more stable and can be stored for a longer duration. This process also results in a slightly higher purity [73]. To achieve crystallinity, it is important to controllably add the non-solvent and to slowly mix it.

Filtration

Filtration, unlike the other separation methods presented, is used for heterogeneous mixture, i.e. when there are two or more phases present [36]. This method is applicable once the dye has been precipitated and converted back into a solid. The principle is that a porous medium retains the solid particles while allowing the fluid to pass through. After the mixture has been filtered, the dye can be collected as a “cake” on top of the filter, either manually or by applying air pressure to release the solids.

3.4.2 Recovery process from the literature review

Among the reviewed studies in 3.3, only one described a recovery process for both the extracted dyes and the solvent that seemed industrially scalable. This process is presented by Mu et al. in Section 3.3.3, which described how BA was used as a solvent for extracting dyes from polyester [58]. After the extraction, the polyester fabric was washed with ethanol to remove any lasting dye impurities and BA. This solution was then distilled to recover BA and the washing media. Followingly, the coloured BA solution is mixed with 28 times water containing 0.5 wt% BA. 30 minutes later, almost all dyes had precipitated and were then recovered by filtration. In the report, the dyes were even reused to colour the resulting recycled polyester.

Continuously, two different options were used to separate water from BA after the filtration [58]. The first one was a simple distillation at reduced pressure and 50 °C. It removed the water first due to its lower boiling point, leaving pure BA which can be reused in the dye-removal cycles. The other option is a liquid-liquid extraction where another chemical is introduced. Twice the amount of dichloromethane (DCM) compared to BA is here added to the solution. DCM extracts BA from the solution as it preferentially dissolves into the DCM phase. Remaining, is the aqueous layer that retains only 0.5 wt% of BA, which is the exact same concentration used to precipitate the dyes and could therefore automatically be reused for this specific step. Followingly, the DCM and BA mixture is distilled at 40 °C, which is the approximate boiling point of DCM, therefore leaving a pure concentration of BA. However, DCM is unfortunately toxic and needs to be handled with care. In the PRIO-guide it is considered to be a priority risk reduction substance [59]. Lastly, 5 % of the BA may be lost in processing [58].

3.4.3 Supercritical carbon dioxide with co-solvent

The articles named in Section 3.3.4 did unfortunately not name the recovery of scCO₂. However, as scCO₂ is different from the other solvents, due to its high pressure and supercritical state, its recovery process is different and is therefore explained separately in this report.

In order to lower the energy consumption of a plant using scCO₂ it is crucial to recover and reuse it [74]. CO₂ is usually recycled in the liquid state. Therefore, the CO₂ recovery is performed by firstly depressurising the system so that the CO₂ expands to form a two-phase region and releases the extracted solute. The CO₂ is then heated to go to a single-phase state, its gaseous state, and is then subcooled by a chiller unit to condense it back to its liquid state. Lastly, the liquid CO₂ is pumped back and heated to the required extraction pressure and temperature, thus regenerating its supercritical state. However, if the pressure in the system is below 30 MPa, it is more energy efficient to recover CO₂ as gas. In this case, instead of the heating step, the CO₂ is compressed to a higher pressure than the critical pressure after the expansion. Continuously, the CO₂ is subcooled by a cooling tower, before entering the pump.

In this reports case, the solubility of the dyes in scCO₂ is below 0.5 %, and the system operates above the critical pressure [75]. Under these conditions, CO₂ can instead be directly recovered

as supercritical carbon dioxide [74]. Therefore, only a slight expansion is necessary to make the solute precipitate. As a result, no phase change happens, leaving no obligation to heat and subcool the CO₂. The CO₂ can then be recompressed to the required conditions for dye extraction. However, the presence of a co-solvent in the system adds a certain complexity. After the expansion step, the system has typically two different phases [76]. The CO₂ is in a gaseous state, and the co-solvent and dye are in a liquid state. Therefore, an additional unit like a receiver vessel is needed to separate the two phases. The CO₂ is then filtered, dried and recompressed for reuse and the co-solvent is typically distilled to recover the co-solvent and the solute.

3.5 Process modelling and evaluation

Now that solvents and some separation techniques have been introduced as possible options for a pre-treatment step for the Rewin process chain, it is time to investigate their feasibility and performance through both process modelling and parameters. The modelling aims to visualise the pre-treatment steps, assess the material requirements and to identify critical parameters. This modelling work complements the literature review by using its data to provide an industrial process point of view on the subject as well as analysing its possible industrial implementation with an economic analysis.

3.5.1 Hansen solubility parameters

The first step when choosing a solvent for a specific system is to make sure that the solvent is adequate for its use. This can be done by comparing the Hansen or Hildebrand solubility parameters of the polyester with the solvent. Table 2 displays the Hansen and Hildebrand solubility parameters of the solvents analysed in this report and of polyester. The solubility parameters of an anthraquinone are also present in the table to provide a reference for comparison.

Table 2: Hildebrand and Hansen solubility parameters of the studied solvents and PET.

Solvent	δ_D (MPa) ^{1/2}	δ_P (MPa) ^{1/2}	δ_H (MPa) ^{1/2}	Hildebrand/total solubility parameter (MPa) ^{1/2}
DMSO [49, 61]	18.4	16.4	10.2	26.6
Cyrene [10]	18.8	10.6	6.9	22.7
Water [49]	15.5	16.0	42.3	47.8
Benzyl alcohol [58]	18.4	6.3	13.7	23.8
Ethylene carbonate [49]	19.4	21.7	5.1	29.6
Tetramethylurea [49]	16.7	8.2	11.0	21.6
CO ₂ [49]	15.7	6.3	5.7	17.9
DMF [49]	17.4	13.7	11.3	24.8
PET [10, 61]	18.3	6.7	6.7	21.7
Anthraquinone [49]	20.3	7.6	4.8	22.2

With these parameters, the interaction radius (R_a) of each solvent to polyester can be calculated using Equation 4. Furthermore, knowing that the R_o of polyester is $5 \text{ MPa}^{1/2}$, the suitability of the solvents for the purpose of swelling the polyester can be calculated with Equation 5 [49]. However, three of the solvents named in the articles are composed of a mixture, Cyrene with water, EC with TMU and scCO_2 with co-solvent. Therefore, their solubility parameters need to be recalculated for the mixture using Equation 6. However, for the scCO_2 -systems, RED-calculations are not performed as its supercritical state may alter interaction behaviour in ways that makes this method unreliable.

Equation 6

$$\delta_{\text{Mix}} = \phi_1 \cdot \delta_1 + \phi_2 \cdot \delta_2$$

Where ϕ is volume fraction of each solvent in the mixture [49]. Equation 6 can be used to calculate δ_D , δ_P and δ_H for the mixtures. Followingly, Equation 4 is used to calculate the R_a and Equation 5 the RED.

In 3.2.1, it is explained that if RED is less than 1, the solvent used is considered to be good. However, in the case of dye removal, this is not the case. Under 1, the solvent dissolves the polyester and strongly swells the polymer [49]. Therefore, a RED over 1 is necessary. However, there is little to no information about an optimal RED value for the swelling of polyester. But a study conducted by Nielsen & Hansen mentions that a solvent shows sufficient swelling properties on an elastomer, which is a polymer, when the RED of the system is under 1.7 [77]. Therefore, an optimal RED-value for the swelling of polyester is assumed to be around 1-2.

3.5.2 Parameter definition

Once the solvents have been evaluated with the HSP to be adequate for swelling the polyester and extracting the dyes, it is time to construct the flowsheet for the whole pre-treatment process that is compatible with the five different solvent-based pre-treatment option that this report chose to investigate further:

- DMSO
- Cyrene with water 75:25
- Cyrene with water 50:50
- Benzyl alcohol
- Ethylene carbonate with tetramethylurea

ScCO_2 is not included in this analysis due to its higher complexity degree and different process design requirements.

Before constructing the flowsheet, some parameters need to be introduced for the process. For the input of polyester, Rewin has designed their pilot to handle 5000 kg/h of fabric, which will be the fabric flow used in this report. This flow is assumed to be homogeneous and constant. Additionally, as this inflow is made of coloured polyester, it contains both disperse dyes and polyester, requiring determination of their respective fractions. The reviewed reports are all done in laboratory scales, thus the input polyester in these is much smaller than for the pilot-scale process at Rewin. Therefore, for the results from the reviewed reports to be applicable to their process, the parameters must be scaled up so that it matches an inflow of 5000 kg/h of polyester.

Table 3 shows the input streams, with the detailed information provided in text in Section 3.3. A thing to note is that for DMSO, the input comes from Mu and Yang as Sharma et al. used textile waste [9, 52]. As the other research articles used polyester pieces dyed by themselves, it is important to use Mu and Yang as they also included this step in their research rather than Sharma et al. Furthermore, every scenario is assumed to contain 2 wt% dye on the fabric, as this is a frequently reported value in the analysed reports.

Table 3: Stream input for industrial implementation.

	Dye on polyester %	Dye	Polyester	MLR	Solvent
DMSO	2 wt%	100 kg/h	4900 kg/h	1:5	25,000 kg/h
Cyrene:water (75:25)	2 wt%	100 kg/h	4900 kg/h	1:10	50,000 kg/h
Cyrene:water (50:50)	2 wt%	100 kg/h	4900 kg/h	1:10	50,000 kg/h
Benzyl alcohol	2 wt%	100 kg/h	4900 kg/h	1:4	20,000 kg/h
EC:TMU (7:3)	2 wt%	100 kg/h	4900 kg/h	1:5	25,000 kg/h

3.5.3 General flowsheet

The pre-treatment process flowsheet is done by using Draw.io, an online diagramming software that allows to build process flowsheets with the use of different blocks and streams [78].

Firstly, a separation step is implemented to show the separation between the dye and the polyester. This is done by applying three reactors as the reviewed literature usually named three cycles as the optimal number for dye-removal. This separation step has then two outlets: one with solvent and dissolved dye and the other with polyester and some remaining dye. In the latter outlet, a small portion of the solvent is retained, which needs a washing step in order to separate the remaining solvent from the polyester. This step is included in the Draw.io flowsheet, where the polyester is cleaned using a specific washing medium to remove the remaining dyes and solvent. The washing medium can then be recovered through distillation.

Next, this project has chosen to use the strategy in Section 3.4.2, where the separation between the dye and BA is done through precipitation. However, the solvent amounts for the pre-treatment options are rather high, Table 3. If 28 times water are needed for precipitation, reported for the BA article, enormous quantities of water would be required, which would exceed Rewin's handling capacity. Therefore, before this step, an evaporation step is added to remove parts of the solvent beforehand. This leaves a higher concentration of dye within the remaining solvent in the bottom product, which facilitates the precipitation of the dye with the addition of an anti-solvent. The anti-solvent used in this project is chosen to be water.

To visualise the process of precipitation, a precipitation tank is implemented which has the bottom product of the evaporator and water as inflows. The precipitation tank is where the precipitation takes place and then a filtration unit is applied to the flowsheet to separate the solid dye from the anti-solvent and solvent mixture. Finally, to separate water from solvent, a distillation tower is used, enabling recovery of both. This corresponds to the first approach

named in 3.4.2, as the second named strategy requires an additional solvent, therefore representing an additional cost. Furthermore, heaters and coolers are used to increase and decrease the temperature at the required locations in the flowsheets.

3.5.4 Aspen Plus properties

To obtain additional information about the thermodynamics and other key process properties for the pre-treatment process, Aspen Plus V14 (Aspen) is used. Aspen is a chemical process simulation software provided by Aspen Tech, that allows the user to model, analyse and optimise chemical processes [79]. In the tool, modelling of various chemical reactions, separation processes, heat exchangers, pumps, and so on can be performed with one or multiple streams. The software then predicts energy and mass balances based on kinetic and thermodynamic models which in turn is based on a specific physical property method provided by the user.

The chosen property method for the modelling in this report is Non-Random Two-Liquid (NRTL). NRTL is an activity coefficient-based model and is common for simulations of liquid-phase reactions with non-ideal mixtures, such as a mixture between a polar solvent and a non-polar disperse dye molecule [36]. An activity coefficient model means that for the modelling of different separation techniques, there needs to be a calculation of how much of each component ends up as a vapor and how much remains as liquid at equilibrium. To calculate this, an activity coefficient is used, which describes how much a real solution differs from the ideal behaviour. Thus, NRTL estimates this coefficient and assumes that the distribution of molecules is not random, meaning that some molecules experience more intramolecular forces, such as hydrogen bonding, than what other molecules that are further away can experience.

The polyester for the modelling is assumed to be a solid, whilst both the dye and the solvent are simulated as liquids. This is because the dye is dissolved in the liquid. Not all disperse dyes mentioned in the literature review are available in the Aspen databases, so for all the simulations the dye with the most information in both the Aspen database and in literature is used, which is the anthraquinone Disperse Red 60 (DR60). Therefore, DR60 is used as representative test dye for all dyes, allowing its result to be used as an indication of the behaviour of all disperse dyes.

3.5.5 Solubility analysis

The first thing analysed in Aspen is the solubility of DR60 in the solvents. This is done to predict the dye's precipitation behaviour, as a solute remains dissolved in a medium only when its concentration in the system lies below its solubility limit. However, no experimental solubility data could be found in the literature for these systems. Therefore, solubility is estimated using Aspen by means of the group contribution method UNIFAC (Universal Quasichemical Functional-group Activity Coefficients), which estimates the activity coefficients and predicts the phase equilibria of a system when experimental data is not available [36]. It does so by attributing functional groups such as $-\text{CH}_3$, $-\text{CH}_2$, $-\text{OH}$ to the chosen molecules, assuming that the behaviour of a functional group is independent of the molecule it belongs to.

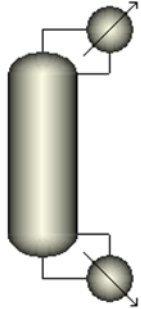
The assigned functional groups for each solvent and DR60 can be seen in the Appendix, Table 11. This gives an estimation of the activity coefficients necessary to produce solubility plots for the dye in the different solvents. However, some information about DR60 is lacking from the Aspen databases and therefore its heat of fusion, 22.56 kJ/mol, and melting temperature, 185 °C, are added to the system [21]. Furthermore, the function "estimate missing parameters using UNIFAC" is used to fill in missing NRTL binary parameters.

Lastly, the plots for the solubility of the dye in the different solvents for a range of temperature are made. Complementary plots are also generated where the system is mixed with varying concentrations of water. These plots help to evaluate how the addition of water alters the solubility of the system, therefore obtaining a possible water-to-solvent ratio allowing dye precipitation. The solvent showing the best results from the plots, based on our process, is then selected for a more detailed process flowsheet in Aspen.

3.5.6 Aspen Plus modelling

To construct a process flowsheet in Aspen, different unit operation blocks are connected with streams, typically under the assumption of steady state. For modelling of the pre-treatment process of the solvent showing the best results in the previous analyses, five fundamental blocks are employed. An overview of these blocks, including their icons, description, uses and key assumptions, can be seen in Table 4. For the data input, parameters from Table 3 are used.

Table 4: Description of Aspen blocks [80].

Block	Icon in Aspen	Description	Use	Key assumptions
Separator (SEP)		Divides one or more inlet streams into two or more outlet streams according to specified split fractions or mass/molar flows.	-Bleed valves -Solid stream splitters	User-defined splits, no reaction or heat-transfer and negligible pressure drop.
Flash (FLASH2)		Describes vapor-liquid equilibrium. Performs a flash calculation at a specified temperature, pressure and/or duty to determine vapor and liquid fractions and compositions in the two outlet streams.	-Evaporators -Flashes -Knockout drums -Free water	System is at thermodynamic equilibrium, steady-state operation and negligible heat losses.
Distillation (DWSTU)		Simulates multistage vapor-liquid separation using equilibrium stages. Performs mass and energy balances with specified feeds, products and columns conditions.	-Distillation column -Refinery towers -Absorbers/strippers	Equilibrium stages (or specified efficiencies), steady-state operation, negligible heat loss, and no reactions unless added.
Heater (HEATER)		Adds or removes heat from an inlet stream by specifying the outlet temperature, duty or energy balance.	-Heaters -Coolers -Pumps -Valves -Compressors	Adiabatic operation unless duty is specified, no chemical reactions and no pressure drop.
Mixer (MIXER)		Combines multiple inlet streams into one outlet stream using overall mass and energy balances.	-Blend streams -Combine recycle and fresh feed	No reactions, negligible pressure drop, adiabatic unless specified, perfect mixing

3.5.7 Aspen flowsheet representation

The Aspen modelling of the pre-treatment step builds on the Draw.io flowsheet explained in 3.5.3., but it also allows for further analysis of additional parameters. Due to the limited amount of data about dye-removal processes, the Aspen modelling in general maintains a certain computational simplicity.

The polyester entering the process is assumed to be an inert solid in the Aspen model. It has no interaction with the dye, and no swelling behaviour is modelled. Therefore, a series of separation blocks is implemented in Aspen Plus to model the separation of dyes from polyester. The split fractions used in the model are based on values reported in the analysed literature and are presented in Section 3.3. The washing step presented in 3.5.3 is omitted from the Aspen flowsheet due to the complexity of modelling the solid-liquid interaction between the polyester, the solvent and the washing medium. Therefore, after the extraction process, no remaining solvent on the polyester is assumed.

Continuously, the evaporator, which is modelled using a flash unit, uses the best water-solvent ratio calculated from the solubility analysis in 3.5.5 as a base to remove a larger part of the solvent. Furthermore, a sensitivity analysis is done on this block to determine its optimal operating temperature and pressure. A sensitivity analysis is a tool available in Aspen that tests different user-defined values of certain independent parameters, such as pressure, to see how it impacts a specific dependant variable in the model, like the temperature of the outlet stream for example [80].

Once the evaporation is done, water is introduced via a mixer block. The amount of water added is determined according to the calculation made in the solubility analysis. A separator block is then employed to represent a precipitation tank, where all dyes are assumed to precipitate and leave the system as bottom product. Finally, to separate water from solvent, a distillation block is used, enabling recovery of both. The parameters used for this final block are the following: 10 stages, water as light key with a recovery of 0.999 and the solvent as heavy key with recovery of 0.001, pressure of 1 bar. These values are just assumed to illustrate the process, and no optimisation is performed.

3.5.8 Economic analysis

Finally, to add another depth to the discovery of which solvent suits Rewin's process best, it is relevant to consider the economic benefit, or loss, that comes from introducing the pre-treatment step. Here, all the selected solvents are reviewed to create an additional means of comparison. This economic analysis is based on estimating the cost of treatment for the waste stream containing dye and other impurities from the current Rewin process, thus the hazardous chemical waste. Then, the dye-removal processes presented in this thesis receive a cost estimation based on the cost of solvent for the plant. Lastly, the savings from minimising the waste are compared with the cost of implementing the pre-treatment, thus providing an evaluation of the economic feasibility of the treatment.

Firstly, there are some key concepts to consider when investigating the economic aspects of an industry, namely the type of expenses. The expenses can be divided into two different categories, capital expenses and operational expenses [81]. Capital expenses occur in the beginning of a new operation, such as the investment of new equipment and machinery. These expenses are investments in assets that will provide long-term benefits to the company. In contrast, operating expenses are recurring expenses, and these costs can be further categorised into fixed or variable operating expenses. Fixed expenses are costs that do not change with production

output, such as labour, whilst variable operating expenses do change with production volume, such as materials and energy. For this report, the capital expenses are not considered, only briefly discussed, and only some of the operational expenses are calculated and discussed.

To estimate the cost of treatment for hazardous waste in the Rewin process, the amount of waste needs to be considered. Rewin aims to recycle 5000 kg/h of polyester and wishes to operate 8000 h/year, which leads to a total recycling of polyester of 40,000 tonnes/year [43]. In the process, the waste stream containing dyes comes after the catalytic reactor, Figure 21. This stream has a yearly flow of 160,000 tonnes and contains mostly MEG, some BHET, water, DEG, TEG and lastly some complex impurities. The impurities contain degraded dye, acids and salts, and accounts for 0.1 % of the total flow, which is about 160 tonnes/year.

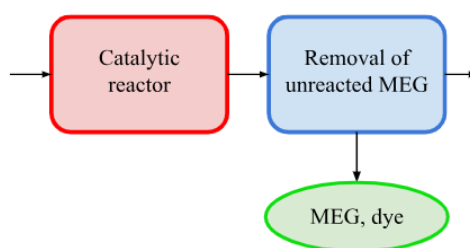


Figure 21: Waste stream containing dye in Rewin Textiles process.

The handling of this waste is not specified by Rewin. However, as the stream contains many different chemicals, where some are degraded and some are not, the whole stream needs to be disclosed as hazardous waste and sent to licensed incineration facilities to be incinerated [82]. To estimate the cost for the waste treatment of hazardous waste, a case study by Lyu et al. has been used [83]. In this study, the third-party tax fee for incineration costs 3000 CNY per tonnes waste, which has then been used to estimate the expense for treatment of Rewin's waste stream. For calculations of the cost savings, see Appendix, where the conversion rate of CNY to SEK is 1.34 SEK/CNY [84].

Lastly, to establish some of the expenses for the proposed processes in this thesis, an estimation of a few of the operating expenses is performed. Based on the proposed flowsheet, the cost of solvents is assumed, with the cost of each solvent provided in Section 3.3 and in Table 10 in the Appendix.

4 Results and Discussion

This section presents and discusses the results obtained from the solvent selection, process modelling and economic analysis performed in this study. The results are discussed in relation to solvent efficiency, sustainability and process feasibility for the dye removal process implementation at Rewin Textiles AB.

4.1 Dye extraction step and solvent discussion

The solvents identified through the literary study are here evaluated for their potential to remove disperse dyes from polyester without damaging the fibre or the dye. This is done by first discussing the HSP, removal efficiencies as well as discussing the environmental evaluation of the solvents.

4.1.1 Hansen solubility parameters

The HSP are commonly used to predict how well a solvent interacts with a given solute. By comparing the dispersion, polar and hydrogen-bonding parameters of each solvent with those of polyester, it is possible to comprehend why certain solvents have higher dye-extraction efficiencies than others. Therefore, this part aims at explaining the swelling capacities of the solvents regarding their HSP compared to the ones of polyester, Table 2.

Starting with the dispersion solubility parameter, δ_D , Fernando et al. describes in the Cyrene article that if a solvent and a polymer have similar δ_D -values, the swelling capacity of the polymer is enhanced [10]. The reason to this is that δ_D represents the dominant cohesive force for polyester, which relates to its van der Waals bonds. Therefore, when δ_D for a polymer and a solvent are close, the solvent can interact with the polyester with roughly the same energy as the polyester interacts with itself, facilitating the disruption of dye-polymer bonds as these are also van der Waals bonds. All of the solvents studied in this report have δ_D -values that are relatively close to the one of polyester, with DMSO, Cyrene and BA showing the closest matches.

Continuously, regarding the polarity solubility parameter, δ_P , Mu et al. in the BA article mentions that this value should be similar between the solvent and the polymer [58]. Furthermore, the article names that δ_P is the most important solubility parameter to calculate the interactions between organic molecules. This is why the article chose to further examine the role of BA as a solvent for dye extraction from polyester. However, from the investigated solvents, only BA, CO₂ and TMU have a somewhat similar polarities to polyester. The others exhibit much stronger polarities, with DMSO and EC having the highest ones. Therefore, it seems that different strategies can be had on the polar solubility parameter. This is supported by Fernando et al. as they mention in their article that dye-extraction strategies were commonly done by polar aprotic solvents [10]. However, polar aprotic solvents can involve toxic chemicals, which is why they investigated Cyrene. Therefore, more strongly polar solvents can also be used for the purpose of extracting dyes, as the polar functional groups on the solvent can form strong possible interactions with the ester groups in polyesters.

Lastly, the hydrogen-bonding solubility parameter, δ_H , is also an important parameter to consider. Fernando et al. mentions that the similarity between the δ_H of Cyrene and polyester is a reason to the efficacy of the solvent as it allows for hydrogen-bonding interactions between

Cyrene and polyester, which supposedly enhances the swelling process [10]. As could be expected, water is the solvent with the highest hydrogen-bonding capacity by far, followed by BA, TMU and DMSO. The other solvents show low δ_H parameters. However, Fernando et al. also names that the forces quantified in δ_H are not the driving forces of dye-extraction but that these come from the other solubility parameters instead.

As mentioned before, the solubility parameters of a solvent should be close to those of the polyester, but not so close that it dissolves the polymer, since the goal here is only to swell the polyester. This makes it hard to exactly define which parameter values are ideal or how close each one should be of polyester, because the effect depends on the combined contribution of all three parameters. For this reason, it is more practical to look at the RED values of the solvent with the solute.

Table 5 displays the results of the calculated R_a and RED of the chosen solvents. As what can be seen, all the solvents and solvent mixtures have a RED value over 1. This is to be expected, as a value under 1 would mean that the solvent dissolves the polyester. With an optimal RED of between 1 and 2 as described in 3.5.1, it puts BA as the most optimal candidates regarding this criterion.

Table 5: Results of the calculated δ_T , R_a and RED of the solvents.

Solvents	δ_T (MPa) ^{1/2}	R_a (MPa) ^{1/2}	RED
DMSO	26.6	10.31	2.06
Cyrene:water (75:25)	26.7	10.48	2.10
Cyrene:water (50:50)	32.8	19.22	3.84
Benzyl alcohol	23.8	7.01	1.40
EC:TMU	26.5	10.97	2.19

Furthermore, DMSO, Cyrene (75:25) and EC:TMU all have very similar RED values, at around 2-2.2. Since most solvents lie in that range, while still showing to experimentally swell the polyester with a high efficiency, it can be reasoned that a RED of 2.2 is completely appropriate for swelling polyester and extracting dyes. This therefore expands the initially defined range. Furthermore, even a RED of 3.84, like for Cyrene (50:50), also experimentally swells the polyester and could also be regarded as good enough for this purpose. However, its dye extraction efficiency is much lower than that of the other solvents and is therefore not optimal for this system. These results suggest that a RED range of 1-2.3 is suitable for polyester swelling and dye extraction purposes.

4.1.2 Evaluation of solvent efficiency based on the literature review

The solubility parameters only give a theoretical prediction on which solvents could be appropriate for such a system. Therefore, experimental analysis is necessary to study which solvent is optimal for this system, which is why this report includes experiments from other research reports. In the reviewed literature, the extraction efficiencies for disperse dyes from polyester

by a solvent depended on solvent polarity, swelling capacity and operating conditions. The reported extraction efficiencies are shown in Table 6. Furthermore, Table 9 in the Appendix displays the pictograms of the reviewed solvents to evaluate their toxicities and Table 10 shows the cost for each solvent.

Table 6: Extraction efficiencies for the solvents listed in the reviewed literature review.

Dye removal %	Type of disperse dye	Cycle 1	Cycle 2	Cycle 3
DMSO* Sharma et al. [52]	Textile waste (not disclosed)	29 % 130 °C	68 % 130 °C	87 % 130 °C
DMSO Mu & Yang [9]	Anthraquinone	87 % 100 °C	No information	No information
Cyrene:water (75:25) Fernando et al. [10]	Anthraquinone	68 % 98 °C	85 % 98 °C	96 % 98 °C
Cyrene:water (50:50) Fernando et al. [10]	Anthraquinone	36 % 98 °C	58 % 98 °C	71 % 98 °C
Benzyl alcohol Mu et al. [58]	Monoazo	95 % 130 °C	98 % 130 °C	99.8 % 130 °C
ScCO ₂ & DMF Huang et al. [61]	Monoazo & diazo	86 % 120 °C	94 % 120 °C	97 % 120 °C
ScCO ₂ & benzyl alcohol Ren et al. [64]	Anthraquinone & monoazo	95 % 120 °C	No information	No information
EC:TMU Mu & Yang [9]	Anthraquinone	88 % 90 °C	98 % 90 °C	99 % 90 °C
EC:TMU Mu & Yang [9]	Anthraquinone	94 % 120 °C	100 % 120 °C	No information

**All the values in this row are approximated from Sharma et al., calculations made in Appendix, Section 7.3.1 [52].*

DMSO showed acceptable results with 87 % dye-removal efficiency after three cycles for Sharma et al. and 87 % after one cycle for Mu and Yang [52, 9]. If Mu and Yang would have focused on DMSO instead of EC:TMU, data for additional cycles would have been obtained which would likely have given removal efficiencies that are comparable to EC:TMU and BA. The difference in removal efficiencies between the two DMSO articles can be explained by that Sharma et al. uses textile waste, where the dyeing process has been carried out under industrial conditions whereas Mu and Yang dyes their own fabric in a laboratory [52, 9]. Industrially, the conditions are more extreme, with higher temperatures or pressures, resulting in the dyes diffusing more deeply into the amorphous regions of the fabric. Furthermore, the fabrics undergo finishing treatments to strengthen their wash-fastness properties which is not something that is done in the laboratory [25]. This can also be a reason to the different operating extraction times

and MLR ratios discussed in the articles. Sharma et al. reported 1 hour and an MLR of 1:18, whereas Mu and Yang reported 30 minutes and an MLR of 1:5, likely because more incrustated dyes require longer extraction times and larger solvent volumes [52, 9]. Therefore, the Sharma et al. article gives a plausible indication of what Rewin can expect on the removal efficiency of DMSO and the other solvents studied on textile waste.

In polycotton blends, DMSO may also swell the cellulosic fibres without dissolving the fibres, but with a low dye-extraction efficiency due to the strong covalent bonds between reactive dyes and cotton [52]. If the dye used to colour cotton fabric was a direct dye instead, DMSO showed potential to remove the dye due to the weak bonds between the fibre and the dye [9]. But Rewin only aims at separating cotton from polyester in the textile waste to resell it, rather than on decolouring the fibres. Therefore, as long as the cotton structure remains intact, the process is compatible with Rewin's production chain.

Depending on the amount of water mixed in with Cyrene, the dye-extraction efficiency differed [10]. With 25 % water, the efficiency after three cycles is 96 % whereas with 50 % water, the efficiency only reached 71 %. When water is added, the polarity of the overall solution is increased but the swelling capability is decreased, which is shown by the RED calculation of 3.84 shown in 4.1.1. Due to Cyrene being the agent that enables the dye-extraction process, it is expected that when Cyrene is more abundant, its extraction efficiency improves. However, when there is more Cyrene in the solution, the overall viscosity is increased, which could have a negative impact on the desorption time of the dye particles. Furthermore, Cyrene is the liquid solvent studied that has the highest inflow requirement, which is 50,000 kg/h.

BA is the second-best solvent for dye extraction analysed in the literature study as it resulted in 98 % dye removal after two cycles and 99.8 % dye removal after three cycles [58]. This suggests that the third cycle is not necessary as the dye is almost entirely extracted from the polymer after two cycles. Furthermore, Mu et al. tested the dye-extraction process on a high-energy dye, Disperse Blue 79, and concluded that the high-removal efficiency achieved for this dye indicates that lower-energy dyes should be even easier to extract using this technique. This is an interesting aspect to consider as it ensures the removal of most types of disperse dyes.

Solvent-based decolourisation can be found to face scalability issues due to excessive use of solvents and a high environmental impact depending on which solvents is being used. Therefore, many articles online have evaluated the efficiency of scCO₂ to extract dyes, and this report has included an analysis of two articles about scCO₂ together with a co-solvent. This is because scCO₂ primarily serves to swell the polyester, while the co-solvent is responsible for extracting the dyes from the polymer matrix. This explains why Ren et al. emphasises the importance of the similarity in the solubility parameters between the co-solvent and the dye compared to between the polymer and the solvent like in the other articles [64]. The role of the co-solvent is not to swell the polyester but to make the extraction of dyes more efficient, so therefore the focus is here on similarity of solubility parameters between the dye and the co-solvent instead.

Huang et al. utilised DMF as a co-solvent, which resulted in a 97 % removal rate after three cycles and Ren et al. used BA as a co-solvent, which resulted in a 95 % dye removal after one cycle [61, 64]. Both these removal efficiencies are high and compatible with a dye-extraction process. Furthermore, Huang et al. mentions in their article that all disperse dyes have different activation energies which is an important information to consider in the analysis [61]. The activation energy of a disperse dye is generally related to its size, with larger particles tending to have higher activation energies and these require longer extraction times. This is consistent with

the theory presented by Mu et al. regarding BA [58]. However, due to the extremely negative environmental impact that DMF has, this dye-removal option is removed from this analysis. Furthermore, Ren et al. uses a bath ratio of 1:500 and an operation time of 3 hours, which are not realistic for industrial implementation and contradicts the purpose of using scCO₂, which is to reduce solvent requirements [64]. Therefore, this dye-removal option is not considered desirable as well and more research is needed on dye removal with scCO₂.

Lastly, the combination of EC with TMU resulted in a 99 % removal rate after a second cycle at 120 °C and a near 100 % removal rate after the third cycle at 90 °C [9]. This puts this solvent as the most efficient system at extracting disperse dyes from polyester, which is attributed to the synergistic effect of the solvent mixture. EC and TMU have very different HSP, as can be seen in Table 2. EC is a highly polar substance that efficiently swells the polymer, while TMU enables the disperse dyes to dissolve and to remain stable, likely due to its high hydrogen-bonding capability. This is consistent with the theory stated by Ren et al., who argues that in a binary solvent system, one component should mainly interact with the polymer, whereas the co-solvent should focus on the dyes and therefore have solubility parameters similar to the dye [64]. In this system, EC swells the polymer whereas TMU acts as the co-solvent and is also shown to have a similar total solubility parameter as an anthraquinone, Table 2. Because disperse dyes are non-ionic and have low polarity and hydrogen-bonding capacity, it is usually enough to look at the total solubility parameter for comparison. However, EC is a solid at room temperature which complexifies its handling and recovery process. Furthermore, this solvent mixture seems to act better in practice than in theory. While the RED-calculations for EC:TMU is within the defined acceptable range, it is close to the upper limit, indicating only marginal predicted suitability. This does not fully reflect the experimental performance reported by Mu and Yang. Therefore, the HSP should only be used to assess which solvents should be tested but not to reliably predict which solvent will perform best.

4.1.3 Environmental evaluation of solvents

The environmental and safety performance of the solvents is a critical factor for the industrial implementation of this pre-treatment process. Out of the analysed solvents, Cyrene is the one with the most sustainable approach. It is both biodegradable and produced from renewable sources as well as having lower carbon dioxide emissions than traditional solvents. Continuously, scCO₂ is considered to be a green solvent due to its non-toxic and non-flammable properties as well as its efficient separation from products through depressurisation. However, scCO₂ requires an extensive amount of energy for the maintaining of its critical state and its recovery. Furthermore, it requires a co-solvent in order to extract the disperse dyes from the fibres. In the literary review, BA and DMF are the solvents employed for that reason and they are both listed as hazardous compounds in the PRIO-guide.

Moving on to the less sustainable solvent alternatives, BA is also used as a standalone solvent. Even though it is listed in the PRIO-guide due to its allergenic properties, it is not a phase-out substance like DMF and thus remains a possible option for the pre-treatment stage. However, proper handling precautions are required, but its biodegradability adds an environmental aspect to the solvent. DMSO has a rather low toxicity, but it is known to penetrate the skin and persist in the body, making it essential to handling it carefully. Nonetheless, it has a lower boiling point than the other solvents apart from TMU, making its recovery possibly more energy efficient. Lastly, the EC:TMU mixture presents a moderate environmental profile. EC, which is the most

abundant substance in the mixture, is relatively safe and biodegradable, but TMU is carcinogenic and presents reproductive hazard properties. Although TMU is not classified in the PRIO-guide, careful handling is required to minimise its environmental impact.

An additional thing to mention when discussing environmental evaluation of solvents, is if leakage to water bodies were to happen. This is because it is important to consider how the presented solvents can behave in an aquatic environment. For example, solvents with a high-water solubility, such as DMSO and Cyrene, disperse faster into surface waters, whilst more hydrophobic solvents, such as BA, can bind to soil particles and remain in the environment for a longer period of time [85]. Due to Cyrene and EC being biodegradable, it can lead to an increase in biochemical oxygen demand (BOD) to decompose the chemical. A high BOD indicates that there is less dissolved oxygen available for microorganisms and other aquatic organisms [86]. Furthermore, CO₂ release into waters can cause local acidification, affecting pH-sensitive organisms and BA release can disrupt cell membranes of aquatic invertebrates, leading to acute toxicity. Another issue with TMU is that there is little to no information on how this solvent affects water, and thus, information on the environmental hazards of the compound in water needs to be studied.

4.1.4 General solvent discussion

Although the EC:TMU mixture shows the highest dye-removal efficiency, the toxicity that is associated with TMU makes this solvent not ideal for a process that is implemented for sustainability reasons. On the other hand, BA is the second most efficient solvent, it could also be considered as a great solvent for this purpose. However, its classification in the PRIO-guide, makes it a less desirable as a primary option. Furthermore, Cyrene is a great option if one wants to focus on an environmental solvent, but its inferior dye-extraction efficiency and large inflow requirements reduces its economic viability. Continuously, scCO₂ offers a sustainable and efficient dye-removal approach, when combined with a co-solvent. Nonetheless, the amount of scCO₂ required for this purpose is too substantial for a company like Rewin and the co-solvents options explored do not prioritise sustainability. Furthermore, the implementation of a high-pressure vessel has a substantial cost, especially if it needs to handle a large inflow of fabric.

In contrast, DMSO shows a great balance between extraction performance, solvent amount and environmental characteristics. Even though the extraction efficiency is not the highest in the article from Sharma et al., the second article written by Mu and Yang shows great potential for DMSO to efficiently extract disperse dyes. Furthermore, the low toxicity of DMSO makes it a reasonable alternative. Additionally, the required MLR for DMSO to remove disperse dyes is also feasible for a company like Rewin. This concludes that, compared to the other solvents, DMSO appears as the most suitable candidate for the removal of dyes from polyester fabrics.

4.2 Process flowsheet

In this section, the proposed process flowsheet developed from the literature review is presented and discussed. First, the overall flowsheet is introduced, Figure 22, followed by a more detailed explanation of each process step, Figure 23 to Figure 25. As a reminder, the proposed process in this thesis is a pre-treatment step to the Rewin Textiles AB process chain, meaning that the textile waste is assumed to undergo no prior treatment. Furthermore, the textile waste that goes in consists mostly of polyester. A thing to note is that, although scCO₂ is a part of the analysis, a flowsheet for it is not developed, as it differs greatly from the other processes.

4.2.1 General process flowsheet

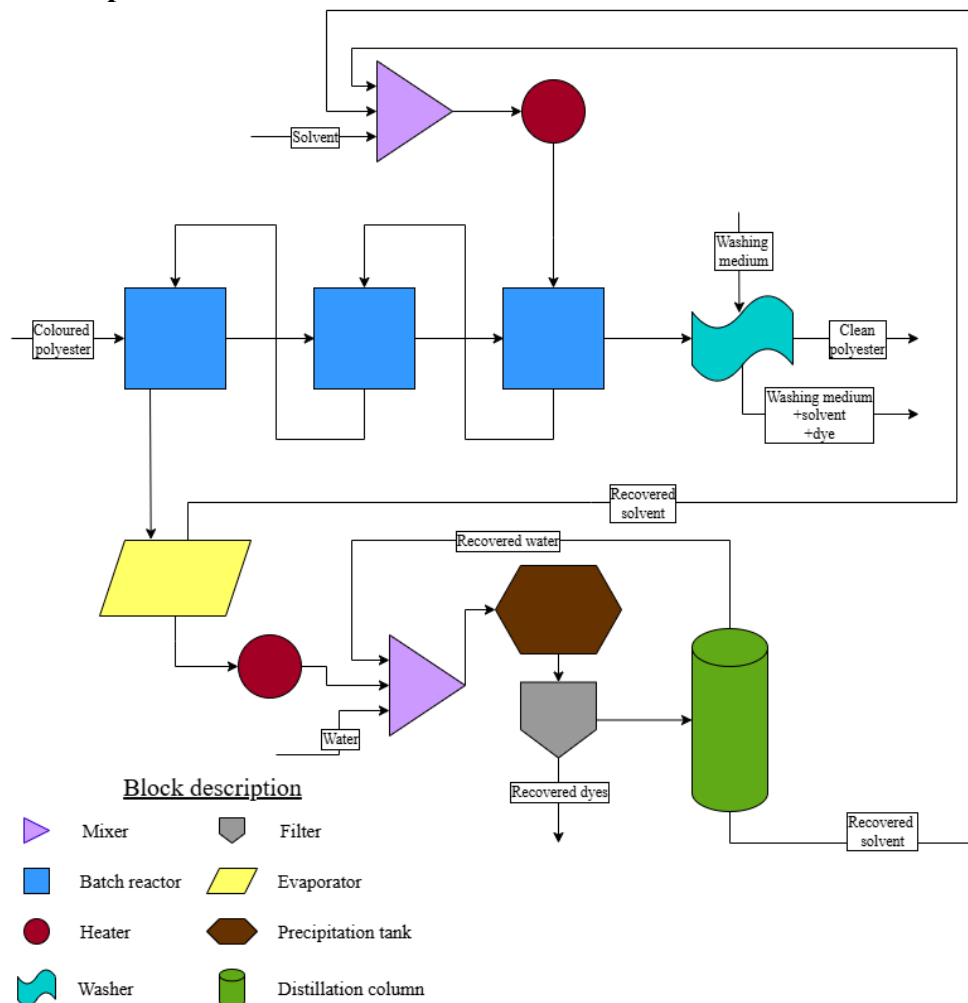


Figure 22: General structure of the dye removal process.

The coloured polyester waste is first cut down into smaller constituents to ensure proper distribution of solvent surrounding the fibres. The size of the polyester is matched to the Rewin size, therefore around 10 cm x 10 cm. The cut textile is then submerged into the solvent that is heated in three consecutive batch reactors, where the residence time for each reactor is 5-30 minutes, depending on which solvent used. The decoloured polyester is then sent to a washing step to remove any remaining dye and solvent, after which it proceeds into the Rewin recycling process as a fully decoloured polyester.

The second part of the flowsheet consists of the separation of the dissolved dye from the solvent, where the first step is to remove a portion of the solvent in an evaporator. This is done to recover some solvent into the dye-removal process described in the text above, as well as to minimise the flow going into the next part of the process, namely the precipitation. Here, the mixture is first cooled down to room temperature before mixing with water as an anti-solvent. Water changes the solubility of the mixture and causes the dye to precipitate, which then falls out as a solid. This solution is then filtered out to isolate the now solid dye, and the remaining water and solvent is separated via a distillation tower, with water and solvent recycled back into the process.

4.2.2 Dye removal from polyester flowsheet

The flowsheet of the dye-extraction step, which constitutes the first part of the process, is presented in more detail in Figure 23.

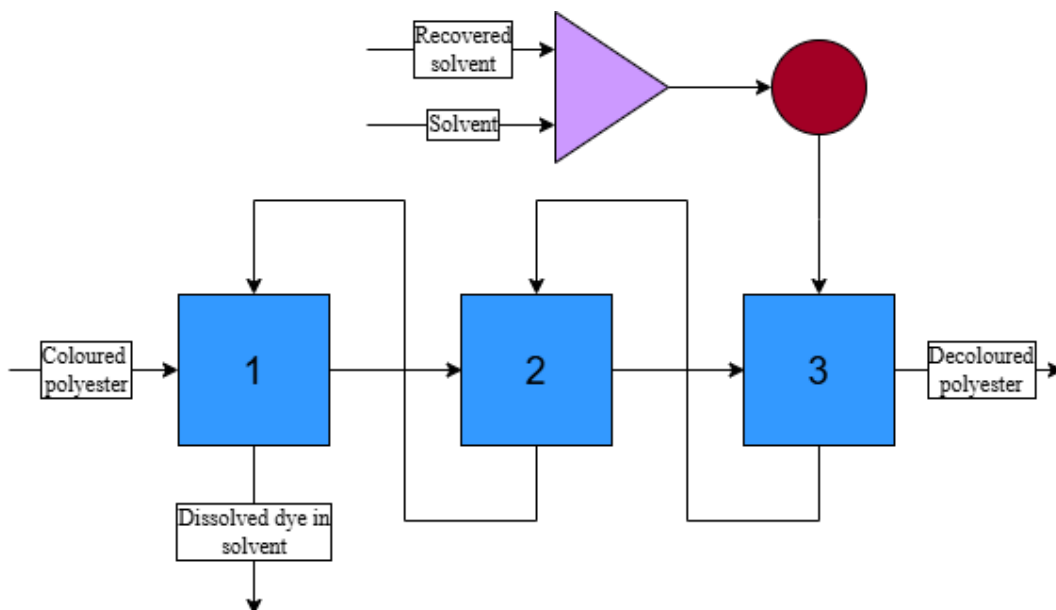


Figure 23: Separation of dye from polyester.

The solvent entering this process consists of both fresh and recovered solvent. This is because solvents are expensive and to continuously purchase fresh solvent would be financially unrealistic. It would also generate large volumes of waste solvents, which adds another expense. Additionally, to recycle the solvent adds more circularity into the process, which is an important principle in modern process design. However, it is not possible to recover all the solvent as it would lead to a gradual accumulation of dye [87]. Trace amounts of dye will always remain in the recovered solvent, and if all solvent were to be recycled, then these traces would accumulate into much higher concentrations. This would eventually lead to a less efficient uptake of dye by the solvent, which is not a desirable trait. Therefore, a recycling rate of 95 % with a 5 % addition of new solvent have been decided for this system. This rate is chosen because Mu et al. indicated in their report that about 5 % BA was lost to processing [58]. Obviously, it is possible to change this partition, by either increasing or decreasing the recycling ratio, depending on how the process behaves in reality. Additionally, solvents tend to be quite volatile at higher temperatures, which places added pressure on keeping a leak-free process in both pipes and reactors [36]. However, leakage is a risk in almost any process, therefore it is reasonable to assume it can happen for this process as well.

The solvent is then heated up to the temperatures disclosed in the reviewed articles, before entering the dye-extraction reactors. The heated stream is then sent to batch reactor 3, which is the last reactor the polyester reaches. This type of configuration of batch reactors is called a counter-current batch process, where the textile first enters batch reactor 1 and the solvent first enters batch reactor 3. According to the reviewed articles, the textile needs to have a specific residence time for each dye-extraction step as well as ensuring proper heating, and the best type of reactor for this is a batch reactor [36]. A batch reactor is a vessel in which the solvent and textile are loaded and mixed, after which the system is sealed, ensuring that nothing can enter or leave the tank during the reaction time. The substrates are heated and mixed in the vessel, to

guarantee proper distribution of the solvent on the fabric, and once the reaction is done, the vessel is emptied. However, the required flowrates of polyester and solvent might be too large for this type of reactor and therefore this limitation could be addressed by employing multiple counter-current batch reactors arranged in parallel.

The counter-current flow is decided upon as it is a more efficient way of using solvent for dye-extraction purposes. In a standard three-step batch process, fresh solvent is required for all three stages. However, if a counter-current flow is introduced, fresh solvent is only required once at the final step. In this configuration, the cleanest solvent contacts the most decoloured polyester in the last reactor, batch reactor 3. This enables the solvent to almost entirely decolorise the polyester without reaching the dye-saturation concentration in the solvent, as described in Section 2.3.1 with the Nernst isotherm. After the reaction time has passed, this already-used solvent is transferred to batch reactor 2 to decolorise a polyester that contains a higher concentration of dyes. This decolourisation is possible because the solvent is not saturated with dye after batch reactor 3, leaving a capacity of the solvent to extract more dyes. Lastly, the solvent is moved on to batch reactor 1, where it encounters the polyester with the highest concentration of dyes, untouched textile waste. The solvent here extracts dyes to its maximum ability.

Additional advantage to the counter-current process, is that the solvent becomes more concentrated with the dye once leaving batch reactor 1, due to less solvent in the system, which makes it easier to separate it from the solvent in subsequent steps. Furthermore, this process allows the solvent to be used to its maximal ability without wasting fresh solvent at stages where it is not needed. However, the reviewed literature did not mention a counter-current process, and they instead decided to add fresh solvent at each cycle. Therefore, this process presented will probably result in some other removal efficiencies than the results presented in the articles.

The duration of batch operating times differs between the solvents, with BA only needing 5 minutes per batch reactor, whilst EC:TMU, DMSO and Cyrene needing 30 minutes according to the literature review. Additionally, the solvents all use different dye-extraction temperatures, which can be seen Table 6. There, it can be seen that BA uses the highest temperature out of all the solvents, at 130 °C, and thus needs a higher energy input for heating than the other solvents but for a much shorter period. Dye removal using DMSO occurs at 100 °C and Cyrene is heated at roughly the same temperature, 98 °C, and due to the similar batch operating times of the two solvents, they require roughly the same amount of energy for the dye-removal step. EC:TMU extracts both at 90 °C for three cycles and 120 °C for two cycles.

The outlets of this process step leave in two different streams: one containing dissolved dye in solvent and the other with small cut pieces of decolourised polyester. The dissolved dye in solvent is discussed further in Section 4.2.4, where the focus is on separating dye from the solvent instead, while the washing of polyester is discussed below.

4.2.3 Washing of polyester

After the removal of dye from polyester, the output from batch reactor 3 is mostly decolourised polyester containing some small portion of solvent and dye. Prior to sending this polyester to the Rewin recycling process, it is important to remove these impurities, as otherwise they can interfere with their process. The setup for the washing of polyester can be seen in Figure 24.

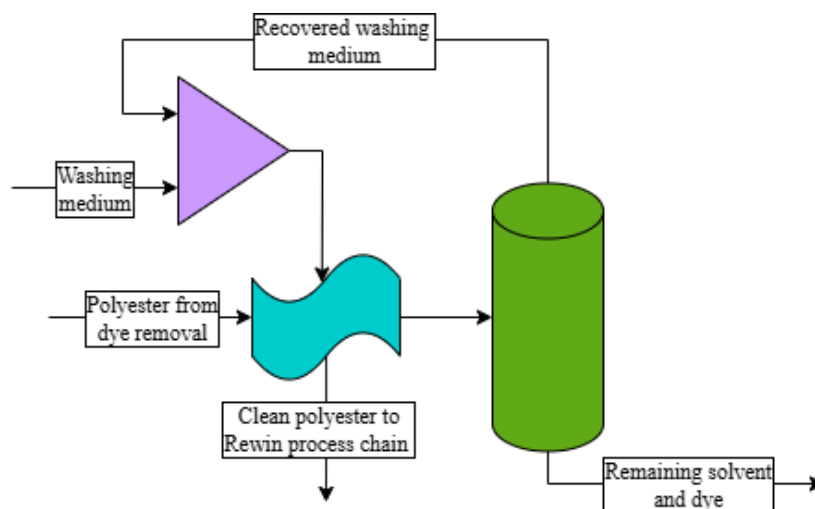


Figure 24: Washing of polyester to remove remaining dye and solvent.

A washing medium is used to remove any remaining dye and solvent from the clean polyester, which is then dried and sent off to the Rewin recycling process. The washing step is especially necessary for BA, as any remaining solvent can interfere with the ethylene glycol (EG), which is used for glycosylation [58]. This can create undesired side effects such as minimising the yield of recovered polyester. Cyrene is also a solvent that can react with EG by creating ketals, which also reduces the yield [54]. Additionally, EG can open the ring in EC, thus consuming the EG, which is needed for depolymerising polyester [88]. Both DMSO and TMU are not as reactive with EG and do not necessarily affect the yield of recovered polyester.

The articles reviewed for the literature study have included which washing medium was selected, except for Cyrene. Continuously, the washing medium needs to be miscible with the solvent. BA is only slightly miscible with water, but more miscible with organic solvents and therefore ethanol is used as a washing medium [58]. DMSO as well as EC:TMU uses water to rinse of the polyester fabric, as specified by Mu and Yang [9]. DMSO is highly miscible with water and causes the solvent and dye mixture to separate easily from the polyester. TMU is also highly miscible with water, whilst EC is not as miscible as DMSO and TMU, but still enough. Cyrene is also miscible with water, and thus this report assumes that water is a good washing medium for this solvent. Water as a washing medium is extremely cheap, but less energy is needed to distillate ethanol after the washing step as it has a lower boiling point of 78.5 °C and a lower enthalpy of vaporisation than water [21].

Once the polyester is rinsed and sent to depolymerisation, the remaining washing medium mixed with some dye and solvent needs to be separated from each other. This separation occurs in a distillation column where the top product is recovered washing medium, which is recirculated back into the process. To make up for any loss during the process and decrease the risk of accumulation of dye and solvent in the system, a portion of new washing medium of 5 % is applied. The bottom product is then leftover dye, solvent and some washing medium, which this report assumes to be 5 %. Since it is not known how much bottom product there is, it is not possible to say whether it should be recovered or not. If the amount is very small, the costs outweigh the benefits of recycling the product, but if it is a large quantity, it is possible to mix the remaining solvent-dye mixture with the output from batch reactor 1 in Figure 23. This report has assumed that the fraction is small enough so that it can be handled as a waste stream and thus be discarded after being disclosed as hazardous waste.

4.2.4 Separation of dye from solvent

Once the dye has been separated from the polyester fabric, the dye is dissolved in the solvent and leaves as an outflow stream from batch reactor 1 in Figure 23. This outlet stream is described in this section, which deals with how the dye is in turn separated from the solvent. The procedure presented is an extension of the processes explained in Section 3.4.2, with the addition of an evaporator prior to precipitation, Figure 25.

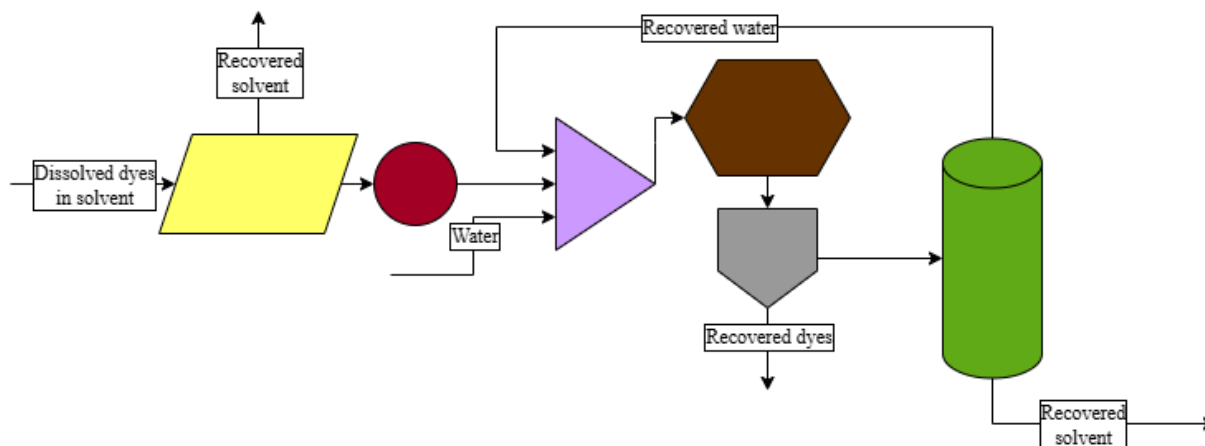


Figure 25: Separation of dye from solvent through precipitation.

The amount of solvent used in the whole process is fairly large, ranging from 20,000 kg/h to 50,000 kg/h, and because the dye-solvent separation step involves the addition of water, it is necessary to first remove some of the solvent. Therefore, an evaporator system is added before the addition of water. A larger part of the solvent is here evaporated, but more details on how much will be explained in Section 4.3.2, with how much water that is needed to make the dyes precipitate. The removed solvent is then recycled back into the process. It is also important to note that even though most of this recovered stream contains solvent, it is possible for trace amounts of dye to remain in the solvent, contributing to the accumulation previously described.

An evaporator system is used instead of a distillation tower because the stream contains dissolved solid in the solvent. If the process is to have a distillation tower instead, some of the dye could precipitate. This is due to less solvent on the trays closer to the bottom of the column, by the reboiler, which can therefore cause clogging [89]. Additionally, the evaporators need to operate at low pressures, to not thermally degrade the dye in the solvent. Otherwise, the temperatures would approach the boiling temperatures for the solvents, which all range from 176.5 °C to 248 °C, and thermal degradation of azo dyes has been seen at temperatures above 130 °C. This will be further studied in Section 4.3.

However, evaporating a larger part of the solvent requires an extensive amount of energy and steam, and therefore this report has applied a multi-stage evaporation (MSE) system, Figure 26. This approach is a common strategy to minimise steam demands in industries [71]. In an MSE, fresh steam is only applied once to the first evaporator, while the solvent vapor generated in each stage is reused as the heating medium for the subsequent stage. The feed enters evaporator 1, which has the highest pressure, together with fresh steam, causing part of the solvent to evaporate. The resulting liquid stream then follows to evaporator 2, while the solvent vapor from evaporator 1 serves as the heating steam for evaporator 2. This principle is repeated across all stages, and only the vapor from the final stage is condensed in an external condenser. Furthermore, the pressure is lowered for each evaporator, where the last evaporator has the lowest

pressure. This is advantageous when the solution is heat-sensitive, which the dye is in this case, as well as ensuring sufficient boiling with the vapour in the subsequent stages. As a result, fresh steam is required only once, and only a single condenser is needed at the third evaporator, significantly reducing the overall thermal and energy demand of the system. Additionally, it is important to collect the solvent condensate from evaporator 2 and 3 and solvent vapor from the third evaporator, so that the solvent can be recycled back into the process. The MSE used for this process contains 3 towers. This choice is motivated by the capital cost increases approximately linearly with additional towers, while the small efficiency gains of evaporation diminish beyond three stages, making further expansion economically unjustified.

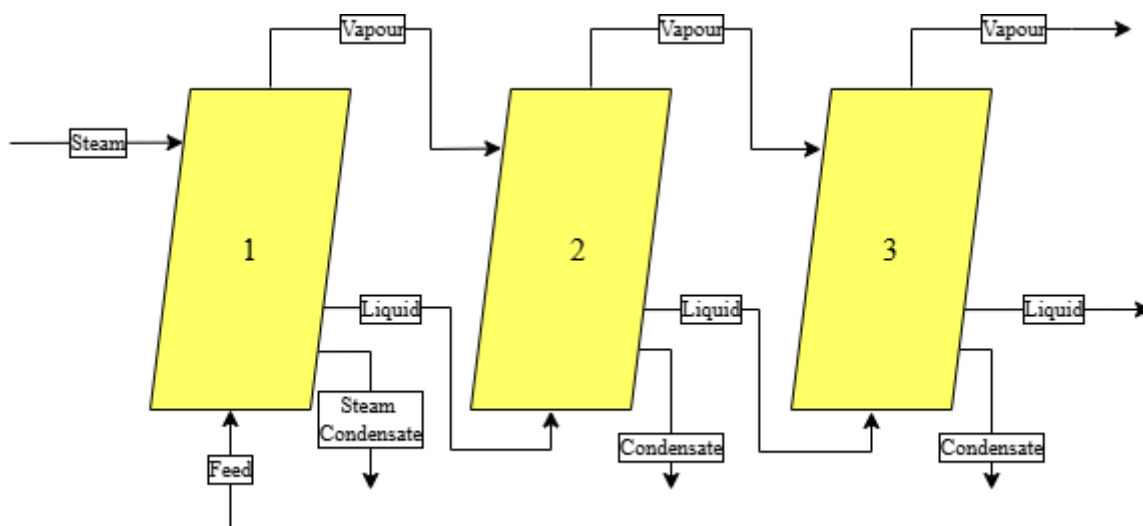


Figure 26: Three-stage evaporators with co-current flow feeding.

The liquid outlet of the third evaporation tower releases dissolved dyes along with a smaller portion of the solvent. This stream is cooled down to 25 °C before being mixed with water, Figure 25. This solution then enters a precipitation tank in which the dye precipitates and solidifies again with the help of mixing. It is also possible to cool down the stream even more, to decrease the amount of water required for precipitation, due to the solubility of solutes usually being lower at decreased temperatures [90]. The residence time in the precipitation tank is set to 30 minutes, which is the same amount of time as for the BA article and is therefore assumed to be sufficient to make all the dyes precipitate [58].

Once the dye has solidified, a filtration unit is installed to collect the precipitated dye. As the dye is milled to a size of $<1 \mu\text{m}$ during its production, the filter needs to have pores that can catch particles of this size, whilst allowing for the liquid to pass through. Therefore, a crossflow microfiltration unit is employed, where a pressure difference of 1 to 5 bar is used to drive the separation forward [36]. It is also possible to use flocculants in order to form larger flocs of the very fine particles, to then allow a filter press to press out the liquid. However, the process in this report uses the former option to reduce the need for additional chemicals and also increase dye purity. The collected dye can then be used to dye fabrics again, which has been demonstrated to be possible by two of the research articles studied. Thus, Rewin can sell this recovered dye to textile manufacturers.

The final part of the process is a simple distillation column to separate the solvent from the water. The water leaves the tower as a top product due to its higher volatility compared to the solvent and can then be recirculated back into the process. The bottom product consists of the

solvent, which can be mixed with the stream of recovered solvent leaving the evaporator and then be recycled back into the process to remove dyes from polyester again.

4.2.5 Challenges with the proposed process flowsheet

The proposed process flowsheet poses some challenges, especially for the two-component solvent options, EC with TMU and Cyrene with water. This challenge is especially noticeable at the evaporation step, where a fraction of the solvent is being removed. For Cyrene with water, water has a much lower boiling point, 100 °C, than Cyrene, 203 °C, leading to near total removal of water and only some of Cyrene. The next step is to add water to precipitate the dye, which is problematic because water has just been removed in a prior step. As the removal of water is quite energy-intensive, the ideal scenario would be to not remove water at all, due to it being added in subsequent steps. However, it is necessary because the inflow of Cyrene is the largest out of the studied solvents. Another issue that then presents itself is that Cyrene is quite viscous and requires water to flow more freely.

Furthermore, by removing water from Cyrene, the process removes the component that minimises the solubility of the dyes in the mixture. Therefore, by removing water, the solubility of the dye in the solution is increased. This means more anti-solvent needs to be applied in the precipitation step. If the aim is to use a two-component mixture, it is then better to have the solvent that solubilises the dyes to have a lower boiling point and therefore be removed first than the solvent that instead swells the polyester. This can be seen for the other two-component solvent option in this report, namely EC:TMU.

Continuously, EC has a boiling point of 248 °C and TMU has a boiling point of 176.5 °C. This means that during the evaporation step, most of TMU is removed from the mixture, while only a small fraction of EC is removed, leading to a lower solubility of the dye in the mixture. Some TMU stays in the solvent mixture due to the molecule binding to the dyes as well as to EC. An evaporator is well suited for separating one fluid from a dissolved compound but does not work as effectively for a binary system of liquids [71]. Therefore, entering the precipitation tank, the mass ratio between the solvents is unknown and it becomes complicated to estimate how much water is needed. It could lead to either too much or too little water being added. Additional issues that arise are after the filtration of dyes; the distillation needs to handle a tertiary system instead. A solution to this problem would be to add a distillation column upstream of the evaporation unit to first completely remove TMU. This is possible due to the multiple stages of the distillation column, which allow for the low-boiling compound to be recovered at the top, while the high-boiling compound is retained at the bottom. However, dissolved dye will end up in the bottom-product along with EC, which might cause some issues if the dye starts to precipitate as well as fouling on the equipment. Then, the process still needs to remove a portion of EC, as the mixture only contains 30 % TMU. Therefore, the evaporation stage is still necessary, but with a preceding distillation unit, leading to a much higher energy demand for the system.

Lastly, a challenge that is not due to two-component mixtures is that the proposed flowsheet alters the type of batch reactor from standard forward-flow batch processes to counter-current batch reactors. This is more appealing from an industrial point of view, due to less fresh solvent being added and used. However, it will most probably result in different extraction efficiencies throughout the cycles, with the hope that the extraction concentration saturation is not met before the last extraction stage. If that is the case, one solution could be to add the 5 % fresh solvent into tank 1 or 2 instead of before tank 3. However, nothing ensures that 5 % fresh solvent will raise the saturation limit sufficiently to separate all dyes and, therefore, experiments need to be carried out using industry equipment to test this percentage.

4.3 Aspen Plus modelling

To get additional information about the process design of the pre-treatment step, multiple analysis tools are used on Aspen. This section aims at describing and discussing the results of these analyses to improve the process implementation of the separation step.

4.3.1 Solubility analysis results

The solubility analysis of DR60 in different solvents is performed in Aspen and the results according to temperature is depicted in Figure 27.

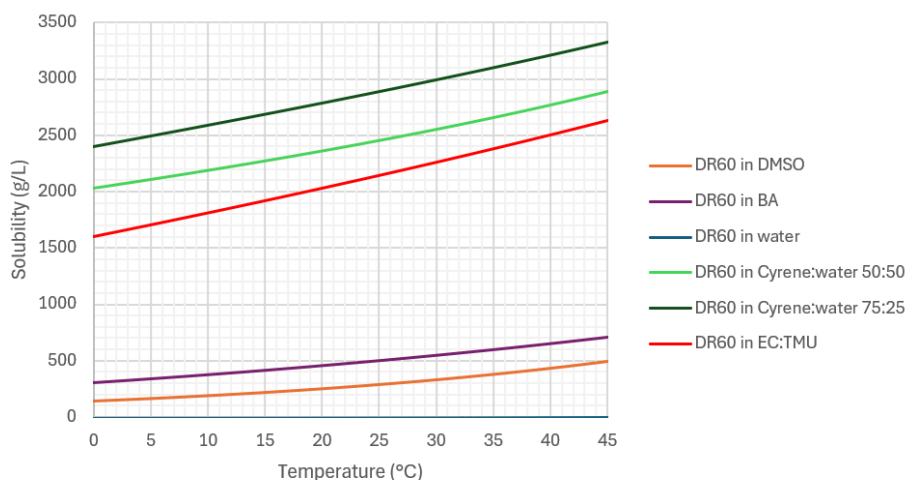


Figure 27: Solubility of DR60 in multiple solvents.

All the solubility curves are increasing with temperature which is an expected result. This is because dissolving a solid is typically an endothermic process, meaning that it requires energy which can be brought by heat [90]. Continuously, DR60 has the lowest solubility in water which is to be expected due to the particle's hydrophobicity. These findings are a first indication on the possible reliability of this model. However, no experimental data could be found on the solubility of DR60 in the different solvents, apart from water. The solubility in water is 1×10^{-6} mol/mol, which can be translated to 0.018 g/L, calculations in Appendix, Section 7.3.2 [21]. This is 2.2 lower than the modelled value of 0.041 g/L in Figure 27 at 25 °C. Although a difference of a factor of 2.2 from the reported value is not ideal, it is still within a range that can be considered workable for modelling. Furthermore, the solubility value is really low, meaning that a deviation of this magnitude does not drastically alter the overall trend. Therefore, the model is considered good enough for this type of analysis.

DMSO exhibits the lowest solubility of DR60, followed by BA. After these solvents, the solubility increases sharply with EC:TMU dissolving DR60 much more effectively and with Cyrene displaying the highest solubility overall. As an attempt to explain this, the total solubility parameter (δ_T) is used because DR60 is mostly non-polar and non-hydrogen-bonding, making δ_T adequate, as explained in 3.2.1. These are listed in Table 2 and Table 5, with DR60 using the solubility values of an anthraquinone, which has a δ_T of 22.2 MPa^{1/2}. As mentioned previously, the “like-solves-like”-principle states that when the solubility parameter of the solvent is similar to the solute, the solvent has a good solubility capability. Starting with DMSO (26.6 MPa^{1/2}), it has the δ_T value furthest from that of the dye, which corresponds to what is being displayed in Figure 27. Secondly, BA (23.8 MPa^{1/2}), has a better DR60 solubility than DMSO, which again is consistent with the figure.

However, for the two-component systems, the calculated δ_T -values shown in Table 5, shows to be inconsistent with the principle and the solubility plot. 75 % Cyrene (26.7 MPa^{1/2}) has a δ_T close to DMSO, whilst showing a much higher solubility of DR60 in the plot. Furthermore, based on the total solubility parameters, 50 % Cyrene (32.8 MPa^{1/2}), would be expected to show much worse solubility than what DMSO has, which is not seen in the figure, as it appears as the second best at solubilising the dye. However, considering Cyrene (22.7 MPa^{1/2}) on its own rather than in a mixture with water, it has a δ_T much closer to DR60. This explains why it dissolves the dye better than the other solvents. Nevertheless, when it is mixed with water that has a much higher δ_T (47.8 MPa^{1/2}) the overall mixture ends up with a δ_T further from the anthraquinone. This would imply that the calculation for δ_T of a mixture cannot be used reliably as a comparative tool for mixed-component systems. Furthermore, it is possible that Aspen first calculates the solubility contribution of each solvent in the two-component mixture separately, Cyrene and water, and then sums these contributions. This could explain why the predicted solubility of Cyrene with water in Figure 27 is so much higher than for BA and DMSO.

Another discrepancy arises in the predicted solubility of DR60 in EC and TMU separately, which can be seen in Figure 32 in the Appendix. According to this figure, EC is the solvent that has the higher DR60 solubility because at 25 °C, TMU has a solubility of 500 g/L and EC has a solubility of 3200 g/L. This result contradicts both literature data and the HSP of both components. A likely explanation for this discrepancy is that EC is a solid at temperatures under 36 °C. This is not something that is included or represented in the Aspen model, as no change of solubility occurs at that temperature in Figure 32, where the phase transition of EC would normally be shown by the solubility data. Why Aspen does not account for EC as a solid at these temperatures is probably due to EC being defined as a liquid in the database and the NRTL binary parameters between DR60 and EC being for a temperature of 25 °C, a temperature at which EC would normally be a solid. This probably leads to an overestimation of the solubility of DR60 in EC. Therefore, this report concludes that this model is not appropriate for the EC:TMU system, which is therefore excluded from further Aspen analysis. Furthermore, the rest of the solubility values should be interpreted with caution, especially for the mixtures of solvents and they should be considered as overall trends rather than precise predictions.

Moving on, the modelled data presented in Figure 27 is used to analyse the precipitation performance of DR60 in the different solvents, except for EC:TMU. The values that are of interest here are at 25 °C, as it is the chosen temperature to work with for precipitation, and these are presented in Table 7. In the same table, the concentrations of DR60 in each solvent for the presented process can be found. These values are calculated in the Appendix, Section 7.3.4.

Table 7: Solubility and concentration of DR60 in each solvent from the process flowsheet.

Solvent	Solubility of DR60 at 25°C (g/L)	Concentration of DR60 (g/L)
DMSO	289	4.4
BA	497	5.21
Cyrene:water (75:25)	2450	2.35
Cyrene:water (50:50)	2883	2.22

As all the calculated concentrations for DR60 are under the solubility values, the dye is dissolved in the solvents. This is because if the concentration was to be above the solubility, the solvent would be oversaturated with dye, which would thus precipitate. Any value below, means in theory that the solvent is not saturated with the dye and dissolves it instead. Therefore, to separate the dissolved particles from each solvent, precipitation is implemented. To do this, an anti-solvent in the form of water is added. Figure 28 shows the relationship between the solubility of the dye and the mass fraction of water in the solution.

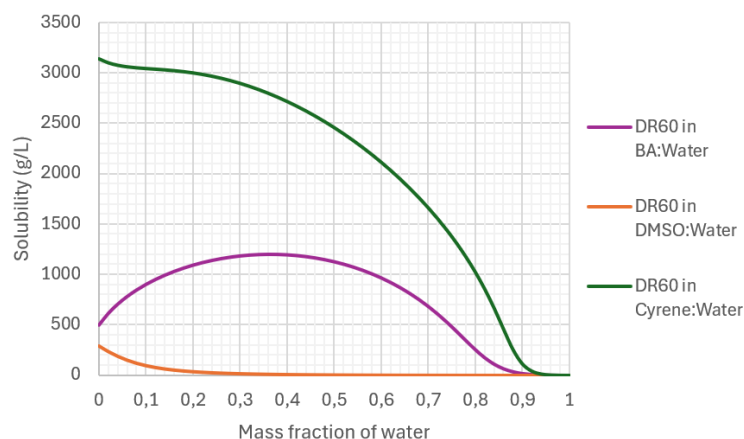


Figure 28: Solubility of DR60 in the chosen solvents with varying concentration of water.

As seen in Figure 28, DMSO and Cyrene have a decreasing solubility of DR60 with the addition of water. However, Cyrene initially displays a high solubility of DR60, and its solubility has only a small decrease until it reaches about 25 % water, to then decrease more rapidly. On the other hand, DMSO exhibits extremely low solubility of DR60 with the addition of water. For BA, the solubility first increases and reaches a maximum, to finally decrease. An attempt to explain this is that by the increase of polarity and hydrogen-bonding capacity that can result from the slight addition of water, creating more favourable conditions for dissolving DR60, whose structure contain polar groups despite its overall hydrophobicity. However, with too much water, the mixture becomes too polar to stabilise the dye molecules, leading to a reduced solubility at higher water mass fractions. Furthermore, DMSO does not result in an initial increase of dye solubility due to the already high polarity of the solvent. The addition of water instead disrupts the molecular structure of DMSO by binding to the heteroatoms of the compound and strengthens water-water interactions, making the mixture less induced to dissolve the dye particles [91].

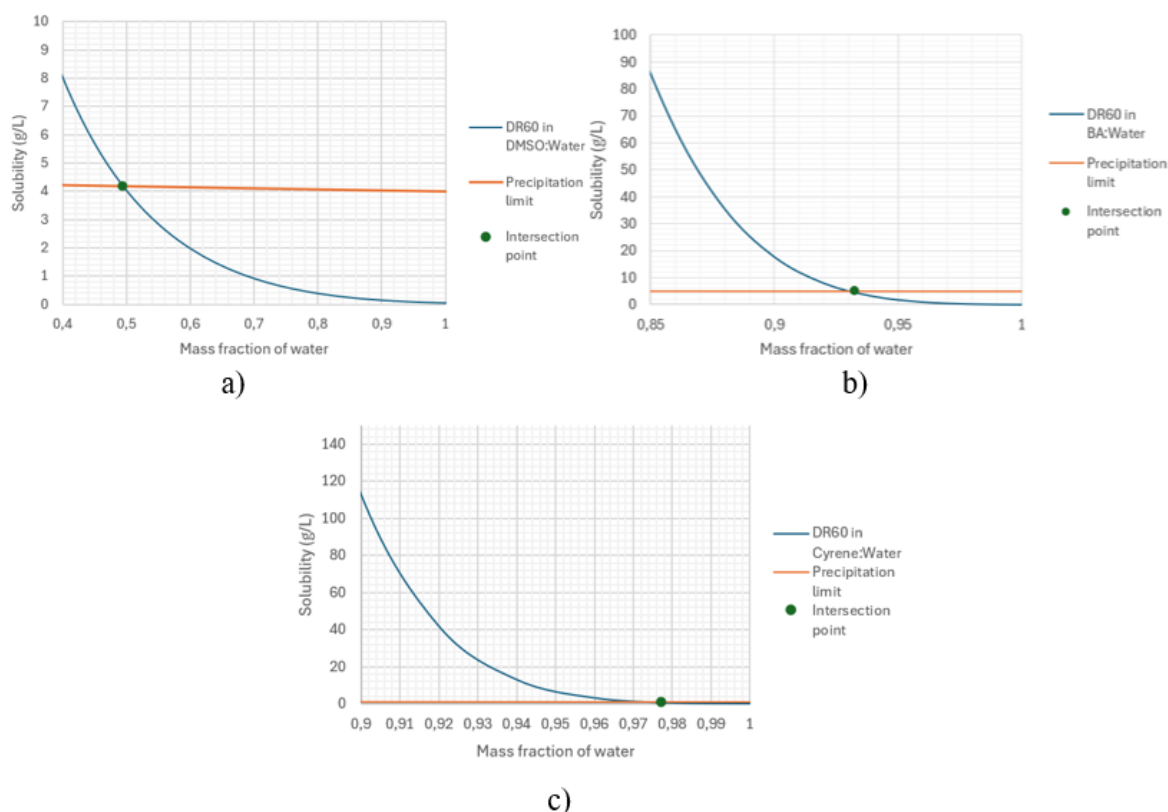


Figure 29: Precipitation limit for DR60 in a) DMSO b) Benzyl alcohol & c) Cyrene against the water mass fraction. Note the difference in the x-axis.

Figure 33 to Figure 35 in the Appendix display Figure 28, but individually for each solvent with their respective precipitation thresholds. Figure 29 then shows the zoomed-in plots of the precipitation limits for each solvent. The precipitation threshold is the concentration of DR60 in each solvent as water is added, while an equal amount of solvent is removed to keep the total mass constant. The calculation used to determine the precipitation limit is shown in the Appendix, Section 7.3.4. Figure 29 shows that the solvent with the highest potential to efficiently separate the dye from the solvent through precipitation with the addition of water as an anti-solvent is DMSO. At a water mass fraction of 49 %, the system reaches the precipitation limit. This means that, when the total mass of the system is kept at 25,000 kg/h, the system requires 49 % of water and 51 % of DMSO to make DR60 begin to precipitate. Under the same assumption of constant total mass, the water mass fraction for the BA system is 93 % and for the Cyrene system is 98 %. These values are much higher than the one for DMSO, demonstrating its superiority compared to the other solvents based on solubility on top of the other factors named in Section 4.1. Therefore, the rest of the calculations and process modelling focus on DMSO rather than on the other solvents.

4.3.2 Evaluation of water addition

According to the modelling, DMSO is the solvent that needs the least amount of additional water to make the dye precipitate. However, the amount of added water depends on the amount of solvent evaporated beforehand. Therefore, this thesis has performed calculations to model the mass of solvents and water needed in order to reach the solubility values of DR60 at each water mass fraction. These are in the Appendix, Section 7.2.4 and they allow the exhibit of Figure 30 for DMSO.

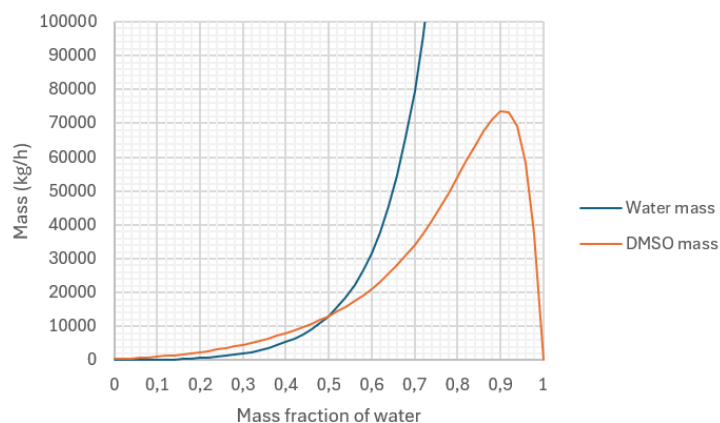


Figure 30: Mass of DMSO and water necessary to reach the solubility limit against the water mass fraction.

Continuously, Figure 30 gives an indication of how much water is needed for precipitation depending on the amount of DMSO in the system, but it gives no estimation on what the optimal system can be. Therefore, calculations about the heat duty required for DMSO removal, along with the heat duty needed to subsequently remove the corresponding amount of water for this specific water fraction, has been performed in the Appendix, Section 7.3.6. These calculations show that removing 94 % of DMSO and adding 240 kg/h of water is the most energy-efficient scenario. However, if one were to remove 94 % of DMSO, only 1470 kg/h solvent would be left in the system, which could introduce complications, such as premature dye precipitation in the evaporator or other dye behaviour changes. Furthermore, according to the calculations, no substantial change in heat duty occur after 84 % DMSO removal, Figure 36. Therefore, a 90 % removal of DMSO appears more reasonable, which results in a precipitation system with 2500 kg/h DMSO and 660 kg/h of water, which are the parameters used for the modelling of the DMSO system in Aspen.

4.3.3 Key parameters and sensitivity analysis results

Most of the parameters for the DMSO system have been introduced, making it possible to construct its flowsheet in Aspen to test additional parameters. Figure 31 is the representation of its process flowsheet in Aspen. The molar vapor fraction of the block “EVAP”, which is the percentage of a stream that leaves the evaporation tower as vapor, is chosen to be 0.8993 as this fraction results in approximately 2500 kg/h DMSO staying in the system after the evaporation unit. The vapor fraction parameter is also varied in Aspen to make sure that the software agrees with the results from the heat duty calculation made. Each vapor fraction value corresponds to an amount of DMSO staying in the system which corresponds to an amount of water to be added to induce precipitation. Therefore, for several vapor fractions, the heat duty for the distillation unit as well as the heat duty for the evaporation unit are compared to the results from the calculations made in 4.3.2. These tests confirms that the optimal removal occurs in the same vapor fraction range as calculated. Moreover, one thing to point out is that the “SEP” block should in reality be constituted of three batch reactor with a counter-current flow like described earlier in 4.2.2, but due to extraction data only being available for one cycle, just one process is being represented in the flowsheet.

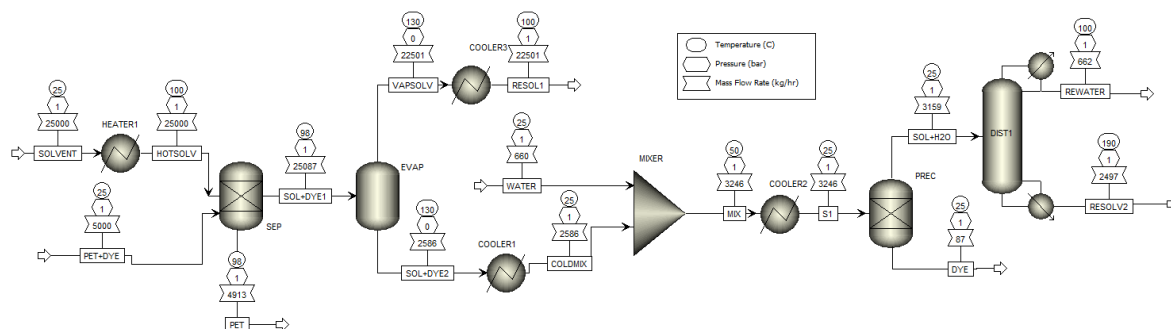


Figure 31: Aspen process flowsheet of the DMSO system.

In Figure 31, the “EVAP” block represents all the three units of the MSE, and a sensitivity analysis is conducted on this block to investigate the relationship between boiling temperature of DMSO and pressure of operation. As a temperature above 130 °C is not desirable, due to the risk of degrading dyes, this temperature is used as a criterion. The sensitivity analysis, Figure 37 in the Appendix, shows that, in order to maintain a temperature of 130 °C or lower, a pressure of maximum 0.16 bar is required. Therefore, this pressure is chosen as the pressure of the first stage of the multi-stage evaporation system, as the highest pressure should be used in the first stage. The pressure and temperature of the two subsequent stages are not yet defined but should be lower than those of the initial stage. They require further optimisation and depend on the company’s preferences. However, if temperatures of 110 and 100 °C are for example chosen for the subsequent steps, the corresponding pressures are 0.075 and 0.05 bar, Figure 37. These low pressures correspond to vacuum conditions, which allows the liquid to boil at much lower temperatures but requires vacuum equipment.

No sensitivity analysis is performed on the distillation tower “DIST” as little to no dyes should remain in the system at that stage. Therefore, the operating temperature and pressure can be altered and optimised by the company according to its preferences. Furthermore, no azeotrope between water and DMSO can be found in Aspen, Figure 38 in the Appendix, meaning that the separation between the two only requires one distillation unit. The detailed results of the evaporation tower, the distillation unit and the composition of the outlet streams of the respective units can be seen in the Appendix, Table 12 to Table 14.

Continuously, the Aspen model shows that the mixing of DMSO with water results in a release of heat, indicating that it is an exothermic reaction. This result is supported by literature and implies that an additional cooler needs to be placed after the mixing takes place, to ensure temperature control and to facilitate the precipitation process [92].

4.4 Economic analysis results

The economic analysis first presents the results for the potential savings Rewin can obtain by avoiding the incineration of waste coming out of the catalytic reactor, followed by the cost of each solvent. The discussion then considers these factors while also addressing additional other investments and variable expenses associated with implementing this report’s ideas of dye-removal methods. A thing to note is that the economic analysis is performed for all the solvents, not only DMSO.

4.4.1 Results of the economic analysis

The equations for both the cost of incinerating the waste stream from Rewin's process and the cost of each solvent can be found in Appendix, Section 7.3.7. The results from the calculations can be found in Table 8.

Table 8: Cost estimation for waste stream from Rewin Textiles AB and cost for each solvent.

	Annual cost (SEK)
Waste stream	643 million
DMSO	351 million
Benzyl alcohol	160 million
EC:TMU	1328 million
Cyrene:water (75:25)	6316 million
Cyrene:water (50:50)	4211 million

As seen in Table 8, the estimated incineration fee for the waste stream after the catalytic reactor costs Rewin about 643 million SEK each year. Furthermore, the solvent cost is based on the yearly solvent consumption of the presented process in this thesis. Among the evaluated solvents, BA has the lowest solvent cost annually out of all the presented solvents, with DMSO being more than twice the cost than BA. Furthermore, both ratios of Cyrene and the mixture of EC and TMU costs more than what the company can save for not treating the waste stream. However, it is important to note that all of these costs are estimated values and come with some uncertainties.

4.4.2 Discussion of the economic analysis

The cost for incinerating the waste stream is associated with great uncertainty. The calculation is based on a study from an industrial site in China, which has other regulatory laws surrounding waste treatment than Sweden. China has higher fees than Sweden, so 643 million SEK per year for treatment of chemical waste is potentially too high for Rewin [93]. However, it is not possible to find an exact number on the expenses of incinerating hazardous chemical waste in Sweden, thus this report assumes a maximum decrease of 25 % of the cost. This leads to a cost between 482-643 million SEK for treatment of the waste stream.

Moreover, the stream contains complex impurities, which is the basis for its classification as hazardous waste, but not all the complex impurities are dye or degraded dye. As mentioned in Section 3.5.8, the stream also includes some salt, organic acids and other degraded products. Therefore, by applying a pre-treatment step, only the dye is removed from these impurities, and thus the total cost of treating the waste stream is only reduced but not eliminated. Therefore, this report has after discussion with representatives from Rewin estimated that about half of the complex impurities are removed from the waste stream, leading to a reduction of waste treatment cost with 50 %. This instead implies that Rewin can save between 241-321.5 million SEK with a pre-treatment step implementation.

The next aspect considered is the expected cost associated with implementing a pre-treatment step, with the focus on solvent usage. As seen in Table 8, solvents are quite expensive and most of the solvents presented in this report cost more than what the company can save. Firstly, Cyrene is the most expensive solvent, which is due to its limited commercial availability. However, the cost of this solvent is based on laboratory scale prices, and the actual bulk price of Cyrene is likely lower than 420 SEK/kg. The second most expensive solvent is a mixture as well, EC:TMU. EC is relatively inexpensive, with an estimated cost of 45 SEK/kg, but the overall cost of the mixture is dominated by TMU as it costs 325 SEK/kg. This is due to its expensive synthesis and the strict regulations regarding its handling, due to its toxicity. Therefore, this report concludes that the expenses for both of these systems are economically unsuitable for industrial implementation at Rewin and other solvents should be used instead.

According to this report's estimations, both BA and DMSO are much cheaper than the other solvents discussed above. Especially BA, which is assumed to be the least expensive out of all of the solvents. This is mainly due to the availability of the raw material of the synthesis of BA, toluene, as well as BA having a wide range of industrial uses, leading to a high production volume of BA [58]. DMSO is estimated to cost about twice as much as BA and even having a higher estimated cost than what the company can save with this process. This is mostly due to the more complex and regulated synthesis of DMSO, which is done by oxygenation of dimethyl sulphide [9].

Therefore, according to this report's calculations, BA is the only solvent that costs less than the amount the company would save from not removing dye from polyester. However, if the process could effectively recirculate 99 % rather than 95 %, the cost of solvent would be drastically minimised. For example, DMSO would instead cost 70 million. Nonetheless, changing the recirculation ratio comes with a great uncertainty, as it accounts for both leakage and removal of solvent to ensure no accumulation occurs. Still, aiming to have a recirculation of 95-99 % benefits the financial constraint that comes with adding a pre-treatment step.

If the process is supplied with polyesters of pre-defined colours, such as only red-dyed polyester for example, then the recovered dye can potentially be sold to textile manufacturers. From the literature review, both Mu and Yang and Mu et al. managed to redye polyester fibres with the extracted dyes, suggesting that Rewin could also take advantage of this property [9, 58]. Furthermore, if Rewin were to find someone wanting to purchase the recovered dye, they would generate more income, making the process more financially viable. Mu et al. performed an economic evaluation in their report, where they included an estimated market value for the recovered dye at 100 SEK/kg. In the Aspen modelling, the material flow for dye is around 100 kg/h, which corresponds to 80 million SEK of revenue per year on the recycled dyes alone, demonstrating that this potential income stream is economically significant.

Another consideration is the additional benefits for Rewin that comes from implementing a pre-treatment step. In their depolymerising process of polyester, Rewin uses MEG together with a catalyst. The catalyst aids in the process and operates well as long as it can, before losing its activity and thus needing to be removed, regenerated or replaced. A common deactivation process for a catalyst is through poisoning, which is caused by contaminants in the reactor binding to the catalyst and therefore blocking the active sites of the catalyst. The contaminants in this process are the complex impurities, thus dye and degraded dye. Therefore, by removing dyes as a prior step, less contaminants can poison the catalyst, which increases the lifetime of catalysts. This, in turn, leads to reduced catalyst regeneration requirements and saves Rewin money.

However, the cost of solvent is not the only expense that is expected from the proposed flow-sheet. Further operational costs such as labour, water, heating demand, steam and so on are also needed. Therefore, these costs also need to be considered when thinking about adding a pre-treatment step to Rewin's process and if it is financially justifiable. However, this report has chosen not to quantify this figure as the focus is to find which solvent is best. Additionally, the solvents all have a similar design in processes and thus the expenses are alike between the solvents, except for the multi-component systems that might require additional units and therefore additional costs. This is also the reason to why investment costs such as reactor vessels, pipes, separation towers, heat exchangers and others are not included. However, it is important to note that the solvent needs to be less expensive than the savings gained from handling the hazardous waste, to make room for the other operational expenses.

Although scCO₂ is not a part of either the flowsheet representation, process modelling or the calculated economic assessment, it is still interesting to consider this option and its associated cost. As mentioned previously in Section 3.3, carbon dioxide as a solvent is not expensive, where the price is at around 12 SEK/kg. In comparison to the other solvents, it is much cheaper, with the closest expense being BA for 20 SEK/kg. However, the issue with using scCO₂ is the initial cost of equipment, which causes it to have a higher capital expense than the other processes presented. This is due to the need for high-pressure compressors, specialised heat exchangers and reinforced pressure vessels [94]. This is consistent with broader techno-economic analyses of scCO₂ technologies. For example, Heller et al. showed that scCO₂ systems exhibit at least a 10 % higher cost than comparable steam-based processes. Additionally, as the system needs a co-solvent, another expense is added to the system. Therefore, this report concludes that using scCO₂ as a method to remove dye from polyester is not as cost-effective as the other solvents presented.

4.5 Further discussion

The following section discusses the remaining challenges of the implementation of such a pre-treatment process as well as uncertainties and questions that have emerged throughout this thesis. Future work opportunities are also mentioned here since this thesis focuses primarily on theoretical feasibility but still needs experiments to control the discussed data and processes.

4.5.1 Industrial implementation discussion

Based on the discussions in Sections 4.1 to 4.4, DMSO appears to be the best-suited candidate for the implementation of a dye-extraction pre-treatment process at Rewin, due to its greater balance in terms of sustainability, cost and water requirements. However, several uncertainties remain and many of them apply across all pre-treatment options discussed.

One important uncertainty concerns the type of textile Rewin receives. As mentioned in 2.4.1, there exists different types of textile waste and therefore different types of textile inflows can enter the Rewin-recycling process. If the type of waste is post-consumer, the textiles are typically mixed in terms of colour or composition. This makes the recovery of dyes complicated because the extracted dyes will probably form dark or mixed-coloured solution, which makes its reuse or selling challenging. However, if the waste is pre-consumer or industrial, then the textiles are usually much more uniform in their materials and colours. In those cases, the dye-extraction batches may contain fabrics dyed with similar colours, which increases the recovery possibility of dyes. Furthermore, this would mean that the dyes could be reused or potentially

be sold. Nevertheless, selling the dyes would require meeting some purity and quality requirements, which can be difficult to achieve in practice, especially since a single-coloured fabric usually consists of a mixture of several dyes [95].

Furthermore, one more notion to address on textile waste is that little to no fabrics are fully composed of polyester. Therefore, even if the pre-treatment process focuses on polyester textiles, the incoming textile waste is not limited to polyester fabrics, as these can also be partially composed of nylon, elastane, wool and cotton. However, the dyes present on these textiles do not necessarily need to be extracted, as these are either discarded or sold, while the Rewin process goes on with the decoloured polyester only. Rewin intends to sell the recovered cotton and therefore, the chosen solvent cannot damage the cotton to maximise its selling price. Even if DMSO swells cotton, both Sharma et al. and Mu and Yang demonstrated that DMSO did not damage the cotton fibres at the temperature range of dye-extraction. Furthermore, it has been demonstrated Cyrene does not dissolve cotton at temperatures under 140 °C, which is above the working temperature for the proposed process [10]. Due to the crystallinity of cellulosic fibres, it is usually not dissolved in common solvents and because no specific information about the other solvent's capacity of dissolving cotton could be found, they are therefore assumed to not dissolve the material as well [96]. However, experiments need to be conducted to confirm this supposition.

A last additional uncertainty is that the experiments conducted in the reviewed articles are on a laboratory scale and not an industrial one. Therefore, the scaling of the experiments in matter of solvent ratios, temperature, pressure and so on might not be consistent or realistic with what is expected of an industry. Even if most of the reviewed articles investigated the optimal MLR ratio for dye-extraction, it might not be the same on an industrial scale, as what could be seen with the DMSO articles [52, 9]. These studies showed that textile waste required a much larger MLR ratio compared to textiles dyed in the laboratory probably due to the superior fastness properties of dyes on textile waste. This suggests that laboratory experiments might underestimate some operating conditions of the dye-removal process, particularly the required MLR and operating times, in order to be applicable in industrial settings.

4.5.2 Recommendations for future work

Even if the proposed flowsheet displays an initial strategy on how the dye-extraction process could look like at Rewin, much more is still needed to make this process reliable. Consequently, several aspects require further investigation and practical experiments.

Most of the reports focused on one or two types of disperse dyes, therefore giving only valuable data about the removal efficiency of these specific disperse dyes. Nothing ensures that a solvent removes as efficiently other disperse dyes, especially bigger and structurally different ones. However, due to the bonds between disperse dyes and polyester being physical and not chemical, a solvent capable of removing one disperse dye is likely able to remove most of the disperse dyes available, however with varying efficiencies. Furthermore, if other or a wider range of dyes are considered, their precipitation thresholds or solubilities may differ from the one examined in the report. Therefore, a recommendation is to do experiments on a mixture of several disperse dyes with DMSO to measure the dye-extraction efficiency of the solvent as well as testing the amount of water to be added to trigger precipitation of a dye-mixture.

An interesting thing noticed during the modelling of dye solubility in solvent together with added water, is that for BA, the solubility of DR60 increased. It reached a maximum solubility at 35 % water and 65 % BA. This adds an interesting possibility of a two-component solution

for dye removal. If the solubility of the dye in the solvent is higher with the slight addition of water, then it possibly becomes easier to extract dyes, therefore resulting in less solvent needed for the system. Furthermore, if water is already in the solution, then less water is needed to be added to induce precipitation in the subsequent step. As a result, less water must be removed in the distillation unit, as some of it is required for the dye-extraction process. This could lead to a more efficient system. However, there is no saying how well this newly composed mixture swells the polyester. Furthermore, the presented flowsheet in this thesis presents complications for a two-component solvent process, but this discovery provides valuable insight regarding future work.

Furthermore, Section 4.3.2 showed that a removal of approximately 90 % of DMSO resulted in an optimal scenario for the process design. However, a 100 % solvent removal in the evaporator, would instead yield solid dyes directly, meaning that the precipitation tanks and subsequent distillation would be unnecessary. This would lead to less investment costs on equipment as well as potentially lower operational costs. Nonetheless, this could instead introduce other operational challenges such as fouling and the final stages of solvent-removal being more energy intensive. Due to these uncertainties, this option was not selected for the process design but is identified as a potential area for future investigation.

Continuously, this thesis conducts some simulations and modelling in Aspen, with the property model NRTL. The NRTL property model, the UNIFAC functional groups chosen or Aspen's limited data on the solvents and dyes can all be reasons for some discrepancies between theory and the Aspen model. Considering the assumptions made throughout this thesis, NRTL as a property model seems like the right fit for the model. However, if the dye is not assumed to be a liquid, another model would have perhaps been more suitable. A popular property model for systems with complex chemicals, such as pharmaceuticals for example, is COSMO-SAC [97]. COSMO-SAC is a predictive thermodynamic model that does not rely on fitted binary parameters, making it more attractive for systems with poorly characterised compounds such as dyes. Therefore, the solubility predictions could be improved with such a model compared to NRTL. The use of COSMO-SAC was considered in the thesis but ultimately not implemented, due to the required parameters being available only through external databases that were not accessible. Furthermore, this thesis has not attempted to fully optimise the proposed flowsheet, which could see improvements by the addition of heat exchangers, more appropriate temperatures, pressures or MLR ratios. Even if some parameters are optimised through a sensitivity analysis for example, much more can still be done.

Another promising area for future work concerns scCO_2 . Due to its different operating conditions than the other reviewed solvents, scCO_2 is only briefly discussed and for most part omitted from this thesis. However, its non-toxicity, recyclability and low environmental footprint as well as great reported extraction efficiencies make it an attractive long-term alternative. Its biggest downside is the required equipment necessary for its demanding conditions as well as required amount of scCO_2 , which may be challenging to justify for a company of Rewin's current scale. The co-solvents used in the reviewed reports are not the most environmentally desirable, indicating that further work is needed to identify more sustainable co-solvent alternatives which would be compatible with scCO_2 . Furthermore, during a discussion with a representative from SiO_x Machines, which utilises liquid CO_2 in various industrial applications, suggestions were made about the possible swelling efficiency of liquid carbon dioxide instead [98]. If liquid CO_2 were to be used instead, the cost of operation would be substantially decreased due to lower

energy inputs. Although this suggestion is very promising, it lies outside the scope of this report but represents a valuable direction for future experimental work on dye-extraction processes.

One direction that this report has investigated is the use of mixed-solvent system for dye-removal purposes, namely the mixture of EC with TMU, Cyrene with water and scCO₂ with co-solvent. Due to drawbacks of this mixed system with the proposed flowsheet as well as its comparatively higher cost, the mixed systems are not considered as optimal for Rewin. However, a discussion with a researcher from RISE emphasised the potential of this strategy, as a mixture of solvents can contribute to complementary properties. For example, EC is very efficient at swelling the polyester, whereas TMU acts on the stabilisation of the dyes in the solvent. Therefore, mixed-solvent systems represent a promising future perspective, as long as the chosen solvents are both practical and less hazardous than those considered in this report.

Lastly, insights from RISE suggest that a dye-removal step after the catalytic reactor may be more worth to investigate, as their experimental work showed high MLR requirements for the removal of dyes as a pre-treatment step. This alternative is briefly discussed in Section 3.1.2, but the focus of this thesis ultimately continued with pre-treatment strategies for various reasons. Nevertheless, it is undoubtedly a strategy that can be looked into further. Furthermore, even though some of the reviewed literatures named high MLR for pre-treatment processes, most of the articles had reasonable MLR, which could be adapted to a small industry.

5 Conclusions

The aim of this thesis is to identify a dye-extraction process as a pre-treatment step that is compatible with Rewin's polyester recycling facility. Due to the weak bonds between disperse dyes and polyester, the chosen extraction method is a simple solvent-based extraction process. This project continues with studying multiple solvents for this purpose: DMSO, benzyl alcohol, Cyrene, supercritical carbon dioxide and ethylene carbonate together with tetramethylurea. The best solvent found, is based on results from a literature study, Aspen Plus modelling and a simple techno-economic analysis.

Across all evaluated aspects, DMSO shows to be the most promising candidate. DMSO displays great swelling capacity of the polyester and dye-extraction efficiency as well as balanced environmental profile. Furthermore, the modelled solubility analysis exhibits advantageous properties for separation of dyes via precipitation. The economic analysis also demonstrates that DMSO is one of the cheaper solvents if a high recycling ratio is maintained. However, its cost surpasses the savings generated from the pre-treatment implementation, which is a significant limitation. Even though DMSO is not the best solvent in each of the reviewed categories, it presents the most compelling overall option. Therefore, this study proves that a solvent choice should not be solely made on extraction potential, as other parameters such as cost, practicality and toxicity are equally important.

Selecting DMSO as the extraction solvent, the presented process flowsheet exhibits different separation stages to ensure compatibility with Rewin's existing process and efficiency. Firstly, the dye extraction from polyester takes place in a counter-current batch system to reduce the total solvent consumption. Afterwards, the polyester is cleaned, and the dye is separated from DMSO through precipitation by addition of water. Nevertheless, due to large solvent volumes, a higher fraction of it is removed through evaporation in a prior step to precipitation. Lastly, the precipitated dye is filtered out and the DMSO and water are recovered back to the process through distillation.

Although DMSO is considered to be the strongest candidate, this report also highlights several uncertainties and limitations. The modelling in Aspen Plus, the extraction efficiencies, the type of textile waste recycled, and the behaviour of the solvent under repeated cycles all introduce uncertainties that must be validated experimentally. Furthermore, other solvent options are equally as promising as DMSO but not compatible with the presented process chain and were therefore not considered as much as DMSO. This includes the two-component solvents as well as the use of supercritical carbon dioxide, which necessitates further research. Another perspective of research would be to include the dye-separation step at the catalytic reactor instead, due to a possible reduced investment cost.

To conclude, this thesis demonstrates that having a solvent-based pre-treatment step is a feasible process to improve dye removal in polyester recycling at Rewin Textiles AB. However, more experiments need to be conducted to ensure this statement and its industrial feasibility. The benefits of such a pre-treatment step are the inhibition of catalyst poisoning, minimised hazardous waste and potential recyclability of dyes. This leads to an enhanced circularity approach, which is a necessary step towards a more sustainable future and in line with EU's waste directive.

6 References

- [1] Textile Heritage Museum, “A Timeline of Textile History,” [Online]. Available: <https://textileheritagemuseum.org/textiles-ancient-times-to-modern-day/>. [Accessed 21 October 2025].
- [2] J. Lee, “How long does it take to sew a t-shirt?,” Modaknits, 25 April 2025. [Online]. Available: <https://modaknits.com/how-long-does-it-take-to-sew-a-t-shirt/>. [Accessed 21 October 2025].
- [3] S. Imran, M. A. Mujtaba, M. Z. Zafar, M. A. Kalam, A. Hussain, A. Mehmood, U. E. Farwa, T. Korakianitis, H. Fayaz and c. A. Saleel, “Assessing the potential of GHG emissions for the textile sector: A baseline Study,” *Heliyon*, vol. 9, no. 11, November 2023.
- [4] J. Agarwal and Sonia, “Dyes and Dyeing processes for natural textiles and their key sustainability issues,” in *Fundamentals of Natural Fibres and Textiles*, Chandigarh, The Textile Insitute Book Series, 2021, pp. 439-472.
- [5] Naturvårdsverket, “Textilavfall,” 18 August 2025. [Online]. Available: <https://www.naturvardsverket.se/amnesomraden/avfall/avfallslag/textilavfall/>. [Accessed 21 October 2025].
- [6] E. P. a. Council, “Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives,” Official Journal of the European Union, Brussels, 2023.
- [7] G. Sandin, M. Lidfeldt and M. Nellström, “Exploring the Environmental Impact of Textile Recycling in Europe: A Consequential Life Cycle Assessment,” *Sustainability*, vol. 17, no. 5, 2025.
- [8] D. Damayanti, L. A. Wulandari, A. Bagaskoro, A. Rianjanu and H.-S. Wu, “Possibility routes for Textile Recycling Technology,” *Polymers*, vol. 13, no. 21, 2021.
- [9] B. Mu and Y. Yang, “Complete separation of colorants from polymeric materials for cost-effective recycling of waste textiles,” *Chemical Engineering Journal*, vol. 427, 2022.
- [10] P. R. Fernando, A. Hebden, C. Du and P. Goswami, “Focused parameter study of dye removal from PET textiles using Cyrene: Toward sustainable textile recycling,” *Environmental Challenges*, vol. 20, 2025.
- [11] “DyeRecycle,” [Online]. Available: <https://www.dyerecycle.com/>. [Accessed 19 November 2025].

- [12] M. Clark, *Handbook of Textile and Industrial Dyeing*, Leeds: Woodhead Publishing, 2011.
- [13] Textile Exchange, “Materials Market Report,” Textile Exchange, 2024.
- [14] U. Schlöter-Schrehardt, N. Polisetti, J. Menzel-Servering and F. E. Kruse, “Tissue Engineering for Reconstruction of the Corneal Epithelium,” in *Ocular Surface Disease: Cornea, Conjunctiva and Tear Film*, Expert Consult, 2013, pp. 347-360.
- [15] Sustainability Directory, “Why is Polyester so common in Fast Fashion?,” 6 May 2025. [Online]. Available: <https://fashion.sustainability-directory.com/question/why-is-polyester-so-common-in-fast-fashion/>. [Accessed 8 September 2025].
- [16] B. L. Deopura and N. V. Padaki, “Synthetic Textile Fibres: Polyamide, Polyester and Aramid Fibres,” in *Textiles and Fashion: Materials, Design and Technology*, Woodhead Publishing Series in Textiles, 2015, pp. 97-114.
- [17] A. Smelik, “Polyester: A Cultural History,” *Fashion Practice*, vol. 15, no. 2, pp. 279-299, 2023.
- [18] U. Ellervik and O. Sterner, *Organisk kemi*, Lund: Studentlitteratur, 2014.
- [19] J. Militky, “The chemistry, manufacture and tensile behaviour of polyester fibers,” in *The Handbook of Tensile Properties of Textile and Technical Fibres*, Woodhead Publishing Series in Textiles, 2009, pp. 223-314.
- [20] S. H. Park and S. H. Kim, “Poly(ethylene terephthalate) recycling for high value added textiles,” *International Journal of Interdisciplinary Research*, vol. 1, no. 1, 2014.
- [21] CAS Scifinder, “CAS Scifinder,” American Chemical Society, 2025. [Online]. Available: <https://scifinder-n.cas.org/>. [Accessed 30 September 2025].
- [22] A. Abel, “The history of dyes and pigments: From natural dyes to high performance pigments,” in *Colour Design (Second Edition)*, Woodhead Publishing Series in Textiles, 2012, pp. 557-587.
- [23] A. I. o. Chicago, “Ushabti (Funerary Figurine) of Psamtek by Ancient Egyptian,” Rawpixel, [Online]. Available: <https://www.rawpixel.com/image/8938202/ushabti-funerary-figurine-psamtek-ancient-egyptian>. [Accessed 16 October 2025].
- [24] A. Gürses, M. Açıkyıldız, K. Güneş and M. S. Gürses, “Classification of Dye and Pigments,” in *Dyes and pigments*, Springer, Cham, 2016, p. 31–45.
- [25] W. Schindler and P. Hauser, “Finishes to improve colour fastness,” in *Chemical Finishing of Textiles*, Woodhead Publishing in Textiles, 2004, pp. 144-156.

- [26] “National cancer institute,” [Online]. Available: <https://www.cancer.gov/publications/dictionaries/cancer-terms/def/affinity>. [Accessed 10 September 2025].
- [27] T. E. o. E. Britannica, “Britannica,” 22 10 2021. [Online]. Available: <https://www.britannica.com/science/sublimation-phase-change>. [Accessed 10 september 2025].
- [28] J. Chakraborty, “Dyeing with basic dye,” in *Fundamentals and Practices in Colouration of Textiles*, Woodhead Publishing India, January 2010, pp. 184-191.
- [29] M. K. Sayyed H. Hashemi, “Azo dyes: Sources, occurrence, toxicity, sampling, analysis, and their removal methods,” in *Emerging Freshwater Pollutants: Analysis, Fate and Regulations*, Elsevier, 2022, pp. 267-287.
- [30] J. Koh, “Dyeing with disperse dyes,” in *Textile dyeing*, IntechOpen, 2011, pp. 195-220.
- [31] R. Hamprecht and A. Westerkamp, “Disperse Dyes,” in *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, Germany, Wiley-VCH, 2000, pp. 331-344.
- [32] “Disperse Dyes Market Size, Share, Industry Trends, Growth Drivers, Opportunities, Key Players Analysis, Regional Outlook and Forecast Report (2025–2032),” MMR, June 2025. [Online]. Available: <https://www.maximizemarketresearch.com/market-report/global-disperse-dyes-market/92431/>. [Accessed 15 September 2025].
- [33] A. R. Choudhury, “Dyeing of synthetic fibres,” in *Handbook of Textile and Industrial Dyeing, Volume 2*, Serampore, Woodhead Publishing Series in Textiles, 2011, pp. 40-128.
- [34] T. L. Nguyen and M. A. Saleh, “Thermal degradation of azobenzene dyes,” *Results in Chemistry*, vol. 2, 2020.
- [35] K. Ryberg, A. Goossens, M. Isaksson, B. Gruvberger, E. Zimerson, M. Bruze and L. Persson, “Patch testing of patients allergic to Disperse Blue 106 and Disperse blue 124 with thin-layer chromatograms and purified eyes,” *Contact Dermatitis*, vol. 60, no. 5, pp. 270-278, 2009.
- [36] R. Smith, *Chemical Processes Design and Integration*, Manchester: Wiley, 2016.
- [37] L. Pei, Y. Luo, X. Gu, H. Dou and J. W. 1, “Diffusion Mechanism of Aqueous Solutions and Swelling of Cellulosic Fibers in Silicone Non-Aqueous Dyeing System,” *Polymers*, vol. 11, no. 3, 2019.
- [38] Sustainability Directory, “Textile Industry Waste,” 25 April 2025. [Online]. Available: <https://pollution.sustainability-directory.com/term/textile-industry-waste/>. [Accessed 21 October 2025].

- [39] Å. Östlund, H. Wedin, L. Bolin, J. Berlin, C. Jönsson, S. Posner, L. Smuk, M. Erkinsson and G. Sandin, "Textilåtervinning," Naturvårdverket, Bromma, 2015.
- [40] S.-L. Loo, E. Yu and X. Hu, "Tackling critical challenges in textile circularity: A review on strategies for recycling cellulose and polyester from blended fabrics," *Journal of Environmental Chemical Engineering*, vol. 11, no. 5, 2023.
- [41] M. Babaei, M. Jalilian and K. Shahbaz, "Chemical recycling of Polyethylene terephthalate: A mini-review," *Journal of Environmental Chemical Engineering*, vol. 12, no. 3, 2024.
- [42] Rewin Textiles AB, "Rewin Textiles," Rewin Textiles AB, [Online]. Available: <https://www.rewintextiles.com/>. [Accessed 16 September 2025].
- [43] K. Nyström, S. Barring, I. Kristensson, P. Wacker and S. Ljungman, "Study of Treatment and Recovery of Waste Streams for the Rewin Polyester Recycling Process," Lund, 2024.
- [44] G. Gorreta, C. Maesani, S. Alini, M. Blangetti and C. Prandi, "Towards fiber-to-fiber recycling of synthetic textile wastes: the problem of decolorization," *Waste Management*, vol. 205, 2025.
- [45] Y. Li, J. Shen, Q. Liu, Y. Zhu, Z. Pang and M. Ge, "Zinc-doped ferrite nanoparticles as bi-functional catalysts for decolorization of disperse dyes in glycolysis of colored poly(ethylene terephthalate) fabrics," *Journal of Environmental Chemical Engineering*, vol. 11, no. 3, 2023.
- [46] J. Huang, D. Yan, H. Dong, F. Li, X. Lu and J. Xin, "Removal of trace amount impurities in glycolytic monomer of polyethylene terephthalate by recrystallization," *Journal of environmental chemical engineering*, vol. 9, no. 5, 2021.
- [47] K. T. Savjani, A. K. Gajjar and J. K. Savjani, "Drug Solubility: Importance and Enhancement Techniques," *International Scholarly Research Notices*, vol. 2012, no. 1, 2012.
- [48] W. Zeng, Y. Du, Y. Xue and H. L. Frisch, "Solubility parameters," in *Physical Properties of Polymers Handbook*, New York, Springer, 2007, pp. 289-304.
- [49] C. M. Hansen, Hansen Solubility Parameters : A User's Handbook, CRC Press, 2007.
- [50] S. Herrlich, T. Lorenz, S. Spieth, S. Messner and R. Zengerle, "Solvent Bonding of a Drug Delivery Device by Using Hansen Solubility Parameters," in *8th International Conference on Multi-Material Micro Manufacture*, Villingen-Schwenningen, 2011.
- [51] American Chemical Society, "Molecule of the Week Archive: Dimethyl sulfoxide," American Chemical Society, 20 September 2021. [Online]. Available:

<https://www.acs.org/molecule-of-the-week/archive/d/dimethyl-sulfoxide.html>.
[Accessed 30 September 2025].

- [52] E. Sharma, M. K. Hadrojoprano, P. Gunawan, Z. S. G. Leng, D. T. C. Yong, N. Gupta, L. Y. Nan and X. Hu, "Solvent assisted approach for greener decoloration of textile and fashion waste," *Cleaner Engineering and Technology*, vol. 27, 2025.
- [53] Made-in-China, "DMSO Price," Made-in-China, [Online]. Available: https://www.made-in-china.com/products-search/hot-china-products/DMSO_Price.html. [Accessed 10 November 2025].
- [54] D. Kong and A. V. Dolzhenko, "Cyrene: A bio-based sustainable solvent for organic synthesis," *Sustainable Chemistry and Pharmacy*, vol. 25, 2022.
- [55] Sigma-Aldrich, "Merck," Sigma-Aldrich, [Online]. Available: <https://www.sigmaaldrich.com/GB/en>. [Accessed 2 October 2025].
- [56] T. Brouwer and B. Schuur, "Dihydrolevoglucosenone (Cyrene), a Biobased Solvent for Liquid–Liquid Extraction Applications," *ACS Sustainable Chemistry & Engineering*, vol. 8, no. 39, 2020.
- [57] F. Brühne and E. Wright, "Benzyl Alcohol," in *Ullmann's encyclopedia of industrial chemistry*, Wiley-VCH, 2003, pp. 83-91.
- [58] B. Mu, Y. Shao, L. McBride, H. Hidalgo and Y. Yang, "Rapid fiber-to-fiber recycling of poly (ethylene terephthalate) and its dye from waste textiles without damaging their chemical structures.," *Resources, Conservation & Recycling*, vol. 197, 2023.
- [59] Prioguiden, "Search for properties hazardous to human health and the environment," *Kemikalieinspektionen*, 23 September 2025. [Online]. Available: <https://www.kemi.se/prioguiden/>. [Accessed 13 October 2025].
- [60] Intratec, "Benzyl Alcohol Prices Worldwide," Intratec, 2025. [Online]. Available: <https://www.intratec.us/solutions/primary-commodity-prices/commodity/benzyl-alcohol-prices>. [Accessed 10 November 2025].
- [61] T. Huang, X. Wei, S. Qu, W. Zheng and L. Zhao, "Enhanced decolorization behaviors of colored PET textiles by supercritical carbon dioxide as part of the recycling process," *The Journal of Supercritical Fluids*, vol. 222, 2025.
- [62] P. Yadav, M. Agrawal, A. Alexander, R. Patel, S. Siddique, S. Saraf and Ajazuddin, "Polymer production and processing using supercritical carbon dioxide," in *Green Sustainable Process for Chemical and Environmental Engineering and Science*, Elsevier, 2020, pp. 1-16.

- [63] Made-in-China, "Carbon Dioxide Price," Made-in-China, [Online]. Available: https://www.made-in-china.com/products-search/hot-china-products/Carbon_Dioxide_Price.html. [Accessed 10 November 2025].
- [64] J. Ren, Y. Tsuji, I. Tabata, T. Hori and K. Hirogaki, "Decolorization of dyed polyester fabrics by synergistic effect of supercritical carbon dioxide fluid and co-solvent," *Journal of Environmental Chemical Engineering*, vol. 13, no. 3, 2025.
- [65] M. I. Chaudhari, A. Muralidharan, L. R. Pratt and S. B. Rempe, "Assessment of Simple Models for Molecular Simulation of Ethylene and Propylene Carbonate as Solvents for Electrolyte Solutions," in *Modeling Electrochemical Energy Storage at the Atomic Scale*, Springer, Cham, 2018, pp. 53-77.
- [66] Made-in-China, "Ethylene Carbonate Prices," Made-in-China, [Online]. Available: https://www.made-in-china.com/products-search/hot-china-products/Ethylene_Carbonate_Price.html. [Accessed 10 November 2025].
- [67] N. Gupta, S. Kalla and Z. Murthy, "Effect of Tetramethylurea (TMU) on polysulfone Membrane Performande for Atrazine-containing Waste water Treatment," *Journal of Polymer Materials*, vol. 40, no. 3-4, pp. 317-328, 2023.
- [68] Thermo-Fisher, "1,1,3,3-Tetramethylurea," Thermo-Fisher Scientific, [Online]. Available: <https://www.thermofisher.com/order/catalog/product/138491000?>. [Accessed 10 November 2025].
- [69] M. C. Lee, P. K. Pak and H. H. Cho, "Swelling Properties of Poly(ethylene terephthalate)," *Journal of the Korea Society of Dyers and Finishers*, pp. 17-16, 1994.
- [70] Q. Wan, H. Wang, S. Li and J. Wang, "Efficient liquid-phase exfoliation of few-layer graphene in aqueous 1, 1, 3, 3-tetramethylurea solution," *Journal of Colloid and Interfeace Science*, vol. 526, pp. 167-173, 2018.
- [71] R. Billet, "Evaporation," in *Ullman's Encyclopedia of Industrial Chemistry*, Weinheim, Wiley-VCH, 2000, pp. 585-619.
- [72] The Editors of Encyclopaedia Britannica , "chemical precipitation," Encyclopedia Britannica, 21 February 2025. [Online]. Available: <https://www.britannica.com/science/chemical-precipitation>. [Accessed 15 October 2025].
- [73] C. F. Poole, "Crystallization," in *Encyclopedia of Separation Science*, Detroit, Elsevier, 2000, pp. 64-86.
- [74] J. L. Martinez and S. W. Vance, "Supercritical Extraction Plants Equipment, Process and Costs," in *Supercritical Fluid Extraction of Nutraceuticals and Bioactive Compounds*, Boca Raton, CRC Press, 2007, pp. 25-49.

- [75] H. D. Sung and J. J. Shim, "Solubility of C. I. Disperse Red 60 and C. I. Disperse Blue 60 in Supercritical Carbon Dioxide," *Journal of Chemical & Engineering Data*, vol. 44, no. 5, pp. 985-989, 1999.
- [76] K. Leitch, G. Hartigan and R. D'Orazio, "CO₂ Recovery Process for Supercritical Extraction". USA Patent US 6,960,242 B2, 1 November 2005.
- [77] T. B. Nielsen and C. M. Hansen, "Elastomer swelling and Hansen solubility parameters," *Polymer Testing*, vol. 24, no. 8, pp. 1054-1061, 2005.
- [78] "Draw.io," Northampton, 2005-2025.
- [79] Aspen Tech, "Aspen Plus," Aspen Technology, [Online]. Available: <https://www.aspentech.com/en/products/engineering/aspen-plus>. [Accessed 17 October 2025].
- [80] K. I. Al-Malah, ASPEN PLUS Chemical Engineering Application, New Jersey: John Wiley & Sons, Inc., 2016.
- [81] R. Leng and J. Anderson, "Techno-economic analyses," in *Integration and optimization of Unit Operations*, Elsevier, 2022, pp. 373-412.
- [82] G. O. o. Sweden, "Miljöbalk (Environmental Code)," Government Offices of Sweden, Stockholm, 1998.
- [83] Y. Lyu, K. Yan, J. Tian and L. Chen, "High cost of wate treatment calls for systematic thinking: A case study for a chemical industrial park in China," *Journal of Industrial Ecology*, vol. 27, no. 1, pp. 362-375, 2022.
- [84] Riksbanken, "Sök räntor och valutakurser," Riksbanken, 20 November 2025. [Online]. Available: <https://www.riksbank.se/sv/statistik/rantor-och-valutakurser/sok-rantor-och-valutakurser/>. [Accessed 21 November 2025].
- [85] K. Koziół, K. Kozak and Ż. Polkowska, "Hydrophobic and hydrophilic properties of pollutants as a factor influencing their redistribution during snowpack melt," *Science of the Total Environment*, Vols. 596-597, pp. 158-168, 2017.
- [86] Atlas Scientific, "Atlas Scientific - Environmental Robotics," 1 May 2024. [Online]. Available: <https://atlas-scientific.com/blog/what-causes-high-bod-in-wastewater/>. [Accessed 1 December 2025].
- [87] P. M. Doran, "Material Balances," in *Bioprocess Engineering Principles*, Elsevier Ltd, 2013, pp. 87-137.
- [88] J.-C. Lee and M. H. Litt, "Ring-Opening Polymerization of Ethylene Carbonate and Depolymerization of Poly(ethylene oxide-co-ethylene carbonate)," *Macromolecules*, vol. 33, no. 5, 2000.

- [89] S. Ramchadan, "Minimize Trapped Components in Distillation Columns: here is how one plant remedied a distillation difficulty by analyzing, then counteracting, the chemistry that had led to the problem," *Chemical Engineering*, vol. 113, no. 3, 2006.
- [90] P. W. Atkins, J. D. Paula and J. Keeler, *Atkins' physical chemistry*, Oxford: Oxford : Oxford University Press, 2023.
- [91] B. Yang, X. Cao, C. Wang, S. Wang and C. Sun, "Investigation of hydrogen bonding in Water/DMSO binary mixtures by Raman Spectroscopy," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 228, 2020.
- [92] H. Fan, A. Rapikov and E. Benassi, "Agglomeration in dimethyl sulfoxide and water binary System: A comprehensive study through thermodynamics, vibrational spectroscopy, quantum mechanical calculations and morphology," *Journal of Molecular Liquids*, vol. 408, 2024.
- [93] IEA Bioenergy, "Swedish Waste Incineration Tax Abolished," IEA Bioenergy, [Online]. Available: <https://task36.ieabioenergy.com/news/swedish-waste-incineration-tax-abolished/>. [Accessed 25 November 2025].
- [94] L. Heller, S. Glos and R. Buck, "Techno-economic selection and initial evaluation of supercritical CO₂ cycles for particle technology-based concentrating solar power plants," *Renewable Energy*, vol. 181, pp. 833-842, 2022.
- [95] C. S. Whewell, "Dyeing and printing," Britannica, 31 October 2025. [Online]. Available: <https://www.britannica.com/topic/textile/Dyeing-and-printing>. [Accessed 26 November 2025].
- [96] S. Acharya, S. Liyanage, P. Parajuli, S. S. Rumi, J. L. Shamshina and N. Abidi, "Utilization of Cellulose to Its Full Potential: A Review on Cellulose Dissolution, Regeneration, and Applications," *polymers*, vol. 13, no. 24, 2021.
- [97] S. Z. Mahmoudabadi and G. Pazuki, "Investigation of COSMO-SAC model for solubility and cocrystal formation of pharmaceutical compounds," *Scientific reports*, vol. 10, 2020.
- [98] "About SiOx Machines AB," SiOx Machines AB, [Online]. Available: <https://www.sioxmachines.com/about-siox-machines-ab/>. [Accessed 2025 November 28].
- [99] Svenskt Vatten, "Vad kostar vatten?," [Online]. Available: <https://www.svensktvatten.se/om-oss/verksamhet-och-strategi/fakta-om-vatten/vad-kostar-vatten/>. [Accessed 13 January 2026].
- [100] HunterLab, "What Is CIELAB Color Space?," Hunter Associates Laboratory, Inc, 4 November 2025. [Online]. Available: <https://www.hunterlab.com/blog/what-is-cielab-color-space/>. [Accessed 8 January 2026].

- [101] B. Becerir, E. Karaca and S. Omeroglu, "Assessing colour values of polyester fabrics produced from fibres having different cross-sectional shapes after abrasion," *Coloration Technology*, vol. 123, no. 4, pp. 252-259, 2007.
- [102] M. Alveteg, Handbook Physical properties, correlations and equations, Lund: MediaTryck, 2024.

7 Appendix

7.1 Additional tables

Table 9: Pictograms of the reviewed solvents [55].

DMSO	Cyrene	Water
None	 Reason: eye irritation.	None
Benzyl alcohol	Carbon dioxide	Ethylene carbonate
 Reasons: harmful if swallowed, may cause an allergic reaction, causes eye irritation.	 Reason: contains gas under pressure.	  Reasons: harmful if swallowed, eye irritation, may cause damage to organs if swallowed.
Tetramethylurea	DMF	
   Reasons: harmful if swallowed, skin irritation, eye damage, may damage the unborn child.	   Reasons: flammable, harmful in contact with skin or inhaled, eye irritation, may damage the unborn child.	

Table 10: Cost for each solvent.

Solvent	Cost
DMSO [53]	35 SEK/kg
Cyrene [56]	420 SEK/kg
Water [99]	0.08 SEK/kg
Benzyl alcohol [60]	20 SEK/kg
CO ₂ [63]	12 SEK/kg
Ethylene carbonate [66]	45 SEK/kg
Tetramethylurea [68]	325 SEK/kg

Table 11: Functional groups of the analysed chemicals in Aspen.

Compound	Functional group description	Amount
DMSO	DMSO (dimethyl sulfoxide)	1
Cyrene	>CH-	1
	>CH ₂	1
	-CH ₂ -CO- (ketone group as any group other than second carbon)	1
	>CH-O- (ether)	1
	-CH ₂ -O- (ether)	1
Water	H ₂ O	1
Benzyl alcohol	Aromatic -CH=	5
	Aromatic C-CH ₂ -	1
	-OH (primary alcohol)	1
Ethylene carbonate	>CH ₂	1
	-CH ₂ -O- (ether)	1
	-COO-	1
Tetramethylurea	CON(CH ₃) ₂	2
	-CH ₃	1
	CH ₃ -N<	1
Disperse Red 60	Aromatic -CH=	13
	-CH ₂ -CO- (ketone group as any group other than second carbon)	2
	Phenolic =C-OH	1
	Aromatic C-NH ₂	1
	>CH-O- (ether)	1

Table 12: Evaporation tower results in Aspen Plus V14.

Parameter	Value
Outlet temperature	130.3 °C
Outlet pressure	0.16 bar
Fluid phase vapor fraction (Mole)	0.8993
Fluid phase vapor fraction (Mass)	0.8969
Heat duty	4.27 MW
Pressure drop	0.84 bar

Table 13: Distillation tower results from Aspen Plus V14.

Parameter	Value
Minimum reflux ratio	0.065
Actual reflux ratio	0.29
Minimum number of stages	5.17
Number of actual stages	10
Feed stage	4.31
Number of actual stages above feed	3.31
Reboiler heat duty	0.87 MW
Condenser heat duty	-0.54 MW
Distillate temperature	99.67 °C
Bottom temperature	189.99 °C
Distillate to feed fraction	0.53

Table 14: Stream results for "EVAP" and "DIST". From Aspen Plus modelling.

After "EVAP"	VAPSOLV	SOL+DYE2
Total Mass Flows	2586 kg/h	22,501 kg/h
DMSO	2499 kg/h	22,501 kg/h
DR60	87 kg/h	1.6×10^{-5} kg/h
WATER	0	0
After "DIST"	REWATER	RESOLV
Total Mass Flows	662 kg/h	2497 kg/h
DMSO	2.5 kg/h	2496,5 kg/h
DR60	0	0
WATER	660 kg/h	0.66 kg/h

7.2 Additional figures

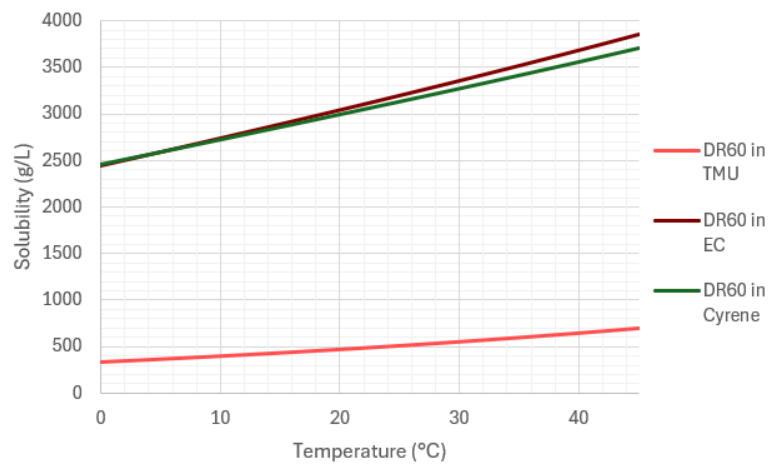


Figure 32: Solubility of DR60 in TMU, EC and Cyrene against the temperature.

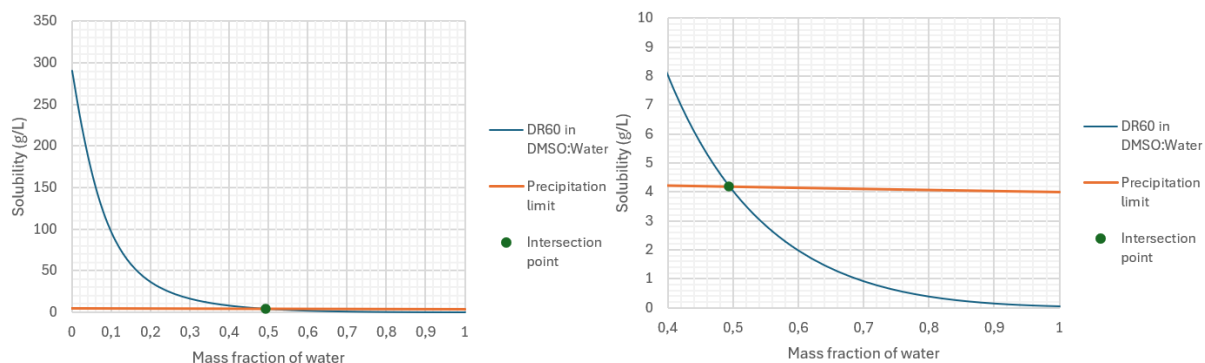


Figure 33: Solubility plot of DR60 in DMSO:water against the mass fraction of water with the right figure as the zoomed-in version.

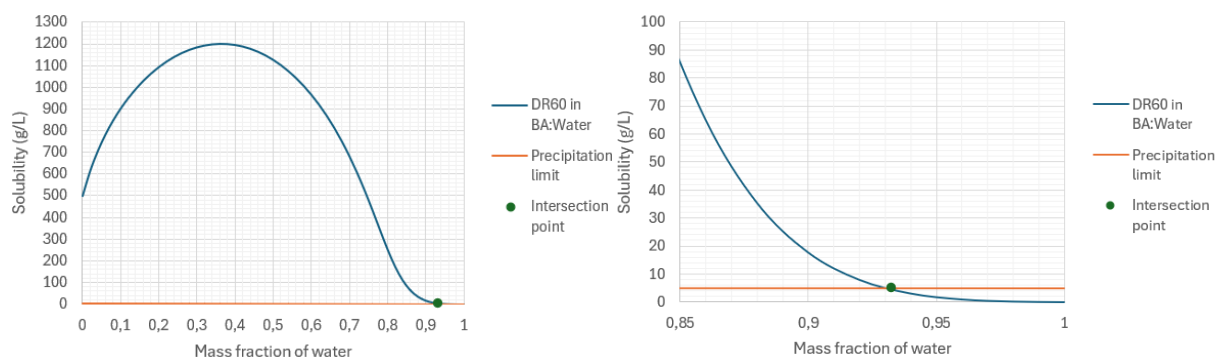


Figure 34: Solubility plot of DR60 in BA:water against the mass fraction of water with the right figure as the zoomed-in version.

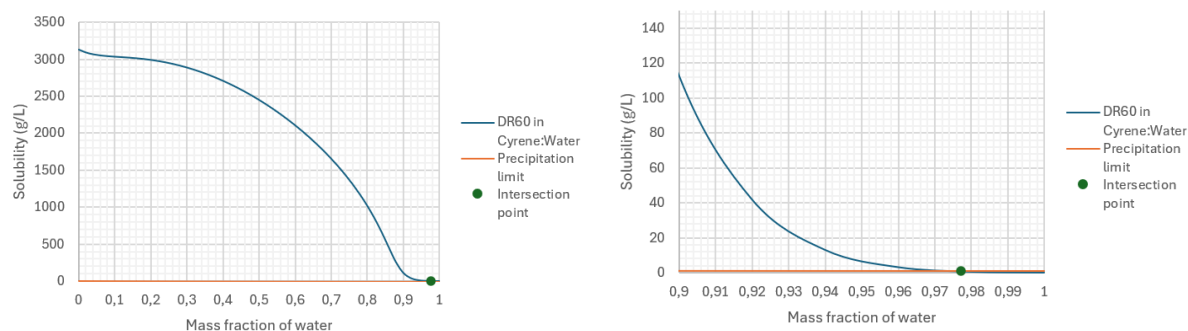


Figure 35: Solubility plot of DR60 in Cyrene:water against the mass fraction of water with the right figure as the zoomed-in version.

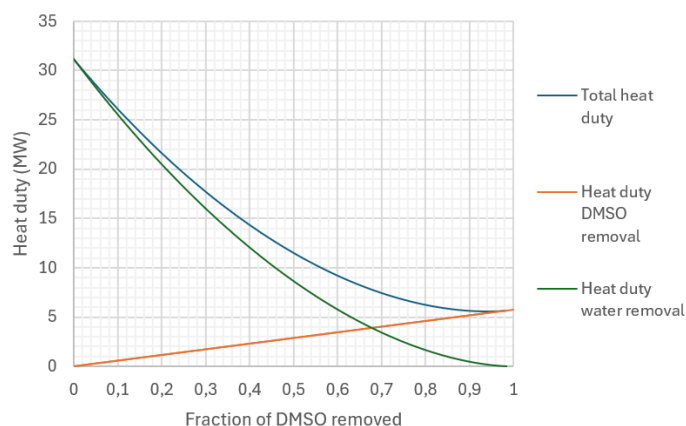


Figure 36: Heat duty results of DMSO system at different DMSO removal mass fractions.

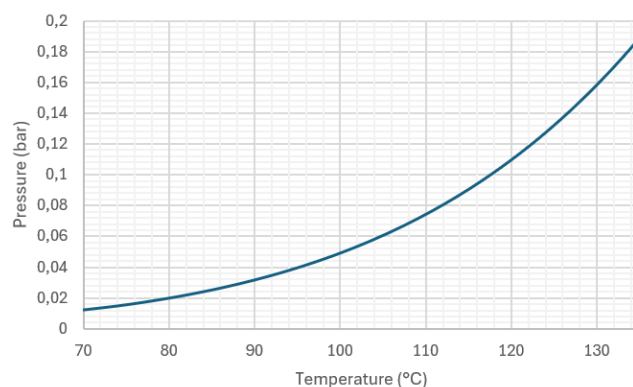


Figure 37: Result of sensitivity analysis showing boiling point of DMSO depending on pressure.

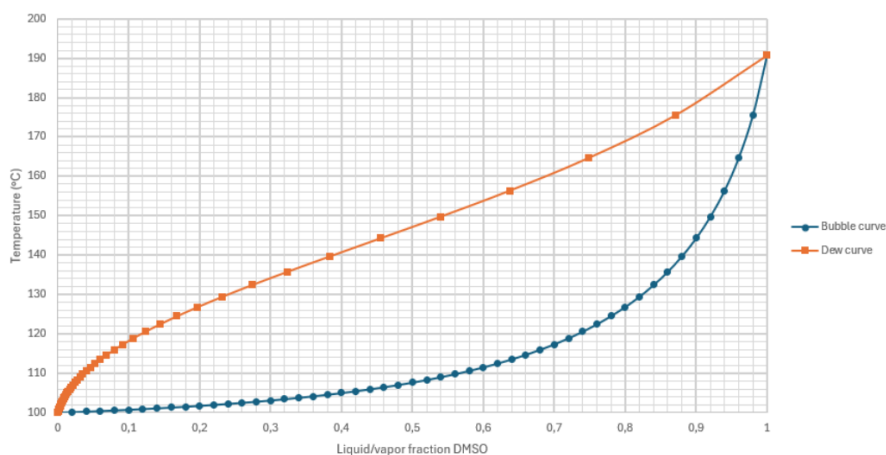


Figure 38: Vapour-liquid equilibrium (T - x - y) diagram made in Aspen for the water/DMSO system at atmospheric pressure.

An azeotrope would be observed in Figure 38 if the two curves intersected, which is not the case here, therefore no azeotrope is present for this system [36]. The bubble curve represents the temperatures at which the liquid mixture starts to boil, and the dew curve represents the temperatures at which the vapour mixture starts to condensate.

7.3 Calculations

If mentioned, the calculations are done in excel and are therefore accessible through the following link. Observe that the graphs are not accessible via the link due to transfer of data from excel to google spreadsheet to facilitate its display through the link:

https://docs.google.com/spreadsheets/d/1wBDLHPsFq0ty9Xpnn5OhqWq-BQGCohb0p_Em77ssYw/edit?usp=sharing

7.3.1 Dye removal percentage for DMSO from Sharma et al. 2025

The article from Sharma et al. does not disclose how much dye that is removed from the polyester fabrics in percentage [52]. This is due to the substrate in their experiment being textile waste, and therefore, the authors do not know the concentration of dye on the fibres. However, they instead measured L^* , which corresponds to the perceptual lightness in the colour space [100]. This colour space is represented in the CIELAB, which is a three-dimensional space that assigns a numerical value to every perceptual colour.

To assign a dye removal percentage to the reported L^* values from Sharma et al., a simple normalisation was made. The L^* value of the dyed polyester prior to treatment was used as the initial reference, while the L^* value of undyed polyester in the literature was taken as the fully decoloured state. The cumulative dye removal after each treatment cycle was calculated as the fraction of the total achievable increase in lightness according to Equation 7.

Equation 7

$$\text{Dye removal (\%)} = \frac{L_{\text{cycle}}^* - L_{\text{dyed}}^*}{L_{\text{undyed}}^* - L_{\text{dyed}}^*} \times 100$$

This calculation provides an approximative measure of dye removal based solely on changes in lightness and the value for the undyed L^* is assumed to be 95 [101]. The other values can be seen in Table 15, taken from the article provided from Sharma et al. [52].

Table 15: Reported L^ values for polyester taken from Figure 6 in Sharma et al. [52]*

	L^*
Dyed	18
After cycle 1	40
After cycle 2	70
After cycle 3	80

7.3.2 Translation calculation of the experimental solubility value

DR60 has a solubility of 1×10^{-6} mol/mol in water at an unknown temperature, assumed to be 20 to 25 °C. DR60 has a molar weight of 331.32 g/mol and water has a molar weight of 18.02 g/mol and a density of 997 g/L [21, 102]. Therefore, the solubility of DR60 can be translated to the following:

$$Sol_{DR60} = \frac{10^{-6} \frac{mol_{DR60}}{mol_{water}} \cdot 331.32 \frac{g_{DR60}}{mol_{DR60}} \cdot 997 \frac{g_{water}}{L_{water}}}{18.02 \frac{g_{water}}{mol_{water}}} = 0.01833 \frac{g_{DR60}}{L_{water}}$$

7.3.3 DR60 concentration calculation in the different solvents

By dividing the mass of the solvents with their densities, it is possible to get the volume of each solvent, Table 16. Continuously, for the solvents that are composed of a mixture, the volumes are added together to get the total volume of the solution. Therefore, Cyrene with water (75:25) has a total volume of 42 537.6 L/h, Cyrene with water (50:50) has a total volume of 45 075 L/h and EC:TMU has a total volume of 20 292 L/h. Lastly, to obtain the actual concentration of DR60 in the solvent, one has to divide the mass of DR60, 100 kg/h, with the volume of solvent. The results are displayed in Table 16.

Table 16: Calculations of the DR60 concentration in the various solvents.

Substance	Density (kg/L)	Mass (kg/h)	Volume (L/h)	Concentration of DR60 (g/L)
DMSO	1.1	25 000	22 727	4.4
Benzyl alcohol	1.0413	20 000	19 207.5	5.21
Cyrene (75)	1.25	25 000	20 000	2.22
Water (25)	0.997	25 000	25 773.2	
Cyrene (50)	1.25	35 000	28 000	2.35
Water (50)	0.997	15 000	15 045.1	
EC	1.4	17 500	12 500	4.93
TMU	0.962	7 500	7 792	

7.3.4 DR60 concentration calculations in mixture of solvent and water

These calculations are performed in Excel to determine the DR60 concentration at the different water mass fractions, represented in Figure 33 to Figure 35 as the “precipitation limit”. It is called precipitation limit as, once the solubility of DR60 crosses this curve, the concentration of DR60 in the system becomes sufficient for precipitation to occur. To do the necessary calculations, the total mass of the system is assumed to remain constant, meaning that if water is added, the mass of solvent is decreased accordingly to maintain a constant overall mass. This assumption is done to make it possible to represent the precipitation limit. The threshold is determined by first calculating the volume of each component at every water mass fraction, where the mass of each component is divided by its corresponding density. Taking BA for example, at a water mass fraction of 0.5, there is 50 % water and 50 % BA in the system, corresponding to 12,500 kg/h each. Dividing these masses with each of their densities yields their volumes at this specific mass fraction. The volumes of the solvent and water for each water mass fraction are then summed to obtain the total volume of the mixture. Continuously, the mass of DR60 in the system is then divided by the total volume, resulting in the concentration

of DR60 in the system, which marks the solubility limit at which precipitation becomes possible.

7.3.5 Water evaluation calculations

These calculations are also done in Excel and are made to produce the plot in Figure 30. Compared to Figure 33 to Figure 35, this plot does not assume a constant total mass of the system and instead of plotting the solubility of DR60 in the mixtures, it plots the required mass of solvents to reach the solubility values of DR60. Therefore, the first step is to translate the solubility value to a volume by dividing the mass of DR60 (kg/h) by the solubility values (kg/L) for each water mass fraction (x_w). Continuously, Equation 8 is used to calculate the total mass of the system:

Equation 8

$$m_{tot} = \frac{V_{tot} \cdot \rho_w \cdot \rho_{sol}}{\rho_w \cdot x_{sol} + \rho_{sol} \cdot x_w}$$

Followingly, the mass of each component can be calculated by multiplying the total mass with the components mass fraction, which can then be modelled against the mass fraction of water, Figure 30.

7.3.6 Heat duty calculations

These calculations are also done in excel. The pre-treatment process aims at evaporating parts of DMSO, making it easier for the dye to precipitate once water is added in the system. However, this water needs to subsequently be removed from the rest of DMSO by distillation to allow the recovery of both. Therefore, with the mass of each component calculated in 7.3.5, it is possible to perform simple heat duty calculations to estimate the energy required to remove the components in the process. This allows to find the optimal water mass fraction for the process enabling the lowest heat duty possible. However, the calculations should not be taken as an absolute value but rather as an indication on the overall heat duty, as these for example omit the reboiler heat duty of the distillation tower.

Firstly, the amount of DMSO removed for each water mass fraction needs to be calculated, which is done by subtracting the mass of DMSO at each mass fraction to the initial amount of solvent in the system. The amount of water to be distilled is known, as all water needs to be separated from DMSO. Continuously, Equation 9 is used to calculate the heat duty of DMSO and water removal separately, where T_2 is the boiling temperature of the component and the other parameters necessary can be found in Table 17.

Equation 9

$$Q = m \cdot c_p \cdot (T_2 - T_1) + m \cdot \Delta H_{vap}$$

Lastly, by adding the two heat duties together, all the heat duties for the different water fractions can be compared to find the lowest one for the system. This gives indications about the most energy-efficient amount of water to add. This results in a removal of 94 % of DMSO (leaves 1470 kg/h DMSO in the system) with an addition of 240 kg/h of water being the optimal ratio as it resulted in the lowest total heat duty, which is of 5.585 MW, Figure 36. This result lies approximately within the same range as the sum of the heat duties of the “EVAP” and ”DIST” blocks from the Aspen modelling, Table 12 and Table 13, indicating that the calculation results are reasonable. The difference between the total heat duties can be because of a difference in c_p

between Aspen and the calculations performed here, as well as Aspen performing more advanced calculations.

Table 17: Parameters for heat duty calculation.

Component	c_p (kJ·kg ⁻¹ ·K ⁻¹)	ΔH_{vap} (kJ/kg)
Water [102]	4.184	2260
DMSO [21]	2.026	648

7.3.7 Cost estimation

To estimate the savings associated with handling the waste stream leaving the Rewin Textiles process as Stream 2, the calculations are as follows. The third-party incineration fee, i_{fee} , is multiplied with the amount of waste coming out of Stream 2, m_{st2} , see Equation 10.

Equation 10

$$\text{Saving Stream 2} = i_{fee} \cdot m_{st2} = 3000 \left(\frac{\text{CNY}}{\text{tonnes}} \right) \cdot 160000 \left(\frac{\text{tonnes}}{\text{year}} \right) = 480 \text{ million } \frac{\text{CNY}}{\text{year}}$$

Furthermore, the cost of solvents is based on a 95 % recycling ratio, and the cost is an estimation based on Rewin Textiles' assumption of their annual processing capacity. The first part of Equation 11 is the initial cost for the process, a one-time payment to start of the process. The second part accounts for the annual operating hours, including a 5 % solvent makeup per hour to compensate for losses due to leakage and solvent removal to prevent dye accumulation. The cost/kg term refers to the cost of the solvent from Table 10 and the results can be seen in Table 8.

Equation 11

$$\text{Cost of Solvent} = m_{\text{solvent}}(\text{kg}) \cdot \frac{\text{cost}}{\text{kg}} + 0.05 \cdot m_{\text{solvent}} \left(\frac{\text{kg}}{\text{h}} \right) \cdot 8000 \left(\frac{\text{h}}{\text{year}} \right) \cdot \frac{\text{cost}}{\text{kg}}$$