Depolymerization of Polyester and Nylon 6 in a Co-Process using Neutral Hydrolysis

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Depolymerization of Polyester and Nylon 6 in a Co-Process using Neutral Hydrolysis

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Chemical Recycling of Synthetic Textile Waste

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Abstract:

In this study, depolymerization via neutral hydrolysis has been used to co-process polyester and nylon 6 into its constituent monomers. While the study has been performed as a pure literature study, it has been concluded that co-processing of the two polymers is feasible. The recovery of the monomer products by phase separation has been investigated with the objective of retaining high yield and product purity utilizing Aspen Plus V9. TPA and CL have been identified as the main products of the process based on which the solid-liquid phase separation to retrieve the monomers has been implemented. 605.3 kg TPA/hr has been recovered with 99.9% purity and 484.7 kg CL/hr as liquid with 91.2% purity. The separation of water and EG has been modelled additionally to give the possibility of recycling a portion of the process water within the system. To improve energy recovery, a pinch analysis has been conducted to identify the optimum HEN of the model.

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Summary

With the increasing amount of consumed textile products per capita over the recent decades and the trend towards fast fashion and a shortened product lifetime, the accumulation of textile waste is growing rapidly. This development in the consumerism of textiles affects not only their production, but causes likewise consequences in the management and treatment of the accruing waste. The annual generation of textile waste from European households alone has been estimated to around 5.8 million tonnes [1]. Thereby, the majority of the waste is either landfilled or incinerated, which causes environmental pressures due to the low biodegradability of incorporated synthetics and the creation of emissions. Following the ambitions stated by the European Commission for a reduction in the EU's greenhouse gas emissions and in line with the Sustainable Development Goals for climate action, this project aims for the development of a chemical recycling mechanism for polyester and nylon, which contribute as the two most used synthetic textile materials to the mentioned concerns originating from textile waste.

Throughout the development of this project, a depolymerization process for polyester and nylon 6 to produce their constituent monomers by co-processing has been established, which is followed by the definition of a phase separation mechanism in order to separate the resulted monomer products. The model has been generated utilizing the simulation program Aspen Plus V9, with the main objective to retrieve high monomer yields after the depolymerization and separation, with preferably high purity suitable for the re-utilization of the monomer products in subsequent new production processes. The depolymerization reaction has been defined as a neutral hydrolysis in sub-critical conditions, due to the high process performance, low environmental impacts, high yields of the individual polymers and the ability to process different types of polymers. The chemical reactions for the depolymerization of each polymer and the corresponding kinetics have been specified. For the simulation of the reactor model, a plug flow reactor has been chosen to implement a continuous reaction and due to higher conversion efficiency. Because this study is based on theoretical considerations and available data found in literature, certain assumptions have been defined for the development of this recycling process. The most important assumption is the hypothesis of no interaction between polyester and nylon during the depolymerization process.

Based on the depolymerization reaction, terephthalic acid and ϵ-caprolactam have been identified as the main monomer selling products of the plant, from which the solid terephthalic acid was decided to be separated first from the multi-phase mixture stream. Therefore, the utilization of three hydrocyclones arranged in series has been proposed, with an additional subsequent purification of the solid stream

by means of a flash. Due to this solid phase separation and purification, 99.8% of the terephthalic acid could be recovered with a purity of 99.9%. Based on this finding, the depolymerization of polyester and the corresponding separation of terephthalic acid could be determined feasible. The remaining liquid stream after the solid phase separation is consisting of ϵ-caprolactam, aminocaproic acid, ethylene glycol, water and a fraction of not fully depolymerized nylon. ϵ-Caprolactam has been separated from this liquid stream utilizing a distillation column and a subsequent flash in order to purify the monomer product due to the reduction of the water content. The monomer could be recovered by 96.6% with a purity of 91.2%, which is assumed as not pure enough for a direct re-utilization in some production processes. Thereby, the main impurity of the monomer could be identified as ethylene glycol residues with about 6.5%, which demonstrates a direct effect on the product's outcome due to co-processing of the two polymers.

Due to a high amount of ethylene glycol remaining in the liquid stream after the separation of the main selling products, an additional separation of ethylene glycol by means of a distillation column has been suggested. Thereby, 79.2% of the ethylene glycol could be recovered from the process stream. Additionally, this further separation gave access to the possibility of recycling a portion of the process water stream back to the reactor input in order to reduce the overall water consumption of the plant.

To improve the heat recovery within the system, a pinch analysis on the process model has been investigated and an improved heat exchanger network has been devised by reducing the applied external hot and cold utilities for the recycling process. This analysis could optimize the heat integration in the model for an improved energy consumption.

Contents

Preface

This Master thesis has been written by the group TEPE4-1003 in the study programme Energy Engineering with the specialization in Thermal Energy and Process Engineering at Aalborg University. The project has been conducted in the period from February 1st until May 28th 2021.

The objective of this study was the development of a recycling co-process of polyester and nylon with the motivation of understanding and defining a possible pathway for the depolymerization and separation of the stated polymers. Polyester and nylon have been chosen because of their broad utilization in synthetic textiles. The aim of the process was a preferably high yield of separated monomer products, with a sufficient monomer purity to enable the re-utilization of the recycled fibres in new production processes. Therefore, an optimization study on the individual phase separation mechanisms for the solid and liquid product phases has been conducted. For the optimization of the plant's energy consumption, a heat exchanger network has been defined. Initially, this project has been planned as an experimental investigation on the depolymerization behaviour of polyester and nylon under different reaction conditions, however due to special circumstances, the study has been conducted solely theoretical. Therefore, the simulation program Aspen Plus V9 has been utilized to model the depolymerization in a co-process as well as the connected phase separation.

Alongside with the individual project work, the study group has participated in a Mega Project entitled "the Circular Region", organized by the Aalborg University. It emphasizes project work oriented on the Sustainable Development Goals (SDGs) and encourages the scientific exchange of experiences and ideas between students from different faculties working on their own projects.

The group would like to thank *Antonio Jaime Azuara* for his continuous support and the supervisors *Thomas Helmer Pedersen*, Associate Professor, and *Saqib Toor*, Associate Professor, for the enlightening discussions and inspiring ideas.

Reading Guide

Throughout this report, abbreviations have been used. When the abbreviation is introduced for the first time, the full word is written out followed by the associated abbreviation in brackets. A list of all abbreviations as well as a nomenclature with the used symbols is given. The reference style for this project is based on the IEEE standard. The placing of a reference before or after the full stop indicates if the reference is associated with the foregoing sentence or the paragraph respectively.

The complete list of literature used in this study is given at the end of the thesis report. The reference numbers used in the thesis are hyperlinks in the digital version. The figures and tables throughout the study are defined by the chapter number followed by a consecutive numbering of the figure/table/equation. For instance, the second figure in chapter 2 is denoted as figure 2.2. Cross-references to figures, tables, equations or sections mentioned in the report text are likewise hyperlinks in the digital version.

Aalborg University, May 28, 2021

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Abbreviations

Acronym	**Description**
ACA	Aminocaproic acid
AEA	Aspen Energy Analyzer
CL	ϵ-Caprolactam
CSTR	Continuous stirred tank reactor
DIST	Distillation column
EG	Ethylene glycol
FL	Flash separator
HC	Hydrocyclone
HEN	Heat exchanger network
NRTL	Non random two-liquid
PET	Polyethylene terephthalate
PFR	Plug flow reactor
POLYNRTL	polymer Non random two-liquid
TPA	Terephthalic acid
SDG	Sustainable Development Goal

Nomenclature

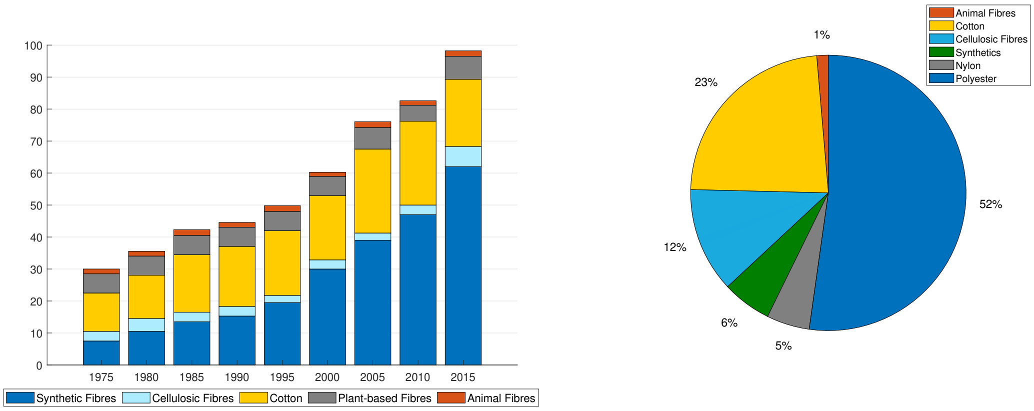
Symbol	**Description**	**Unit**
A	Pre-exponential factor	$\frac{1}{mol \cdot min}$ | $\frac{1}{s}$
α	Relative volatility	-
α_{ave}	Average relative volatility	-
E_a	Activation energy	$\frac{kJ}{mol}$
F_B	Buoyancy force	N
F_C	Centrifugal force	N
F_D	Drag force	N
d	Particle diameter	m
k	Rate constant	$\frac{1}{mol \cdot min}$ | $\frac{1}{s}$
μ	Viscosity	$\mathrm{Pa} \cdot \mathrm{s}$
N	Number of stages	-
N_{min}	Minimum number of stages	-
R	Universal gas constant	$\frac{J}{mol \cdot K}$
R	Reflux ratio	-
R_{min}	Minimum reflux ratio	-
R^2	Coefficient of determination	-
r	Orbit radius	m
ρ	Density	$\frac{kg}{m^3}$
T	Temperature	K | °C
u_t	Tangential velocity	$\frac{m}{s}$
x	Stream composition	-

1 Introduction

1.1 Background and Motivation

Textiles are an important part of daily life. With a great variety of properties, they can be found in clothes, furniture, bedding and carpets as well as work- and sportswear, car tyres, safety belts and others. With a decreasing lifespan and the price of clothes falling relative to inflation, the consumption of textile products have increased immensely over the recent decades and continues to rise further. In 2017, European households alone consumed about 13 million tonnes of textile products according to the European Environment Agency, whereof 5.8 million tonnes are discarded as waste every year [1]. This corresponds to an annual textile waste accumulation of 11 kg per capita in the EU.

Also the textile industry itself produces waste, which incurred during different stages of the production process. Most of these wastes can be reused directly in different sections of the production line or for other types of products. However about 25% requires additional treatment before it can be reused, which has been estimated to a waste accumulation of about nine million tonnes every year on a global scale. [2]



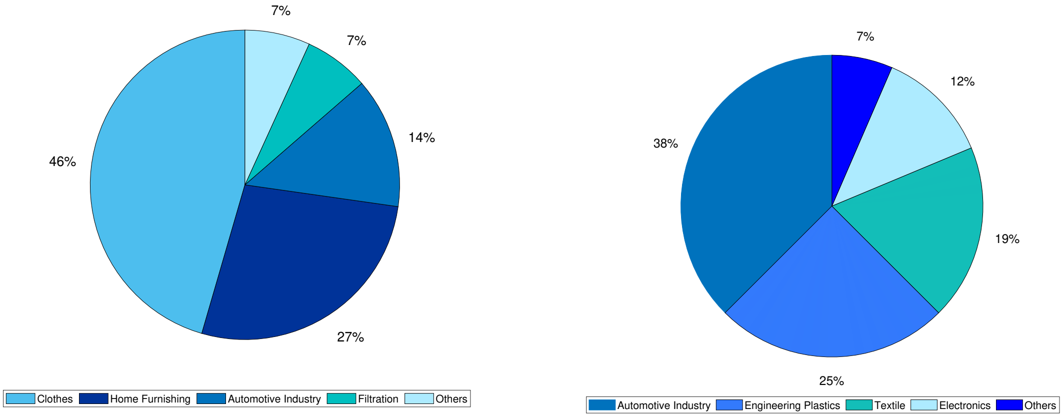
(a) Global fibre production development in million metric tonnes.

(b) Distribution for global production of 110.5 million metric tonnes fibres in 2019.

Figure 1.1: Global fibre production development from 1975 to 2015 and their proportional share in 2019, data based on [3].

The immense increase in the textile consumption is mainly driven by the intensified production of synthetic fibres, which can be seen in the figure 1.1a. Hereby, the most common synthetic fibre nowadays is polyester, which surpassed cotton as the leading textile material in the late 1990s. Today, about 63% of the global textile fibres are synthetic, with polyester taking more than 50% of the global share as illustrated in the figure 1.1b. With a production rate of over 5 million tonnes of nylon (polyamide) in 2018, it is considered the second most common synthetic fibre after polyester. [1], [3] An estimate of the application distribution of polyester and nylon is given in the figure 1.2. This illustrates the main economical sectors to which fibres of polyester and nylon contribute to, demonstrating their everyday importance.

The strong increase in the consumption of textiles creates different environmental effects. Especially the piling of synthetic waste in landfills is detrimental due to the low degradation rate of plastics. Whereas some synthetic materials such as polyester degrade very slowly, over the duration of several years, others are non-degradable. Also the production of textiles in general has different environmental impacts. The cultivation of cotton creates pressure on land and water use, eutrophication and use of mineral resources, whereas synthetics affect climate change and the use of fossil fuel resources through their generation. The utilization of plastics and synthetic textiles however can also contribute to more sustainability in individual sectors, such as the reduction of vehicle weight in the automotive industry.



(a) Global application of polyester staple fibres in 2016, data based on [4].

(b) Global application of nylon in 2019, data based on [5] .

Figure 1.2: Distribution of polyester and nylon application.

With the goal of reducing the EU's greenhouse gas emissions and climate neutrality by 2050, the European Commission specified textiles as one of the key value chains in their composed Circular Economy Action Plan from 2020 as part of the EU Green Deal [6], [7]. Due to the stated reasons, the consumption of textiles in the EU has been defined as the fourth highest contributor on the use of raw materials and water after food, housing and transport and comparably high rankings in the use of land and generation of greenhouse gas emissions [8]. This classification gives textiles an important role in the EU's ambitions for more sustainability. From which a significantly larger but indirect impact of the EU's textile consumption has to be considered, generated in other parts of the world, through the production and import of mainly clothes and footwear.

The utilization of recycled textiles could reduce these environmental pressures, however the share of reused materials is currently negligible in the global market and less than one percent of the overall global textiles is being recycled [9]. This leads to the majority of textile waste being incinerated or landfilled. As one solution strategy, the European Commission announced an extended producer responsibility and an additional obligation for separate textile waste collection in the EU member states by 2025 [7]. Therefore, the overall objective should be to prevent waste accumulation, followed by re-utilization and recycling. The necessary sorting of materials and products before reusing and recycling is a labour intensive process and therefore costly, but also creates possibilities for job positions and the development of circular economies.

In terms of recycling strategies, chemical recycling has the advantage over mechanical recycling as it recreates material fibres similar to the virgin fibres without downgrading of the material. This way, the recycled fibres can be reintroduced to new production processes without quality losses in the final product.

A more holistic approach for more sustainability and climate action in a global context is given by the 2030 Agenda for Sustainable Development, which is created by the United Nations and incorporates 17 Sustainable Development Goals with different targets. An introduction to this idea and how it is connected to the presented study will be given in the following section.

1.2 Sustainable Development Goals

In addition to the described study, this project has been involved in a Mega Project organized by the Aalborg University, which encourages students from different scientific fields for the interdisciplinary exchange of ideas and experiences based on different goals. The discussed challenge thereby has been the development of a circular region, which emphasises a systematic change in circular economy and ideas for more sustainability in the utilization of materials and energy. With this background, the relation of the presented individual project to the Sustainable Development Goals (SDG) will be presented.

The United Nations' 2030 Agenda for Sustainable Development is a universal plan of the United Nations member states for direct action to end poverty and other deprivations as well as to improve health and education, reduce inequality and support economic growth, while tackling climate change and preserve the natural environment on land and sea. For this ambitions, 17 SDGs with different focus have been identified and further refined by associated targets for each goal. [10] With the presented background and the motivation for more sustainability in the textile industry, this project has the potential to contribute to some of the defined SDGs. The individual SDGs related to the objective of this study will be herewith introduced.

With the recycling of textile waste, a more sustainable industrial infrastructure through the re-utilization of different resources will be created. Additionally, regained materials are made available. The recycling process itself requires a previous sorting of the textile waste, which gives the possibility of new workplaces and the cooperation between different countries.

As previously mentioned, the general consumption of synthetic textiles is drastically increased over the recent past, which also includes the private consumption and has led to the significant amount of textile waste per capita. Therefore, an efficient waste management including the separate collection of textile waste is a key step for a more circular economy in textiles and strictly necessary for the implementation of a chemical recycling process.

The aim of recycling textiles is reducing the accumulation of unused waste materials and likewise to making them accessible for re-utilization. With the opportunity of reintroducing recycled fibres to the production line of new products, the consumption of textile products would become overall more sustainable, due to the reduced utilization and depletion of fossil resources. Thereby the opportunity to enhance circular economies will be established.

Through the development of a process to recycle polyester and nylon, a concrete starting point to a possible pathway of tackling the previously described environmental problems caused by the tremendous consumption of textile products will be given. This approached solution incorporates different facets of climate action, such as the reduction of environmental hazards, tackling climate change and raise awareness for more sustainable consumption.

With the introduced actions and the overall goal for more sustainability in the textile industry, general measurements to protect the existing ecosystems and the therein living wildlife have been described. With an efficient sorting mechanism of textile waste, the entry and spreading of these wastes into open environments is to be prevented. Additionally, the generation of emissions during the production process of virgin fibres and the depletion of fossil resources should be reduced. Therefore, environmental hazards and the pollution of land and sea should be decreased.
The textile industry is a global economy. This should not only comprise the production line for new products but also incorporate an international cooperation in waste management. This partnership could embrace the collection of textile waste, the sorting of the different materials, the recycling of these wastes and finally the re-distribution of recycled fibres to the production factories.

1.3 Objective

Considering the high amount of textile waste and the large portion of incorporated synthetic materials, which are not or only insufficiently biodegradable, efficient strategies for the handling and recycling of this waste have to be developed. Recycling of textile waste has the potential to lower the different environmental impacts occurring during the production of new products mentioned previously as well as lowering the overall waste accumulating in landfills. Therefore, textiles should primarily be reused, recycled and only incinerated as a last possibility.

For the stated reasons, the objective of this study is to design a process for the chemical recycling of synthetic textiles. With polyester and nylon previously mentioned as the two globally most utilized synthetic textile materials, the process will be developed for the recycling of these materials. The aim is to achieve fibres similar to the original fibres used in the generation of polyester and nylon respectively, from which new products could be produced. With the development of such a process, a potential pathway for a more sustainable waste management and circular economy, in line with the presented SDG goals could be introduced.

2 Problem Analysis

The difficulties for the textile industry due to environmental concerns and an increasing global demand has been introduced. Thereby, polyester and nylon could be defined as the two most commonly used synthetic fibres on a global scale. Even if the combination of nylon and polyester is not a widely utilized textile blend, high accumulation of those in the textile waste is to be expected due to their broad application. In general, due to the different blends of materials and the presence of many chemicals, additives, or resins, the recycling of different textile products remains challenging. To establish a recycling mechanism in the coming years that can deal with a realistic textile waste distribution, understanding the behaviour of different synthetic materials in such a recycling mechanism is of importance. Therefore, analysing and designing a recycling process that can handle the two mostly used synthetic materials polyester and nylon in a co-process could be of high interest.

In this chapter, the theoretical background necessary to understand and develop a possible solution for the recycling of polyester and nylon will be discussed. Therefore, an overview of the planned process will be given. This will be followed by an introduction to the synthesis reactions of polyester and nylon. These reactions will be utilized to estimate the respective depolymerization reactions by reverse engineering, from which the behaviour of the two polymers in a hydrolysis depolymerization will be discussed. Finally, possible separation methods for the resulting product phase streams will be analysed. At the end of each section, a summary of the findings will be given and this chapter will be followed by a concluding problem statement. The implementation of the theoretical findings to the simulation programme and their optimization will be discussed in following chapters.

2.1 Overview of the Process

Different recycling processes have been utilized in the polymer industry. Some common recycling methods in the plastic industry are primary, secondary, and tertiary processes, however, these processes are not completely adapted in the textile industry. For the recovery of carbonaceous materials from textiles, physical and chemical recycling are the preferred methods whereas incineration for energy recovery and land-filling methods should be avoided. In physical recycling, the polymers are subjected to shredding and melting to remodel the polymer, but there is limited use for these resulting polymers due to the degradation of the polymer's properties with each life cycle as a result of the low molecular weight of the recycled resin. This issue is caused by chain-scission reactions as a result of interaction with water [11]. In the case of chemical recycling, this process is capable of recovering the pure chemicals or monomers from polymers without any degradation in properties which preferably can be reused as raw materials for the production of new polymers or even chemicals. Due to these advantages, there are multiple attempts for the development of different depolymerization processes such as hydrolysis, glycolysis and pyrolysis in the scientific community [11].

This study will focus on the development of a co-processing mechanism for polyester and nylon utilizing hydrolysis for the depolymerization. Therefore, it is crucial to understand the differences and similarities of the two materials to identify feasible reaction conditions and estimate the composition of the products. Different studies for the depolymerization of the single polymers could be found in the literature, however, there is no currently available literature or experimental data for co-processing polyester and nylon. Therefore, existing data for the single polymers with best fit to the described problem will be utilized as a starting point, from which the co-process reaction will be approximated.

As the discussions made in this study are based on the data found in literature and theoretical considerations, certain assumptions have to be made within the scope of this project. One crucial assumption is the hypothesis of no direct interaction between the two polymers during the depolymerization process. Furthermore, the feed polymers will be assumed as pure materials, without impurities or other incorporated residues. Based on this assumption, possible side reactions or byproducts will be neglected.

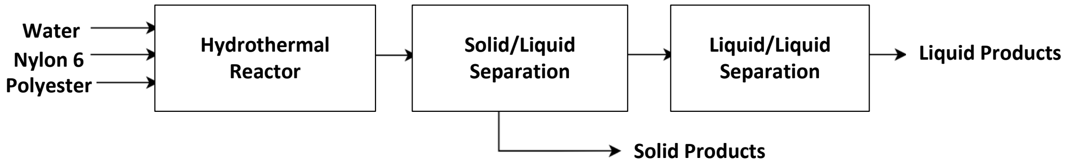


Figure 2.1: Overview of the recycling process.

An overview of the general process is given in the figure 2.1. This illustrates a simplified version of a possible recycling plant, not including necessary heaters or a previous separation of the utilized waste material. Therefore, the main components presented in the process can be narrowed down to the hydrothermal reactor to decompose the respective polymer chains and the following separation mechanisms for solids and liquids, utilized to separate the different products from each other. A detailed description of each component and its implementation to the simulation will be given.

The objective in the development of this recycling process is the optimization of the co-process for maximal product yield, which in this case means a maximum amount of separated monomers. Additionally, the retrieved monomers should not only reach a preferably high quantity, but also stay within certain quality constraints which are necessary for the re-utilization of the monomers in new production processes for synthetic textile fibres or other plastic products.

By establishing the presented recycling process, a holistic approach for the depolymerization and separation of two combined synthetic textile materials will be given, which could lead to a further development of new pathways for the recycling of plastics and textiles. Therefore, it is of high interest to understand the possibilities as well as the limitations evolving through the development of this process.

In the subsequent section, the depolymerization of polyester by reverse engineering the synthesis reaction will be discussed, followed by the depolymerization of nylon.

2.2 Depolymerization of Polyester

Polyesters are currently the most important thermoplastic polymers as illustrated in the figure 1.1b in the introduction and are used in a large variety of applications. These range from food and other plastic packaging, over the automotive industry to clothes and different components in daily life products. Depending on their main chain composition, they can be classified as aliphatic, semi-aromatic or aromatic polyesters corresponding to different material characteristics. Therefore, different aromatic diacids and aliphatic diols can be combined. For the utilization in textiles, the most common polyester is the semi-aromatic polyethylene terephthalate (PET) with its chemical formula $(C_{10}H_8O_4)_n$ and a melting point at about 260°C. It is synthesized by the reaction of terephthalic acid (TPA) and ethylene glycol (EG) to polymer chains. Polyester fabrics made of PET have the advantages of a strong fiber, elasticity and resistance to abrasion and wrinkling [12]. Compared to nylon fibres, polyester is typically not as strong, however, it has the advantage of significantly lower production costs. It is often combined with other fibres such as natural cotton fibres in textile blends to improve the textile's properties.

2.2.1 Synthesis of Polyester

Textile polyester fibres are produced by polycondensation of its monomers TPA and EG. Therefore, the functional carboxyl ($-COOH$) and hydroxyl ($-OH$) end groups of TPA and EG respectively join via an ester link as illustrated in the figure

2.2. During the polymerization reaction, water is released which is constantly removed to shift the equilibrium reaction towards the product side. Hereby, a higher degree of polymerization is ensured. The reaction is often performed in stages with increasing pressure and temperature to achieve higher molecular weights. For the synthesis of polyester, the temperature ranges between 258°C and 290°C but should not exceed 300°C at which point a rapid decomposition reaction occurs [13].

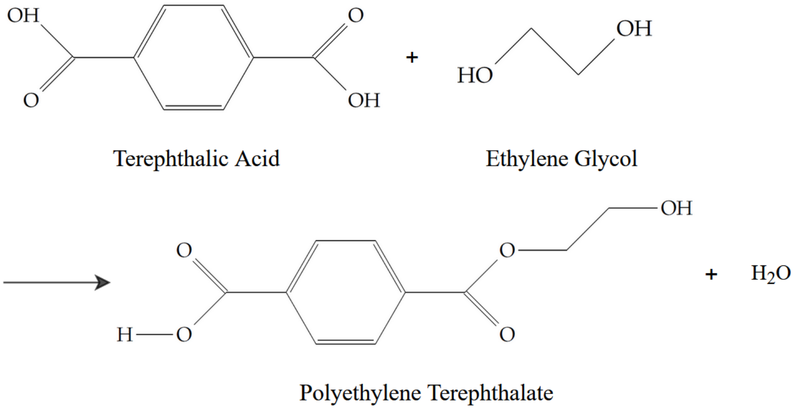


Figure 2.2: Polymerization of polyester.

2.2.2 Depolymerization Summary

The depolymerization of polyester can be related to the reverse reaction of the here described synthesis reaction. This time the PET polymer chain should split up by breaking the ester links. For this purpose, water should be added under high temperature and high pressure, and reform the carboxyl and hydroxyl end groups with the respective monomers. The high pressure is necessary to induce breaking of the polymer chains. A more detailed analysis of the reaction conditions for the depolymerization will be given in section 4.3.2. Ideally, PET only breaks into its two primary products TPA and EG, however, also secondary byproducts will form in a realistic depolymerization process. Nevertheless, the amount of secondary products appears to be relatively small and high product purities could be found in literature especially for TPA [14]. For this reason, the assumption will be made that these secondary products can be neglected in the following considerations. Hence, the depolymerization reaction for polyester can be defined as follows:

$$(C_{10}H_8O_4)_n + H_2O \longleftrightarrow C_8H_6O_4 + C_2H_6O_2 \tag{2.1}$$

2.3 Depolymerization of Nylon 6

Nylon is a synthetic aliphatic amide and therefore, classified as a polyamide. The variety of existing nylon types makes it an attractive material for many industries due to its specific applicability and high performance properties. The particular type of nylon is indicated by its given numbering, specifying the number of carbon atoms in its monomers. Depending on the type of nylon, it is industrially produced either by the reaction of a diacid with a diamine or by ring-opening polymerization of lactams. Therefore, the main synthesis reactions can be summarized as step-growth polycondensation, ring-opening polymerization and polyaddition reactions. The result is an individually sized polymer with high strength and thermal stability. With its characteristics of high elasticity, durability, the ability to be dyed and its robustness, nylon is preferably utilized in the automotive industry, followed by engineering plastics and textiles such as carpets as shown in the figure 1.2b in the introduction section. Hereby, the two most commonly used types of nylon and therefore most important are nylon 6 and nylon 6,6 whereas nylon 6 holds an overall slightly higher market share and can be expected to promote the nylon market growth due to its broad variety of application [5]. Because of its slightly higher market share and the tendency of a higher rising demand, this report will concentrate on the depolymerization of nylon 6.

2.3.1 Synthesis of Nylon 6

Nylon 6, or also polyamide 6 or polycaprolactam, is industrially synthesized by ring-opening polymerization of its cyclic amide monomer ϵ-caprolactam (CL) and has the chemical notation $(C_6H_{11}NO)_n$. Its melting point is at about 220°C. The polymerization mechanism can be induced by hydrolytic, cationic or anionic initiators. However, the cationic polymerization is often not preferred due to a lower conversion rate and lower molar mass of the resulting polyamide [15]. For this reason, cationic polymerization will not be included in further discussions. In the following, the synthesis of nylon 6 via anionic and hydrolytic ring-opening will be described, from which the depolymerization reaction will be derived by reverse engineering.

Anionic Ring - Opening Polymerization
The anionic ring-opening polymerization of CL to nylon operates under anhydrous conditions and is considered as the fastest polymerization method for nylon due to lower activation energy, which makes it an interesting industrial mechanism [15]. The polymerization mechanism can be described in a three step reaction. First, the acidic $H-N$ proton is abstracted from the CL, initiated by the presence of a strong base such as alkali metals, metal hydrides or metal amides, for example sodium (Na). This abstraction forms an activated monomer anion in the initial step

which in turn attacks another cyclic lactam molecule to induce ring-opening in a second step. The resulting very reactive primary amide anion abstracts likewise in a third step the $H-N$ proton from another lactam monomer, forming an amino-acyllactam and an activated lactam anion which as well can continuously react with the formed dimer. This reaction can successively continue by the activation of further lactams to grow longer polymer chains, similar to the mechanism of polyaddition. [16], [17] The described reaction scheme is illustrated in figure 2.3 below.

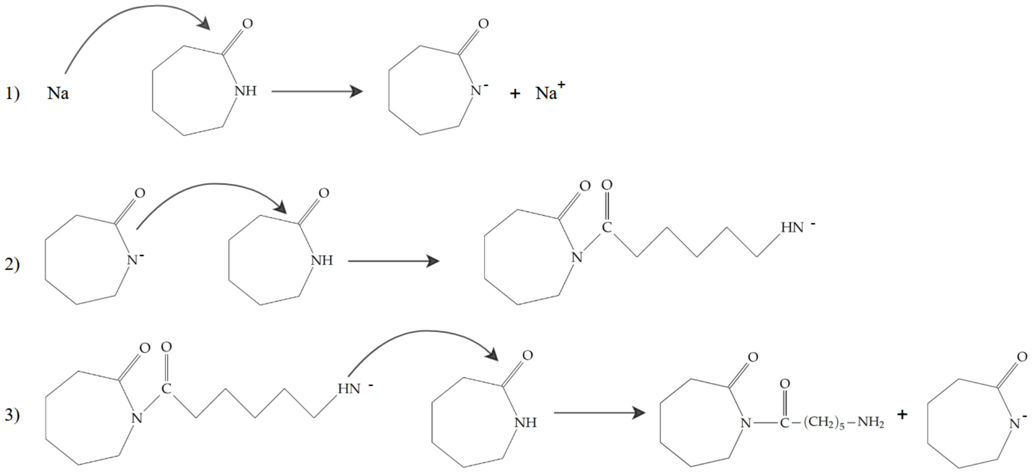


Figure 2.3: Anionic ring-opening polymerization of nylon 6.

For the anionic ring-opening polymerization of nylon, different factors such as the reaction time and temperature as well as the nature and concentration of the initiator are of importance. In case of polymerization without any initiator, or else an already activated anionic monomer, a high reaction temperature above the melting point of 220°C is necessary. Hereby, the concentration of activated anions increases with temperature and reaches predominance at about 150°C. The resulting nylon product is of comparatively lower crystallinity. With addition of an initiator, the reaction temperature as well as the time can be significantly reduced, leading to an increase in the reaction rate and reduction of side reactions. The same effect could be observed for the utilization of a catalyst. The temperature range for polymerization with an initiator or catalyst could be determined as 130 to 180°C with a 94% conversion rate at temperatures above 130°C. However, reactions below 130°C resulted in low conversion into nylon and low molecular weight, and nylon synthesized at 150°C showed higher crystallinity [15], [18]. In terms of the backward reaction, a high reaction temperature above 310°C is favoured to shift the equilibrium to the left side [19].

Hydrolytic Ring - Opening Polymerization

As indicated by the name, the hydrolytic ring-opening polymerization of nylon is initiated by the addition of a small amount of water (1 - 2 wt%) [19]. Hereby, the characteristics of nylon for moisture absorption which causes a plasticizing effect has to be considered, for which reason high amounts of water should be avoided. The hydrolytic reaction is a reversible reaction, which favours the backward direction due to the higher stability of the cyclic ring structure. Similar to the previously described anionic polymerization, the nucleophilic alcohol group of water attacks the CL monomer to induce ring-opening and forms a carboxyl end group ($-COOH$). The remaining hydrogen bonds to the nitrogen, forming an amino end group ($-NH_2$). The result is an aminocaproic acid (ACA) as illustrated in the figure 2.4 below. Due to the reaction of functional electrophilic and nucleophilic groups present, a large amount of smaller oligomer chains are built at first which then connect to longer polymer chains. This reaction can also be described as polycondensation, in which amide groups are formed by the nucleophilic attack of amino end groups on carboxyl end groups [19], [20]. Therefore, both reactions polyaddition and polycondensation occur in the hydrolytic ring-opening polymerization and in the case of reverse polymerization are followed by an additional step for ring closing. The reverse reaction of polycondensation can be enforced by high temperatures and a high amount of water, even if it is not thermodynamically favoured. In industrial processes, hydrolytic polymerization is typically performed under atmospheric pressure and at a temperature range of 250 to 280°C, reaching an efficiency of about 90% [19]. However, a two stage reaction process with adjusted pressure and water input is often favoured to optimize the polymerization results. Similar to the anionic polymerization, the reaction mechanism of hydrolytic polymerization can likewise be improved by the addition of a catalyst.

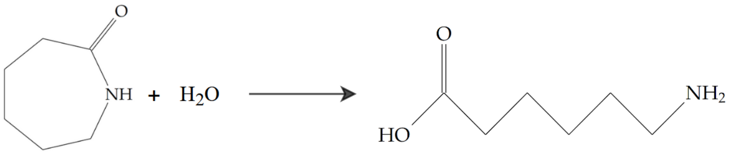


Figure 2.4: Hydrolytic ring-opening of ϵ-caprolactam.

2.3.2 Depolymerization Summary

In comparison to the process of polyaddition, which occurs under anhydrous conditions, polycondensation has a slower reaction rate which is also the case for the backward reaction. This is because the polyaddition reaction is thermodynamically favoured and less random than polycondensation. Although backward polyaddition requires high temperatures above 310°C, it is relatively insensitive towards pressure changes. Since this reaction happens under anhydrous conditions, it can be considered as the thermal degradation of the nylon polymer. Despite the faster reaction of polyaddition, polycondensation can be enhanced with the presence of a high amount of water and high temperatures [19]. In this reaction, ACA will be produced as an intermediate step. Therefore, both reactions could be utilized for the depolymerization of nylon into its monomer CL.

For the depolymerization reaction of polyester in 2.2.2, the presence of water is necessary in order to break the polymer chains and form the respective monomers. Therefore, the absence of water and consequently having anhydrous conditions would be infeasible for the co-process. For this reason, the hydrolytic depolymerization of nylon will be applied. This depolymerization can be summarized as followed, with the formation of ACA as the intermediate:

$$(C_6H_{11}NO)_n \ + \ H_2O \ \longleftrightarrow \ C_6H_{13}NO_2 \ \longleftrightarrow \ C_6H_{11}NO \ + H_2O \tag{2.2}$$

2.4 Assessment of the Hydrolysis Reaction

When the addition of water reacts with one or more compounds in such a way that it can form two or more products by scission of bonds, this process is known as hydrolysis. Hydrolysis can be carried out under acid, basic or neutral conditions, which will be discussed individually for each polymer in this section to define the most suitable reaction for the co-process. For polyester, hydrolysis is expected to produce its monomers TPA and EG under high pressures and temperature. For the cleavage of the amide bond in polyamides such as nylon 6, to produce monomers like CL, hydrolysis is considered the major decomposition method. Hence, to identify common reaction conditions by understanding the differences in the behaviour of the individual polymer is considered a key step towards the development of a combined recycling reaction.

2.4.1 Acid Hydrolysis

Polyester
Acid hydrolysis of polyester is applied using sulfuric or nitric acids, which are the most common acids used as they permit reactions at high temperatures with low activation energy and retention time [21]. However, this process is considered expensive and high risk due to the utilization of concentrated acids in large quantities and the necessary removal of those from EG for purification. Usage of strong acids can be hazardous especially with the disposal of these toxic chemicals after treatment which could pose significant risk to human health and environment ecosystems if proper chemical waste management practices are not followed. Based on the studies conducted by Mancini and Zanin [21] and Yoshioka et al. [22], it is reported that acid hydrolysis of polyester with sulfuric acid resulted in high yields of up to 80% of TPA.

Nylon
Nylon is likewise subjected to acid hydrolysis with presence of superheated steam to produce ACA which then undergoes further conversion to CL under acidic conditions [23]. In this process, inorganic or organic acids such as nitric, benzoic, hydrochloric, and formic acids can be used for the hydrolysis. Catalysts such as boric and orthophosphoric acid are often applied to the process at temperatures around 250 - 350°C. The output is fractionally distilled in a base in order to recover the CL by concentrating up to 70% liquor after the process. Approximately 93 - 95% of CL can be produced at the given temperature range by passing superheated steam through molten nylon in the presence of phosphoric acid [24].

2.4.2 Alkaline Hydrolysis

Polyester
Under alkaline conditions, hydrolysis of polyester is capable of converting the gained EG further into carbon dioxide and oxalic acid, which has more value than the former product [25]. Therefore, this process seems economically feasible due to the increased value in the product as well as using inexpensive bases like NaOH or KOH at concentrations of 4 - 20% acting as a solvent in the reaction without the requirement of pressure equipment. Additionally, the process can incorporate coloured PET feedstocks and produce colourless products, which proves the possibility to oxidize the dye present in the feedstock. Despite these advantages however, alkaline hydrolysis alone is not capable of forming the acidic monomer TPA, for which reason the primarily formed disodium terephthalate has to be acidified to be converted into the desired TPA. For this purpose, Ügdüler et al. [26] used sulfuric acid in their study and could achieve good coversion of TPA. Nevertheless, they could also determine a significant amount of formed sodium sulphate, even

considerably exceeding the amount of formed TPA. The high amounts of acids required for the conversion of TPA as well as the high amount of formed inorganic salts as by-product make the utilization of alkaline hydrolysis unfavourable.

Nylon

For nylon, alkaline hydrolysis is not commonly applied as polyamides are much more resistant to it compared to strong acids [27]. For this reason there is not as much literature available on the alkaline hydrolysis of nylon. Studies were conducted with barium hydroxide and KOH at high temperatures, but the results showed a very low yield and long retention time of about one to three hours [28]. However, an improvement to this process could be the utilization of superheated steam as a catalyst in the presence of alkalis under high pressure. It corresponds to higher yields and faster reaction times of the depolymerization.

2.4.3 Neutral Hydrolysis

Neutral hydrolysis of polymers have great potential, especially with high temperature and pressure of water at near sub- and supercritical conditions. Supercritical conditions of water could enhance the reactions considerably in comparison to subcritical conditions due to properties and behaviour changes with the phase transition. Water becomes a good solvent as the dielectric constant of sub/supercritical water is in the range of 2 to 30 which is very low compared to a dielectric constant of 80 for water at ambient conditions [29]. Hence, the hydrolysis process appears very effective as water takes a dual role exhibiting behaviours both as acid and alkali catalysts. Therefore, hydrolysis in sub- and supercritical conditions is getting much attention for the recycling of waste polymers.

Polycondensation polymers are subjected to depolymerization to produce monomers through processes such as hydrolysis as these polymers contain ester, ether, or acid amide bonds which can be cleaved by hydrolysis in sub/supercritical water. The use of sub/supercritical water has advantages in monomer recovery of plastics such as high process performance, a low environmental impact and the capability to process different types of plastics and waste incorporated plastics [14]. The advantage of neutral hydrolysis is the utilization of water as a solvent instead of any chemicals. However, the drawback of this process is that all the impurities contained in the feedstock accumulate with the solids, which in this case is TPA, causing the product to have less purity compared to other hydrolysis methods.

Polyester
Polyester can be processed in neutral conditions with high pressure of 15 - 90 bar, high temperature of 200 - 300°C and excess of water, producing a high yield of TPA and EG. In the studies conducted by Colnik et al. [14] and Cata et al. [30], high yields of TPA up to 90% were obtained for colourless PET feedstock in sub-critical conditions of 300°C. The former also conducted experiments on coloured PET waste in the same conditions and resulted in a lower yield with 85% compared to the colourless PET due to the presence of the additives, however demonstrating the ability of neutral hydrolysis to process PET from different sources [14]. By the comparison of sub- and supercritical conditions, a slightly higher yield of TPA with around 5 - 7% and less secondary products such as carbon dioxide, isophthalic acid, benzoic acid, etc. could be observed in the sub-critical conditions, which suggests that sub-critical conditions would be ideal to obtain the most yield of the monomer.

Nylon
Hydrolysis of nylon in sub/supercritical water has been of major interest as water can participate in the process simultaneously as a catalyst and co-reactant. In their experimental study, Motonobu et al. [31] conducted a hydrolysis process of nylon 6 at reaction conditions around 380°C and high pressure of 200 bar with a retention time of up to 10 minutes in a batch reactor. The yield of monomer CL and ACA obtained was 86% and 5.5% respectively. The higher the reaction temperature, the faster is the formation of CL until a maximum yield value is reached within the supercritical region and then it decreases with further increase in temperature as it produces other byproducts such as ACA or cyclic dimer [29]. Different studies have been found conducted in the temperature range of 300 to 400°C and a pressure range of 150 to 350 bar, suggesting that increasing reaction temperature contributes to faster CL production rate and resulting in better conversion of nylon. The results obtained by Motonobu et al. and Iwaya et al. demonstrate that sub-critical conditions are more favorable than supercritical conditions for the hydrolysis of nylon as it is almost completely transformed with yields up to 85% and shows better stability. However, despite high energy and equipment requirements, supercritical water also provides certain advantages due to effective depolymerization with high yields and lower residence time [19].

2.4.4 Hydrolysis Summary

With considerations of a cost efficient and environmental friendly process for the recycling of textile waste, the advantages of neutral hydrolysis show good arguments for its utilization. Acidic and alkaline hydrolysis however show certain drawbacks in their application for at least one of the two polymers of interest. The involved acids and bases in these hydrolysis reactions set the requirement for further purification processes such as the acidification of TPA or the recovery of CL due to a fractional distillation. For the stated reasons, neutral hydrolysis is preferred for the utilization in this process. Additionally, it could be determined that the treatment in sub-critical conditions is suitable for polyester as well as nylon and might be beneficial in terms of higher product yields. Another advantage of sub-critical conditions is the lower energy demand. Therefore, the application of neutral hydrolysis in sub-critical conditions is chosen for the further development of the recycling co-process for polyester and nylon. A detailed discussion about the reaction conditions applied in the simulation, will be given section 4.3 in the upcoming chapter.

2.5 Product Phase Separation

After the hydrolysis of polyester and nylon, the reactor's output stream will consist of a multi-phase mixture including the different depolymerization products. For the re-utilization of these products in a production process of new plastics and synthetic textiles, the corresponding product streams have to be separated from each other. Therefore, the products and their respective phases have to be identified first. Based on the polymer synthesis of polyester and nylon described previously, TPA and EG could be defined as the corresponding monomers of polyester, whereas CL is the monomer of nylon. It is also possible that residues of the intermediate ACA may be present in the outlet stream. The respective monomers are the products of the polymers after depolymerization and separation.

TPA will be present as solid particles in the reactor's product stream, whereas EG, CL and ACA will be dissolved in the water and therefore present in the liquid phase. The different phases in which the respective products occur call for different separation methods, which will be discussed in the following sections. Hereby, the solid phase will be separated first, followed by the separation of the components found in the aqueous phase. The objective is a high efficiency of the individual separation methods to achieve a preferably high purity of the monomer products. TPA, EG and CL can commonly be found in purity levels between 96% and 99%. However, for the production of most PET products purified TPA is preferred. The presence of additives and resins within the monomers are not considered as their amount and type require experimental analysis in order to define appropriate separation methods. Additionally, the selling price of all three monomers increases with higher purity. Therefore, an efficient separation of the multi-phase mixture stream would increase the feasibility for recycling polyester and nylon in a co-process. Special considerations will be given to the separation of TPA and CL which are considered as the main selling products of the recycling plant due to their higher market value.

2.5.1 Separation of Terephthalic Acid

For separation of the solid TPA particles from the primarily liquid product stream, different separation techniques such as filters, cyclones, centrifuges or membranes could be utilized. For low maintenance and easier implementation in a continuous process, the utilization of cyclones and centrifuges is preferred over filters and membranes, therefore, a cyclone will be utilized in this project. Due to the high liquid content and little to no gas phase present in the stream, a hydrocyclone will be used. The functional principles of a hydrocyclone will be elaborated in the following.

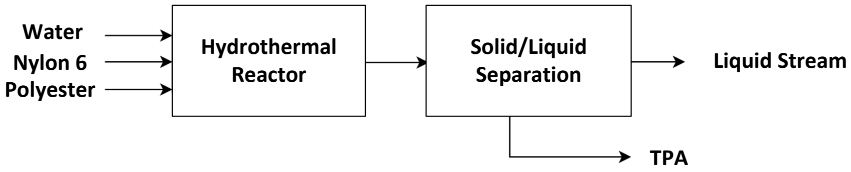


Figure 2.5: Solid - liquid separation block scheme.

Hydrocyclone

The hydrocyclone is a commonly used separation method for mixtures of solid particles or droplets from liquid carrier streams. The separation is based on differences in densities and caused by centrifugal forces and characteristic flow patterns. The mixture flow will tangentially enter the cylindrical vessel, which typically merges into a conical body as illustrated in the figure 2.6. The tangential entry of the flow and fluid pressure causes a rotational motion of the fluid, which results in the development of a vortex. The fluid travelling through the chamber develops a secondary inward radial motion towards the axial overflow outlet, causing two opposing forces on the dispersed particles. One is the centrifugal acceleration forcing the particles in an outwards direction, whereas the radial inward moving fluid creates a drag force. The resulting opposite movement of particles and fluid in a radial outward and inward direction causes separation. This radial flow movement and therefore, the separation efficiency is influenced by the size of the particles, the density of the particles as well as of the fluid and the viscosity of the fluid. The liquid fluid will exit the hydrocyclone through the axial overflow outlet, whereas the more dense solid particles will exit through the underflow. The underflow outlet can be peripheral to the chamber, however, it is commonly placed axial and opposite to the overflow outlet. The overflow is directed by a cylindrical outlet, also known as the vortex finder. [32]

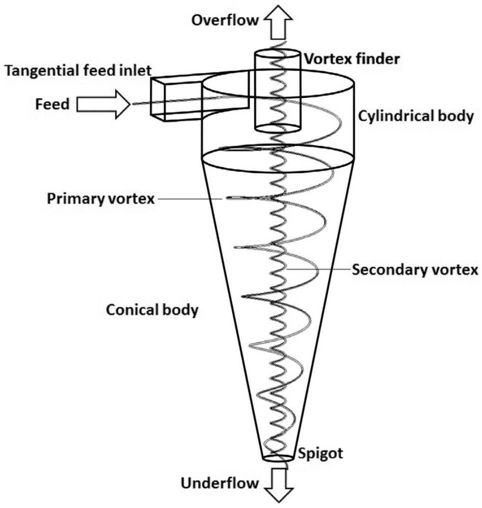


Figure 2.6: Schematic of a hydrocyclone, taken from [33].

As previously mentioned, the solid particle separation from the liquid stream is induced by different forces acting on the particle. Therefore, the centrifugal force F_C guiding the particle in an outward direction should be greater than the buoyancy F_B or drag force F_D guiding the particle towards the inward direction along with the liquid stream. Hereby, the main driving factor of the drag force is the liquid viscosity, whereas the buoyancy and centrifugal force are mainly driven through differences in the solid and liquid densities as can be seen in the equations 2.3 and 2.4 respectively. The different forces acting on the particles are illustrated in the figure 2.7 below. Hence, the solid separation is enhanced through higher density differences between the liquid and the solid particles. Since the aqueous phase of the reactor's output consists of multiple fluids, the respective densities have to be considered. Nevertheless, due to the high water to polymer ratio of the reactor's feed, the majority of the liquid fluid is water.

$$F_C = \frac{\pi\, d^3}{6}\, \rho_s\, \frac{u_t^2}{r} \tag{2.3}$$

$$F_B = \frac{\pi\, d^3}{6}\, \rho_f\, \frac{u_t^2}{r} \tag{2.4}$$

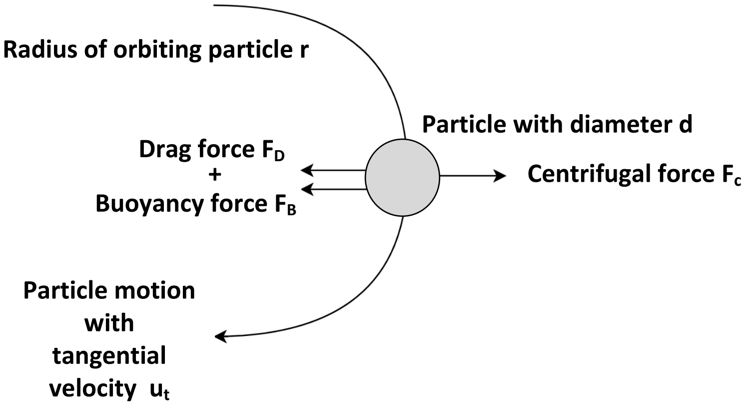


Figure 2.7: Schematic of the different forces acting on a spherical particle in the hydrocyclone.

As can be seen from the figure 2.8, the densities of the liquid products and water decrease with temperature from which a higher separation efficiency at elevated temperatures can be assumed. ACA is hereby not considered since a significantly lower quantity in the reactor's output stream can be assumed and due to the high similarity to CL. Because EG is highly dissoluble in water due to its hydroxyl end groups, an aqueous solution containing 75% EG is used for the comparison. It can be determined that under atmospheric conditions, the liquid densities remain below the solid density of TPA with about 1520 $\mathrm{kg/m^3}$. Therefore, it can be assumed that the overall difference in densities at high operating temperature is sufficient for the separation of the solid TPA particles.

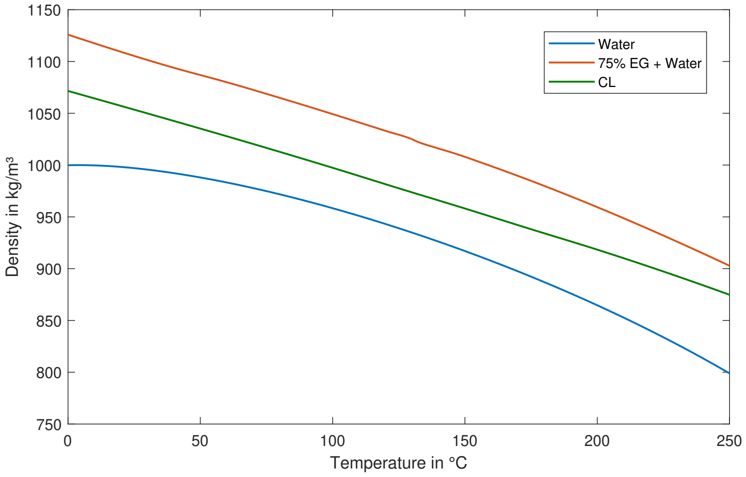


Figure 2.8: Densities of caprolactam, water and an aqueous ethylene glycol solution as function of temperature, data based on [34]–[36].

Another important property of the carrying fluid is its viscosity, which has an influence in the equation 2.5. Similar to the densities, a reduced viscosity is advantageous for the separation. Figure 2.9 illustrates the viscosity of CL, EG and water as a function of temperature. It can be seen that with increasing temperature, the viscosity of each component decreases in a similar manner. Additionally, the lowest viscosity can be read for water. With the high water amount of water necessary for the depolyerization reaction, the reactor's output stream is expected to contain about 3% EG and 6% CL from which it can be concluded that the overall stream will have a viscosity similar to water.

$$F_D = 3\,\pi\,d\,\mu\,u_r \tag{2.5}$$

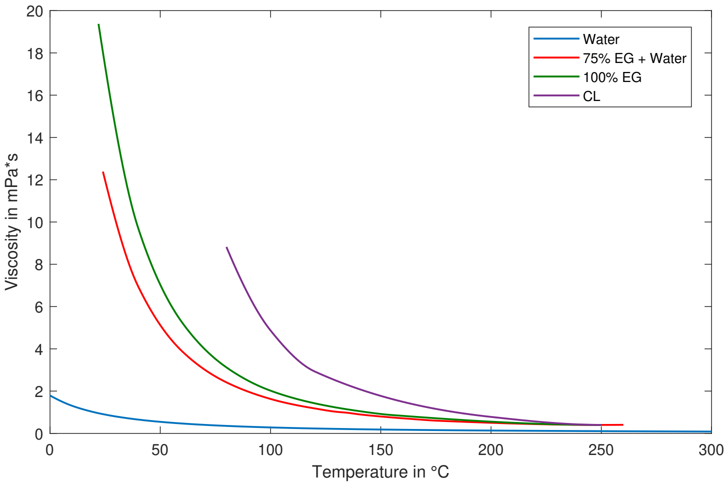


Figure 2.9: Viscosities of caprolactam, water, ethylene glycol and an aqueous ethylene glycol solution as function of temperature, data based on [35]–[37].

Finally, only the size of the hydrocyclone and of the particles are left as influencing factors of the separation efficiency. The inside diameter of the cylindrical feed chamber of a commercial hydrocyclone can commonly vary between 10 mm and 2.5 m. Typically, the hydrocyclone is capable of separating particles in the size range of 1.5 to 300 μm [38]. TPA has a particle size distribution of 50 to 150 μm and lays well within this range [39]. For a continuous flow, it can be assumed that the particle size distribution will statistically tend towards a normal distribution. For this reason, the mean particle size of TPA can be determined as 100 μm.

In this section, the hydrocyclone could be defined as a suitable method to separate the solid TPA particles from the multi-phase mixture stream exiting the hydrothermal reactor. The subsequent separation of the liquid components will be discussed in the following section, with focus on the separation of CL. A detailed investigation on the separation efficiency of TPA and its optimization will be given in section 5.1.

2.5.2 Separation of ϵ-Caprolactam

After the solid TPA particles have been removed from the stream, a liquid mixture containing EG, CL and water remains for further separation. This liquid stream can possibly also contain small amounts of unconverted ACA. The following liquid separation will be discussed for the ideal case, considering only EG, CL and water.

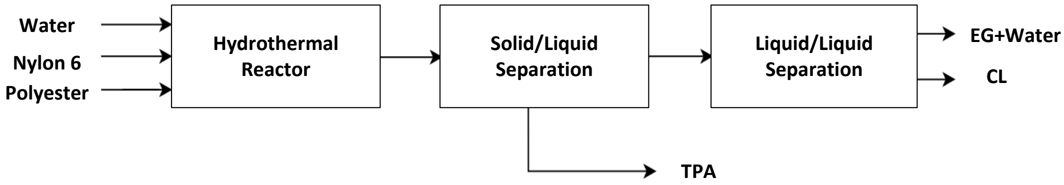


Figure 2.10: Liquid - liquid separation block scheme.

For the separation of liquid streams, different methods such as extraction, flash separation and distillation are the most commonly used. In liquid-liquid extraction, often two liquids are separated from each other due to their relative solubilities by adding a solvent. This method however, creates certain disadvantages when utilizing it in the presented study. The added solvent in the mixture would need to be removed from the stream again after separation in order to not affect the purity of the products. This solvent removal would cause higher energy consumption and the requirement of additional equipment. Additionally, more than one solvent may be required due to the characteristics of the different components present in the mixed stream. For these reasons, the utilization of liquid-liquid extraction is determined as infeasible in this case. In the following, the liquid stream separation through the application of a flash separator and distillation column will be discussed. With CL being one of the main selling products of the process, it should primarily be separated from the liquid stream. The ideal result would then be a single stream containing only CL and one stream containing EG and water.

Flash Separation

The separation of liquids by utilizing a flash separator is a relatively simple and commonly applied method. The separation is based on the different boiling points and volatilities of the respective liquid components. For the separation, the pressure and temperature in the liquid feed as well as in the flash chamber need to be considered. The more volatile component vaporizes and is taken off the overhead, whereas the less volatile component remains in liquid state and drains to the bottom of the chamber. To prevent liquid droplets from being entrained in the vapor, a demister is often added. Additional factors to consider are the flow rate, the feed composition and the size of the flash chamber. Next to its simplicity, flash separation has the advantage of a rapid vaporization of the volatiles, however, the extend of separation can be limited.

For the separation of the previously mentioned liquid mixture, the different boiling points have to be considered. With about 100°C, water has the lowest boiling point of the liquid stream under atmospheric conditions, whereas EG with about 197°C and CL with about 270°C have a comparatively high boiling point. Because CL has the highest boiling point, it should be separated from the stream first. This is also beneficial for the objective of the liquid separation to gain a single stream of CL. Since CL is one of the main selling products, a high purity is of importance which could be reached by the evaporation of EG, water and possible other volatile impurities in the stream. As a result, CL should exit the flash chamber through the bottom stream whereas a mixture of EG and water should take off through the overhead. Equally, the possible accumulation of heavier impurities in the bottom stream has to be considered. Therefore, a series of flash separations may be beneficial to achieve the desired product purity. Overall, a temperature below 250°C with a certain safety margin has to be maintained during the separation process to avoid a possible degradation or polymerization of CL. Additionally, the application of vacuum pressure could be considered to evaporate EG and water at an already lower temperatures.

Distillation Column

Similar to a flash separator, a distillation column is based on the different boiling points and the volatilities of a binary or multi-component liquid mixture. Under the application of a certain temperature and pressure, separation is induced. The more volatile component with a lower boiling point will evaporate and flow upwards, whereas the component with a higher boiling point remains liquid and drains downwards to the bottom of the column. The vapour and liquid stream will then exit the column through the overhead and bottom indicated in the figure 2.11. Packing or plates within the column increases the surface contact and hence, the separation efficiency. The up-streaming vapor gets in contact with the plates, which have a lower surface temperature, and condenses partially. Hereby, the newly formed and further uprising vapour will be enriched with the more volatile component. Likewise, the downward streaming liquid is enriched with the heavier component. Due to the repeated development of evaporation and condensation reactions, a distillation column is often referred to as a series of flash units. An advantage of a distillation column over a flash separator is the higher degree of separation. To ensure a continuous separation by a steady flow and increase the efficiency, a small amount of the overhead and bottom stream is recirculated as reflux to the column as illustrated in the figure 2.11.

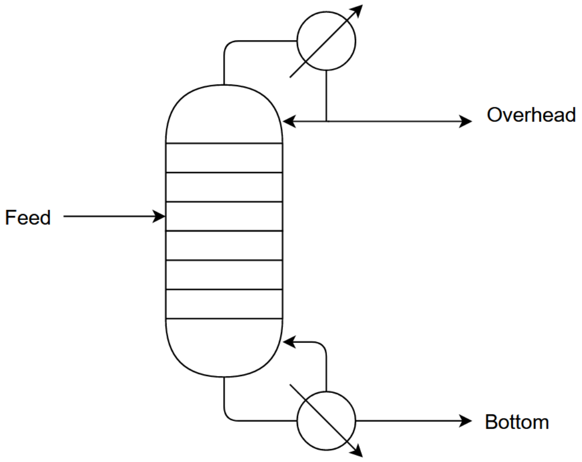


Figure 2.11: Schematic of distillation column.

Many simulation programmes apply shortcut methods to estimate this reflux ratio. These preliminary estimations are often based on the Fenske-Underwood-Gilliland equation for binary and multi-component mixtures to make a first estimation for a minimum number of stages as well as a minimum reflux ratio. These approximations are further used by the programme as a starting point, to estimate a correlation to the actual number of stages and actual reflux.

In order to calculate a first estimation of the necessary minimum number of stages N_{min} for a sufficient separation, the Fenske equation is commonly applied:

$$N_{min} = \frac{log\left[\left(\frac{x_D}{(1-x_D)}\right)\left(\frac{1-x_B}{x_B}\right)\right]}{log\,\alpha_{ave}} \tag{2.6}$$

$$\alpha_{ave} = \sqrt{\alpha_B \cdot \alpha_D} \tag{2.7}$$

It is based on the output composition of the overhead (distillate) and bottom stream divided with the average relative volatility α_{ave}. The average relative volatility is dependent on the relative volatility of the lighter key component relative to the heavier key component at the bottom of the column and at the distillate respectively and is therefore a function of temperature and vapour pressure. [40]

For the estimation of a minimum reflux ratio R_{min} of binary mixtures, a graphical approach can be applied and is often preferred due to its relative simplicity.

For multi-component mixtures however, the graphical estimation can not always be applied for which reason a mathematical approximation based on the Underwood equation for multi-component mixtures is the most common method. In this estimation, the distillation column is divided into different fractionating sections indicating the composition of the key components. The relative volatility can vary throughout the column, but is constant within one section. With the known component compositions and the relative volatilities, a minimum reflux ratio can be estimated. [41]

With the first two estimations made the minimum number of stages and minimum reflux ratio can be correlated to determine the actual values by means of the Gilliland correlation method. Although the Gilliland method is only an estimation of the real values, its utilization has been proven useful. To determine the values for the actual number of stages N and the reflux ratio R, either a graphical approach or else an estimation via calculations can be utilized. For a mathematical approximation of the correlation, a number of equations have been suggested over the past. However, for the estimation of R, a multiplication factor such as $R = 1.5 \cdot R_{min}$ is often assumed. [40] A similar assumption can also commonly be seen for the estimation of N, whereby preliminary calculations are significantly shortened. It becomes apparent, that due to the complexity of a more precise estimation for a distillation column design, detailed calculations by means of a simulation are inevitable.

In this section, the separation of the liquid stream by means of a flash separation as well as a distillation column have been examined. Whereas the application of a liquid-liquid extraction has been rejected in advance, both here discussed separation methods appear feasible for the utilization in the presented process. Certain advantages and disadvantages of the two separation methods such as the rapid flash separation as well as the respective extend of the separation have been mentioned. A detailed discussion about the separation efficiency of each method and the overall optimization of the liquid phase separation will be given in section 5.2.

3 Problem Statement

The continuously increasing consumption of textile products causes a globally growing problem in their production as well as in the handling of accumulating waste. The rising trend towards fast fashion and shorter product lifetimes, also for other textile products such as draperies and furniture, play a crucial part in this development. In the introduction, especially the growing portion of synthetic textiles in the overall mix of textile materials could be identified as the driving factor of the increasing production rate of textile products. Furthermore, different environmental and economical consequences could be assessed in relation to the globally growing demand, with a specifically high impact on the consumption of resources and on climate change.

One solution to the stated problem could be the chemical recycling of the textile materials that cannot be further reused and would otherwise end up as waste in incineration or landfills, thereby a circular economy could be created. Whereas the research on the recycling of other plastic materials such as plastic bottles is already established and implemented to a certain extend in real life application, investigations on the recycling of synthetic textiles is comparatively limited in the current state. Most research studies focus on the recycling of a single synthetic material or on the recycling of polyester-cotton blends. With the fast rising share of synthetic textiles in the overall material mix, an efficient recycling has the potential to lower the described environmental pressure and gives the possibility to make the production of new textile products more sustainable.

With polyester and nylon being the most commonly used synthetic textile materials, it has been assumed that these will consequently accumulate the most in the overall synthetic textile waste. For this reason, this project focuses on the chemical recycling of these two materials to identify a new pathway for the depolymerization of two different synthetic waste materials in a co-process and to define a possible separation mechanism of the resulting monomers. The objective is to achieve sufficient depolymerization and separation of the monomer products to give the possibility of selling these monomers or reintroducing them to a following production processes of new textile or plastic products. Due to the extend of this project, certain assumption have been made for the development of this recycling process.

Assumption statements:

- The feed materials of the recycling plant are previously sorted and are considered as pure.
- The two polymers do not directly interact with each other during the depolymerization process.
- The product separation focuses on the main monomer selling products ϵ-caprolactam and terephthalic acid.
- Possible side products and intermediates are not considered.

Based on the defined objective, a continuous depolymerization process and a subsequent separation mechanism of the product phases is to be designed. For the depolymerization of polyester and nylon in a co-process, hydrolysis in neutral conditions has been chosen. Furthermore, it has been decided to separate the solid particles first, followed by the separation of the liquid components. An overview of the recycling process is given in the figure 3.1 below.

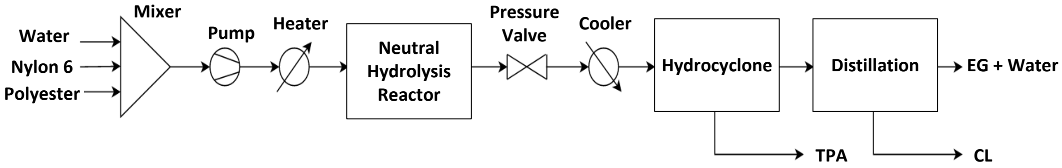


Figure 3.1: Overview of the depolymerization process and phase separation mechanism.

Before entering the hydrothermal reactor, the three feed streams consisting of water, nylon 6 and polyester need to be well mixed with each other, as well as heated up and set under pressure to approach the operating conditions of the reactor. This is done to get the feed stream into molten state for a higher conversion and to ensure a constant reactor environment for a steady hydrolysis reaction. Following, the high temperature and high pressured stream can be depressurized and cooled after the hydrolysis reaction for further treatment. The solid TPA particles are separated from the liquid stream by means of a hydrocyclone. After the first separation, the second main selling product, CL, is separated from the remaining liquid stream with a distillation column. A detailed discussion about the optimization of each separation component in terms of product yields and purities will be given.

4 Modelling of the Co-Process in the Reactor

This chapter discusses the co-processing simulation model of polyester and nylon through hydrolysis. The complete model from the hydrothermal reaction to the separation of the monomer product streams is designed and simulated based on available literature data. This simulation model has been developed utilizing the software Aspen Plus V9, which is commonly used for chemical process simulations. The process design software contains inbuilt components and databases for compounds and species with pure and binary regressed parameters. It is able to simulate chemical processes by calculating the process performance on specified operation conditions using thermodynamic and mathematical models.

Engineers in petrochemical, pharmaceutical, polymer, and thermodynamic process industries utilize Aspen Plus for optimizing existing design processes or predict the outcome of new processes by calculating mass-energy balances on the unit operations. Physical and chemical characteristics of all species generated or consumed during the chemical process are retrieved from the extensive component database. Due to the availability of a thermodynamic database of compounds and prominent operating components as well as chemical property packages for the polymer process, Aspen Plus is ideal for simulating the depolymerization process.

4.1 Property Method

To model the simulation, different compounds taking the role of reactants, products, solvents, etc. were selected from the Aspen Plus component database. The fluid package POLYNRTL was chosen as the property method for calculating the properties of these components. This polymer-NRTL model is an extension of the non-random two-liquid (NRTL) model for interactions with polymer segments and co-polymers [42]. As one example, the POLYNRTL method can be utilized to describe a vapor-liquid and liquid-liquid equilibrium for different polymer solutions. It is considered for the presented simulation as it is suitable for homo-polymers, co-polymers, and polymer blends based on the operating conditions of this system.

4.2 Feed Stream

The raw materials inserted to the simulation model are water, nylon 6, and polyester. The feed polymers are considered to be pure polymers without any impurities. Therefore, the necessary pre-treatment of the waste materials would be needed to consider for a practical implementation of this process, due to the extend of this study however this aspect will not be discussed. Before entering the reactor, the feed stream needs to be mixed, heated up and pressurized to a similar level as the operational conditions of the reactor. This is done to ensure constant operational conditions for the continuous hydrolysis reaction. The polymer streams enter the process in molten form, therefore an extruder is assumed prior to the feed entrance. The extrusion process melts the polymers, which are then assumed to directly enter the mixer together with the water stream and proceed further into the reactor. The melting points of nylon 6 and polyester are 220°C and 260°C respectively, therefore, the extruder is assumed to operate at 270°C and 100 bar. The high pressure is applied to break down the polymer chains and additionally ensure a liquid phase stream. The mixed stream is then heated and pressurized to the respective operational conditions of the PFR before entering the reactor as illustrated in figure 4.1.

4.3 Reactor Model

4.3.1 Selection of the Continuous Reactor

To implement a continuous process and accomplish complete formation of the monomer products, continuous reactors are preferred for industrial processes. The reactor should also be capable to maintain and perform isothermally at high temperatures and possibly long residence time to get the desired conversion and products. The most common used continuous reactors are the plug flow reactor (PFR) and the continuous stirred tank reactor (CSTR). In a PFR, the reactants travel along the tube as a plug compared to the continuous stirring in the CSTR. As the plug of compounds moves throughout the PFR, the compounds are transformed into products. The PFR reactor is considered to have a theoretically higher conversion efficiency compared to a CSTR with the same volume. This means the reaction will be completed to a higher percentage in a PFR than in a CSTR as the former begins at a high reaction rate and then decreases gradually towards the end, whereas the latter operates always at low reaction rates. Considering high flow rates and high fractional conversion, the reactor volume that would be required utilizing a CSTR would be considerably higher compared to the reactor volume of a PFR at the same conditions [43]. Because the reactor volume can be considered the main criteria for the choice of the reactor as the capital investment required can be reduced for economical benefits, a PFR is chosen for the implementation in this model.

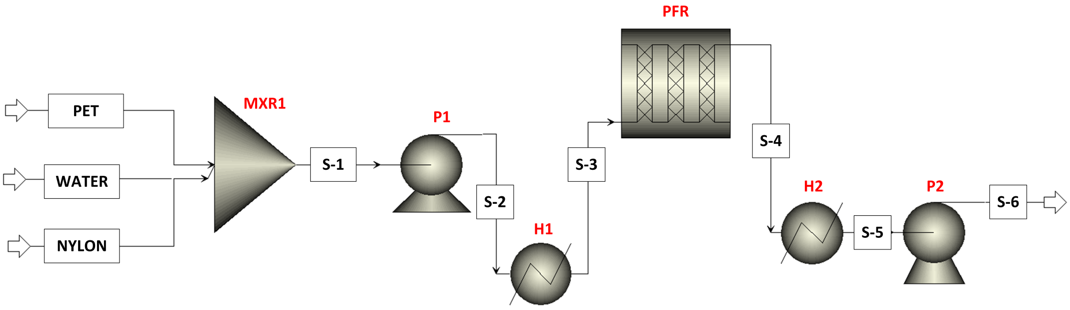


Figure 4.1: Flow diagram of the PFR model in Aspen Plus.

To represent the PFR, the Aspen Plus block RPlug is selected. It is designed for rate-controlled reactions with known kinetics. It requires a specification for the type of reactor such as specific temperature, adiabatic, or cooled. An overview of the PFR model is given in the figure 4.1. The reaction type specified in the Aspen reaction set is the power law method. For this method, either the reaction kinetics or equilibrium conditions are required to be previously defined. The respective reactions and kinetics for the depolymerization of polyester and nylon in the PFR are discussed in the following two sections.

4.3.2 Kinetics of Polyester

As described in the section 2.2.1, polyester is synthesized through the linkage reaction of the respective functional carboxyl- and hydroxyl end groups of its monomers. Consequently for the depolymerization, these polymer ester links have to be broken under water consumption. The resulting products are the previously introduced monomers TPA and EG as illustrated in the equation 4.1, which has been previously introduced. Emerging oligomers and small amounts of side products will not be considered.

$$(C_{10}H_8O_4)_n + H_2O \longrightarrow C_8H_6O_4 + C_2H_6O_2 \tag{4.1}$$

Even though it could be found in literature that a classic first- or second order reaction does not always describe the depolymerization reaction perfectly, a first order reaction could often provide feasible results and will be assumed in this study. It could be found that the hydrolysis reaction of polyester is accelerated in molten state, hence the reaction temperature should be above its melting point and minimum 220°C. The study by Colnik et al. [14] determined 300°C as the optimal reaction temperature for a high yield of TPA with a retention time of 30 minutes, however, good results could also already be determined after 10 minutes reaction time with a TPA yield between 80 and 90%. Similar results could be found by Sato et al. [44], who additionally determined a maximum reaction temperature of about 350°C above which the production rate of EG rapidly decreases due to decomposition. Therefore, a sufficient residence time for a reaction at 300°C can be concluded as 10 minutes after which the yield of EG likewise decreases, whereas TPA reaches stability after 20 minutes as can be seen in figure 4.2.

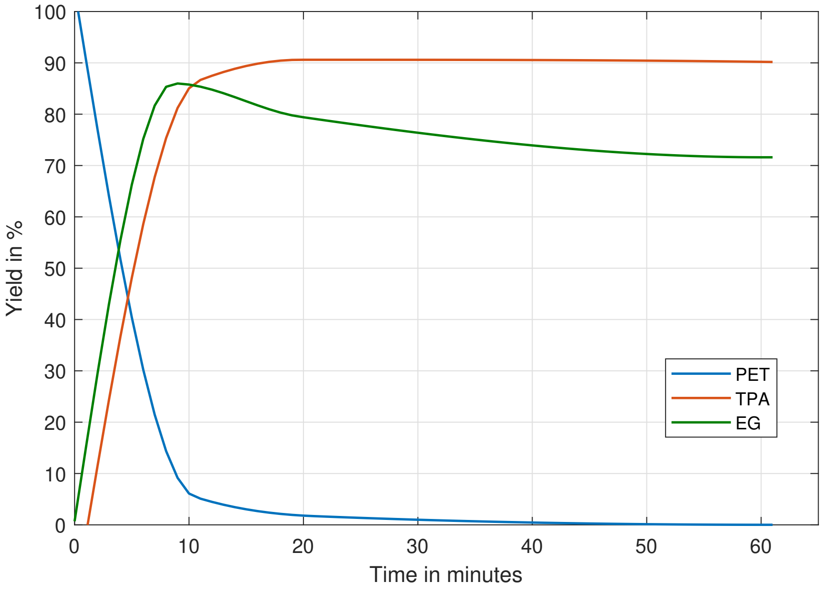


Figure 4.2: Conversion yield of PET into TPA and EG as function of time at a reaction temperature of 573 K and water to PET ratio 10:1 (wt/wt), based on the work by Sato et al. [44].

Next to the temperature and retention time, the charge ratio of water:polyester (water:PET) appears to have a high impact on the monomer recovery as well. By increasing the water content, the rate of collision is raised which automatically enhances the reaction. The higher water content additionally shifts the reaction equilibrium towards the products side. However, the increase in liquid volume also leads to higher energy costs due to necessary heating which would need to be considered. Kao et al. [45] and Campanelli et al. [46] investigated the effect of different charge ratios at different temperatures on the depolymerization efficiency of PET due to the presence of carboxylic acids. With 2 mol ester linkages per each mol of repeat unit in the virgin PET, a full depolymerization of PET corresponds to 10.4 mmol COOH/g PET [46]. With values of 10.0 and 10.3 mmol COOH/g PET, charge ratios of 6:1 and 10:1 (wt/wt) showed good results respectively [45]. For charge ratios below 5.1:1 the establishment of an equilibrium could be observed, which is to avoid for the purpose of depolymerization [46]. For the application in this study a charge ratio of 10:1 is chosen.

In order to develop a simulation of the polyester depolymerization, further kinetics have to be determined. These include the activation energy Ea for the reaction and the rate constant k which are to be investigated experimentally. Based on the work of Campanelli et al., an Arrhenius plot shown in the figure 4.3 could be developed with a coefficient of determination $R^2 = 0.9994$, from which the corresponding pre-exponential factor A and the activation energy could be calculated. Therefore, the natural logarithm of the Arrhenius equation stated in the equation 4.2 and the universal gas constant $R = 8.3145$ J/mol·K were used. Following, the rate constant could be calculated as $k = 0.75$ g PET/mol·min for a temperature of 573 K which corresponds to the previously defined optimal temperature of 300°C.

$$k = A \cdot e^{-Ea/R \cdot T} \tag{4.2}$$

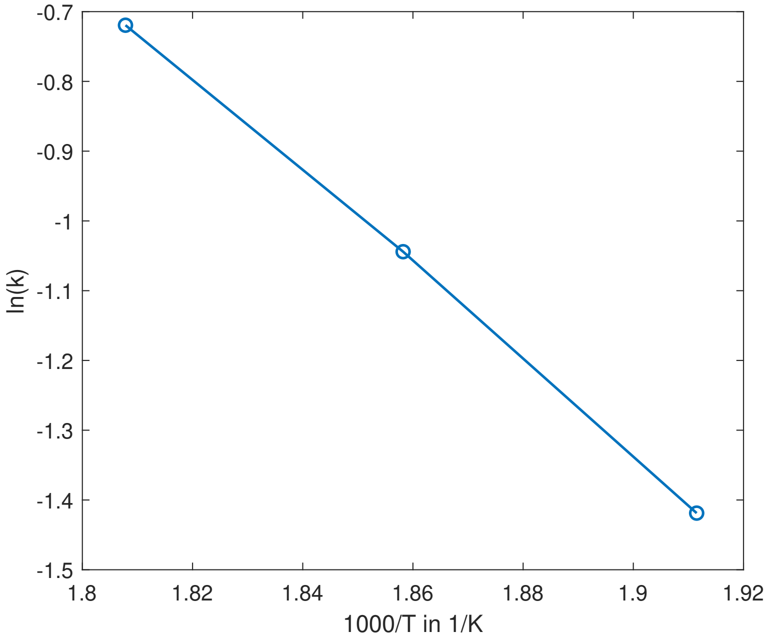


Figure 4.3: Arrhenius plot for the depolymerization of polyester with a water to PET ratio of 10:1, based on [46].

The kinetics for the depolymerization of polyester have been discussed in this section. A summary of the determined values is given in table 4.1 below.

Table 4.1: Reaction kinetics of polyester.

$A\ [\frac{1}{mol \cdot min}]$	$Ea\ [\frac{kJ}{mol}]$	T [K]	$k\ [\frac{1}{mol \cdot min}]$	Water:PET [wt/wt]
$97.34\ x10^3$	56.11	573	0.75	10:1

4.3.3 Kinetics of Nylon 6

Similar to the implementation of the polyester depolymerization reaction, the reaction mechanism and the kinetics for nylon have to be defined. The study carried out by Iwaya et al. [29] achieved good results for the depolymerization of nylon 6 with a maximum yield of 85% CL after 60 minutes retention time. The remaining compounds were specified as mainly ACA and a mixture of various dimers and oligomers. Due to their very small fraction in the product mixture, oligomer and dimer by-products have been defined as insignificant which leaves CL and ACA as the main products of consideration. The depolymerization reaction could be defined as a consecutive reaction with the degradation of nylon to ACA and further cyclodehydration to CL. Hereby ACA functions as a product of unreacted or not fully depolymerized nylon as well as an intermediate reactant which can transform further into CL by ring-closing reactions. This conclusion corresponds to the findings made by the synthesis reaction in the section 2.3.1. By comparison of the activation energies for the degradation of nylon and the cyclodehydration of ACA, it could be found that the activation energy for the degradation reaction has a significantly higher value. For this reason, the assumption of a pseudo-first order reaction can often be found in literature. Nevertheless, for the implementation of the depolymerization reaction of nylon, a two step reaction should be applied in order to incorporate the formation of ACA as an intermediate. Additionally, the simulation software will be able to detect possibly unreformed ACA in the product output. Therefore, the depolymerization will be described as stated in reactions 4.3 and 4.4 below.

$$(C_6H_{11}NO)_n + H_2O \longrightarrow C_6H_{13}NO_2 \tag{4.3}$$

$$C_6H_{13}NO_2 \longrightarrow C_6H_{11}NO + H_2O \tag{4.4}$$

The kinetics for the nylon depolymerization reaction could be determined in a similar manner as the method applied in the previous section. For this purpose, the study conducted by Iwaya et al. [29] has been utilized. Based on this work, the corresponding activation energies and pre-exponential factors for both steps could be calculated through the Arrhenius plot. For the depolymerization reaction, the activation energy and pre-exponential factor have been calculated as Ea_1= 99.77 kJ/mol and A_1= 6.23x10^5 1/s and for the ring-closing reactions the values are determined as Ea_2= 16.87 kJ/mol and A_2= 0.39 1/s respectively.

In section 2.3.1 it could be determined, that a high amount of water would be beneficial in the hydrolytic depolymerization of nylon to enforce the reverse reaction of polycondensation. In literature, often an applied charge ratio of 15:1 (wt/wt) water to nylon could be found. However, Iwaya et al. could observe that the influence of water density and the amount of water charged in the reactor is of less importance for the reaction in sub-critical conditions. Therefore, the influence of temperature and reaction time can be valued higher. This impact can be seen in the figure 4.4 for temperatures ranging from 553 to 603 K and is based on the work by Chen et al. [47]. Whereas a reaction temperature of 603 K could achieve the highest yield of CL with the shortest reaction time, longer reaction times let the yield decrease again, for which reason it has been assumed that the monomer cannot separate from the close reaction system and even decomposes again with increasing time. Below a temperature of 603 K this behaviour has not been observed. Hence, the highest yield of CL under stable conditions could be achieved at 573 K after a reaction time of about 100 minutes with a yield of 77.96% [47].

The pressure applied in nylon depolymerization often ranges between 100 and 350 bar. For the case of a pseudo-first order reactions and similar cases to the one discussed in this section, a pressure of 150 bar showed good responds to the results by Iwaya et al. [29] and Chaabani et al. [48].

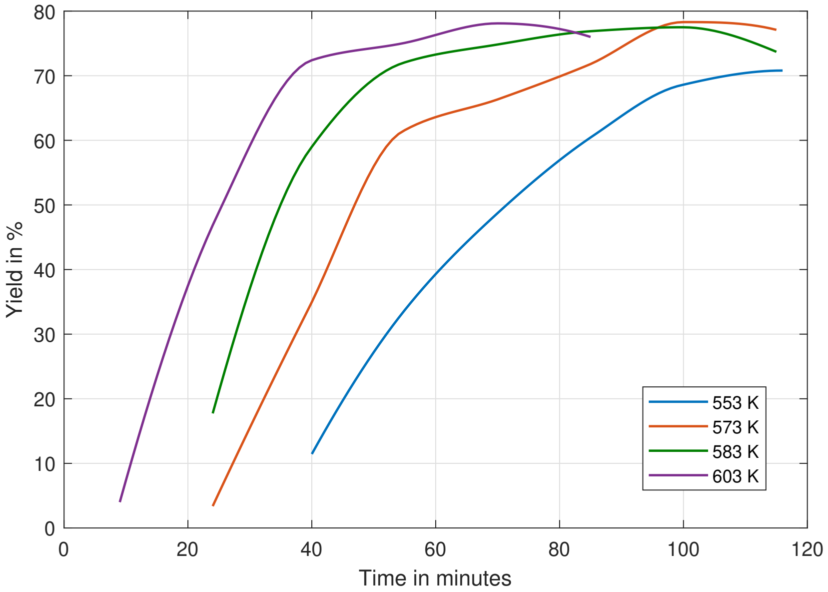


Figure 4.4: Conversion yield of ϵ-caprolactam as function of time with different temperatures and water to nylon 6 ratio of 15:1, based on the work by Chen et al. [47].

The kinetics for the depolymerization of nylon 6 have been discussed in this section. A summary of the kinetics found for the depolymerization of nylon is given in table 4.2 below.

Table 4.2: Reaction kinetics of nylon 6 with constant temperature and water to nylon ratio.

Reaction	A $[\frac{1}{s}]$	Ea $[\frac{kJ}{mol}]$	T [K]	k $[\frac{1}{s}]$	Water:Nylon [wt/wt]
Depolymerization Ring-Closing	$6.23\ x10^5$ 0.39	99.77 16.87	573	$5.0\ x10^{-4}$ $1.1\ x10^{-2}$	15:1

4.3.4 Summary of the Co-Process

The reaction conditions for polyester as well as nylon have been discussed. While some kinetic variables such as temperature have the same value for both depolymerization processes with about 300°C (573 K) or are in the same range, other variables such as the retention time in the reactor differ strongly. One possible factor for considerations about the feasibility of the co-process could be the respective economical significance of each monomer as well as the polymer itself. For example is the production of nylon generally more cost intensive compared to polyester and the monomer TPA is often considered as more valuable than EG. From the findings of this chapter, it can be concluded that the depolymerization of polyester is much faster with about 10 minutes compared to nylon with about 100 minutes. Nevertheless, from figure 4.2, it can be seen that the yield of TPA remains stable even over longer retention times, whereas the yield of EG decreases after less than 20 minutes. Hence, it could be concluded that if the yield of TPA is rated of higher importance for the overall product mixture compared to EG, the co-processing of polyester and nylon is feasible. Additionally, the type of the utilized reactor is of importance to consider. The discussed times of reaction are based on experimental measurements using a batch reactor whereas the reactor in this study will be designed for a continuous recycling plant to resemble a more realistic recycling facility. Reactions in a PFR are usually based on the reactor volume, different to the batch reactor, which is based on time. Whereas the batch reactor has a constant volume and converts the reactants over a certain residence time, the conversion in a PFR will be constant over time and change along the axial length of the reactor. For this reason, the mentioned reaction times are only applicable to a certain extend and will most likely be reduced due to the characteristics of the continuous reactor.

4.3.5 Implementation of the Depolymerization Reactions

As previously mentioned calculations related to the PFR are based on the reactor volume, therefore the reactor dimensions such as the length and diameter need to be defined, which was determined by observing the mass composition of the product formation and reactant consumption along the length of the reactor. For this purpose, the depolymerization reactions and kinetics of polyester and nylon defined in the previous sections have been implemented to the PFR model. The potential simulation plant is considered to have a capacity to process overall 80,000 tonnes per year. Therefore, in the simulation model, the flow rate of water in the feed is 68,800 tonnes/yr (7848.51 kg/hr) whereas the flow rate of polyester and nylon is 6,720 (766.60 kg/hr) and 4,480 tonnes/yr (511.06 kg/hr) respectively. These flow rates correspond to the previously defined charge ratios.

At 220 m length and 0.1 m diameter, the rate of the formed products reached a maximum. A further increase in the reactor length showed no significant change in the product's mass composition. The mass composition profile along the reactor length is given in the figures 4.5 and 4.6 for polyester and nylon respectively. Here, the two y-axes have to be pointed out, which correspond to the mass fractions of the polymer and monomers on the left axis and the mass fraction of water on the right axis. This has been done because of the high water content in the feed stream in comparison to the mass of polymer.

In the figure 4.5, the depolymerization of PET along with the corresponding water consumption can be seen. Additionally, the parallel formation of TPA and EG is illustrated, which corresponds to the findings by Sato et al. shown in the figure 4.2 and can be transferred to the dissociation of the polymer chains. The PET shows a rapid decomposition reaction, which can be related to the fast reaction time of the PET hydrolysis mentioned earlier. The apparent higher amount of TPA is related to the higher mass fraction of TPA in comparison to the smaller EG monomer. The water increase after the polyester depolymerization at about 40 meter is related to the parallel nylon depolymerization reaction, shown in figure 4.6.

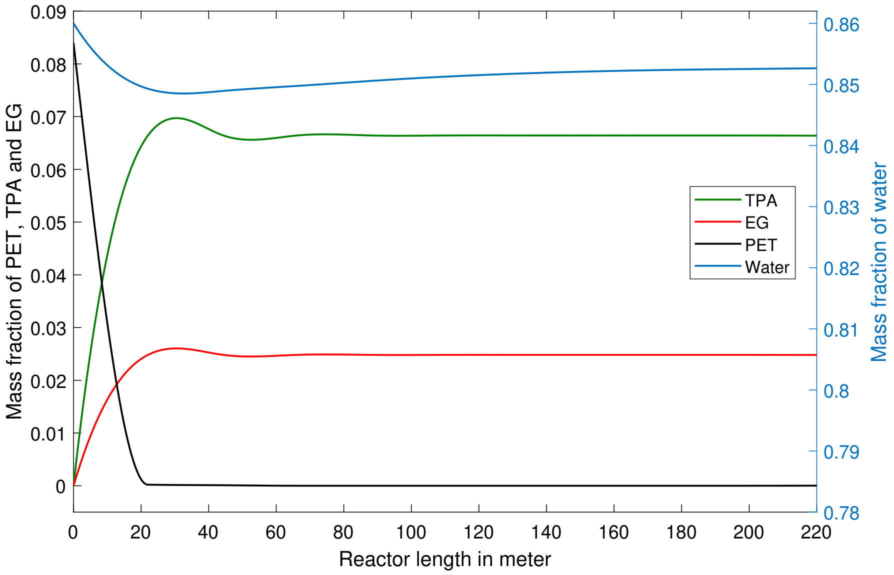


Figure 4.5: Mass composition profile for the depolymerization of polyester as function of the reactor length, with the mass fraction of water given on the right side.

Figure 4.6 illustrates the depolymerization reaction of nylon, from which a clear reduction of the polymer can be seen over the length of the reactor. Additionally, the two steps of the reaction with the formation of ACA as an intermediate is depicted in the graph. It can be seen that some CL is formed already at the beginning of the process, however the formation significantly increases with the reaction of ACA to CL. The deformation of the ACA intermediate is in direct correlation to the reformation of water in the reactor, which can be transferred to the ring-closing reaction of CL in which water is released.

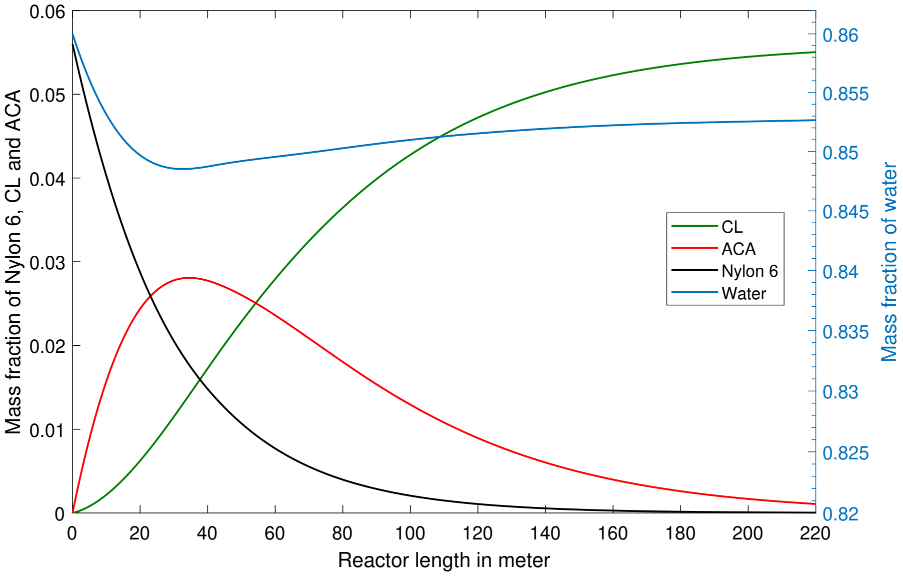


Figure 4.6: Mass composition profile for the depolymerization of nylon 6 as function of the reactor length, with the mass fraction of water given on the right axis.

As it has been illustrated previously in the figure 4.1, the output from the PFR reactor after depolymerization is further processed by reducing the temperature to 200°C and depressurized to 30 bar for product separation. The PFR output stream has mainly four products: TPA, CL, EG, and ACA and also water, along with the presence of a small amount of unprocessed nylon. The mass flow of the PFR input stream <S-3> and output stream <S-4> is given in the table 4.3.

Table 4.3: Mass flow of the Input and Output stream of PFR

Component	Input Stream <S3> $[kg/hr]$	Output Stream <S4> $[kg/hr]$
Water	7848.51	7781.52
Polyester	766.60	-
Nylon	511.07	0.29
TPA	-	606.18
EG	-	226.47
CL	-	502.94
ACA	-	9.09
Total	9126.18	9126.49

It was assumed that co-processing of nylon and polyester does not affect the individual yields of the formed products. The products in the output have mainly two phases: solid, and liquid phase. The highest product formed is TPA with a flow rate of 606.17 kg/hr followed by CL with 502.94 kg/hr. The secondary products especially EG show a significant presence with 226.47 kg/hr compared to ACA, which is the lowest product formed with around 9.09 kg/hr. Due to the high water to polymer ratios and the formation of water during the ring-closing reaction to CL, a high water amount of 7781.52 kg/hr can be found in the PFR output stream. The solid product TPA needs to be separated first from the liquid stream and the separation of products within the liquid phase require additional treatment, which will be discussed in the next chapter.

5 Modelling of the Phase Separation Process

The different depolymerization products from the reactor's output stream require further treatment to distinguish the products into separate monomer streams. As mentioned in the section 2.5, the stream consists of a multi-phase mixture and the separation of the different products requires additional components to make sure that the final product contains the least amount of impurities to obtain highly pure monomers suitable for the re-utilization in production processes. Additionally, a higher product purity often raises its selling price, therefore a higher separation efficiency could increase the process feasibility, which is especially important for TPA and CL as they are the main selling products. The product phases have been identified earlier, with TPA being the only solid in the stream and other products like CL, EG and ACA are present within the liquid and aqueous phase. Based on the theoretical considerations made in section 2.5, the separation of the solid and liquid phase have been investigated and optimized individually. At first the solid separation will be discussed, followed by the liquid separation. A final arrangement for the combined phase separation will be presented at the end of this section.

5.1 Recovery of Terephthalic Acid

As mentioned in the previous section, the PFR output stream is cooled and depressurized to 200°C and 30 bar respectively. With this change in the operational conditions, the overall energy consumption will most likely be reduced while keeping the stream in liquid phase to prevent it from uncontrolled separation in the pipe as well as possible degradation of the products. In order to first separate the solid TPA from the stream, a hydrocyclone has been implemented as described in section 2.5.1. The objective of utilizing a hydrocyclone is a preferably high TPA yield and still keeping the rest of the stream in liquid phase throughout the separation process.

The total mass flow entering the hydrocyclone is defined by the stream <S-6>, which is the same composition as <S-4>, and corresponds to around 9126 kg/hr. After the separation of the stream via a hydrocyclone, 538 kg TPA/hr could be removed through the bottom outlet stream. Around 68 kg/hr of the TPA is not separated and exits together with the top outlet stream. This separation corresponds to an efficiency of 88.75% for TPA. Because there is still a significant amount of TPA present in the top outlet stream, it would be of interest to separate this amount from the top stream before continuing with the separation of the liquid components. Therefore, an investigation on optimizing the solid separation efficiency by implementing serial hydrocyclones as depicted in the figure 5.1 has been performed. In this investigation the amount of nylon residue in the stream is neglected due to its very small amount stated in the table 4.3.

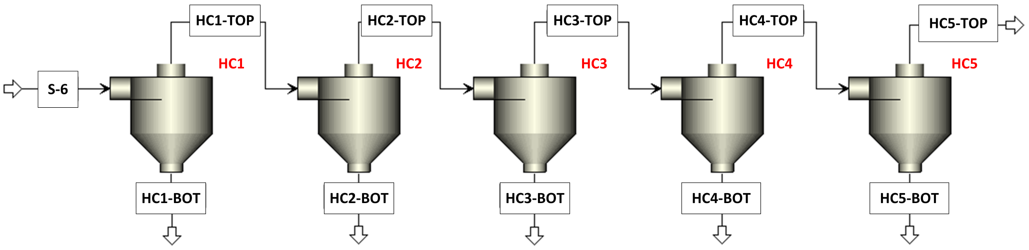


Figure 5.1: Flow diagram for serial hydrocyclones.

Table 5.1: Investigation on serial hydrocyclones for solid phase separation, with A) representing the top outlet composition and B) representing the bottom outlet composition.

A)

Component	HC1 Top [kg/hr]	HC2 Top [kg/hr]	HC3 Top [kg/hr]	HC4 Top [kg/hr]	HC5 Top [kg/hr]
Water	7695.76	7610.54	7525.85	7441.69	7358.07
TPA	68.18	7.67	0.86	0.10	0.01
CL	497.40	491.89	486.41	480.97	475.57
EG	223.98	221.50	219.03	216.58	214.15
ACA	8.99	8.89	8.79	8.69	8.59
Total	8494.6	8340.8	8240.4	8148.3	8056.7

B)

Component	HC1 Bot [kg/hr]	HC2 Bot [kg/hr]	HC3 Bot [kg/hr]	HC4 Bot [kg/hr]	HC5 Bot [kg/hr]
Water	85.76	85.22	84.69	84.16	83.62
TPA	538.00	60.51	6.81	0.76	0.09
CL	5.54	5.51	5.47	5.44	5.40
EG	2.50	2.48	2.46	2.45	2.43
ACA	0.10	0.10	0.10	0.10	0.10
Total	631.9	153.8	99.5	92.9	91.6
Efficiency in %	88.75	88.75	88.79	88.37	90.00

Table 5.1 shows the stream results for five hydrocyclones connected in series as illustrated in the figure 5.1 with the stream composition of the upper outlet in table section A) and the bottom outlet in table section B). It can be seen that a good amount of TPA is separated in the first two hydrocyclones, however, the efficiency of separation remains on a comparatively high level for all five hydrocyclones in series. The stated efficiency is here related to the separation of TPA in the individual hydrocyclone in series. It can also be seen that the water content in the bottom stream is the second component of high importance due to its quantity and even exceeds the amount of TPA in the bottom stream from the second hydrocyclone onward. If it is possible to fully remove this water content from the bottom stream, the TPA purity would increase to 98.5%, 88.2% and 46.0% for the first three hydrocyclones respectively, whereas the remaining impurity is due to the presence of CL, EG and ACA residues. Nevertheless, when removing the water incorporated in the bottom stream, an additional partial reduction of these impurities is also possible.

The amount of CL, EG and ACA residues as well as the water content in the bottom stream is relatively constant throughout the series of hydrocyclones. From this observation, it can be concluded that the selection of the number of hydrocyclones is mostly dependent on the amount of TPA in the bottom stream and in the top stream itself. In the bottom stream, it is considered as a product, whereas in the top stream it is considered as a residue which could possibly affect the purity of the following liquid products and their separation process. After the second separation through the hydrocyclone, the TPA residue in the top stream is less than 0.1% and reduces to only 0.01% of the top stream after the third hydrocyclone. Interesting to point out is the bottom composition of the third hydrocyclone. As the amount of TPA in the bottom stream after the second hydrocyclone was substantially higher than the amount of CL, the difference after the third hydrocyclone is significantly reduced. In the following bottom streams of hydrocyclone four and five, the contained TPA is even less than 1 kg/hr. Therefore, the utilization of four or five hydrocyclones in series can be determined as infeasible, considering the required effort for separation and possibly subsequent treatment of the high water content for a higher product purity.

Due to the high solubility of CL, EG and ACA, it can be considered that these residues can be removed to a good extent along with the water from the bottom stream. In order to achieve a high overall yield of TPA, three hydrocyclones are determined as the most suitable solution for the separation of solid TPA from the mixture stream. Nevertheless, the output of the third hydrocyclone might be considered separately for the reason of ensuring a high product purity. This causes the consideration of a alternated arrangement of the three hydrocyclones. Since the first hydrocyclone is already able to separate a fair amount of around 89% of the TPA input stream, it would be of interest to increase the quality of this stream. By implementing another hydrocyclone after the bottom stream of HC1, an improvement of the product purity may be achieved with a low energy component such as a hydrocyclone. In the table 5.1, it can be seen that also the top stream of HC1 still contains a considerable amount of TPA, which should be separated from this stream. Therefore, a third hydrocyclone will be utilized for the top streams. The result is a triangular arrangement of three hydrocyclones as illustrated in the figure 5.2. A comparison of the separation results in terms of the bottoms stream outlets from the first arrangement with three hydrocyclones in series to the alternated arrangement in triangle is given in the table 5.2 below.

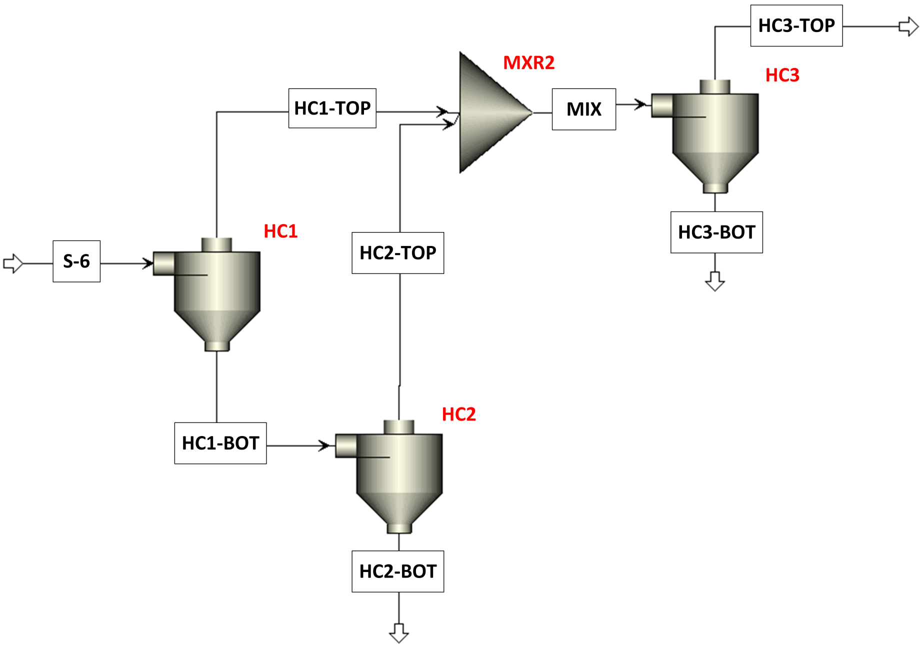


Figure 5.2: Flow diagram of triangular arrangement of the hydrocyclones.

Table 5.2 states the bottom stream results for the solid separation, utilizing the described arrangement of three hydrocyclones in series and three hydrocyclones in a triangle. It can be seen that the combination of HC1 and HC2 in the triangle arrangement has a high impact on the purity of TPA, which exits the bottom stream of HC2 with a purity of more than 98%. Therefore, a further treatment with a flash or similar components to reduce the water content in the outlet stream appears not necessary. The TPA leaving this stream has a mass of about 480.4 kg/hr and an additional 111.6 kg/hr TPA can be retrieved with HC3, which results in a total mass of TPA of 592.0 kg/hr. The TPA exiting from HC3 however requires further treatment in order to reduce the water content and improve the current purity of

Table 5.2: Solid separation results using hydrocyclones in series and triangle arrangement

		HC1 Bot	HC2 Bot	HC3 Bot
Series	Mass flow water [kg/hr]	85.8	85.2	84.7
	Mass flow TPA [kg/hr]	538.0	60.5	6.8
	Mass fraction TPA [%]	85.1	39.3	6.8
Triangle	Mass flow water [kg/hr]	85.8	6.4	85.7
	Mass flow TPA [kg/hr]	538.0	480.4	111.6
	Mass fraction TPA [%]	85.1	98.6	54.3

around 54%. With a TPA feed of 606.18 kg/hr coming from the PFR, as stated in table 4.3, around 14 kg/hr TPA could not be removed from the liquid stream and exits the third hydrocyclone of the triangle arrangement as waste through the top outlet. For the serial arrangement, the resulting bottom streams could be treated separately to reduce the respective water content for which the relating purities have been stated previously. Nevertheless, it appears beneficial to combine these three output streams for further purification to minimize the necessary equipment to only one flash separation, filter or similar method. The combined TPA mass flow of the three hydrocyclones in series is around 605.3 kg/hr, which means a loss of 0.88 kg/hr TPA exiting through the top outlet of HC3. The combined purity of the stream is 68.4% and could be raised to 96.1%, assuming complete reduction of water, which is comparable to the result in the triangular arrangement. However, when applying a further treatment of the liquid content, other impurities dissolved in the water stream may be reduced as well, raising the purity of TPA even higher. The small loss of TPA with less than 1 kg/hr forms a strong argument for the utilization of three serial hydrocyclones. However, a huge drawback is the high water content in the combined bottom outlet stream with 255.7 kg/hr, which significantly increases the energy consumption for the subsequent purification of TPA in comparison to the lower amount of liquid in the outlet stream of the third hydrocyclone <HC3-Bot> from the triangular arrangement. A summary of the described findings is given in table 5.3. The here stated values are related to the combined bottom output stream before further purification treatment for the serial arrangement and the bottom output stream of HC2 for the triangular arrangement.

Table 5.3: Summary of the comparison between solid separation using three hydrocyclones in series and triangle without further purification.

Arrangement	Mass of TPA [kg/hr]	Water content [kg/hr]	Loss of TPA [%]	Product purity [%]
Series	605.3	255.7	0.15	68.4
Triangle	592.2	85.7	2.31	98.6

It can be concluded that both arrangements have certain advantages and disadvantages, which have been discussed in this section. The overall decision on one of these two arrangements can be narrowed down to the amount of TPA recovery from the feed stream and the difference in the water content present after separation which could lead to high energy consumption in subsequent purification processes. Considering the overall objective of the described separation method to achieve a preferably high amount of TPA solid, the serial arrangement will be selected. Hereby, the difference between the amount of not separated TPA exiting with the liquid flow from the top of the third hydrocyclone is of high relevance, because it would mean a considerable loss of one of the main selling products with an additional impact on the purity of the second selling product CL which separation will be discussed in the following. The main drawback of the serial arrangement is the high amount of water content in the output stream, which needs to be reduced in order to achieve the demanded high purity of TPA and thus causes a high energy consumption. This energy consumption might be reduced by more simplified separation methods for the purification, for example with a filter. A summary of the solid phase separation with three hydrocyclones in series and a subsequent purification utilizing a flash separator is given in the table 5.6.

5.2 Recovery of ϵ-Caprolactam

For the separation of the liquid components, flash separation and the utilization of a distillation column could be defined as most feasible in section 2.5.2. Additionally, the reaction conditions could be determined with certain constraints to prevent CL from degradation or polymerization. In flash separation as well as distillation, pressure and temperature have a high impact on the separation efficiency and are directly in correlation to each other. Therefore, these are the parameters that needs to be investigated. Due to the large amount of water that needs to be evaporated for the separation, both methods will have a high energy consumption relevant for the feasibility of each process. The upper outlet stream of the third hydrocyclone <HC3-Top> given in the table 5.1 from the previously selected solid separation process is considered as the input stream to the respective liquid separation. Therefore, the liquid input stream may be adjusted in temperature and pressure according to the operational conditions of the liquid separation method by means of a heater and pump respectively before entering the separation chamber or column. With the percentaged amount of ACA of 0.11% and 0.01% TPA in the input stream, only water, CL and EG will be considered for this investigation. This assumption is also done based on the similarity of ACA and CL, and TPA being a solid, this will however occur in the bottom output and will therefore be considered in the overall conclusion of the combined phase separation process.

5.2.1 Flash Separation

To determine a possible optimization of the liquid stream separation via a flash separator, the temperature dependence of the process has been analysed. Therefore, the pressure has been set to a constant value of 0.1 bar and the temperature has been varied between 50 and 100°C. Within this temperature range and with the given pressure, the water content should be evaporated and exit through the flash overhead. Additionally, the degradation of CL should be prevented. Since EG has a higher boiling point as water, its behaviour under these conditions is of special interest. It represents here the main impurity possibly affecting the product quality of CL. With CL having the highest boiling point in comparison to EG and water, the product stream should be taken from the bottom flow of the flash chamber. The stream distribution of CL and EG into the overhead (Top) and bottom stream (Bot) is illustrated in the figure 5.4. The mass fraction is given in percent and is based on the corresponding input mass stream of CL and EG respectively.

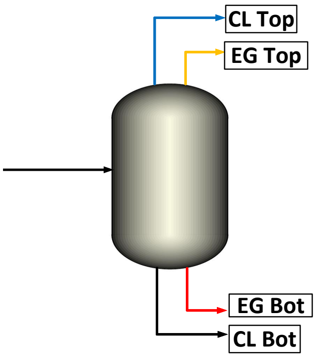


Figure 5.3: Flow diagram of the flash separator illustrating the output streams related to figure 5.4.

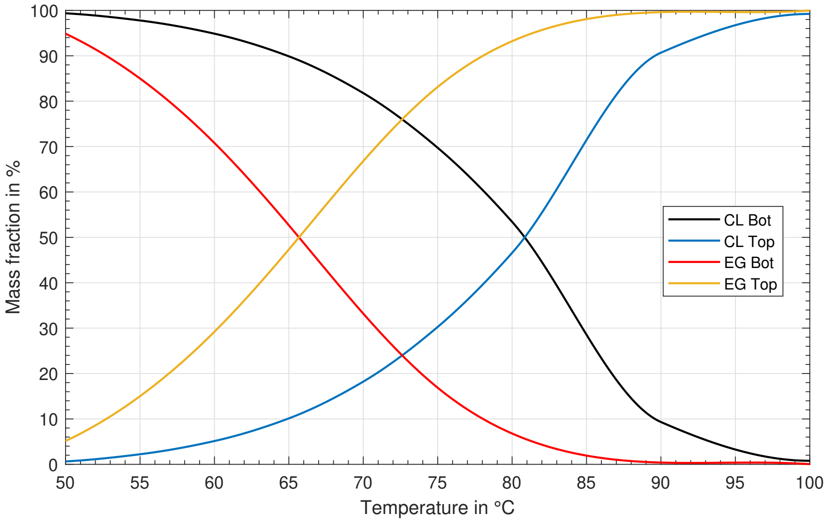


Figure 5.4: Distribution of CL and EG in the flash bottom (Bot) and overhead (Top) stream based on the respective feed, as function of temperature at 0.1 bar.

From the figure 5.4, a distinct and similar temperature dependence can be seen for CL and EG. As it was expected, EG responds stronger and already at a lower temperature to the temperature changes compared to CL. The breakover point at which 50% of the EG feed stream will evaporate towards the overhead and 50% will drain towards the bottom of the chamber is reached at a temperature of around 66°C. For CL, the breakover point is reached at a temperature of about 81°C, therefore the flash separator should operate at temperatures below 80°C above which a higher portion of the CL stream would exit with the overhead which is undesired. By lowering the temperature, the amount of CL in the bottom stream will increase. However, the amount of EG will also continuously increased up to the breakover point after which an even higher amount of EG will remain at the bottom of the flash chamber than evaporates and exits with the overflow. Hence, the increasing amount of EG in the bottom stream not only affects the CL product purity, but likewise the separation efficiency. For this reason it can be concluded that a full separation of CL from the liquid stream with a single flash is not possible, therefore a separation with multiple flash separators in series or in combination with other separation methods would need to be considered. Additionally, a certain amount of water evolving in the bottom of the chamber has to be considered when lowering the temperature for a higher CL yield, because of the approximation of the saturation line. This could potentially have an additional effect on the CL purity. Although this fraction of water is most likely to be small in comparison to the water contained in the feed stream of the flash, the proportional amount in comparison to the amount of CL might be high due to the overall high water ratio in the stream. This proportional increase of evolving water content in the bottom of the chamber can be seen from the respective values in table 5.4 with segment A) stating the overhead mass composition and segment B) representing the bottom composition for the case of 0.1 bar.

Table 5.4: Mass composition flow for a single flash separation as function of temperature with constant pressure of 0.1 bar

A)

Temperature [°C]	CL Top [kg/hr]	EG Top [kg/hr]	Water Top [kg/hr]
50	3.1	11.3	6903.4
60	24.9	64.0	7378.4
70	88.6	146.3	7474.6
80	226.6	204.2	7513.5

B)

Temperature [°C]	CL Bot [kg/hr]	EG Bot [kg/hr]	Water Bot [kg/hr]
50	483.3	207.8	622.5
60	461.5	155.1	147.5
70	397.8	72.7	51.3
80	259.8	14.9	12.4

As can be seen from the table 5.4, the evolving water content in the bottom stream (Bot) of the flash separation is only marginal in comparison to the water amount in the overhead stream (Top). Though, compared to the amount of CL in the bottom stream, the water content is of high importance at lower temperatures. At 50°C, the amount of water is even higher than the amount of CL present. Also with the high amount of EG at the same temperature, the product quality of CL would be insufficient. This consideration does not include the possible accumulation of ACA and TPA residues. Therefore, a combination of either multiple flash separations or in combination with a different liquid separation method seems to be inevitable in order to achieve the desired product purity.

5.2.2 Distillation

The distillation column has similar functional properties as the flash separation and operates based on similar separation principles. EG could be determined as the main impurity remaining in the stream and should be specifically analysed for separation efficiency considerations. Also in the distillation column, CL will exit as the bottom product due to its higher boiling point in comparison to water and EG which means that the objective is to improve the separation of EG and water residues from the bottom of the column. Therefore, the pressure at the condenser is kept constant at 0.1 bar corresponding to a temperature of 45°C whereas the bottom temperature is varied between 90 and 230°C, which corresponds to a self-regulated pressure between 0.01 and 1.1 bar.

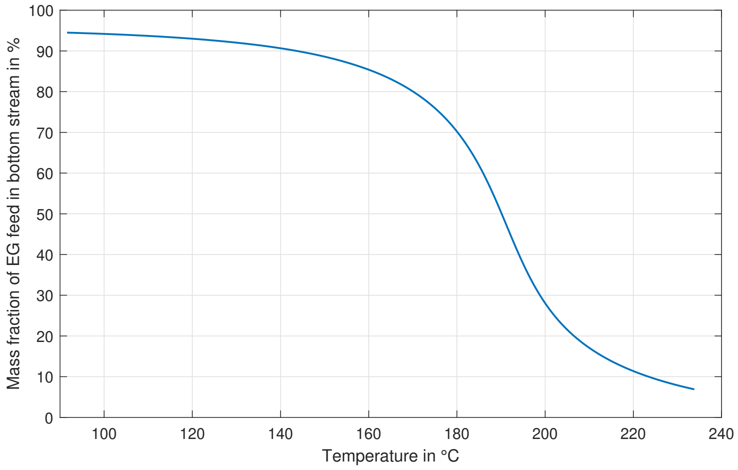


Figure 5.5: Mass fraction of EG in the bottom outlet relative to the amount of EG in the feed stream as function of temperature.

In the figure 5.5, the relative amount of EG draining to the bottom of the distillation column relative to the amount of EG in the distillation feed stream is given as a function of temperature. As it could be expected, the EG starts to partially evaporate and rise as vapour towards the distillation's overhead at about 160°C. The vapour fraction significantly increases close to EG's boiling point at about 190°C which corresponds to an operational pressure of 0.62 bar. A similar effect can be observed for the purity of CL.

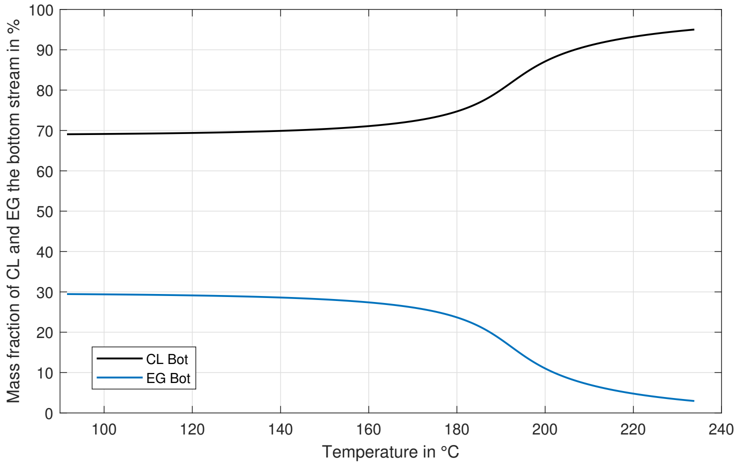


Figure 5.6: Mass composition of CL and EG in the bottom stream as function of temperature.

As illustrated in the figure 5.6, the mass fraction of CL increases in reaction to the decreasing EG from a relatively constant 70% to a maximum of about 95% at 230°C. This behaviour of direct response confirms the assumption of EG representing the main impurity. The remaining 5% impurity comprises the remaining liquid components in the bottom stream such as water, ACA and not fully separated EG. This analysis does not include solids, which in this case is TPA residue from the previous solid separation with hydrocyclones and corresponds to 0.86 kg/hr as stated in table 5.1 or residues of nylon. TPA and nylon residues will remain in the bottom stream of the column and not separate from the CL product stream via distillation or flash separation. The purity of the CL monomer stream containing TPA and nylon residues will therefore be reduced to 89.8%. The amount of CL coming from the subsequent hydrocyclones for solid separation could with 99% almost be fully recovered. From the initial PFR output stream with 502.94 kg CL/hr given in table 4.3, 96% of CL could be recovered, which means that around 4% and 17 kg CL have been lost due to the previous solid separation process. A summary of the distillation bottom output is given in the table 5.5, including the amount of TPA and nylon residues.

From the analysis described in this section, it can be concluded that a single flash separation would be insufficient for the separation of CL and the remaining liquids. Several flash separators in series would be necessary to achieve the demanded CL product purity, however from the separation characteristics shown in the figure 5.4, it can be assumed that also with a serial arrangement of multiple flash separators, the product quality may be reduced due to the direct correlation of EG affecting the yield and purity of CL. For this reason, the utilization of a distillation column is favoured. The values stated in table 5.5 show good results for the recovery of CL at relatively low pressure ranges. A possible further improvement of the distillation output could possibly be achieved by the addition of one flash separator after the distillation column to reduce the remaining water content and a portion of the EG residue. A summary of the results combining the distillation column in combination with a flash separator is given in table 5.7.

Table 5.5: Mass composition of the distillation's bottom stream at 0.1 - 2.0 bar

Component	Total	Water	CL	EG	ACA	TPA	Nylon
Mass stream [kg/hr]	540.45	7.53	485.92	37.93	8.79	0.86	0.28
Mass fraction [%]	100	1.4	89.8	7.0	1.6	-	0.05

In this section, the different phase separation methods have been discussed in detail and a possible optimization of each component has been investigated. The overall objective of the respective phase separation methods was a preferably high product recovery with sufficient or good monomer purity. The discussed separation methods are considered for an ideal case scenario without losses in temperature and pressure. A summary of the finalised phase separation process is given in the following section.

5.3 Summary of the Phase Separation Process

In the previous section, the utilization of three hydrocyclones in series were determined as an optimized solution for the separation of TPA solids from the liquid stream. Due to the high water content remaining in the TPA output stream, its evaporation through a flash has been suggested. Following, it could be determined that a flash separation would not give a sufficient separation of the liquid phase in terms of the quality demands on the CL monomer for further re-utilization in production processes as well as in terms of the CL yield. However, it was found that a flash separation might be beneficial to use for the reduction of water residue in the outlet stream of a distillation column. The distillation column has shown good results for the separation of CL from the liquid phase stream and is therefore preferred.

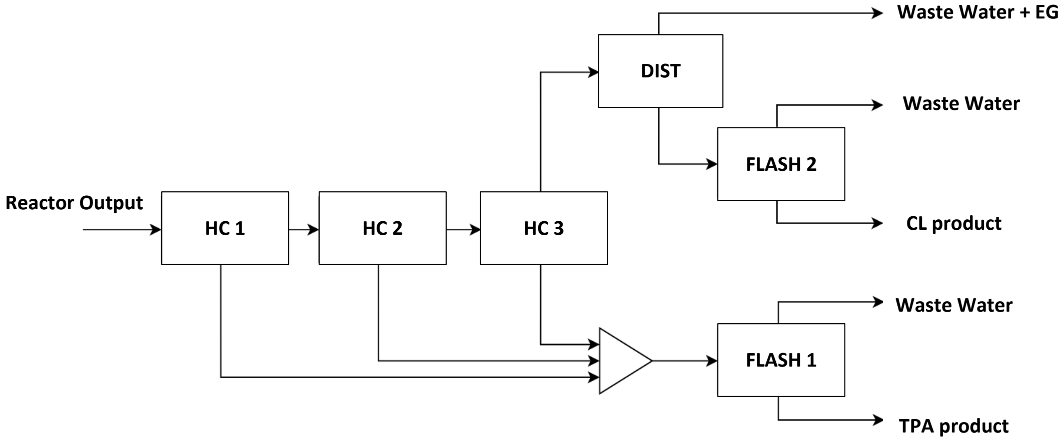


Figure 5.7: Flow diagram of the combined phase separation process.

In the figure 5.7, the combination of the selected phase separation processes is illustrated, with a summary of the stream results and component conditions given below in table 5.6 for the solid phase separation and in table 5.7 for the liquid phase separation. The reactor output stream is taken as the inlet flow for the hydrocyclone, followed by the solid separation section in which each top outlet stream of the hydrocyclones is passed on to the next component. The received bottom outlet streams are combined to a single TPA product stream, which is further purified through the reduction of the water content. The top stream of the third hydrocyclone is further transferred to the distillation column for liquid phase separation with a subsequent purification of the CL product stream through water reduction with a flash separation.

Table 5.6: Summary of the solid phase separation for 606.18 kg/hr TPA input.

Component	HC 1	HC 2	HC 3	Flash 1
Property	200°C, 30 bar	200°C, 30 bar	200°C, 30 bar	150°C, 1 bar
TPA [kg/hr]	538.00	60.51	6.80	605.32
Purity [%]	85.1	39.3	6.8	99.9

Table 5.7: Summary of the liquid phase separation for 502.94 kg/hr CL input.

Component	Distillation	Flash 2
Property	0.1 - 2.0 bar	105°C, 0.05 bar
CL [kg/hr]	485.92	484.73
Purity [%]	89.8	91.2

5.4 Further Optimization of the Recycling Process

With the previously described phase separation mechanism, the main selling products TPA and CL could be effectively recovered from the multiphase mixture stream exiting the PFR. In figure 5.7 of the previous section, three different waste water streams can be seen exiting the system, from which one however also contains EG. Even if EG is not one of the main selling products of the recycling process, recovering this EG content could be an addition to the selling products and thus beneficial for the economical feasibility of the plant. This assumption would presume, that the amount of recovered EG from this stream is satisfactory, considering the additional energy demand for the separation. A summary of such a separation of EG by means of a distillation column is given in table 5.8 below. Nevertheless, a second advantage could be accomplished by this addition. Since most of the other compounds from the multiphase mixture stream have already been separated before, the main products from this additional separation would be EG and water. This could give the possibility to recirculate the resulting water stream after the separation of EG to the beginning of the process and reintroduce it to the input stream of the PFR. With this recycling stream an overall reduction in the water consumption of the plant may be achieved, which could additionally reduce the overall operating costs. One factor worth to mention as well would be an increase in the sustainability of the plant due to the internal circularity of one of the feed materials. For the separation the differences in the volatilities of EG and water are beneficial for a higher purity of the recirculating water stream since unseparated residues would be expected to accumulate with the heavier EG. Nevertheless, supplementary heating, pressurizing and mixing of the recirculating water with the original stream would be required. Additionally, the effect of possible residues in the recirculating water stream on the depolymerization as well as on the product purities would need to be investigated, with additional considerations on the maximal fraction of recirculation tolerable for the process.

Table 5.8: Summary of EG separation by distillation

Property [bar]	EG In [kg/hr]	EG Bot [kg/hr]	EG Top [kg/hr]	Purity [%]
0.5 - 15.0	181.1	179.3	1.8	70.3

6 Overview of the Process and Flow Diagram

Over the past chapters of this report, the depolymerization and separation of polyester and nylon in a co-process has been developed. Thereby, the main focus has been set on high yields and purity of the main selling products TPA and CL. In the previous section, an additional separation of EG has been proposed in order to increase the plant's economical feasibility and to give the opportunity of an internal water recirculation for a supplementary decrease of the operational costs and a possibly increased sustainability due to lower water consumption.

The recycling process described throughout this report has been developed with the objective of defining an applicable depolymerization mechanism and an optimal separation of the product phases. Therefore, the aspect of energy consumption has not been considered. An analysis of the energy integration by a heat exchanger network is given in the subsequent chapter.

An overview of the final plant is given in figure 6.1 on the next page. Thereby, the previously mentioned additional separation of EG is integrated. This has been decided due to the stated benefits of the separation. However, the also described recirculating water stream from this second distillation column to the PFR has not been included, because the implementation would require additional investigations on the effects and limits of such, exceeding the extend of this project. Nevertheless, a mass stream of around 7443 kg water/hr could be detected, exiting the second distillation's overflow with a purity of around 99% which confirms the feasibility of this proposal. A summary of all streams is given in the appendix A.

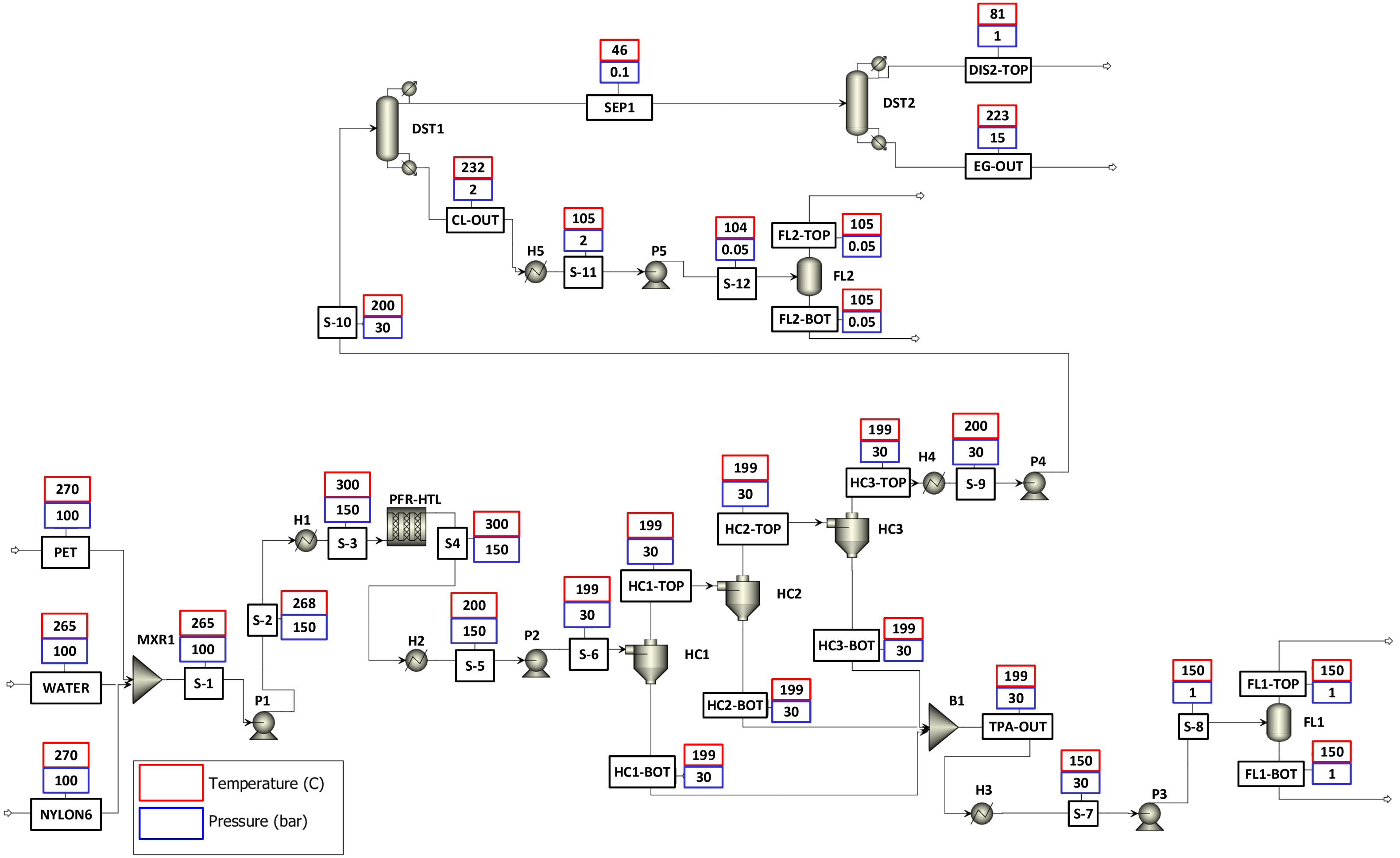


Figure 6.1: Flowsheet of the Aspen Model.

7 Energy Recovery

In the previous chapters, a complete model consisting of the depolymerization and the separation of the formed products has been designed in Aspen Plus. The entire plant simulation consists of multiple components and operations that require energy inputs to ensure proper functioning at the desired operating conditions. In this chapter, the optimization of the model's energy consumption is carried out by integrating the heat generated within the system to minimize the utilization of external utilities for the system's operations.

7.1 Heat Exchanger Integration

The different process components utilized in the simulation have multiple flow streams between them, which require specific temperature conditions to maintain the operational conditions in the individual components. This is aided by the supply of either heating or cooling through hot and cold utilities such as cooling water, air, high-pressure steam, etc. The reactants need to be heated to meet the operational conditions of the PFR and further, the product streams need to be cooled down for the separation process. The Aspen Plus model does not consist of any automated heat exchangers, which can be considered as an inefficient design in terms of the energy consumption. In order to improve the energy efficiency of the model, a heat exchanger system can be implemented. The heat exchanger aids in utilizing the energy within the different flow streams of the process, with the objective of reducing the requirement of external hot or cold utilities.

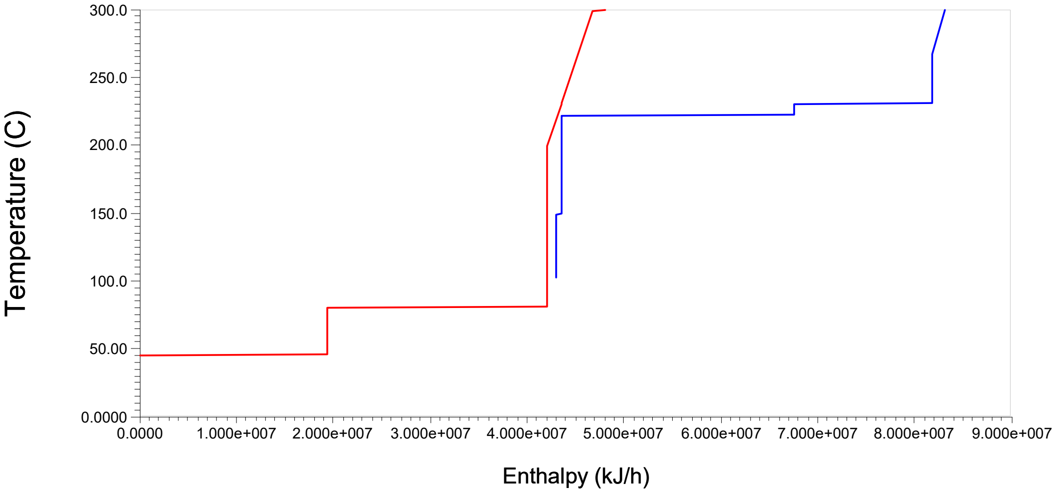


Figure 7.1: Composite curve of the process streams

For this purpose a pinch analysis has been performed utilizing the add-on Aspen Energy Analyzer (AEA). Thereby, the positions within the process, at which regenerative heat exchangers could be installed in order to improve the heat recovery efficiently, have been located to design a heat exchanger network (HEN). Thus, existing heat exchangers could be modified and added to the system for optimal heat integration. With the process streams representing the heat sources and sinks, a composite curve analysis has been generated to identify the pinch points. To consider multiple process streams within the system, the heat loads of all the streams are added together over temperature to represent a single composite of the complete hot and cold streams. Composite curves denote the connection between the temperature and enthalpy of the system's process streams. The composite curve generated for this project is illustrated in the figure 7.1 above, where the hot and cold composite curves are represented by the red and blue lines respectively. The hot composite curve represents the heat that is removed from the process streams to cool them down whereas the cold composite curve represents the heat that is required to heat the streams. The minimum temperature difference between the hot and cold streams, known as the minimum approach temperature, is set as 10°C.

For the development of the HEN, a grid diagram illustrating the hot and cold process streams has been generated. Therefore, the grid diagram for the recycling process developed throughout this report has been generated first as the initial case and is displayed in the figure 7.2. In the HEN grid diagram, the blue and red dots represent heat exchangers connecting the process streams with the cold and hot utility streams respectively. Due to the utilization of the AEA, multiple HEN designs based on the imported data and results of the previously defined process simulation could be compiled, from which the most suitable design has to be determined. Therefore, the heat exchanger network performance and cost index of each design have been taken as the selection criteria, which indicate the possibility of corresponding savings in the hot and cold utilities of the model. In the selection process for the most feasible HEN design, considerations about the total energy used for the heating and cooling utilities, the number of heat exchangers required as well as their area have been included. Additionally, the indication for the operating cost per second as well as the capital and total cost of the HEN have been included, which can be directly related to the reduction in the applied hot and cold utilities.

With the main objective of the HEN to optimize the energy consumption of the recycling process by reducing the external hot and cold utilities, the total costs of the utilities including the capital and operational costs should be reduced. Therefore, both network performance and cost index of the design will be considered for selecting the optimal HEN design. These parameters are additionally analyzed by the inclusion of target values, which are theoretical values of an ideal condition. The target value is beneficial to understand how close the design is to the minimum energy requirement. Based on the described criteria, an improved HEN design could be identified as shown in the figure 7.3. In this figure, three heat exchangers have been placed between the process streams for efficient heat recovery integration within the system. The heat exchangers are represented by silver dots and a highlighted connection line between the streams. The differences in the properties of the initial and improved HEN setup are listed in the tables 7.1 and 7.2. All listed parameters have reached the target values by approximately 100%.

Table 7.1: Comparison of the initial and improved HEN based on performance.

Model	Hot Utility [kW]	Cold Utility [kW]	No. of Units
Initial setup	11,160	13,380	12
Improved setup	10,020	12,240	15

Table 7.2: Comparison of the initial and improved HEN based on the cost index

Model	Operating Cost Index [cost/sec]	Capital Index [cost]	Total Cost Index [cost/sec]
Initial setup	0.02481	24,21,000	0.0495
Improved setup	0.02362	23,56,000	0.0486

From the summaries in the table 7.1 and 7.2, an improvement in the utilization of hot and cold utilities can be seen in terms of the energy performance as well as the cost index. From table 7.1, the reduction in the energy consumption by hot and cold utilities due to the improved HEN design could be determined as 11.4% and 8.5% respectively. Despite the increase in the number of heat exchangers from 12 to 15 units in the improved design, it is worth mentioning that the capital cost for the improved setup is still less compared to the initial design. Additional improvements can be observed for the operational and total cost index, even though these changes are relatively small. The decrease in the operational cost index with about 0.8% can be related to the reduction of the external utility consumption due to the optimized heat integration. The stated findings, lead to the conclusion that the improved HEN is more efficient in terms of the energy performance and the cost. Therefore, the implementation of the improved HEN to the process is suggested.

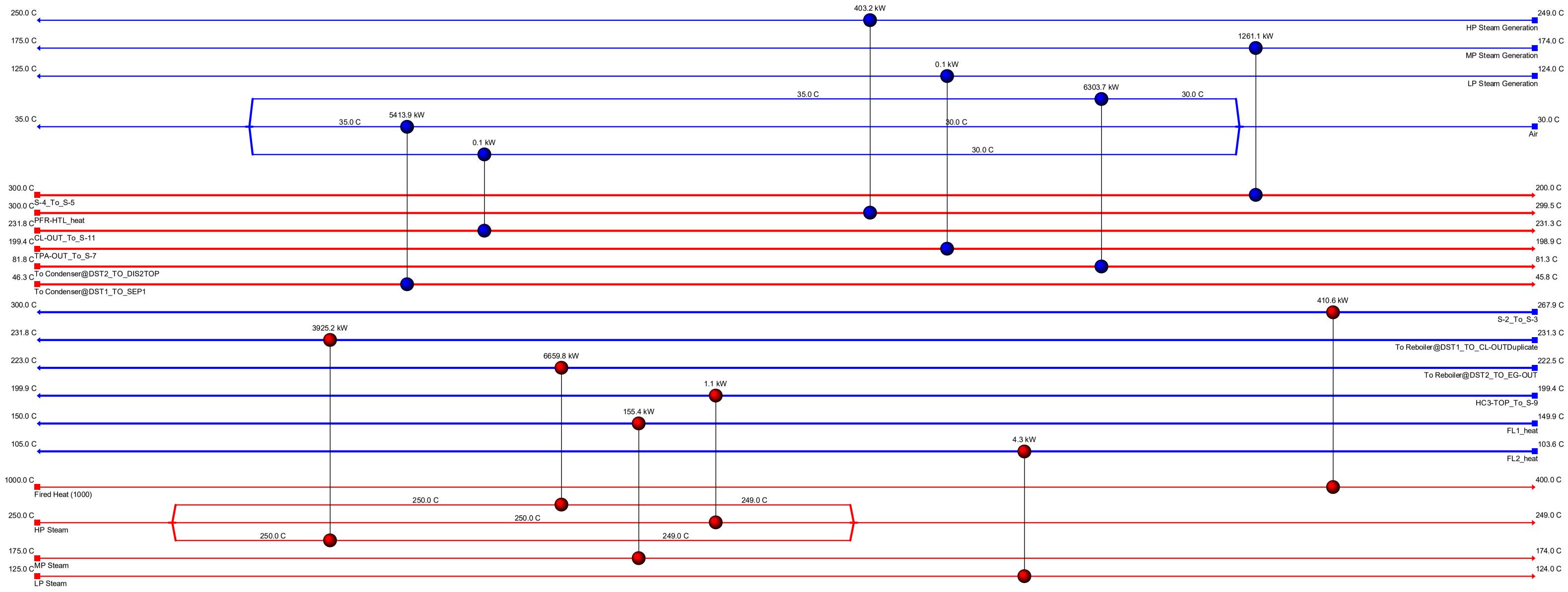


Figure 7.2: Initial HEN grid diagram of the recycling process.

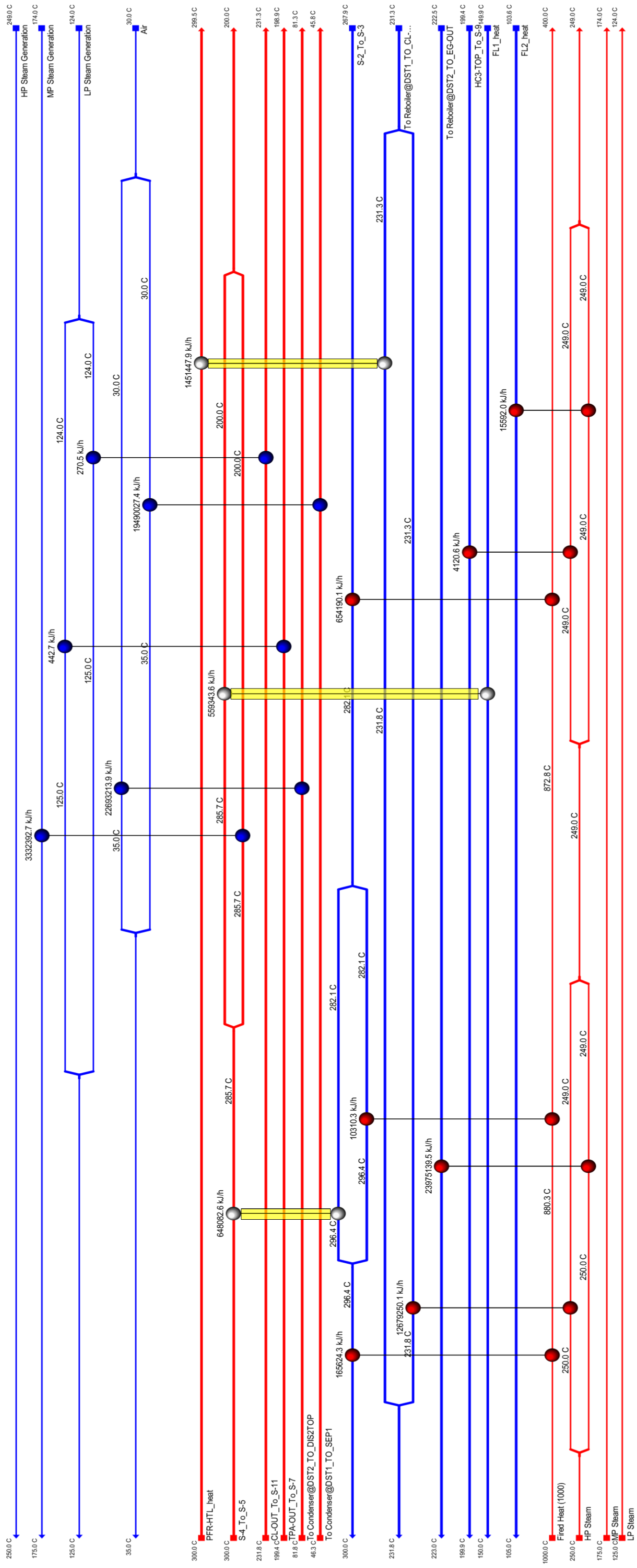


Figure 7.3: Improved HEN grid diagram with added heat exchangers.

8 Conclusion

In this report, a recycling mechanism for the depolymerization of polyester and nylon could be developed with a subsequent recovery of the monomer products by phase separation. Thereby, the objective was to obtain a high yield of monomer products with sufficient product purity to enable a possible reintroduction of the recycled fibres to new production processes. This chapter will give a summary of the main outcomes of this project.

For the depolymerization of polyester and nylon in a co-process, neutral hydrolysis in sub-critical conditions was determined as the best choice. Therefore, a kinetic model has been developed for the application in a PFR based on data found in the literature. Furthermore, TPA and CL have been defined as the process' main selling products for which the solid and liquid phase separation mechanisms were developed. In order to separate solid TPA particles from the multi-phase stream, the utilization of three hydrocyclones arranged in a series has been proposed. With this method, 605.3 kg TPA/hr could be separated which corresponds to a recovery of 99.8%. Through the utilization of a subsequent flash separation, the purity of TPA was increased from 68.4% to 99.9%. Following, 485.9 kg CL/hr have been separated from the liquid stream through the utilization of a distillation column which is correlated to a recovery of 96.6%. As a result, a purification of the monomer by means of a flash separator has been proposed as well, which resulted in an improvement of the purity from 89.8% to 91.2%. In addition to the separation of the main selling products, the separation of EG using a distillation column has been suggested in order to increase the plant's profitability and to give the possibility of recirculating a portion of the process water stream. From this additional separation, 179.3 kg EG/hr with a purity of 70.3% was retrieved, which corresponds to a recovery of 79.2%.

A significant effect on the product's purity due to the utilization of a flash after each respective phase separation could be observed. The resulting purity of the TPA particles can be assumed as appropriate for the utilization in the new production processes. For this reason, the depolymerization of PET and the separation of TPA is concluded as a feasible solution in regards to the defined objective. The purity of CL however remains under the purity ranges commonly found on the market. Thereby, the EG residue could be determined as the main impurity, with about 34.7 kg EG/hr, which can be related to the described difficulties in separating the liquid stream components. Therefore, a direct effect of the co-process on the product's quality could be observed. Due to the lowered quality of CL and the included impurities in the product stream, a reduction in the selling price of CL has to be assumed and its re-utilization for the production of different products needs further investigation. Therefore, the depolymerization of nylon could be determined as appropriate, however an amount of 0.29 kg/hr non-depolymerized nylon could be detected after the PFR, which remained in the stream. With 0.28 kg/hr, the majority of this non-reacted nylon was found in the product output stream of CL after separation and purification. EG has a considerably lower purity after the separation, which can however be related to the remaining water content in the stream with around 75.2 kg/hr, representing 29.5% of the stream. Therefore, a possible purification of EG by means of a flash could be worth investigating in order to increase its feasibility as an additional selling product. As a result, the established possibility of recirculating a portion of the water stream back to the PFR could be considered as a supporting argument, for the implementation of the additional separation of EG. Nevertheless, the additional energy consumption and cost of necessary heaters, pumps and mixer have to be taken into account for consideration.

The described findings have been compiled under the assumption of no direct interaction between the two polymers during the depolymerization reaction and under ideal conditions. For the validation of these assumptions and findings, experimental investigations on the polymer behaviour would be necessary.

Concluding this report, an analysis on the energy recovery of the process by implementing a HEN through pinch analysis has been conducted. Thereby, the HEN has been optimized due to the addition of three heat exchangers, which has let to a reduction in the external hot and cold utility energy consumption of 11.4% and 8.5% respectively. Based on the found improvements in terms of the energy performance as well as the cost indices for the external utilities, the application of the improved HEN has been suggested.

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A Summary of the Flow Diagram

Table A.1: Summary of the process streams (1)

Stream Name	Units	PET	WATER	NYLON 6	S-1	S-2	S-3	S-4	S-5	S-6
Description										
From Component	-	-	-	-	MXR1	P1	H1	PFR-HTL	H2	P2
To Component		MXR1	MXR1	MXR1	P1	H1	PFR-HTL	H2	P2	HC1
Temperature	°C	270	265	270	264.6	267.9	300	300	200	199.4
Pressure	bar	100	100	100	100	150	150	150	150	30
Mass Flows										
Total	kg/hr	766.6	7848.5	511.1	9126.2	9126.2	9126.2	9126.5	9126.5	9126.5
Water	kg/hr	-	7848.5	-	7848.5	7848.5	7848.5	7781.5	7781.5	7781.5
TPA	kg/hr	-	-	-	-	-	-	606.2	606.2	606.2
EG	kg/hr	-	-	-	-	-	-	226.5	226.5	226.5
PET	kg/hr	766.6	-	-	766.6	766.6	766.6	-	-	-
CL	kg/hr	-	-	-	-	-	-	502.9	502.9	502.9
ACA	kg/hr	-	-	-	-	-	-	9.1	9.1	9.1
Nylon 6	kg/hr	-	-	511.1	511.1	511.1	511.1	0.29	0.29	0.29
Mass Fractions										
Water	-	-	1	-	0.860	0.860	0.860	0.852	0.852	0.852
TPA	-	-	-	-	-	-	-	0.066	0.066	0.0666
EG	-	-	-	-	-	-	-	0.025	0.025	0.025
PET	-	1	-	-	0.084	0.084	0.084	-	-	-
CL	-	-	-	-	-	-	-	0.055	0.055	0.055
ACA	-	-	-	-	-	-	-	0.0009	0.0009	0.0009
Nylon 6	-	-	-	1	0.056	0.056	0.056	<0.001	<0.001	<0.001

Table A.2: Summary of the process streams (2)

Stream Name	Units	HC1-BOT	HC1-TOP	HC2-BOT	HC2-TOP	HC3-BOT	HC3-TOP	TPA-OUT	S-7
Description									
From Component		HC1	HC1	HC2	HC2	HC3	HC3	B1	H3
To Component		B1	HC2	B1	HC3	B1	H4	H3	P3
Temperature	°C	199.4	199.4	199.4	199.4	199.4	199.4	199.4	150
Pressure	bar	29.9	29.9	29.9	29.9	29.9	29.9	29.9	30
Mass Flows									
Total	kg/hr	631.9	8494.6	153.9	8340.7	99.6	8241.1	885.4	885.4
Water	kg/hr	85.8	7695.7	85.3	7610.5	84.7	7525.8	255.8	255.8
TPA	kg/hr	538.0	68.2	60.5	7.7	6.8	0.86	605.3	605.3
EG	kg/hr	2.5	224.0	2.5	221.5	2.5	219.0	7.4	7.4
PET	kg/hr	-	-	-	-	-	-	-	-
CL	kg/hr	5.6	497.4	5.5	491.9	5.5	486.4	16.5	16.5
ACA	kg/hr	0.10	8.9	0.10	8.9	0.10	8.8	0.30	0.29
Nylon 6	kg/hr	0.003	0.28	0.003	0.28	0.003	0.28	0.009	0.009
Mass Fractions									
Water	-	0.135	0.906	0.554	0.912	0.851	0.913	0.289	0.289
TPA	-	0.851	0.008	0.393	0.0009	0.068	0.0001	0.684	0.684
EG	-	0.004	0.026	0.016	0.027	0.025	0.027	0.008	0.008
PET	-	-	-	-	-	-	-	-	-
CL	-	0.009	0.059	0.036	0.059	0.055	0.059	0.019	0.019
ACA	-	0.0002	0.0011	0.0006	0.0011	0.0009	0.0011	0.0003	0.0003
Nylon 6	-	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Table A.3: Summary of the process streams (3)

Stream Name	Units	S-8	FL1-BOT	FL1-TOP	S-9	S-10	CL-OUT	SEP1	S-11	S-12
Description										
From Component		P3	FL1	FL1	H4	P4	DST1	DST1	H5	P5
To Component		FL1	-	-	P4	DST1	H5	DST2	P5	FL2
Temperature	°C	149.9	150	150	200	200	231.8	458.5	105	103.6
Pressure	bar	1	1	1	30	30	2	0.1	2	0.05
Mass Flows										
Total	kg/hr	885.4	605.5	279.9	8241.1	8241.1	540.4	7699.8	540.5	540.5
Water	kg/hr	255.8	0.01	255.8	7525.8	7525.8	7.5	7518.2	7.5	7.5
TPA	kg/hr	605.3	605.3	-	0.9	0.9	-	-	-	-
EG	kg/hr	7.44	<0.01	7.44	219.0	219.0	37.9	181.1	37.9	37.9
PET	kg/hr	-	-	-	-	-	-	-	-	-
CL	kg/hr	16.5	0.14	16.4	486.4	486.4	485.9	0.49	485.9	485.9
ACA	kg/hr	0.30	0.007	0.30	8.79	8.79	8.79	<0.01	8.79	8.79
Nylon 6	kg/hr	0.009	0.009	<0.001	0.28	0.28	0.28	-	0.28	0.28
Mass Fractions										
Water	-	0.289	<0.01	0.914	0.913	0.913	0.014	0.976	0.014	0.014
TPA	-	0.684	0.999	-	0.0001	0.0001	-	-	-	-
EG	-	0.008	<0.001	0.027	0.027	0.027	0.070	0.023	0.070	0.070
PET	-	-	-	-	-	-	-	-	-	-
CL	-	0.019	0.0002	0.059	0.059	0.059	0.898	<0.001	0.898	0.898
ACA	-	0.0003	<0.0001	0.0010	0.0011	0.0011	0.0162	<0.0001	0.0162	0.0162
Nylon 6	-	<0.001	<0.001	<0.001	<0.001	<0.001	0.0005	-	0.0005	0.0005

Table A.4: Summary of the process streams (4)

Stream Name	Units	FL2-BOT	FL2-TOP	EG-OUT	DIS2TOP
Description					
From Component		FL2	FL2	DST2	DST2
To Component		-	-	-	-
Temperature	°C	105	105	223	81.3
Pressure	bar	0.05	0.05	15	0.5
Mass Flows					
Total	kg/hr	531.6	9.4	253.0	7444.9
Water	kg/hr	3.1	4.4	75.2	7443.0
TPA	kg/hr	-	-	-	-
EG	kg/hr	34.7	3.3	179.3	1.8
PET	kg/hr	-	-	-	-
CL	kg/hr	484.7	1.7	0.49	<0.001
ACA	kg/hr	8.7	0.01	<0.01	<0.001
Nylon 6	kg/hr	0.28	<0.001	-	-
Mass Fractions					
Water	-	0.006	0.474	0.295	0.999
TPA	-	-	-	-	-
EG	-	0.065	0.348	0.703	0.0002
PET	-	-	-	-	-
CL	-	0.912	0.177	0.002	<0.001
ACA	-	0.0165	0.0011	<0.0001	<0.0001
Nylon 6	-	0.0005	<0.001	-	-