Modelling of Lyocell fibre production and technical analysis of solvent recovery concepts

Thesis for M.Sc. in Chemical and Process Engineering

by

Andreas Reipsar



Laboratory for Process Design and Systems Engineering Faculty of Science and Engineering Åbo Akademi University

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Abstract

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Author:	Andreas Reipsar		
Thesis supervisors: Dr Eemeli Hytönen			
	VTT Technical Research Centre of Finland Ltd,		
	Espoo Finland		
Prof. Anders Brink			
	Finland		
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Lyocell is a type of man-made cellulosic fibre that is produced via direct dissolution of dissolving pulp in a non-volatile amine oxide or ionic liquid. The dissolved pulp is regenerated into long fibre strings by extruding the dissolved mixture through an airgap into a water bath. The fibres coagulate in the bath and are later drawn into another water bath where they are washed until the solvent is completely removed. The Lyocell process is known as a sustainable way of producing textile fibres due to its low emissions, water consumption and land-usage. It is distinguished by its very high recycling rate of solvent, which in some cases has been reported to be above 99%.

The objective of this thesis was to create a realistic model of the NMMO-based Lyocell process by using the steady-state simulation software Balas®. The model provides data from which the accumulation of impurities in the process loops can be studied. The process impurities are defined as un-utilised pulp components and inorganics. This data combined with overall mass and energy balances are used to analyse five solvent recycling concepts: (1) ion exchange and evaporation; (2) flotation, ion exchange and evaporation; (3) filtration, ion exchange and evaporation; (4) filtration and liquid/liquid-extraction with butanol; and (5) filtration and liquid/liquid-extraction with dichloromethane.

All process concepts were set to perform at a 99% solvent recovery rate, thus creating a scenario for an equal comparison of the pre-requisites for each of the recycling concepts. The concepts were evaluated based on the purity of the recovered solvent, energy demand and overall complexity. Complexity is based on the number of process steps and design parameters, as well as dependence on chemicals. The least complex combination of technologies is Concept 1, followed by Concept 3, 2, 4 and 5. Concept 4 and 5 can provide a highly concentrated solvent stream (99%) with lower amounts of impurities than the other concepts. Concept 1, 2 and 3 result in very similar solvent purity rates. Concept 2 has the lowest steam demand, followed by Concept 1, 3, 5 and 4. The model results are in reasonable accordance to published data on water and energy demand of industrial Lyocell fibre production.

Keywords: Lyocell, regenerated cellulosic fibre, solvent recovery concepts, process modelling, steady-state simulation, technical analysis

Preface

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"Marcet sine adversario virtus"



Abbreviations

- DP Degree of polymerisation
- IL Ionic liquid
- $IX-Ion \ exchange$
- LLE-Liquid/liquid-extraction
- M-M orpholine
- NMM N-methylmorpholine
- NMMO N-methylmorpholine N-oxide
- PHK Prehydrolysis Kraft
- ppm Parts-per-million
- TCF Totally chlorine free
- $TDS-Total\ dissolved\ solids$
- TSS Total suspended solids

Table of Contents

A	bstract	й
P	reface	iv
A	bbreviatio	onsv
Т	able of Co	ntentsvi
L	ist of Figu	res viii
L	ist of Tabl	esX
1	Introd	uction1
2	Literat	ture review4
	2.1 W	Vood and pulp fundamentals
	2.1.1	Cellulose
	2.1.2	Hemicellulose
	2.1.3	Lignin
	2.1.4	Extractives
	2.1.5	Ash-forming elements
	2.2 Se	olubility of pulp
	2.2.1	NMMO9
	2.2.2	Ionic liquids
	2.3 L	yocell process description
	2.3.1	Pre-treatment, pre-mix and dissolution
	2.3.2	Spinning and fibre regeneration
	2.3.3	Washing19
	2.3.4	Drying and finishing
	2.3.5	Solvent recovery methods
	2.3.5	.1 Flotation
	2.3.5	.2 Filtration
	2.3.5	.3 Ion exchange
	2.3.5	.4 Evaporation
	2.3.5	.5 Liquid/Liquid-Extraction
3	Metho	d31
	3.1 R	esearch objective
	3.2 O	verall approach

	3.3	Case study definition				
	3.4	Simulation tool - Balas®				
4	Resu	ılts				
	4.1	Concept 1				
	4.2	Concept 2				
	4.3	Concept 3				
	4.4	Concept 4				
	4.5	Concept 5				
	4.6	Summary				
	4.7	Sensitivity analysis				
5	Disc	ussion and observations				
6	Con	clusions				
7	Swedish summary - Svensk sammanfattning54					
8	References					
A	ppendix	x A – Model implementation63				
A	Appendix B – Model structure and overview73					
A	ppendix	x C – Mass and energy balances				
A	Appendix D – Technical analysis					

List of Figures

Figure 2-1. Molecular structure of cellulose. Reproduced from Sjöström (1993)
Figure 2-2. Lignin monomers. Reproduced from Biermann (1996)6
Figure 2-3. Cellulose molecular structure with inter (dashed lines) and intramolecular (dotted lines)
hydrogen bonds. Reproduced from Festucci-Buselli, Otoni and Joshi (2007)8
Figure 2-4. Proposed dissolution mechanism of cellulose in NMMO. Reproduced from Pinkert, Marsh
and Pang (2010)
Figure 2-5. Proposed dissolution mechanism of cellulose in IL. The anion bonds with a hydrogen ion
and the cation bonds with a cellulose chain. Reproduced from Pinkert, Marsh and Pang (2010) 12
Figure 2-6. Illustration of Lenzing AG's Lyocell fibre production process. Reproduced from Lenzing
Aktiengesellschaft (2019)
Figure 2-7. Ioncell process concept. Illustrated according to Stepan et al. (2016)
Figure 2-8 Illustration of a kneader, used for both premix and dissolution. Reproduced from Lewin
and Pearce (1998)
Figure 2-9 Thin-wall evaporator used for cellulose dissolution. Reproduced from White (2001)17
Figure 2-10 Schematic illustration of dry-jet wet spinning. Reproduced from Liu et al. (2017)
Figure 2-11 End (A) and side view (B) of a perforated drum dryer. a) loading conveyor; b) Perforated
drum; c) Cover plates; d) Fan; e) Heaters; f) Air distributor. Reproduced from Tsotsas, Gnielinski and
Schlünder (2000)
Figure 2-12 Working principle of a liquid/liquid-extraction
Figure 2-13 Static column extractors. Reproduced from Mersmann, Kind and Stichlmair (2011)29
Figure 2-14 Rotating disc columns and mixer-settler extractors. Reproduced from Mersmann, Kind
and Stichlmair (2011)
Figure 3-1 Simplified structure of the simulation model
Figure 3-2 Process configuration for the LLE concept
Figure 4-1 Process data for solvent recovery Concept 1
Figure 4-2 Process data for solvent recovery Concept 2
Figure 4-3 Process data for solvent recovery Concept 340
Figure 4-4 Process data for solvent recovery Concept 4
Figure 4-5 Process data for solvent recovery Concept 5
Figure 4-6 Distribution of organic compounds in the stream entering the ion exchange unit in Concept
1, 2 and 3
Figure 4-7 Summary of energy demand
Figure 4-8 Summary of freshwater demand
Figure 4-9 Sensitivity analysis of freshwater demand, Concept 3
Figure 4-10 Sensitivity analysis of steam demand, Concept 3

Figure 4-11 Sensitivity analysis of organic content in the recovered solvent stream, Concept 346
Figure 4-12 Sensitivity analysis of inorganic content in the recovered solvent stream, Concept 3 47
Figure 4-13 Effect of water content in extracted solvent/dichloromethane-system on steam demand,
Concept 5
Figure 4-14 Effect of variation in LLE pulp-derived organic reject-% on pulp-derived organic content of
the recovered solvent, Concept 5
Figure 4-15 Effect of variation in LLE inorganic reject-% on inorganic content of the recovered solvent,
Concept 5
Figure A-1 Process configuration of fibre regeneration in the model. Red stream represents fibre;
green represents washing water, and blue represents water free from impurities. The cooling unit is
followed by two separation units, which are used to describe compound losses in occurrence with
fibre regeneration
Figure A-2 Example of a separation step in the superstructure67
Figure A-3 Process configuration for the LLE concept71
Figure B-1 Model structure for the dissolution step. Red lines represent the main process flow of fibre,
orange lines represent steam flow, black lines represent wastewater, and green lines represent
process water
Figure B-2 Model structure for the spinning and washing step
Figure B-3 Model structure for the drying step74
Figure B-4 Model structure for the solvent recovery superstructure, levels 1 to 3
Figure B-5 Model structure for the solvent recovery step level 4 evaporation and wastewater
treatment
Figure B-6 Model structure for the solvent recovery step level 4 liquid/liquid-extraction. The purple
lines represent concentrated organic solvent77
Figure D-1 Flotation unit surface area and depth as a function of vertical speed of suspended solids.
Figure D-2 Membrane area and number of modules as a function of transmembrane flux

List of Tables

Table 2-1. Major hemicellulose components. Reproduced from Sjöström (1993)
Table 2-2. Approximate concentration levels of various elements in dry stem wood of softwoods and
hardwoods7
Table 2-3 General pore size and operating pressure per membrane type 24
Table 4-1 Summary of technical requirements43
Table A-1 Summary of model compounds used63
Table A-2 Operating parameters for the dissolution step evaporation 64
Table A-3 Design parameters for the flotation unit, based on literature in Chapter 2.3.5.1. Compound-
% describes the amount removed from the feed stream68
Table A-4 Design parameters for the ultrafiltration unit, based on literature in Chapter 2.3.5.2
Table A-5 Design parameters for the ion exchange unit 69
Table A-6 Operating parameters for the evaporation units
Table A-7 Operating parameters for the LLE and evaporation units. The parameters are the same for
both steps
Table C-1 Process data for Concept 1 Ion exchange & Evaporation, part 1. The energy streams are
calculated by using 0 $^{\circ}\!C$ as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point
calculated by using 0 °C as base point.78Table C-2 Process data for Concept 1 Ion exchange & Evaporation, part 2.79Table C-3 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 180Table C-4 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 281Table C-5 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 182Table C-6 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 183Table C-7 Process data for Concept 4 Filtration & LLE (Butanol), part 184Table C-8 Process data for Concept 4 Filtration & LLE (Butanol), part 285Table C-9 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 186Table C-10 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 287
calculated by using 0 °C as base point
calculated by using 0 °C as base point.78Table C-2 Process data for Concept 1 Ion exchange & Evaporation, part 2.79Table C-3 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 180Table C-4 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 281Table C-5 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 182Table C-6 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 183Table C-6 Process data for Concept 4 Filtration, Ion exchange & Evaporation, part 283Table C-7 Process data for Concept 4 Filtration & LLE (Butanol), part 184Table C-8 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 186Table C-9 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 287Table C-10 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 287Table D-1 Calculated membrane area and number of modules for specific transmembrane fluxes89Table D-2 Distribution of ions in TCF PHK Dissolving pulp.90
calculated by using 0 °C as base point.78Table C-2 Process data for Concept 1 Ion exchange & Evaporation, part 279Table C-3 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 180Table C-4 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 281Table C-5 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 182Table C-6 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 283Table C-6 Process data for Concept 4 Filtration & LLE (Butanol), part 184Table C-8 Process data for Concept 4 Filtration & LLE (Butanol), part 285Table C-9 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 186Table C-10 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 287Table D-1 Calculated membrane area and number of modules for specific transmembrane fluxes89Table D-2 Distribution of ions in TCF PHK Dissolving pulp90Table D-3 Design calculations for ion exchange units in Concept 1, 2 and 390
calculated by using 0 °C as base point

1 Introduction

The textile industry is currently one of the largest and most polluting industries in the world. The industry is continuously growing and the annual global demand for virgin textile fibres is projected to reach 145 million tonnes by the year 2030. Production of textile fibres is very resource-intensive and the high usage of energy, land, and water is regularly discussed. Global Fashion Agenda and Boston Consulting Group addressed this subject in 2017 by writing an extensive report on the topic, which also contained global textile producers' views on the matter. The producers were specifically asked why the industry is not moving faster towards more sustainable ways of working, for which they provided multiple answers. Three very popular answers were consumers' low willingness to pay premium prices for sustainable products, lack of technological innovations, and lack of an economically viable business case. New and innovative process concepts are therefore needed in order to provide consumers with affordable low-emission textiles in the future.

Textile fibres can be divided into two main groups: natural and man-made fibres. Natural fibres are harvested from animals or plants and can immediately be spun into yarn. Man-made fibres on the other hand have to be refined before they can be spun into threads. Man-made fibres can be produced in many ways and are therefore further categorised into synthetic and semi-synthetic fibres. Synthetic fibres, such as Nylon, are purely made from chemicals and are not plant or animal based. Semi-synthetic fibres, such as Rayon, are in general made from material consisting of long polymer chains. All semi-synthetic fibres are chemically modified, and some of them are also partially degraded in the process. A few semi-synthetic fibres can further be categorised as regenerated fibres, which refer to fibres explicitly made from biomaterials. Both Rayon and Lyocell fibres belong to this subgroup as they are made from pulp. Regenerated fibres are generally produced by dissolving the raw material in a liquid solvent to obtain a homogenous mixture, which then is extruded into strings. The strings are directly pulled into a bath that contains an anti-solvent (often water), which will extract the solvent out of the string and let the fibre mixture regenerate into a solid shape.

The negative aspect of some regenerated fibres is the formation of unwanted chemical derivatives. This is the case for both the Viscose and the Cuprammonium method as they both form by-products while trying to produce Rayon. Production of Lyocell fibres does not result in derivative compounds but the solvent used for dissolving pulp, N-methylmorpholine N-oxide (NMMO), is in general prone to degradation at non-ideal process conditions. The Lyocell process is despite this still considered the greenest alternative for producing man-made fibres.

The process for producing Lyocell fibres was developed by Lenzing AG in the 1980s due to a market demand for cheaper and more environmental-friendly cellulosic fibres. Lyocell was originally a trademark but has later become a generic name for all regenerated fibres produced by direct dissolution with organic solvents. The amine oxide NMMO has long been the go-to choice but an alternative to this has always been desired. The search for an alternative escalated greatly when the lignocellulose dissolving capabilities of some ionic liquids were discovered. This later led to the development of a novel process concept for ionic liquids, called Ioncell, developed at Aalto University and University of Helsinki. Regenerated fibres have not yet been produced commercially according to the Ioncell concept, as it has only been tested at lab-scale. Fibres produced according to the Ioncell concept are still considered as generic Lyocell fibres.

The economic feasibility of the Lyocell process relies very heavily on an efficient recovery of the solvent NMMO, for which filtration, ion exchange and evaporation are established key technologies. However, a general study on the recovery of solvent in the Lyocell process does not exist, and the goal of this thesis is therefore to increase understanding in this area. In addition, new potential solvents such as ionic liquids might require other recovery concepts than what is used for the NMMO-based Lyocell process. An essential part of this thesis is therefore to map out and evaluate existing solvent recovery concepts, as well as new potential alternatives. A simulation model is created to obtain mass and energy balances for five chosen solvent recovery concepts.

The benefit of a simulation model is that the resulting mass and energy balances can provide comprehensive information about the process as a whole. However, one small challenge with modelling the Lyocell process is the lack of validation data. The results presented in this thesis are therefore hypothetical as there is no in-depth reference data. The literature review in Chapter 2 provides a background to the process as a whole, while Chapter 3 focuses on methodology. The results are presented in Chapter 4 and discussed in Chapter 5. The model is created by using the steady-state simulation program Balas®, developed by VTT Technical Research Centre of Finland Ltd.

2 Literature review

2.1 Wood and pulp fundamentals

Pulp is a fibre-based material derived from chemically and/or physically broken down lignocellulosic material, typically wood. It is most commonly known as raw material for papermaking, but it is a very versatile material that is used in many applications besides paper. Pulp is generally formed by 3 main constituents, cellulose, hemicellulose, and lignin. Small residues of ash-forming elements and extractives are also normally found. The individual mass fractions usually vary depending wood type and selected refining process. Pulp can for example be produced by the Kraft method, which results in a high hemicellulose content. Kraft pulp is commonly used in papermaking but can also be further refined into dissolving pulp. Dissolving pulp has a hemicellulose content below 5% combined with a cellulose content over 90% and is used as raw material in the Lyocell process. The topic of wood and pulp is widely covered in area-specific literature (Sjöström, 1993; Biermann, 1996; Wertz, Mercier and Bédué, 2010; Gullichsen and Fogelbolm, 2011).

2.1.1 Cellulose

Cellulose is usually the most desired component in pulp production and constitutes for approximately 40-45% of the dry mass fraction in wood. Cellulose is a linear homopolymer chain of β -D-glucose units linked together by β -(1 \rightarrow 4)-linkages. An illustration of the molecular structure can be seen in Figure 2-1 (Sjöström, 1993). The number of β -D-glucose units determine the degree of polymerisation (DP) and can reach up to 10,000 in unprocessed wood. Cellulose can reach that high crystal structures because of their tendency to form intra- and intermolecular hydrogen bonds. Cellulose in unprocessed wood is known as cellulose I, which can be either I_a or I_β depending on the structure. Cellulose I is known as the natural form of cellulose and is one of four types (I to IV). The cellulose types vary in DP and molecular bonds but still consist of the same D-glucose monomers. Cellulose I possess the highest DP and cellulose IV the lowest.



Figure 2-1. Molecular structure of cellulose. Reproduced from Sjöström (1993).

2.1.2 Hemicellulose

Hemicelluloses is a class of heterogeneous polysaccharides usually formed by a group of five (xylose, arabinose) and six-carbon sugars (mannose, galactose, glucose). Hemicelluloses can in some cases also contain small amounts of uronic acids. Hemicelluloses generally have a DP of 100-200 and are due to this easier to dissolve and have a lower thermal stability than cellulose. Some hemicelluloses are even partly or entirely soluble in water, while others require an alkaline solution. Solubility for the major hemicellulose components can be found in Table 2-1 (Sjöström, 1993).

Table 2-1. Major hemicellulose components. Reproduced from Sjöström (1993)

		Amount	Composition				
Hemicellulose type	Occurrence	(% of wood)	Units	Molar ratios	Linkage	Solubility ^a	DP,
Galactoglucomannan	Softwood	5 -8	β-D-Manp	3	$1 \rightarrow 4$	Alkali, water*	100
_			β-D-Glcp	1	$1 \rightarrow 4$		
			a-D-Galp	1	1→6		
			Acetyl	1			
(Galacto)glucomannan	Softwood	10-15	β-D-Manp	4	$1 \rightarrow 4$	Alkaline borate	100
			β-D-Glcp	1	$1 \rightarrow 4$		
			α-D-Galp	0.1	$1 \rightarrow 6$		
			Acetyl	1			
Arabinoglucuronoxylan	Softwood	7-10	β-D-Xylp	10	$1 \rightarrow 4$	Alkali,	100
			4-O-Me-α-D-GlcpA	2	$1 \rightarrow 2$	dimethylsulfoxid	e*,
			α-L-Araf	1.3	$1 \rightarrow 3$	water*	
Arabinogalactan	Larch wood	5-35	β-D-Galp	6	$1 \rightarrow 3$,	Water	200
-					$1 \rightarrow 6$		
			α-L-Araf	2/3	$1 \rightarrow 6$		
			β-L-Arap	1/3	$1 \rightarrow 3$		
			β-D-GlcpA	Little	1 → 6		
Glucuronoxylan	Hardwood	15-30	β-D-Xylp	10	$1 \rightarrow 4$	Alkali,	200
			4-O-Me-α-D-GlcpA	1	$1 \rightarrow 2$	dimethylsulfoxid	e*
			Acetyl	7			
Glucomannan	Hardwood	2 -5	β-D-Manp	1 –2	1 → 4	Alkaline borate	200
			β-D-Glcp	1	$1 \rightarrow 4$		

^a The asterisk represents a partial solubility.

The hemicellulose content of wood typically contributes 20-30% to the dry mass fraction. As seen in Table 2-1 galactoglucomannan is the dominant component in softwood, and it is generally accompanied by small amounts of arabinoglucuronoxylan

and arabinogalactan. Hardwood on the other hand contains glucuronoxylan and glucomannan, where glucuronoxylan is dominant. Other forms of polysaccharides might also appear for both soft and hardwood, but they are very low in quantity and usually have a low DP.

2.1.3 Lignin

Unlike cellulose and hemicelluloses, lignin is not a carbohydrate but an amorphous polymer with an irregular chemical structure. Lignin consists of three building blocks: p-Coumaryl, Coniferyl and Sinapyl, which can be linked in many various ways. Their molecular structure can be seen in Figure 2-2 (Biermann, 1996). Softwoods dominantly contain coniferyl (>90%) together with some sinapyl (<10%), hardwoods also contain both coniferyl and sinapyl but with a more balanced ratio (50/50). Polymerisation of the phenylpropane units is a result of bonds formed between free radicals, usually via C₆ and C₃ precursors. The bonds formed between the elements are either ether linkages (C-O-C) or carbon-carbon (C-C) bonds. The ether linkages are more common and contribute to more than two-thirds of the bonds formed in lignin polymers. Lignin content differs depending on the wood type but is generally about 20-25% for hardwoods and 25-30% for softwoods. The main task for lignin is to act as a binder of fibres in the wood, like a glue between the wood cells for more rigidity.



Figure 2-2. Lignin monomers. Reproduced from Biermann (1996)

2.1.4 Extractives

Extractives are a broad collection of substances with low molar masses, such as fatty acids, fatty alcohols, ethers, esters and aromatics. The primary function of extractives is to help provide nutrition and to protect the wood from degradation and microbiological attacks. Extractives vary in composition from species to species but usually contribute with 1-5% of the dry wood content. Extractives are usually soluble in neutral organic solvents or water.

2.1.5 Ash-forming elements

Ash-forming matter is a composition of inorganic component that usually constitutes between 0.2 and 5% to the mass fraction of trees when taking into account bark, needles and leaves. However, it rarely exceeds 1% for pure wood. Inorganics usually appear as metal salts or ions that are bound to cellulose chains. Inorganics are generally not desired in the pulping process because they might cause corrosion and speed up the degradation of pulp carbohydrates. The majority of inorganics are therefore usually removed from the pulp before key steps in the refining process. Inorganics are usually removed by using either an aqueous acid or chelating agent. Approximate concentration levels of inorganic elements in dry stem wood can be found in Table 2-2 (Gullichsen and Fogelbolm, 2011).

Range, ppm	Elements
400-1000	K, Ca
100-400	Mg, P
10-100	F, Na, Si, S, Mn, Fe, Zn, Ba
1-10	B, Al, Ti, Cu, Ge, Se, Rb, Sr, Y, Nb, Ru, Pd, Cd, Te, Pt
0.1-1	Cr, Ni, Br, Rh, Ag, Sn, Cs, Ta, Os
< 0.1	Li, Sc, V, Co, Ga, As, Zr, Mo, In, I, Hf, W, Re, Ir, Au, Hg, Pb,
	Bi, Sb

Table 2-2. Approximate concentration levels of various elements in dry stem wood of softwoods and hardwoods

2.2 Solubility of pulp

Solubility of lignocellulose has been thoroughly studied since the start of this millennia and is an important aspect for production of Lyocell fibres. Extensive research has therefore been carried out by many researchers in this area (Rosenau *et al.*, 2002; Mäki-Arvela *et al.*, 2010; Hauru *et al.*, 2012). The aim for dissolving pulp when producing textile fibres is generally to obtain a homogenous mixture that later can be extruded and regenerated into fibre strings. An additional benefit that comes from regeneration of pulp is that the chemical structure switches from cellulose I to the more beneficial cellulose II. Both cellulose types are linked by hydrogen bonds horizontally, but only cellulose II is vertically linked. The vertical linkages give cellulose II a stronger structure and higher tensile strength, making it more beneficial for textile fibres than cellulose I. Horizontal intermolecular hydrogen bonds can be observed in Figure 2-3 (Festucci-Buselli, Otoni and Joshi, 2007).



Figure 2-3. Cellulose molecular structure with inter (dashed lines) and intramolecular (dotted lines) hydrogen bonds. Reproduced from Festucci-Buselli, Otoni and Joshi (2007).

Cellulose is dissolved by either breaking apart the D-glucose units from the polymer chains or separating the chain from other chains. The former is merely used to reduce the DP of the polymer, which will also lower the pulp viscosity. The chains can be separated by splitting the intermolecular hydrogen bonds between the chains by introducing a solvent. All hydroxyl groups that formed intermolecular bonds will instead bond with solvent molecules, thus releasing the chains from one another. The chains are regenerated by exposing the solvent/cellulose-mixture to an anti-solvent. The solvent will then leave the cellulose chains and start to interact with the anti-solvent. The cellulose chains can then re-create the intermolecular bonds and form a cellulose II structure. A desired solvent characteristic is therefore strong hydrophilicity, as it makes the solvent more reluctant to bond with water over cellulose. The anti-solvent is in most cases water, but the same concepts apply if the anti-solvent is an alkaline or organic solution.

Solvents used for dissolution of cellulose can be divided into two classes: derivatising or non-derivatising. By using derivatising solvents, unstable chemical compounds will be formed as a result of the dissolution process as opposed to non-derivatising solvents. The absence of by-product formation is what makes the non-derivatising solvents considered as green solvents. Nevertheless, by-products can be formed at non-ideal process conditions due to elevated temperatures or high inorganic content. Dissolution by using non-derivatising solvents is generally called direct dissolution. The solvents types presented in Chapter 2.2.1 and 2.2.2 are both classed as non-derivatising. Derivatising solvents are commonly used in the Viscose and the Cuprammonium process, while non-derivatising solvents are used in the Lyocell process.

2.2.1 NMMO

4-methylmorpholine-4-oxide (NMMO) is an oxidant organic compound that is known for its ability to very efficiently dissolve lignocellulose. NMMO appears in three natural forms: anhydrous NMMO, monohydrate NMMO- $1 \cdot H_2O$ and NMMO- $2.5 \cdot H_2O$. In 1979, Chanzy, Dubé and Marchessault discovered that NMMO- $1 \cdot H_2O$ could act as a solvent for cellulose, the mixture was also found to crystallise after being cooled. Furthermore, they found that cellulose retained the same specific morphology of the solution after the solvent was removed. It was also concluded that anhydrous NMMO formed cellular textures and monohydrate NMMO spherulites. Navard and Haudin (1981) determined the melting points of the three NMMO types to 182.4°C, 75.6°C and 40.5 °C. In 1982, Chanzy *et al.* found that crystalline structures of with anhydrous NMMO were most likely to dominate in solutions with less than 13.3% mass fraction water (Wertz, Mercier and Bédué, 2010). Likewise, it was found that solutions with water content at 13.3-24% would be dominated by monohydrate NMMO crystals. Solutions over 24% would consist of a combination of monohydrate and NMMO-2.5·H₂O.

In order to obtain highly oriented cellulose structures, it is therefore desirable to form a solution dominated by anhydrous NMMO crystals. In 2002, Biganska, Navard and Bédué found that a general crystallisation of NMMO/Cellulose/water-solutions depended on the crystallisation of NMMO, not of cellulose. The study found that the regenerated cellulose, which had been exposed to excess water, showed a higher oriented structure for solutions with lower water concentration. Anhydrous NMMO would therefore seem to be the most beneficial version of NMMO for dissolving NMMO. However, due to the high melting point, it is too prone to by-product formation to be industrially feasible. Due to this, the more stable monohydrate is generally used for dissolving cellulose. A proposed dissolution mechanism of cellulose in NMMO can be observed in Figure 2-4 (Pinkert, Marsh and Pang, 2010).



Figure 2-4. Proposed dissolution mechanism of cellulose in NMMO. Reproduced from Pinkert, Marsh and Pang (2010).

Degradation of NMMO is unavoidable but can be minimised by controlling temperature and adding stabilisers. An extensive study on NMMO degradation has been published by Rosenau *et al.* in 2001, which covers all known reaction paths. The most common degradation products of NMMO are N-methylmorpholine (NMM) and morpholine (M). Degradation is generally sped up after reaching 120°C and becomes uncontrollable after 150°C. Degradation products can be toxic and dangerous, as well as cause discolouration and affect fibre quality. Iron and copper ions in particular, but also metal ions in general, have been reported to have a significant impact on NMMO degradation (Rosenau *et al.*, 2001; White, 2001). Lignin might also to some extent support degradation due to its hydroxyl groups, which can lead to formation of toxic formaldehyde.

2.2.2 Ionic liquids

A general definition of ionic liquids (IL) is a mixture containing (almost) exclusively ions, but it is limited to mixtures with a melting point below 100°C. The liquids are specifically considered room temperature ionic liquids when they can stay liquid below 25°C. Because it only takes two compounds to form an ionic liquid, the number of possible configurations is very large. There are no general classifications or names for dividing IL types into larger groups based on purpose or special characteristics. The chemical name of the anion or the cation is therefore mostly used when describing the type of liquid. An advantage with the great versatility and endless configurations is that it provides a possibility to design task-specific ionic liquids. ILs used for dissolution of lignocellulosic material are examples of this.

Mäki-Arvela *et al.* carried out an extensive study on this specific type of IL in 2010, for which the aim was to specifically investigate the correlation of multiple IL properties on their dissolution capacity. They found that relatively small cations typically are more efficient in dissolving cellulose than bigger cations, with the same applying for anions. The cation also has to be polarising and capable of effectively targeting the cellulose hydroxyl groups. Furthermore, they also noted that the presence of functional groups could have a crucial impact on solubility. Solubility would evidently decrease if the cations were equipped with a hydroxyl end-group of their own.

Ionic liquids typically possess very low vapour pressure and low flammability, which results in a low tendency to form gaseous by-products. It is due to this high chemical stability that they are generally considered as a greener alternative to NMMO. However, when degradation does happen, it is most likely to occur when the liquids are exposed to high temperatures or inorganic compounds. Other negative aspects are usually linked to potential toxicity, corrosivity and price. These things can often be minimised by carefully choosing process parameters, mixture of ions and equipment material.

Phase diagrams and specific composition of IL/cellulose/water-solutions are individual, but experiments have shown that ILs can dissolve cellulose in solutions of up to 25 wt.-% of cellulose (Swatloski *et al.*, 2002). However, solutions closer to 10 wt.-% cellulose are generally more common. The amount of water in the solution has a significant impact on the ILs ability to dissolve cellulose, and especially if the IL is hydrophilic. An advantage with hydrophilic solvents is that they are easier to separate from the regenerated fibre in a later stage as they prefer to bond with water over cellulose. This naturally also comes with the disadvantage that very hydrophilic ILs are more difficult to separate from water. A proposed dissolution mechanism of cellulose in an IL is illustrated in Figure 2-5 (Pinkert, Marsh and Pang, 2010).



Figure 2-5. Proposed dissolution mechanism of cellulose in IL. The anion bonds with a hydrogen ion and the cation bonds with a cellulose chain. Reproduced from Pinkert, Marsh and Pang (2010).

2.3 Lyocell process description

The Lyocell process has been in industrial use since the 1980s and was developed by Lenzing AG, one of the biggest producers of regenerated cellulosic fibre in the world. The commercial name of their Lyocell fibres is Tencel, which can be compared to the trademarked Ioncell. Both products are Lyocell fibres, but Ioncell is based on a slightly modified process concept. Ioncell fibres are also yet to be produced commercially, but studies have been published about fibre properties and manufacturing process (Stepan *et al.*, 2016; Hauru, 2017). The Ioncell concept uses the ionic liquid [DBNH][OAc] for direct-dissolution of cellulose instead of NMMO. A benefit is that this ionic liquid can operate at lower temperatures than NMMO, due to a different thermodynamic profile.

General process data for the NMMO-based process can be found in publicly available literature. According to Lenzing, 46 litres water is used to produce one kilogram of Tencel fibre, covering cradle to production gate (Lenzing Group, 2018). The corresponding water demand for cradle to produced dissolving pulp in Lenzing's pulp mill was reported to be 38 litres/kg (Suhr *et al.*, 2015). The actual production of Tencel fibres from dissolving pulp can therefore be assumed to require 8 litres of water. Furthermore, a life-cycle analysis by Roos (2012) claims that the Lyocell process used by Lenzing has a primary energy demand of 47.6 MJ/kg produced fibre. The general NMMO-Lyocell process is illustrated in Figure 2-6 (reproduced from Lenzing Aktiengesellschaft (2019)) and the Ioncell concept in Figure 2-7.

The difference between the concepts is mostly connected to the raw material used. The Lyocell process is limited to the use of dissolving pulp as raw material, while the Ioncell can use pulp mixtures with higher DP, such as paper grade pulp or recycled paper. The Ioncell process is equipped with a pre-treatment and fractionation step, making it possible to adjust the paper grade pulp to dissolving pulp quality. This might result in the product not necessarily being that much different than for the Lyocell process. It is more a question of process definition as the dissolving pulp used in the Lyocell process is already adjusted to a certain quality. In contrast to the Ioncell concept, where it is included in the process configuration. Common predominating

methods for producing dissolving pulp are pre-hydrolysis Kraft and acid sulphite pulping, which both result in noticeable cellulose yield losses in comparison to the Ioncell concept (Roselli *et al.*, 2014). Ioncell pulp pre-treatment is thoroughly described in papers by Froschauer *et al.*, (2013) and Roselli *et al.*, (2014).



Figure 2-6. Illustration of Lenzing AG's Lyocell fibre production process. Reproduced from Lenzing Aktiengesellschaft (2019)



Figure 2-7. Ioncell process concept. Illustrated according to Stepan et al. (2016).

Besides the difference in raw material, both processes consist of what could be called a fibre line. The fibre line starts with a mixture step where pulp and solvent are formed into a highly viscous mixture called dope by direct dissolution. This is followed by dry-jet wet spinning where the dope is extruded through an air gap into a water bath. The dope is immediately regenerated into fibres when it makes contact with the water and is directly drawn into another bath. The regenerated fibre is then drawn through a long washing stage, where the solvent is washed off by counter-current water flow. The wet fibre can be further processed according to end-usage.

The use of unadjusted paper grade pulp in the Lyocell process has earlier been discussed by Rosenau *et al.* (2001), where it was considered to be theoretically possible but problems with spinnability might occur. Spinnability refers to the ability of the formed mixture to be extruded and drawn into long strings. The influence of hemicellulose on spinnability was later studied by Zhang and Tong (2007). They concluded that the polysaccharides had a positive impact on fibrillation resistance, mechanical properties and overall production speed of Lyocell fibres. They further suggested that this might imply that hemicellulose would act as a plasticiser in the solution, i.e. give the solution a lower viscosity without any addition of enzymes or acids. The use of pulp with high hemicellulose content also results in less production losses, as excess hemicellulose no longer is removed to obtain dissolving pulp.

2.3.1 Pre-treatment, pre-mix and dissolution

Pre-treatment is a required process step for the Ioncell concept in order to obtain a mixture equal to dissolving pulp, and is thoroughly described by Froschauer *et al.* (2013) and Roselli *et al.* (2014, 2016). The big difference between the high DP paper grade pulp and dissolving pulp is the viscosity and cellulose content. Pre-treatment in the Ioncell concept lowers the viscosity of the pulp by addition of enzyme and acid. Enzymes will target hemicelluloses for fractionation before the acid is introduced to reduce DP by hydrolysis. This combination can change the intrinsic viscosity from about 800-900 to ideally 400-500 mL/g. Viscosity and DP adjustment are critical as they strongly affect rheological properties and spinnability.

The addition of acid will not only affect the viscosity, but also the amount of metal ions that are bound to the pulp (Su *et al.*, 2010). By exposing pulp to strong acids, the chemical bonds between the metal ions and the pulp will break. Thus resulting in an increased concentration of free ions in the system. The efficiency of metal removal can be further increased by addition of chelating agents (Räsänen, 2003; Su *et al.*, 2010). Both enzyme and acid treatment take place in kneaders, i.e. a type of mixing devices. Both treatments also end with enzyme and acid being washed off and use filters to separate pulp and chemicals before entering the pre-mix step.

The pre-treatment is followed by a pre-mix, which is mutual for both the Lyocell baseline process and the Ioncell concept. The pre-mix aims to homogenise the pulp/solvent/water-mixture into a slurry before the pulp can be dissolved. Homogenisation takes place in a kneader (see Figure 2-8), which enables ideal mixing by shredding the pulp. Pre-mix is the first step of the NMMO-based process where dissolving pulp is mixed with a 76-78% aqueous amine oxide solution at 70-90 °C (White, 2001). The pulp will not be able to dissolve at this stage as there is excess water present and the temperature is too low. The Ioncell concept is almost identical to the NMMO-based process, apart from the temperature being 60 °C and the pulp being mixed with an 85% IL/water-mixture.



Figure 2-8 Illustration of a kneader, used for both premix and dissolution. Reproduced from Lewin and Pearce (1998).

The Ioncell pre-mix step ends with removal of hemicellulose, IL and water by using filtration, through which a pulp standard equal to dissolving pulp is obtained. Roselli *et al.* (2016) reported a hemicellulose contents of 0.9-2.4% for the modified pulp (depending on wood and hemicellulose type) by using this method. However, even though that both the baseline Lyocell process and the Ioncell concept uses dissolving pulp, the dissolution step slightly differs between the two concepts.

When the NMMO/pulp solution is mixed to a homogenous slurry, it enters an evaporator. The evaporator is set at 90-120 °C and vacuum pressure, which enables efficient evaporation of water.



Product discharge

Figure 2-9 Thin-wall evaporator used for cellulose dissolution. Reproduced from White (2001)

Evaporation of excess water is needed as dissolution will not occur until a feasible composition of pulp, solvent and water is reached. Excess water is removed because the solvent prefers to bond with hydrogens in water rather than hydroxyl groups in cellulose. By reducing the amount of water, the solvent will be forced to start bonding with hydroxyl groups in cellulose. After slowly diffusing into amorphous regions of the polymer structure and making the fibres swell, the solvent can now begin to dissolve the pulp completely. The solvent will gradually continue to dis-integrate crystalline regions near the amorphous cellulose regions by continuously breaking intermolecular hydrogen bonds. This will then result in a fully dissolved and homogenous solution.

Dissolution of pulp in the Ioncell concept needs no evaporation because the water content in the pulp exiting the pre-mix is already sufficiently low, a kneader is utilised once more. An IL mixture with 13 wt% pulp content was reported to have been used by Stepan *et al.* (2016), with kneader parameters at 80 °C and 50 mbar.

2.3.2 Spinning and fibre regeneration

The transformation of dope into regenerated fibres takes place in the spinning step of the process. The highly viscous solution is pumped through a jet consisting of multiple tiny holes, forming strings of the solution. The strings are drawn directly into a water bath where they are regenerated into gelatinous filaments but are almost immediately pulled up again. If there is a small air gap between the jet and the water, the spinning is called dry-jet wet spinning. If there is no air gap, it is called wet spinning. The former is used in both the NMMO-based Lyocell process and the Ioncell concept; the latter is used in the viscose process.

Dry-jet wet spinning provides the fibres with improved strength and elongation properties compared to wet spinning, which enables improved spinnability. The choice of air gap, draw ratio, and anti-solvent temperature plays a key role for the properties of the produced fibres. The draw ratio is determined by the difference in speed of the polymer solution entering and leaving the bath. The speed is increased to lengthen the fibres and straighten their structure as much as possible.



Figure 2-10 Schematic illustration of dry-jet wet spinning. Reproduced from Liu *et al.* (2017).

The regeneration starts immediately when the dope touches the water. Because the solvent is very hydrophilic, it will prefer bonding with water over cellulose. When the solvent is gone, cellulose chains will regenerate intermolecular bonds and form a cellulose II structure. The temperature of the water is typically much colder than the solution, as it helps the regeneration (White, 2001). A study by Hauru *et al.* (2014) shows that a temperature of 15-25° for the water is suitable.

Compound losses in the regeneration step have been studied by Ma *et al.* (2016) and it was found that only small amounts of hemicellulose and lignin are lost. Loss of cellulose was not explicitly mentioned, but the composition of cellulose, hemicellulose and lignin in the regenerated fibre was stated to be very close to the pulp composition before dissolution. This would indicate small or minimal losses of cellulose, which is supported by similar observations from Zhang *et al.* (2009).

2.3.3 Washing

After the fibres are regenerated, the remaining solvent is removed by washing the fibres. Washing is generally done by towing the fibres through a series of wash baths with a counter-current flow of water. The water exits the bath where the fibres enter and is then used in the coagulation bath before being sent to water treatment and solvent recovery. Water is used because it works as an anti-solvent for NMMO and

hydrophilic ILs. This means that it can attract NMMO or a hydrophilic IL by providing free hydrogen ions to bond with, which in return will free the cellulose chains. However, a pre-requisite for removing solvents is diffusion of anti-solvent into the towed fibre. It is only then that the solvent can diffuse out of the fibre, by bonding with the free protons provided by the anti-solvent.

The interaction between solvent and water plays a vital role when studying diffusion through the fibre. A study by Hauru *et al.* (2016) found that the diffusion of solvent on the way out of the fibre generally is slower than the diffusion of water into the fibre. They could therefore conclude that the efficiency of the washing step is heavily timedependent. Washing efficiency can be optimised by keeping the concentration of solvent in the water at a low level. A significant counter-flow of freshwater into the baths is also essential to negate the accumulation of impurities in the bath, and not just to keep a low solvent concentration. Impurities are not desired as they can affect the quality of the fibre, by for example discolouration.

2.3.4 Drying and finishing

When the fibre is washed from impurities, it can be modified according to end-usage. The fibres are always dried after being washed, but can also be combined with stapling, bleaching, dyeing or chemical treatment. Chemical treatment is generally applied to alter the material characteristics such as softness or fibre fibrillation. Fibres produced with NMMO are generally prone to fibrillation. Stapling can be done either before or after the fibres are dried, the same perforated drum dryer technology can be used in both cases. The dryers operate by sucking dry hot air through the holes of the perforated cylinders and thereby also absorb excess water from the fibres. An illustration of a drum dryer can be seen in Figure 2-11 (Tsotsas, Gnielinski and Schlünder, 2000). Lyocell fibres have a natural moisture content of 11.5% in normal air conditions and a water retention ability of 70% (Werz *et al.*, 2001).



Figure 2-11 End (A) and side view (B) of a perforated drum dryer. a) loading conveyor; b) Perforated drum; c) Cover plates; d) Fan; e) Heaters; f) Air distributor. Reproduced from Tsotsas, Gnielinski and Schlünder (2000).

2.3.5 Solvent recovery methods

Efficient purification and recovery of the solvent is necessary to achieve a high-quality fibre and economic feasibility. The process water exiting the regeneration bath will need a versatile combination of separation technologies as the water contains lignin, inorganics, solvent and small amounts of non-regenerated pulp. As in most cases at an industrial scale, it is very hard to achieve a full recovery and 100% purity of chemicals. This also applies to the Lyocell process, where the accumulation of impurities in the process loops might affect fibre quality or trigger by-product formation. The amount of impurities is not necessarily large after one process cycle, but as the solvent is recovered and re-used, accumulation of impurities will occur. However, an efficiency below 100% can be acceptable, as long as the amount of specific impurities can be maintained at a level where the effect of them is dismissible. Metal ions were mentioned in Chapter 2.2.1 to have a negative impact on NMMO and are therefore of high priority in this step.

Lenzing AG claims to have a solvent recovery rate of over 99% but does not mention whether the value is based on the amount of solvent used in the dissolution stage or the amount of solvent exiting the washing stage for re-circulation. Thus not specifying if there are small solvent losses to the produced fibre. Potential losses of NMMO overall in the process are most likely degradation and formation of by-products. Technologies that are used for purifying process water streams are usually evaluated based on their ability to remove total suspended solids (TSS) and total dissolved solids (TDS). This can also be applied for the Lyocell process as both organic and inorganic impurities can be defined as either TSS or TDS. TDS are generally defined as compounds that are small enough to be filtered through a pore size of 2 micrometer. Larger compounds are defined as suspended solids. Cellulose, hemicellulose and lignin can vary in degree of polymerization and polymer size, which means that they can be defined as both TSS and TDS depending on their specific characteristics.

The general Lyocell process solvent recovery consists of two main steps: ion exchange and evaporation. Additional separation technologies can be used to obtain a higher purity rate and lower the load for both ion exchange and evaporation. Some types of resin beds can only tolerate low amounts of suspended solids, meaning that a solid/liquid-separation unit would be beneficial for equipment durability. Flotation and filtration are two basic separation technologies that easily can be combined with the existing concept. The latter is used by Lenzing AG, and the former is commonly used in the viscose process. The Ioncell concept appear to only be using ion exchange and evaporation based on the potential IL-recycling loops exhibited by Stepan *et al.* (2016). From a conceptual point of view, liquid/liquid-extraction could also be a feasible alternative for solvent recovery. The technology is widely used across many industries and will be considered in the applied part of this thesis when comparing process concept alternatives.

All technologies mentioned are described in a public research report by Sorsamäki and Nappa (2015), and additional information on ion exchange is also taken from Harland (1994).

2.3.5.1 Flotation

Flotation can be used to remove suspended solids, free ions and colour from the water. Flotation units are separation technologies based on gravitation, where the lightest compounds can be targeted by separating the surface water. Flotation units can either be based on dissolved air or electrolytic technique. Dissolved air flotation units have air bubbles dispersed from underneath, and their role is to attach on to suspended solids and bring them up towards the surface. The unwanted concentrate, clustered on the water surface, will flow over the edge of the cistern and can be discharged for further treatment. Flotation might require chemical additives such as flocculants or coagulants to work efficiently.

Coagulants are added to neutralise charged solids, as the solids would otherwise repel others of the same charge. The coagulants create a complex of the solid particles were the charged particles are surrounded by the opposite charge than they themselves possess. Thus meaning that the complex is charged, but the particles captured are neutralised. Flocculants are then added, and they possess the opposite charge of the complex. Flocculants can be considered long polymers that can gather all particle complexes formed into a bigger complex. The big complex formed is then easier to separate from the flow. It is worth mentioning that ions are not suspended solids, but dissolved solids.

Electroflotation relies on the same working principle as the dissolved air flotation. However, the bubbles are generated by hydrolysis of water by using electricity caused by an anode and a cathode. The hydrolysis can generate small bubbles filled with oxygen and hydrogen that are about 0.1% the size of the bubbles in the dissolved air flotation. A higher amount of bubbles with smaller sizes generally increases the probability of colliding with a particle.

Flotation is mostly used in the metallurgy industry but can also be utilised for general solid/liquid-separation processes. Flotation can be a suitable technology to use in the Lyocell process because aqueous NMMO and IL systems have a higher density than water alone, meaning that excess water in steady-state would reside in an own phase above the aqueous solvent system. The excess water would also contain suspended solids, as air bubbles would lift them towards the surface. A study by Managó, Vidal and Souza (2016) use process water from the pulp and paper industry to study the effect of a dissolved air flotation unit on chemical oxygen demand, total suspended solids and turbidity. Reported removal rates of total suspended solids varied between 92.9 and 99%, depending on what the water had been used for. COD was reported to decrease by 48% as a result of the flotation.

Flotation can also be used for targeting specific ions. However, it will result in other ions residing in the solution instead. This selectivity often requires adjustment of pH, and the optimum level depends on the ion type. Féris *et al.* (2000) studied separation of the iron complex Fe(OH)₃, where NaOH was used to adjust pH. The result in this case was that sodium became a free ion, while the Fe could form a complex with the OH-group. The study reported recovery rates of up to 96.5% for the complex Fe(OH)₃, without using extra additives. However, it had to operate at a saturation pressure of 3 atm. The pressure could only be reduced if surfactants were included in the process.

Key design parameters for a flotation unit include area, depth, rising speed of air bubbles, rising speed of compounds, and air-to-solids ratio.

2.3.5.2 Filtration

Membrane technologies are very common in water treatment processes due to wide alternatives of pore sizes and overall applicability. Typical pore sizes range from less than 1 nm in reverse osmosis to 10 μ m in microfiltration. The gap between reverse osmosis and microfiltration is covered by ultra and nanofiltration. Membrane efficiency is usually described by the molecular weight cut-off value. The cut-off value is used because it more clearly describes what compounds can pass through the pores, and what compounds that are stopped. The molecular weight generally correlates with the pore size, but it is not always completely precise. Two molecules with equal molecular weight can still slightly differ in physical size, which is usually due to their chemical structure.

Table 2-3 General pore size and operating pressure per membrane type

	Pore size	Operating pressure
Microfiltration	>100 nm	<2 bar
Ultrafiltration	1-100 nm	1-10 bar
Nanofiltration	~1 nm	3-40 bar
Reverse osmosis	<1 nm	10-100 bar

The use of ultrafiltration has been tested on flows containing organic compounds and ions, as well as ionic liquid/water-mixtures (Tavares et al., 2002; Liang, Fu and Chang, 2016). The removal efficiency of ions was reported at 23-29%, although it was discussed that their complexation with organic matter and membrane charge might influence the results (Tavares et al., 2002). Some organic matter is naturally due to its size stopped by the membrane, and an electrically charged membrane can attract free anions and cations to some extent by itself. The tests by Tavares et al. (2002) also showed a significant impact on colour removal, with an efficiency of up to 88.3%. Liang, Fu and Chang (2016) tested two membranes with molecular cut-off values of 0.65 kDa and 1.0 kDa, giving an IL recovery rate of 98.1-97.5% and 96.3-95.8% for the respective membranes. The unit Dalton (Da) is a measure of mass and is equivalent to the average molecular weight of a compound, e.g. 1 g/mole equals 1 Da. It is worth noticing that the ionic liquid used in the study was BmimBr (1-Butyl-3methylimidazolium bromide), which has a molecular weight of about 219 g/mole, i.e. much larger than NMMO monohydrate at 135.16 g/mole. Permeate lignin content varied heavily depending on the IL concentration in the inflow, with 6.1% and 10.4% for 10 g/l, respectively 27% and 62.1% for 100 g/l.

Nanofiltration could also be an option for the Lyocell process as a normal cut-off value is 500 g/mole. NMMO monohydrate would therefore to a large extent be able to penetrate the membrane. The benefit of nanofiltration is that it generally has a very high reject of multivalent ions. Moreover, it has a reject rate of lignin at 78-98% (Weinwurm, Drljo and Friedl, 2015), and it would completely reject cellulose and hemicellulose. The pore size for nanofiltration will probably be too small for a high yield of solvent in the Lyocell process but would give a very pure permeate stream. By combining membranes in series with the retentate stream as a feed for the following stage, a high overall solvent yield might be achieved.

Another interesting possibility is to use flotation and filtration in series, which is what Agarwala, Kanthale and Thakre (2019) conducted a study on. The study aimed to find the optimal type of flocculant for treating spinbath water in a Lyocell process, which also provided information on performance of filtration and ion exchange units. The study found that a combination of flotation and filtration could increase total turbidity

removal from 41% (only filtration) to 94%. Moreover, it was found that the added help of a flotation unit increased the performance of the ion exchange unit by 11%.

2.3.5.3 Ion exchange

The process water in the Lyocell process is concentrated with positively charged metal ions (cations). To target positively charged ions a cation resin bed is used. A cation resin bed already contains positively charged hydrogen ions that easily can be substituted for free cations in the process water. The bed does not have to consist entirely of cations, but can also include resins of opposite charge. A positively charged and a negatively charged bed can of course be used in series if needed, but it is not unusual to have packed beds with positively and negatively charged layers next to each other. The resin can be either strongly charged or weakly charged, depending on the targeted ion and its selectivity. The ion exchange-phenomenon can be described by the following reactions.

$$\begin{aligned} R^-H^+ + A^+ &\rightarrow R^-A^+ + H^+ \\ R^+OH^- + B^- &\rightarrow R^+B^- + OH^- \\ OH^- + H^+ &\leftrightarrow H_2O \end{aligned}$$

Where R^+/R^- represent the charged resin and A^+/B^- the free ions in the solution. The resin bed has a specific operating capacity, which dictates how many free ions it can attract before running out of charge and has to be regenerated. Regeneration is done by backwash, meaning that the bed is washed in counter current to the normal flow. First, the bed is filled with a flow of water, expanding the bed volume by 30-40%, where after an electrolyte solution is injected to react with the collected ions. Positively charged beds are washed with a base solution, to collect the anion captured by the resin and regenerate an OH^- group. Negatively charged resins are washed with acids to remove cations and regenerate hydrogen ions. Potential suspended solids are removed in the same backwash. The resin bed can serve as an absolute filter for incoming solids, but it can have negative effects. Excess amount of stopped solids can lead to clogging of the resin bed. Clogging can lead to a higher pressure drop, a decrease in throughput, and cause channelling. The increased pressure caused by solids in the bed can also lead to resins being destroyed by the force applied.
Industrial ion exchange units can be designed as a column or a tank. The former can be used for continuous processes, while the latter only can be utilised for batch processes. The tank design is non-continuous because the resin is removed and washed when it reaches saturation. The column can be designed either as a fluidised or fixed bed. The latter utilises a downwards flow and acts as a stop for incoming suspended solids. A fluidised bed has an upwards flow that will expand the bed, thus making it easier for solids to enter and possibly exit the bed. A fluidised bed also promotes channelling, which reduces general separation efficiency. A fluidised bed can in general handle a flow with up to hundreds of ppm solids, while suspended solids should be completely avoided for a packed bed (Rousseau, 1987).

The study of pulp components in resin beds is not a widely covered topic and general information of behaviour of TSS and TDS in resin beds is hard to find. However, a study of Wang *et al.* (2016) touched upon the subject of pulp components as they studied the recovery of hemicellulose-derived saccharides by using lime and ion exchange resins. Saccharide losses to the packed resin bed increased when more lime was added, the losses varied between 5% and 25%. The variation was believed to be a direct result of saccharide degradation due to the lime added. This could mean that hemicelluloses can be assumed to behave as dissolved components, as suspended solids in general seem to be stopped by a packed bed.

2.3.5.4 Evaporation

Evaporation is a separation method designed for concentrating non-volatile compounds by vaporisation of volatile components in a liquid-system. Evaporators are usually heated with steam and can operate at a wide range of temperature and pressure conditions. Evaporators are always used in multiple stages if possible, as the pressure and temperature profile can be optimised for a lower overall thermal duty. Lone evaporators are only used if the feed is very low. Steam economy can further be optimised by preheating the feed close to boiling point before entering the evaporator, thus not wasting high energy steam on heating the feed without evaporation occurring. Evaporators can be set in forward or backward feed. Where forward feed is a co-current flow of steam through the stages and backward feed is a counter-current flow.

Evaporators exist in multiple types, but only two types are generally used in the Lyocell process: thin-film and wiped-film evaporator. The thin-film evaporator has a high capacity and is suitable for low viscosity solutions, as it is often designed with multiple long and small vertical tubes where the liquid system flows along the inside wall of the tube. The wiped-film evaporator is often designed as big hollow tubes with rotating blades inside for better distribution and mixture of high viscosity solutions against the walls. The two evaporators work well together, as the mixture viscosity varies according to water content. The wiped-film design is used in the dissolution stage where the viscosity is high, and the thin-film is mainly used in stages with lower viscosity, for example in the solvent recovery step.

2.3.5.5 Liquid/Liquid-Extraction

Liquid/liquid-extraction (LLE) is generally used to extract a solute from a liquid system by introducing the system to another liquid. Thus resulting in a two-phase system in which the solute can migrate from one phase to the other. A pre-requisite for this to work is that the liquids are immiscible, thus are two-phase systems composed of an organic and a water phase widely used. The goal is to influence the system equilibrium by changing pH, temperature and mixture-ratio, thus affecting what phase the solute will prefer to stay in. The extent of the migration is dictated by the system distribution ratio, which describes the relative amount of solvent in the two phases at equilibrium. A general working principle can be seen in Figure 2-12.



Figure 2-12 Working principle of a liquid/liquid-extraction.

There are many alternatives regarding equipment for LLE, as the systems and compounds can have very different requirements or characteristics. Density, throughput, settling characteristics and number of stages required generally influence the possibilities. LLE equipment often takes the shape of a modified column with more or less complex way of working, designed for specific system characteristics. The most general classification of LLE equipment is agitated static columns, pulsed columns and agitated extractors.

The static columns operate by feeding the low-density phase in the bottom below a sieve tray and the high-density phase at the top, and then let the fluids mix by the help of gravity. Due to the tray, the bottom fluid will enter the column as dispersed droplets and thereby increase the efficiency of mass transfer. The pulsed columns have the same working principle, but the column is vertically moved at a specific interval, resulting in more efficient phase mixing. Both column types can vary in filling and inside design. Lastly, the agitated extractors consist of rotating disc columns and mixer-settler, and they are designed to suppress vertical back mixing. Illustrations of the static columns can be seen in Figure 2-13 (Mersmann, Kind and Stichlmair, 2011), as well as rotating disc columns and a mixer settler Figure 2-14 (Mersmann, Kind and Stichlmair, 2011).



Figure 2-13 Static column extractors. Reproduced from Mersmann, Kind and Stichlmair (2011).



Figure 2-14 Rotating disc columns and mixer-settler extractors. Reproduced from Mersmann, Kind and Stichlmair (2011).

LLE can be used for metal extractions and has been studied by Khoutoul *et al.* (2016), where dichloromethane represented the organic phase and metal ions mixed in water the aqueous phase. The results showed that no migration of Fe and Pb-ions from the aqueous to the organic phase would occur if the system pH were below two.

3 Method

3.1 Research objective

The objective of this thesis is to study the resulting accumulation of un-utilised pulp components and inorganic compounds for five distinct solvent recovery concepts in a Lyocell production process. A realistic model of the NMMO-based Lyocell process is therefore created to obtain mass and energy balances for the process. The resulting mass and energy balances are also used to determine the technical requirements for each solvent recovery concept. The concepts are compared based on general process complexity, solvent purity and thermal duty. Complexity is based on the number of process steps and design parameters, as well as dependence on chemicals. The model is created by using the steady-state simulation software Balas®.

3.2 Overall approach

The study follows a traditional case study-type analysis with the following steps:

- 1. Definition of concepts
- 2. Data gathering
- 3. Simulation model development and validation
- 4. Simulation of selected concepts
- 5. Sensitivity analysis

The solvent recovery rate is a key process variable from economic and environmental perspectives. The recovery rate is fixed to 99% for all simulated concepts. This enables a qualitative comparison between the concepts, as all process combinations have to achieve the same result. The new concepts (later referred to as Concept 1, 2, 4, and 5) are hypothetical as no actual process exist with these recovery configurations. Therefore the results cannot be validated with real data. The concept representing the industrially known NMMO configuration (later referred to as Concept 3) is used as fixing point for water and energy consumption of the plant. This enables the

comparison of new potential concepts with the industrial NMMO concept. The net demand for water (8 litre/kg fibre) and energy (47.6 MJ/kg fibre) published by Lenzing AG are used as design values for the industrial NMMO concept (Concept 3).

The solvent recovery step is modelled as a superstructure with four steps, where each step provides certain technologies to use. This enables great versatility as the technologies can be combined in many ways. Every step also has a bypass-option, which means that the technologies in that step do not have to be used in every concept. The superstructure could be subjected to optimization to obtain the most economical or overall best performing combination, but this is not included in this work. A simplified structure of the simulation model is illustrated in Figure 3-1.



Figure 3-1 Simplified structure of the simulation model.

3.3 Case study definition

The model represents a hypothetical process with a yearly production of 50,000 tonnes Lyocell fibre. The process consists of pulp dissolution, regeneration, washing, drying and solvent recovery. The five studied concepts for solvent recovery are: (1) ion exchange and evaporation; (2) flotation, ion exchange and evaporation; (3) filtration, ion exchange and evaporation; (4) filtration and liquid/liquid-extraction with butanol; and (5) filtration and liquid/liquid-extraction with dichloromethane. Each concept is subjected to a technical analysis. Moreover, Concept 3 and 5 are subjected to a partial sensitivity analysis.

The model is designed according to publicly available data found in literature, which is presented in Chapter 2. However, modelling of the liquid/liquid-extraction units are based on unpublished expert opinions. A more detailed description of overall model implementation, parametrization, and structure can be found in Appendix A and Appendix B. The characteristics of the simulation tool Balas® are presented in Chapter 3.4. Functionalities of the Balas® unit operations used in the model are not described in depth.

Totally chlorine-free (TCF) hardwood prehydrolysis kraft (PHK) dissolving pulp is used as raw material for each concept. The composition of the dissolving pulp follows that reported by Blechschmidt *et al.* (2006): cellulose 96.3 wt%, hemicellulose 3.37 wt%, lignin 0.05 wt% and inorganics 0.1 wt%. The incoming pulp has a dry matter of 92% and the produced Lyocell fibre 88.5%. Two types of solvents are used in the study. The considered solvent in Concept 1, 2, and 3 is NMMO. The considered solvent in Concept 4 and 5 is a general non-volatile hydrophilic ionic liquid. Volatile and hydrophobic solvents are thus not included in this model. The mass composition of incoming make-up of NMMO is 86 wt% anhydrous NMMO and 14 wt% water. The corresponding composition for incoming make-up ionic liquid is 99 wt% and 1wt%.

The incoming dissolving pulp is for all concepts mixed to a 50% consistency with freshwater, after which solvent is added according to demand. The dissolution step is modelled using three evaporation units with a co-current flow of steam and a decreasing pressure profile (80kPa, 25kPa, 5kPa), the steam has a temperature of 150°C and a pressure of 450kPa. Excess water is evaporated until a mixture of 15% pulp, 10% water, and 75% solvent is obtained. The spinning step is assumed to produce a loss of solids (pulp) at 2%. Hemicelluloses lost in regeneration are assumed to take the shape of low molecular weight hemicellulose at a rate of 50%, the rest is assumed to be of high molecular weight. The former is considered to behave as dissolved solids,

and the latter as suspended solids. Other solids lost in regeneration (cellulose, lignin, etc.) are assumed to behave as suspended solids.

The regenerated fibre is washed by using a counter-current flow of water and the amount of water needed is controlled by the washing efficiency. The Norden efficiency factor is derived from a hypothetical case where the factor is equivalent to the number of ideal counter-current mixing stages in series. The factor two would thus represent two ideal mixing stages in series. A factor of 1.3 is used for all concepts simulated. This specific value is used because it was fitted for the model in order to obtain the same water and steam demand as the process values published by Lenzing AG. The fibre is assumed to have a water content of 70% when leaving the washing step. It is then dried to 11.5% by using air with a temperature of 100°C.

The flotation unit is modelled with a reject ratio of 96% for suspended organic compounds and 0% for dissolved organic compounds. A 10% reject is set for inorganic components. The corresponding reject-% for filtration units are 100%, 0%, and 26%. The ion exchange reject-% for suspended organics is 99.99%, for dissolved organics 5%, and for inorganics 95%. The ions captured by the resin bed are considered divalent ions, which has an effect on the amount of resin required and the acid demand for regenerating the bed. The evaporation units in solvent recovery step 4 are modelled exactly as in the dissolution step. The LLE setup in recovery step 4 is modelled by using two extraction units and two cascade evaporation units, the configuration is illustrated in Figure 3-2. The first cascade evaporation unit is used for removing excess water and the other for separating IL and organic solvents.



Figure 3-2 Process configuration for the LLE concept.

Evaporation of organic solvents is set at a pressure profile of 100kPa, 15kPa, and 10kPa. The LLE units are assumed to operate with a reject of 99.99% for suspended organics, dissolved organics, inorganics, and water. The extraction efficiency of ionic liquid for butanol is assumed to 68%, and 75% for dichloromethane.

The wastewater produced in the process is assumed to be treated before discharge. A water recovery rate of 80% is assumed, along with a purity rate of 100%. The recovered water is recycled to the washing step. Furthermore, it is assumed that 0.5% of the solvent used in the process is lost to the washed fibre. An additional 0.5% is lost in Concept 1, 2, and 3 to NMMO degradation. The same additional amount is also lost in Concept 4 and 5, but it is lost to the LLE reject stream instead. Thus, resulting in a solvent recovery rate of 99% for all concepts.

3.4 Simulation tool - Balas®

Balas® is a steady-state simulation software mainly designed for chemical and paper industry, but it is also usable in general process modelling. Steady-state simulation is an approach to understand how an integrated system works as a whole and is often used to predict how the process will react to changes. Simulation with Balas® is based on two fundamentals: streams and units. Streams carry matter, energy and information, while units modify what the streams carry. Streams can be connected to units, and the user can specify stream properties or unit parameters.

Balas® provides significant databases of component alternatives, with specific thermodynamic and chemical properties. It is also possible to create user defined databases and components, which enables flexible modelling. Dissolved hemicellulose, NMMO and ionic liquids are examples of compounds that are defined by the user in this study. An important aspect that is dismissed in this model because of this is the miscibility of NMMO and IL in water. Evaporation can only be realistically described if the compound interactions are known because they will affect the vapour/liquid-equilibrium. This model will only give a realistic result if the mentioned compounds do not have any interaction between each other. Balas® uses

Redlich-Kwong-Soave for calculating vapour/liquid-equilibrium, with activity coefficient provided by Reid, Prausnitz and Sherwood (1977). Moreover, solid wood-based model compounds in the Balas® database have their own specific heat coefficient, which is calculated based on values from Paccot (1987).

In addition to basic process simulation Balas® can also be used for different process design problems and process optimization. To do this the user can create specific correlations in the model to describe specific phenomena, for example write a function that describes chemical dosage for a reactor. Parameter functions and design constraints are normally used for this. For increased user-friendliness, Balas® can be linked to excel. Excel can serve as an interface for model parameterization and results handling. Excel can also be used for measurement and process data pre-processing and further result processing using more advanced correlations.

4 Results

The overall mass and energy balances are gathered in Appendix C, and calculations for the technical analysis in Appendix D.

4.1 Concept 1

The first process concept uses an ion exchange resin bed and triple-effect evaporation to remove organics, inorganics and water. The resulting mass flows can be seen in Figure 4-1. The figure depicts water and solvent flows in kilogram per second, and the organic and inorganic flows in gram per second.

The water stream leaving the regeneration and washing step has a solid organic compound concentration of 435 ppm, a dissolved organic compound concentration of 16 ppm, and an inorganic concentration of 23 ppm. The theoretical resin bed charge for capturing 95% of the incoming inorganics for 24 hours is 7891 eq, which equals a resin bed volume of 7.3 m³. The effects that solid organic compounds or dissolved organic compounds would have on the resin bed are not taken into account. For a 24-hour operational period, the resin bed would need 590 kg of sulphuric acid (92 wt%) to regenerate. Multiple resin beds would be needed, as the beds are taken out of usage when being backwashed and regenerated.

The heat exchanging areas of the three evaporation units are approximated to 427 m², 761 m² and 1007 m², from the first effect to the third. The steam demand for this recovery concept is 1758 t/d. The amount of steam required for the dissolution step is 56.8 tonnes/day, and the heat exchanging areas for the evaporation units are approximated to 15 m², 17 m² and 24 m². The recovered solvent has a water content of 14%, an organic concentration of 122 ppm, and an inorganic concentration of 9 ppm.

To put the accumulated organic and inorganic mass flows into context, they are compared to the raw material intake. The organic raw material intake is 1.43 kg/s, and the inorganic 1.43 g/s. The accumulated organic content is equivalent to 0.07% of the incoming organic raw material stream. The inorganic equivalence is 5.13%.



Figure 4-1 Process data for solvent recovery Concept 1.

4.2 Concept 2

A flotation unit is used in Concept 2 to reduce the organic load of the ion exchange unit. The corresponding histogram for the studied process streams can be seen in Figure 4-2. The flotation unit efficiently removes solid organic components at a rate of 96% and result in a load of 17 ppm for solid organics, 16 ppm for dissolved organics, and 23 ppm for inorganics. The required bed volume for a 24-hour period is in that case 7.2 m³ (~7916 eq) and requires 540 kg of sulphuric acid (92 wt%) to regenerate. The dimensions of the flotation unit depend on the horizontal speed and needed retention time. Design values of 5 m/h and 30 min require an area of 44.6 m² and a depth of 2.5 m. An air-to-solids ratio of 35 l/kg would result in an air demand of 92.7 m³/d. The steam demand for the dissolution step is the same as in Concept 1, but 1743 t/d for the recovery step. The corresponding heat exchange areas are 423 m², 755 m² and 998 m². The recovered solvent in this concept has a water content of 14%, an

organic concentration of 120 ppm, and an inorganic concentration of 9 ppm. The organic equivalence to the raw material stream is 0.07%, and the inorganic 5.09%.



Figure 4-2 Process data for solvent recovery Concept 2.

4.3 Concept 3

The flotation unit from Concept 2 is in this concept replaced by a filtration unit, to further reduce the organic load of the resin bed. The resulting filtrate has a dissolved organic concentration of 16 ppm and an inorganic concentration of 17 ppm.

The required membrane area for a specific flow varies with the flux through the membrane. For a flow of 62 kg/s and a flux of $150 \text{ l/m}^2/\text{h}$, the required membrane area is 1488 m². The area is equivalent to 37 spiral wound modules, with a module-specific area of 41 m². The steam demand and the corresponding heat exchange areas are the same as in Concept 1. The sulphuric acid (92 wt%) demand for resin regeneration is 430 kg/d, and the resin bed volume is approximated to 5.3 m³ (~5864 eq). The recovered solvent in Concept 3 has a water content of 14%, an organic concentration of 122 ppm, and an inorganic concentration of 7 ppm. The organic equivalence to the raw material intake is 0.07%, and the inorganic 3.77%.



Figure 4-3 Process data for solvent recovery Concept 3.

4.4 Concept 4

The solvent recovery step in Concept 4 is composed of filtration and liquid/liquidextraction. As presented earlier, the LLE technology consists of two extraction units and two triple-cascade evaporation units. The cascades are used for evaporating water and organic solvents. The process data in Figure 4-4 shows that the recovered solvent contains a dismissible amount of inorganics and pulp-derived organics, but a noticeable amount of butanol.

The filtration unit requires the same membrane area as Concept 3. The resulting packed bed dimensions for the first extraction unit is a height of 5.1 meter and a diameter of 6.9 m. The corresponding dimensions for the second extraction bed is 4.7 m and 0.9 m. The steam demand for the dissolution step is 13.6 t/d and requires evaporator areas of 4.4 m², 0 m² (not needed) and 9.3 m². The evaporation units for removal of water need heat exchange areas of 409 m², 699 m² and 736 m². The corresponding areas for evaporation of butanol are 652 m², 187 m² and 5628 m². The steam demand for water evaporation is 1692 t/d, and 1487 t/d for organic solvent evaporation. The butanol demand is 33.2 t/d.



Figure 4-4 Process data for solvent recovery Concept 4.

4.5 Concept 5

The organic solvent butanol is switched for dichloromethane in Concept 5. The amount of organic solvent in the washwater stream is lower than in Concept 4, which means that a higher percentage of the organic solvent is evaporated in the dissolution step. This is because dichloromethane has a lower miscibility with water than butanol has. However, because the amount of organic solvent in the washwater stream is lower than in Concept 4, the feed of fresh organic solvent is higher in Concept 5. The dichloromethane demand is therefore 31.4 t/d.

The filtration membrane area is the same as in Concept 3 and 4. The height of the first extraction column is 2.6 m and the diameter 4.0 m. The second extraction unit require a height of 2.3 m and a diameter of 0.5 m. The heat exchange areas for water removal are 411 m^2 , 713 m^2 and 736 m^2 . Likewise are the areas for organic solvent evaporation 45 m^2 , 107 m^2 and 2531 m^2 . The respective steam demands for water and organic solvent evaporation are 1707 t/d and 361 t/d. Evaporator areas and steam demand for the dissolution step are the same as in Concept 4.



Figure 4-5 Process data for solvent recovery Concept 5.

4.6 Summary

The results from the simulated concepts are summarised in this chapter by gathering relevant information in three figures and one table.

The simulations for Concept 1, 2, and 3 result in very similar values for the recovered solvent stream due to the efficient ion exchange unit. However, a notable difference among these concepts is the organic load of the ion exchange unit. An overview of the organic compound distribution is thus illustrated in Figure 4-6. 97.2% of the organic load in Concept 1 is TSS and 2.8% TDS. The corresponding for Concept 2 is 75.5% and 24.5%. The organic load of the ion exchange unit in Concept 3 is 100% TDS. Concept 4 and 5 are not included in the figure, as the accumulated organic and inorganic content is dismissible for both concepts. The technical requirements for each solvent recovery concept are summarised in Table 4-1. Steam demand and freshwater demand are illustrated in Figure 4-7 and Figure 4-8.



Figure 4-6 Distribution of organic compounds in the stream entering the ion exchange unit in Concept 1, 2 and 3.

	Concept 1	Concept 2	Concept 3	Concept 4	Concept 5
Flotation		$\begin{array}{c} A=45 \text{ m}^2\\ \text{Depth}=2.5\text{m}\\ \text{Air}=92.7\text{m}^3/\text{d} \end{array}$			
Filtration			A=1488 m ²	A=1488 m ²	A=1488 m ²
Ion exch.	$V=7.3 \text{ m}^3$	V=7.2 m^3	$V=5.3 \text{ m}^3$		
Evaporation	A=427 m ² A=761 m ²	A=423 m ² A=755 m ²	A=427 m ² A=761 m ²		
	$A=1007 \text{ m}^2$	$A=998 \text{ m}^2$	A=701 m A=1007 m ²		
LLE (Evap.)				$1_{H2O}=409m^{2}$ $2_{H2O}=699 m^{2}$ $3_{H2O}=736 m^{2}$ $1_{ORG}=652 m^{2}$ $2_{ORG}=188 m^{2}$ $3_{ORG}=5628m^{2}$	$\frac{1_{\rm H2O}=411 \text{ m}^2}{2_{\rm H2O}=713 \text{ m}^2}$ $\frac{3_{\rm H2O}=736 \text{ m}^2}{1_{\rm ORG}=45 \text{ m}^2}$ $\frac{2_{\rm ORG}=107 \text{ m}^2}{3_{\rm ORG}=2531 \text{ m}^2}$
LLE (Column)				$\begin{array}{c} D_1 = 6.9 \text{ m} \\ H_1 = 5.1 \text{ m} \\ D_2 = 0.9 \text{ m} \\ H_2 = 4.7 \text{ m} \end{array}$	$D_1=4.0 \text{ m}$ $H_1=2.6 \text{ m}$ $D_2=0.5 \text{ m}$ $H_2=2.3 \text{ m}$
Chemical demand	Sulf. acid= 590 kg/d	Coagulants, Flocculants, Sulf. acid= 540 kg/d	Sulf. acid= 430 kg	Butanol= 33.2t/d	Dichlorom.= 31.4t/d

Table 4-1	Summary	of technical	requirements
	<i>,</i>		1



Figure 4-7 Summary of energy demand.



Figure 4-8 Summary of freshwater demand.

4.7 Sensitivity analysis

A complete sensitivity analysis of all model parameters is not included in the scope of this work as it is deemed too vast of a task. However, after running several simulations, it was noted which parameters impacted the results noticeably. Thus, eight parameters are selected for a partial sensitivity analysis. Concept 3 is used to study the effect of five parameters, and Concept 5 is used to study the remaining three parameters. Concept 5 have to be used for three specific parameters because they are connected to the performance of the LLE unit.

The parameters used for sensitivity analysis of Concept 3 are used to study steam and freshwater demand, as well as organic and inorganic compound accumulation. The impact of these five parameters are illustrated in Figure 4-9, Figure 4-10, Figure 4-11, and Figure 4-12 by varying the parameter value by $\pm 50\%$. The parameters and their base values are: 1) the Norden factor is 1.3, 2) the percentage of solids lost in fibre regeneration is 2%, 3) 50% of the hemicellulose lost in fibre regeneration is considered as dissolved components, 4) 5% of this dissolved hemicellulose is captured by the ion exchange unit, 5) the inorganic leakage of the IX unit is 5%.



Figure 4-9 Sensitivity analysis of freshwater demand, Concept 3.



Figure 4-10 Sensitivity analysis of steam demand, Concept 3.



Figure 4-11 Sensitivity analysis of organic content in the recovered solvent stream, Concept 3.



Figure 4-12 Sensitivity analysis of inorganic content in the recovered solvent stream, Concept 3.

The Norden factor appears to be the only parameter that affects the freshwater and steam demand significantly. The accumulation of organic content is more sensitive to relative changes in overall solids lost and how much hemicellulose acts as dissolved compounds than how much hemicellulose is captured in the IX unit.

The parameters that are varied for Concept 5 all have an original parameter value of 0%. Their impacts are therefore studied by increasing the parameter values to 5% and 10%, and not by varying with \pm 50%. The parameters affect steam demand, as well as accumulation of inorganics and pulp-derived organics. Figure 4-13 illustrates what happens to the steam demand when water is extracted by the organic phase in the LLE unit. The steam demand clearly increases when small amounts of water migrate into the organic phase. Figure 4-14 and Figure 4-15 illustrates the accumulation of pulp-derived organics and inorganics when these compounds leak into the organic phase of the LLE unit.



Figure 4-13 Effect of water content in extracted solvent/dichloromethane-system on steam demand, Concept 5.



Figure 4-14 Effect of variation in LLE pulp-derived organic reject-% on pulp-derived organic content of the recovered solvent, Concept 5.



Figure 4-15 Effect of variation in LLE inorganic reject-% on inorganic content of the recovered solvent, Concept 5.

The analysis for Concept 5 shows that steam demand increases if some amount of water is extracted by the organic phase. Extraction of pulp-derived organics to the organic phase shows a small increase in accumulation of pulp-derived organics, but the amount is still smaller than for Concept 3. A more notable result on the other hand is the major increase in accumulation of inorganics. The amount of inorganic content in the recovered solvent after 5% leakage is equivalent to 44.2% of the raw material intake inorganics. A leakage of 10% is equivalent to 67.3% of the raw material inorganics.

5 Discussion and observations

The aim of this thesis was to study five solvent recovery concepts for the Lyocell process and the resulting accumulation of process impurities in the recovered solvent. Additionally, the solvent recovery concepts were also subjected to technical analyses that proposed rough estimations of process equipment sizes. These results, in combination with a sensitivity analysis, provided useful insight into the Lyocell process and its behaviour. The concepts are assessed by comparing them to one another based on recovered solvent purity, energy demand and overall complexity. However, the studied concepts cannot be thoroughly compared before the results are validated and an economic assessment is carried out.

The results show that the accumulation of organics and inorganics is small compared to the amounts entering the process with the raw material, and that Concepts 1, 2, and 3 result in a very similar solvent purity level. The high purity level is a direct result of the ion exchange unit, as it has a very high reject rate of both organic and inorganic impurities. The low hemicellulose and inorganic content in dissolving pulp also contribute to the low accumulations, as those are the compounds that are accumulating. Cellulose will not accumulate because it behaves as suspended solids and can therefore easily be removed from the recovered solvent. Hemicelluloses on the other hand can to some extent behave as dissolved solids, and that makes them harder to eliminate.

Because of the very similar solvent purity and energy demand, the three first concepts are only compared based on complexity and equipment load. Concept 1 only uses two technologies, while Concept 2 and 3 both use three technologies. The organic load of the ion exchange resin bed in Concept 1 is noticeably higher than for Concept 2 and 3. The proportion of TSS in Concept 1 and 2 is notable as suspended solids promote clogging. Concept 3 is in that sense better than Concept 1 and 2, as the IX will run smoother. The downside with Concept 3 is its vulnerability to fouling and the required maintenance. Concept 2 does not require heavy maintenance but is instead dependent on coagulants and flocculants to perform as planned.

Concept 4 and 5 result in a more pure solvent than Concept 1, 2, and 3. The inorganic and pulp-derived organic content are almost dismissible. However, the recovered solvent instead contains a significant amount of organic solvent. The LLE technology used is deemed as very complex due to the uncertainties in mass transfer for organics and inorganics in butanol/water and dichloromethane/water-mixtures. The separation efficiencies rely heavily on overall mixture composition, and partly on influence of pH. This makes the overall LLE efficiency hard to predict, as it relies on partly unknown data at this moment in time. Dichloromethane is more volatile than butanol thanks to its low vapour pressure, which results in a noticeably lower energy demand. Butanol is also more flammable than dichloromethane. However, dichloromethane have worse effects on human health.

The sensitivity analysis showed that freshwater and steam consumption are strongly correlated to the Norden factor. This is quite logical as a lower number of washing steps (higher Norden factor) and less time in contact with water have to be compensated with higher amounts of freshwater. A higher amount of water in the process also means that more water has to be evaporated in the solvent recovery step, i.e. a higher steam demand. The analysis also revealed that the extraction efficiency of inorganics in the LLE unit heavily influences the level of inorganic content in the recovered ionic liquid. The analysis clearly showed that even a small leakage of 5% of inorganics results in a relatively high amount of accumulated inorganic content in the recovered solvent stream. The reason for this could be the LLE configuration used, which operates by using an internal recycling loop. The loop returns about 90% of the flow that exits the water evaporation step back to the inlet to recover more of the ionic liquid, and thus promotes high accumulation within the LLE configuration.

The freshwater and energy demand for Concept 3 is 7.9 litre and 44.6 MJ per kg produced fibre, which are fitted to Lenzing AG's reported process values. The values represent net demand. Because the internal process flows have not been reported, it is not possible to fit or validate the simulation model values. The model water demand is controlled by the efficiency of the wastewater treatment technology, which is set to produce 100% pure water at an 80% recovery rate. A decrease in recovery rate would result in higher freshwater demand, but the demand can be lowered again by increasing the efficiency of the fibre washing step. Improving the washing efficiency can be done

by increasing the Norden factor. The overall freshwater demand can thus be controlled by adjusting two process parameters. This means that the internal water balance cannot be completely determined until the wastewater treatment technology is specified.

The steady-state simulations provided useful knowledge about the Lyocell process as a complete process, which is the type of information that targeted equipment studies are not able to provide. A downside with the model is that it does not take into account in what way accumulated process impurities affect the final fibre quality. Moreover, discolouration and water turbidity are not included in the model, as it requires further knowledge about the process and residing compounds. The complexity of by-product formation is also overlooked in the model, as it is generalised by only having two model compounds that represent liquid and gas-phase degradation products. However, the generalisation made in the model is justifiable, as the scope of this study did not include detailed chemical interactions but merely overall process behaviour.

The results depict five process concepts that are very good at removing organic and inorganic impurities from the recovered solvent. The Lyocell process is known for its closed-loop configuration and efficient usage of solvent, which means that impurities have to be efficiently removed, as they otherwise would have a negative impact on the produced fibre. The results in this study could therefore be seen as plausible. However, in order to obtain more accurate results, the values have to be validated by actual process data or by targeted experimental studies. The results presented in this work can act as a reference for other studies, and the technical analysis calculations can be used for pre-engineering purposes.

There are still a few open questions regarding the Lyocell process that have to be addressed before results of higher accuracy can be obtained. Information on the actual performance of solvent recovery technologies and wastewater treatment is of high interest, as it can have a significant effect on process water quality and accumulation of impurities. Regeneration yield and the resulting spin bath composition are also of particularly high interest for obtaining accurate process simulations. Vapour/liquidequilibrium for solvent/water-mixtures is also a necessity for obtaining an accurate energy balance. Interaction between organic solvents and (in-)organic compounds also have to be further studied.

6 Conclusions

The results showed that Concept 1, 2, and 3 generate very similar levels of accumulated process impurities, and also that the levels in general are very low. Concept 4 and 5 results in higher solvent purity rates than Concept 1, 2, and 3 but assumptions concerning separation efficiencies of inorganics and pulp-derived organics are uncertain. The sensitivity analysis showed that the LLE configuration can promote relatively high accumulations of inorganic compounds at non-ideal performance. Furthermore, the sensitivity analysis also suggested that overall consumption of freshwater and steam can be lowered by increasing the number of washing stages in series (Norden).

Concept 2 has the lowest steam demand, followed by Concept 1, 3, 5, and 4. Concept 1 is considered least complex because it only uses two technologies, but it might not be industrially feasible due to the organic load of the ion exchange unit. Concept 3 is rated as the second least complex, followed by Concept 2. The latter is more complex because of the extra chemistry that coagulation and flocculation add to the process. Concept 4 and 5 are considered more complex than Concept 1, 2 and 3 because of uncertainties in mass transfer of inorganic and pulp-derived organic compounds. Concept 5 is deemed as more complex than Concept 4 because dichloromethane has worse effects on human health than butanol. LLE has the potential to be utilised for obtaining a very concentrated solvent (>99 wt%). A lower steam demand can potentially be obtained if an organic solvent with lower vapor pressure is utilised. The technology has to be further studied to be able to obtain more accurate results.

The choice of steady-state simulation as a tool for studying the Lyocell process supported the objective of the study and provided results that increased understanding about the Lyocell process. The study also identified the following knowledge gaps that hindered more accurate results: fibre regeneration yield, wastewater treatment performance, solvent/water-interaction, and molecular weight distribution of regenerated pulp components - all of which were studied through sensitivity analysis.

7 Swedish summary - Svensk sammanfattning

Textilindustrin är i dagens läge en av världens största förorenare och den årliga globala produktionen av fibrer antas bara växa i takt med ökad levnadsstandard och mängd människor. Industrins inverkan på miljön har länge varit känd och 2007 frågades globala textilproducenter varför de inte börjar använda mer hållbara produktionsmetoder. Den största anledningen var att konsumenterna inte är villiga att betala högre priser för hållbarare produkter. Två andra populära svar var brist på teknologiska innovationer och ekonomiskt hållbara affärskoncept. För att reducera textilindustrins miljöavtryck behövs därför nya och effektiva processkoncept som i synnerhet minskar på vatten-, kemikalie- och markanvändning.

Textilfibrer kan delas in i två grupper och fyra undergrupper. Den första gruppen består av naturfibrer, som kan delas i undergrupperna djurfiber och växtfiber. Till naturfiber hör t.ex. bomull, ull och silke. Den andra gruppen benämns konstfiber, som kan delas in i syntetfiber och regenatfiber. Skillnaden mellan naturfiber och konstfiber är att naturfiber direkt är färdiga fibrer som kan användas i textiler, medan konstfiber artificiellt måste förädlas för att kunna användas. Till syntetiska fiber används ofta råolja som råmaterial, medan regenatfiber ofta består av naturliga material som cellulosa. Regenatfiber är alltså bionedbrytbara, men klassas inte som naturfiber eftersom regenatfiber måste genomgå en förädlingsprocess innan de kan användas till textiler. Detta för att fibrerna måste frigöras från materialet, vilket inte är fallet för naturfibrer som direkt kan användas.

En väldigt känd typ av regenatfiber är RayonTM, produceras enligt viskosprocessen. I viskosprocessen använder man natriumhydroxid och koldisulfid för upplösning av cellulosa. Problemet här ligger dock i kemikalieåtervinningen, där koldisulfid och svavelväte är svårhanterliga. Under slutet av 1900-talet, efter att viskosfiber redan existerat i nästan 100 år, uppfanns en ny typ av regenatfiber som kallas Lyocell. Lyocellfibern är också cellulosabaserad, men använder sig istället av en organisk aminoxid (NMMO) eller en jonisk vätska som lösningsmedel. Fördelen med Lyocell är att man kan ta tillvara upp till 99 % av lösningsmedlet genom att rena processvattnet, detta har dock bara bevisats för konfigurationer med NMMO.

NMMO uppvisar dock instabilitet vid högre temperaturer, som t.ex. kan leda till explosivitet eller formation av kemiska biprodukter. Därför har man i allt större mån börjat undersöka joniska vätskors lämplighet som lösningsmedel. En omfattande undersökning av joniska vätskors löslighet har gjorts av Mäki-Arvela *et al.* (2010) där flera joniska vätskor konstaterades besitta god löslighet. För en god löslighet krävs att lösningsmedlets molekyler effektivt kan bryta cellulosamolekylernas intermolekylära bindningar. Bindningarna kan brytas genom att få vätemolekylerna att binda sig med lösningsmedlet istället för cellulosa.

I Lyocell-processen används dissolvingmassa som råmaterial. Dissolvingmassa har i normala fall en väldigt hög halt av cellulosa (>90%), samt låga halter av hemicellulosa (>5%), lignin (>1%) och oorganiska ämnen (>0.1%). Dissolvingmassa produceras genom att justera innehållet för pappersmassa till de tidigare nämnda gränserna. Därutöver justeras också dissolvingmassans gränsviskositet till en lägre nivå, kring 400-500 mL/g. Viskositeten justeras för att lösningen ska kunna extruderas till trådar utan att deformeras eller gå av. Den inkommande dissolvingmassan blandas med vatten och blir därefter riven till en finfördelad lösning. Lösningen pumpas därefter vidare till en avdunstningskolonn där lösningsmedel tillsätts och överflödigt vatten avdunstar. Lösningen pumpas vidare till en spinneret, som kan beskrivas som ett duschhuvud med många små hål som lösningen pumpas igenom. Trådarna som formas dras direkt ner i ett vattenbad för regenerering. Regenerering betyder i praktiken att de intermolekylära vätebindningarna återuppstår mellan cellulosamolekylerna. Detta händer för att lösningsmedlen föredrar att binda sig med vatten framom cellulosa. Fibern utsätts därefter för ett längre tvättsteg genom att långsamt dras motströms igenom ett stort vattenbad. Lösningsmedlet separeras genom detta från fibern. Vattnet i badet pumpas kontinuerligt bort för att behandlas, samtidigt som färskvatten fylls på för att upprätthålla vattenmängden. När fibrerna är rena, torkas det överflödiga vattnet i fibrerna bort med hjälp av torkcylindrar. Den färdiga fibern kan vid behov färgas eller kemiskt behandlas för att uppnå önskade materialegenskaper.

För tillfället är det endast företaget Lenzing som tillverkar Lyocell, dock under det kommersiella namnet TencellTM. Processtegen är allmänt kända, men alla detaljer och processparametrar har dock inte blivit offentligt publicerade. Målet med denna avhandling är därför att undersöka potentiella koncept för återvinning av NMMO eller

joniska vätskor, för produktion av Lyocellfibrer. Återvinningsmetoderna består av olika kombinationer av allmänna separationsteknologier som flotation, filtration, jonbyte och avdunstning. För att kunna utföra denna typ av utvärdering måste en simuleringsmodell för lyocellprocessen skapas. Modellen skapas med hjälp av simuleringsverktyget Balas®, som opererar i fortfarighetstillstånd (steady-state). Balas® använder Redlich-Kwong-Soave för att beskriva vätskors och gasers termodynamiska beteenden med aktivitetskoefficienter från Reid, Prausnitz and Sherwood (1977). Fasta ämnens termodynamiska egenskaper räknas med hjälp av Paccot (1987). För parametrisering av modellen används publicerade värden för Lyocell processen, okända värden approximeras med hjälp av studier som tangerar tillämpningsområdet. En känslighetsanalys utförs också för att se hur modellen reagerar på förändringar i parametriseringen.

Simuleringsmodellen används för att undersöka fem utvalda processkoncept. Koncepten skiljer sig från varandra endast när det gäller metoden för tillvaratagning av lösningsmedlet, dvs. produktionen av fibrer bibehålls oförändrad. De fem koncepten består av följande kombinationer av separationsteknologier: (1) jonbyte och avdunstning; (2) flotation, jonbyte och avdunstning; (3) filtration, jonbyte och avdunstning; (4) filtration och vätske-vätske extraktion med butanol; och (5) filtration och vätske-vätske extraktion med butanol; och (5) filtration och vätske-vätske extraktion med diklormetan. En heltäckande evaluering av koncepten kan inte göras förrän mass- och energibalanserna är validerade av processdata och en tekno-ekonomisk analys har blivit gjord. Koncepten kan dock jämföras med varandra på basis av det tillvaratagna lösningsmedlets renhetsgrad, sammanlagt energibehov och generell komplexitet. Komplexitetsgrad definieras enligt omfattning av kemiska fenomen, toxicitetsgrad, samt antal processteg och design parametrar. För att alla fem koncept ska vara jämförbara ställs koncepten in så att 99% av lösningsmedlet tas tillvara i processen. Konceptens teknologiska förutsättningar kan då jämföras med varandra eftersom tillvaratagningen alltid är lika effektiv.

Koncept 1 bedöms vara minst komplex, eftersom det bara baserar sig på två processteg. Koncept 3 anses vara näst i tur, följt av 2, 4 och 5. Koncept 2 är mer komplext än koncept 3 för att flotation är en teknologi som kräver kemikalier för att fungera, vilket filtrationen i koncept 3 inte behöver. Koncept 4 och 5 anses vara mer komplexa än koncept 1, 2 och 3, eftersom teknologin är totalt oprövad för Lyocell

sammanhanget. Koncept 4 och 5 baserar sig därför på delvis okänd kemi och ökar därför osäkerheten kring resultatet. Vätske-vätske extraktionen kan påverkas av både pH-värde och flödesinnehållet i de inkommande strömmarna, vilket gör teknologin svårare att reglera. Koncept 4 anses vara mindre komplext än koncept 5 för att diklormetan är mer skadligt för människor, vilket ökar riskfaktorn. Butanol är dock mer brandfarligt och kräver mer energi för att förångas. Koncept 2 har lägst energibehov, följt av 3, 1, 5 och 4. Koncept 1, 2 och 3 har snarlika resultat gällande lösningsmedlets renhetsgrad. Det beror på att hartskolonnen som används för jonbyte är väldigt effektiv på att separera både organiska och oorganiska ämnen. Koncept 4 och 5 kan uppnå en renhetsgrad med nästan obetydliga nivåer av oorganiska ämnen och träbaserade organiska ämnen. Koncept 4 och 5 innehåller dock 1% organiskt lösningsmedlel och det är oklart hur den mängden påverkar resten av processen. Det tillvaratagna lösningsmedlet i koncept 1, 2 och 3 har ett vatteninnehåll på 14%, medan det i koncept 4 och 5 inte innehåller vatten alls.

De simulerade resultaten för koncept 3 är 7,9 liter vatten och 44,6 MJ per kg fiber, vilket är i linje med Lenzing AGs rapporterade värden. Värdena representerar dock nettobehovet för modellen som helhet, vilket betyder att endast den externa vattenoch energibalans kan valideras. Mer information om processen behövs därför för att kunna validera interna procesströmmar. I synnerhet behövs information om materialförluster vid regenereringen av fibrerna och gas-vätska jämviktskurvor för vattenlösningar av joniska vätskor eller NMMO. Utöver detta är det också viktigt att veta hur mycket av avfallsvattnet som kan renas och återanvändas, samt dess renhetsgrad. Dessa faktorer skulle då ge en bra helhetsbild av de interna massbalanserna, samt ett trovärdigt energibehov. Därutöver vore det också viktigt att undersöka om de ackumulerade organiska ämnen kan återanvändas till fibrer när dom följer med lösningsmedlet tillbaka till upplösningssteget. Om ämnenas kemiska tillstånd och struktur har ändrat kan det tänkas påverka deras förmåga att på nytt binda sig till cellulosakedjor.

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Appendix A – Model implementation

The chosen model compounds are summarised in Table A-1.

Solid	Liquid	Vapour
Cellulose	Dissolved cellulose	Water
Hemicellulose (C-5)	Low molecular weight hemicellulose	Degraded solvent (gas)
Hemicellulose (C-6)	High molecular weight hemicellulose	Butanol
Lignin	Dissolved lignin	Dichloromethane
	Inorganic compounds	
	Water	
	Solvent	
	Degraded solvent (liquid)	
	Butanol	
	Dichloromethane	

Table A-1 Summary of model compounds used

Fibre production

The incoming pulp mass flow is used as a design variable to reach a set production speed, which is specified in a design constraint. The raw material pulp composition and water content can be modified by the user, but the inorganic compounds are not individually specified. Instead are all inorganic compounds modelled as one homogenous compound.

<u>Dissolution</u>

Because dissolution conditions can vary when using different solvents, the user must specify the pulp/solvent/water-composition for when dissolution occurs. Complete dissolution of all pulp components is assumed, but the user can specify a lower dissolution rate than 100% if needed. A filter unit after the evaporators will in that case stop the solid components. It is also possible to specify a certain percentage of solvent that will degrade to by-products. Alias components are created for both solvent and

degraded solvent as they do not exist in the Balas® database. The solvent dosage for the dissolution step is controlled by a control-valve and the parameter function

$$\dot{m}_{solvent,in} = \frac{X_{solvent,\%}}{X_{pulp,\%}} \cdot \dot{m}_{pulp,in}$$

After the solvent is added, excess water is evaporated until the specified mixture is reached. A design constraint is used to find the correct water content $X_{water,\%}$.

$$\frac{\dot{m}_{water,evap,out}}{X_{water,\%} \cdot \dot{m}_{total,evap,out}} - 1 = 0$$

The mass flow of steam is used as a design variable. A higher mass flow of steam will evaporate more water and thus lower the water content in the mixture. A three-stage cascade evaporation was chosen in this step to ensure a good steam economy. The three evaporators were set at decreasing pressure profile and with a co-current flow of steam. The steam is set to 150°C and 4.5 bar, which are normal values for low pressure steam in the pulp industry.

Parameter	Value
Pressure (step 1)	80 kPa
Pressure (step 2)	25 kPa
Pressure (step 3)	5 kPa
Steam temperature	150°C
Steam pressure	450 kPa

Table A-2 Operating parameters for the dissolution step evaporation

Spinning and regeneration

Heat and mass transfer are essential when modelling the spinning and washing stages. Heat transfer is important because the temperature plays a vital role in fibre regeneration and mass transfer affects solvent diffusion and pulp losses to the process water. Heat transfer between the dope and a big mass of water is configured by mixing two streams (red and green), as shown in Figure A-1.



Figure A-1 Process configuration of fibre regeneration in the model. Red stream represents fibre; green represents washing water, and blue represents water free from impurities. The cooling unit is followed by two separation units, which are used to describe compound losses in occurrence with fibre regeneration.

A parameter function is created for the control-valve connected to the process water (green stream). The function contains a user-specified fibre-to-water ratio $X_{Fibre / water}$ to calculate the flux of the process water mixed with the incoming dope (red stream).

$$\dot{m}_{Water,bath} = X_{Fibre \, / \, water} \cdot \dot{m}_{Fibre}$$

The temperature of the process water is set by the user and controlled via a design constraint.

$$\frac{T_{Process water}}{T_{Bath}} - 1 = 0$$

The flux of cooling water (blue stream) is used as a design variable for this constraint. The mass transfer concerning pulp losses is connected to the solid/liquid-separation unit in Figure A-1. The losses are assumed to 2% and will affect all pulp components equally. The components lost are assumed to 100% regenerate into solid compounds, apart from hemicellulose. Hemicellulose can be described as low and high molecular weight hemicellulose when they are dissolved, but only high weight hemicellulose is assumed to be regenerated into solid compounds. The low weight compounds are therefore only accumulating in the loops and not contributing to fibre production. Out of the hemicellulose lost in fibre regeneration, 50% is assumed to stay as solids.

Regeneration of pulp components from a dissolved state to solid is specified by using a reactor unit.

Washing and drying

The challenge with modelling the washing step is that the specific freshwater demand per kg dope is unknown. Furthermore, the mass fraction of un-diffused solvent left in the washed fibre is also unknown. These two aspects therefore have to be userspecified, because a general assumption cannot be assumed for all fibre and solvent types. The water bath is modelled by using the Norden efficiency factor. The Norden efficiency factor is derived from a hypothetical case where the number used is equivalent to the number of ideal counter-current mixing stages in series. The amount of solvent left in the fibre $X_{solvent}$ is used to create a design constraint

$$\frac{\dot{m}_{solvent,wet\,fiber}}{X_{solvent} \cdot \dot{m}_{wet\,fiber}} - 1 = 0$$

A solvent amount of 0.5% is assumed to be lost in this stage. The design variable used for this constraint is the valve that controls the counter-current flow of freshwater. The counter-current flow can be also be adjusted by changing the Norden efficiency factor. This gives the model excellent flexibility for describing scenarios with both better and worse washing efficiencies. The results presented in Chapter 4 are simulated with an efficiency factor of 1.3. The wet fibre is assumed to have a dry content of 30% when leaving the bath, after which it is dried to 88.5%. The fibre is dried by using air flotation dryer, which is a Balas® built-in unit operation.

Solvent recovery

To enable smoother transition between the chosen solvent recovery concepts a partial superstructure was created for the recovery step. A partial superstructure comprises of multiple steps, where every step offers selected separation technologies to treat the incoming flow. The separation technologies are placed parallel to each other in every step and the user can then choose which technology to use. This is steered via Excel and a user-friendly logic table. An example of a superstructure step can be seen in Figure A-2.



Figure A-2 Example of a separation step in the superstructure.

Splitters are placed after every outlet streams of every unit and the splitters are connected to the superstructure logic table. The splitters are modelled to let the mass flow through to the next step if the unit is in use but will stop the flow if the unit is not in use. The created Lyocell model has four steps in the superstructure with the following set-up (1) flotation and filtration; (2) flotation and filtration; (3) ion exchange; (4) evaporation and liquid/liquid-extraction. Furthermore, all steps have the option of letting the flow through without any treatment. This is also controlled from the logic table and is based on the same splitter-technique as for the separation units. The superstructure strategy is the most flexible alternative for the model and the user when comparing multiple concepts. All separation parameters presented in this chapter are derived from the information presented in Chapter 2.

<u>Flotation</u>

Flotation exists as a simple separation module in Balas® with the possibility to specify reject consistency and component separation efficiency. The flotation unit works because of the principle that density for aqueous NMMO is higher than for pure water. This means that pure water and flotation rejects can be gathered at the surface of a flotation unit, from where they can be removed. Thus, resulting in a pure aqueous NMMO stream leaving the flotation unit from the bottom of the tank. The process parameters for the flotation unit can be found in Table A-3. Reject efficiencies for the organic compounds are based on the values presented in Chapter 2.3.5.1. The ion rejection rate is based on the assumption that the coagulants and flocculants will capture a small amount of ions.

Table A-3 Design parameters for the flotation unit, based on literature in Chapter 2.3.5.1. Compound-% describes the amount removed from the feed stream

Reject consistency	5%
Cellulose rejected - %	96%
Hemicellulose rejected - %	96%
Lignin rejected - %	96%
Inorganics rejected - %	10%
Dissolved organics rejected-%	0%
Solvent rejected - %	0%

<u>Filtration</u>

The working principle of filtration units in Balas® is that they automatically separate all solid substances. Dissolved and aqueous compounds are assumed to completely flow through the membrane, if not specified otherwise. Ultrafiltration is chosen as the technology used in this model. Nanofiltration was deemed to not be able to reach the needed solvent recovery rate, as for microfiltration it was assumed that not enough organic matter would be removed. The filtration unit is set to separate a certain percentage of cellulose, hemicellulose, lignin, free ions and solvent according to values found in Table A-4.

Cellulose rejected - %	100%
Hemicellulose rejected - %	100%
Lignin rejected - %	100%
Dissolved organics rejected - %	0%
Inorganics rejected - %	26%
Solvent rejected - %	0%

Table A-4 Design parameters for the ultrafiltration unit, based on literature in Chapter 2.3.5.2

Ion exchange

Realistic modelling of a resin bed is challenging, as all ions must be defined in the model. The ion exchange is therefore only described as a simple separation unit with a user-defined general separation efficiency for all inorganic compounds. The resin bed is assumed to operate as a filter, thereby stopping all solids. Dissolved components are assumed to be captured at a user-specified rate.

Because the bed will lose its electrical charge at some point, it has to be regenerated. The acid demand is described by using the ideal reaction

$$R^-H^+ + A^+ \rightarrow R^-A^+ + H^+$$

meaning that the same charge used for capturing a free ion must be used to regenerate the resin. Acid or base is therefore added until all ions are obtained. Regeneration time for a resin bed depends on the size of the bed, i.e. its operating capacity. For ideal regeneration in a theoretical case, the acid or base should provide enough charge to at least match the level of the operating capacity. A resin bed will start to let ions through when the operating capacity reaches zero, i.e. when the bed reaches a neutral charge.

Table A-5 Design parameters for the ion exchange unit

Cellulose rejected - %	99.99%
Hemicellulose rejected - %	99.99%
Lignin rejected - %	99.99%
Dissolved organics rejected - %	5%
Inorganics rejected - %	95%
Solvent rejected - %	0%

Evaporation

The evaporation step is set to operate equivalently to the dissolution step, with three stages, a dropping pressure profile and co-current flow of steam. An equivalent design constraint is used

$$\frac{\dot{m}_{water,evap,out}}{X_{water,\%}\cdot\dot{m}_{total,evap,out}} - 1 = 0$$

and the incoming mass flow of steam is used as a design variable. Process parameters are found in Table A-6.

Parameter	Value
Pressure (step 1)	80 kPa
Pressure (step 2)	25 kPa
Pressure (step 3)	5 kPa
Steam temperature	150°C
Steam pressure	450 kPa

Table A-6 Operating parameters for the evaporation units

Liquid/Liquid-extraction

The LLE is modelled in two steps because both water and organic solvent has to be removed. Organic solvent is added before both LLE steps, which are modelled as simple separation units. The LLE units are set to separate the organic solvent at 100% efficiency and the solvent at a user-specified extraction efficiency. The organic solvent dosage is steered by a control-valve with the following parameter function

$$\dot{m}_{Org.,in} = \frac{X_{Org.1,\%}}{X_{Proc.water,\%}} \cdot \dot{m}_{Proc.water}$$

where $X_{Org.,\%}$ and $X_{Proc.water,\%}$ are user-specified mixture ratios of organic solvent and process water in the LLE unit. The process configuration can be seen in Figure A-3.



Figure A-3 Process configuration for the LLE concept.

The flow of process water recycled back to LLE 1 after evaporation 1 is governed by a splitter, which can divide the flow into two streams. The splitter operates at values between zero and one, where one means that everything is recycled to LLE 1. The splitter value is set by the following parameter function

$$Splitter = 1 - \frac{\frac{X_{Solvent \ loss,\%}}{100 - EE_{Solvent,\%}} \cdot \dot{m}_{Solvent,LLE \ 1,in}}{\dot{m}_{Solvent,LLE \ 2,in}}$$

Where $EE_{Solvent,\%}$ stands for extraction efficiency and $X_{Solvent \ loss,\%}$ for solvent losses to the wastewater, both values are user-specified. Evaporation 1 and 2 have the same set-up as the other evaporators in the model and are controlled by the following design constraints

$$\frac{\dot{m}_{water,evap 1,out}}{X_{water,\%} \cdot \dot{m}_{total,evap 1,out}} - 1 = 0$$
$$\frac{\dot{m}_{Org.evap 2,out}}{X_{Org.2,\%} \cdot \dot{m}_{total,evap 2,out}} - 1 = 0$$

Incoming mass flows of steam are used as design variables for these constraints. Solid components, dissolved components, and inorganics are all assumed to migrate into the organic phase at a dismissible low rate (=0.0001%). The components are assumed to stay in the aqueous phase because they have a higher density than the organic solvent. This in accordance with the principles of an LLE unit as high density compounds will move downwards and light compounds upwards. The impacts of overall mixture composition and pH are not taken into account because of great uncertainty. All parameters can be found in Table A-7.

LLE	Separation
Dichloromethane accept-%	99.99%
Butanol accept-%	99.99%
Cellulose accept-%	0.0001%
Hemicellulose accept-%	0.0001%
Lignin accept-%	0.0001%
Inorganics accept-%	0.0001%
Dissolved organic compounds accept-%	0.0001%
Water accept-%	0.0001%
Solvent (Dichloromethane used), <i>EE</i> _{Solvent,%} accept-%	75%
Solvent (Butanol used), <i>EE</i> _{Solvent,%} accept-%	68%
Solvent losses, X _{Solvent loss,%} accept-%	0.9%
Organic solvent fraction in feed, $X_{Org.\%}$	50%
Process water fraction in feed, $X_{Proc.water.\%}$	50%
Evaporation in LLE	Value
Pressure, H ₂ O (step 1)	80 kPa
Pressure, H ₂ O (step 2)	25 kPa
Pressure, H ₂ O (step 3)	5 kPa
Pressure, organic solvent (step 1)	100
Pressure, organic solvent (step 2)	15
Pressure, organic solvent (step 3)	10
Steam temperature	150°C
Steam pressure	450 kPa
Organic solvent fraction in recovered solvent stream, $X_{0ra2\%}$	1%

Table A-7 Operating parameters for the LLE and evaporation units. The parameters are the same for both steps

Appendix B – Model structure and overview







Figure B-2 Model structure for the spinning and washing step.



Figure B-3 Model structure for the drying step.



Figure B-4 Model structure for the solvent recovery superstructure, levels 1 to 3.



Figure B-5 Model structure for the solvent recovery step level 4 evaporation and wastewater treatment.



Figure B-6 Model structure for the solvent recovery step level 4 liquid/liquid-extraction. The purple lines represent concentrated organic solvent.

Appendix C – Mass and energy balances

Table C-1 Process data for Concept 1 Ion exchange & Evaporation, part 1. The energy streams are calculated by using 0° C as base point.

DISSOLUTION	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Pulp in (pre-treatment)	1.5563	25	5 101	28252.21865	806206206.7	0	88.68468468	3.269269269	0.046046046	0.092092092	0		0	0	0
Mixing water in (pre-treatment)	1.30725	1(101 0	55.08081739	100	0	0	0	0	0	0		0	0	0
Solvent in (Dissolution)	8.32495	49.47414	2 101	204019.1743	13.9990186	85.994014	1.78275E-05	0.006474477	9.30154E-09	0.000475115	0		0	0	0
Solvent recovered	8.27572	70.000035	9 101	203202.7584	13.99816378	85.9888001	3.33555E-05	0.012113838	1.74033E-08	0.000888947	0		0	0	0
Solvent make-up	0.04927	2	5 101	1207.53753	14	86	0	0	0	0	0		0	0	0
Heated stream before dissolution	11.1886	8	101 0	159712.9568	23.20026851	63.6648574	12.33581794	0.459564099	0.00640489	0.013163281	0.319923906		0	0	0
Steam in	0.65744	15(9 450	1806.441905	100	0	0	0	0	0	0		0	0	0
Condensate out	0.80625	50.97900	5 5	2092.692905	100	0	0	0	0	0	0		0	0	0
Puresteam condensate	0.65416	147.9280	4 450	407.7038103	100	0	0	0	0	0	0		0	0	0
Wastewater out	0.84204	73.528812	2 101	259.2310167	99.999853	0	0	0	0	0	0.000146995		0	0	0
Dope out	9.50775	12(101 0	159716.3776	9.999996394	74.9196105	14.51655927	0.540806415	0.007537154	0.015490302	0		0	0	0
SPINNING AND WASHING	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	En zyme-%	
Dope in	9.50775	120	101 0	159716.3776	46£966666.6	74.9196105	14.51655927	0.540806415	0.007537154	0.015490302	0		0	0	0
Pure washwater in	11.2371	10	101 0	473.4580382	100	0	0	0	0	0	0		0	0	0
Recycled processwater in	45.6278	11	101 0	1922.457555	100	0	0	0	0	0	0		0	0	0
Cooling demand	97.725	-,	5 101	2066.837724	100	0	0	0	0	0	0		0	0	0
Processwater out	61.6955	15.00026	9 101	206066.3149	88.4159584	11.5343562	0.044742421	0.002534849	2.33445E-05	0.002384832	0		0	0	0
Wet fibre out	4.67715	10.0970	1 101	28029.67207	69.84996899	0.14999999	28.91907181	1.065914592	0.015013593	3.10138E-05	0		0	0	0
DRYING	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Wet fibre in	4.67715	10.0970	1 101	28029.67207	66896678.69	0.14999999	28.91907181	1.065914592	0.015013593	3.10138E-05	0		0	0	0
Dry fibre out	1.58545	64.46163t	5 100	27832.25079	11.47267847	0.01734079	85.31118225	3.144445113	0.044290062	9.14908E-05	0		0	0	0
RECOVERY STEP 1	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	En zyme-%	
Processwater in	61.6955	14.99026	9 101	206060.1325	88.41595841	11.5343561	0.044742421	0.002534849	2.33445E-05	0.002384832	0		0	0	0
Processwater out	61.6955	14.99026	9 101	206060.1325	88.41595841	11.5343561	0.044742421	0.002534849	2.33445E-05	0.002384832	0		0	0	0
Wastewater out	0	15.01028	9 101	0	0	0	0	0	0	0	0		0	0	0
RECOVERY STEP 2	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Processwater in	61.6955	14.99026	9 101	206060.1325	88.41595841	11.5343561	0.044742421	0.002534849	2.33445E-05	0.002384832	0		0	0	0
Processwater out	61.6955	14.99026	101 9	206060.1325	88.41595843	11.5343561	0.044742421	0.002534849	2.33445E-05	0.002384832	0		0	0	0
Wastewater out	0	15.01028	9 101	0	0	0	0	0	0	0	0		0	0	0

RECOVERY STEP 3	[kg/s]	[Celsius]	[kPa]	Ŵ	W ater-%	Solvent-%	Cellulose-% H	emicellulose-% L	ignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Processwater in	61.6955	14.990269	101	206060.1325	88.41595843	11.5343561	0.044742421	0.002534849	2.33445E-05	0.002384832		0	0	0
Processwater out	61.666	14.990269	101	205531.1548	88.45836254	11.539888	4.47639E-06	0.001625706	2.33557E-09	0.000119299		0	0	0
Wastewater out	0.03625	17.784716	101	534.5457921	1.464543817	0	76.14775534	1.548765983	0.039536737	3.856225199		0	0 16.942979	0
RECOVERY STEP 4	[kg/s]	[Celsius]	[kPa]	ŚW	W ater -%	Solvent-%	Cellulose-% H	emi cellu lose-%	ignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Processwater in	61.666	14.990269	101	205531.1548	88.45836254	11.539888	4.47639E-06	0.001625706	2.33557E-09	0.000119299		0	0	0
Processwater out	8.27571	70	101	203202.5611	13.99815913	85.9888047	3.33555E-05	0.01211385	1.74033E-08	0.000888948		0	0	0
Wastewater out	35.0471	78.807348	101	11565.40531	100	0	0	0	0	0		0	0	0
Steam in	20.3456	150	450	55903.30711	100	0	0	0	0	0		0	0	0
Steam out	18.4449	43.258493	S	47607.6668	100	0	0	0	0	0		0	0	0
Pure steam condensate	20.2439	147.92804	450	12617.063	100	0	0	0	0	0		0	0	0
LLE 1 process water feed	80.7176	19.266894	101	251152.9415	88.45836707	11.5197687	5.58564E-05	0.020285525	2.91432E-08	0.001488609		0 3.42256E	05 0	0
LLE 1 accept	87.6834	19.429233	101	666465.8394	0	7.95345431	5.1419E-11	1.8674E-08	2.66973E-14	1.37035E-09		0 92.046464	24 0	0
LLE 1 reject	73.7518	80	101	70201.36973	96.81321247	3.15195122	6.1132E-05	0.022201456	3.18958E-08	0.001629205		0 0.0109444	89	0
Recycled solution to LLE 1 feed	19.0516	33.1094	101	45621.78671	88.45838174	11.4546469	0.000222162	0.080683303	1.15914E-07	0.005920767		0 0.0001450	06 0	0
LLE 2 process water feed	1.2425	33.1094	101	2975.333858	88.45838174	11.4546469	0.000222162	0.080683303	1.15914E-07	0.005920767		0 0.0001450	06 0	0
LLE 2 accept	1.34912	30.047679	101	10263.6188	0	7.9120424	2.04605E-10	7.43069E-08	1.06233E-13	5.45285E-09		92.087876	05 0	0
LLE WW	1E-07	25	101	1.04899E-05	100	0	0	0	0	0		0	0	0
Organic solvent in	81.9601	20	101	537040.5125	0	0	0	0	0	0		0 99.99912	95 0	0
Organic solvent recovered	81.5952	20	101	534649.6885	0	0	0	0	0	0		0 99.99900	72 0	0
Organic solvent make-up	0.36487	20	101	2390.823981	0	0	0	0	0	0		0	00 00	0
TOTAL	[kg/s]	[Celsius]	[kPa]	ŚW	W ater -%	Solvent-%	Cellulose-% H	emicellulose-%	ignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Pulp in	1.5563	25	101	28252.21865	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0
Fibreout	1.58549	64.461636	100	27832.25079	11.47267847	0.01734079	85.31118225	3.144445113	0.044290062	9.14908E-05		0	0	0
Solvent make-up	0.04927	25	101	1207.53753	14	86	0	0	0	0		0	0	0
Organic solvent make-up	0.36487	20	101	2390.823981	0	0	0	0	0	0		0	00	0
Freshwater in	12.5444	10	101	528.5388556	100	0	0	0	0	0		0	0	0
Steam in	21.0031	150	450	57709.74901	100	0	0	0	0	0		0	0	0
Steam pure condensate out	19.0041	99.899913	101	7956.717573	100	0	0	0	0	0		0	0	0
Evaporated condensate out	21.1452	30	101	2658.074936	100	0	0	0	0	0		0	0	0
Wastewater to purification	57.0705	60.644807	101	15017.25706	99.93741524	0	0.04836354	0.000983664	2.52338E-05	0.002449195	2.168831	-06	0 0.010761	0
Treated wastewater for re-use	45.6278	60.644807	101	11584.86661	100	0	0	0	0	0		0	0	0
Wastewater out	11.4427	60.644807	101	3432.390445	99.68785764	0	0.241213849	0.004906038	0.000125854	0.012215395	1.081715	-05	0 0.0536704	0

Table C-2 Process data for Concept 1 Ion exchange & Evaporation, part 2

NOLLIOSSIG	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	_
Pulp in (pre-treatment)	1.56	5 25	5 101	28252.21558	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0	\sim
Mixing water in (pre-treatment)	1.31	1 1(0 101	55.08081141	100	0	0	0	0	0		0	0	0	~
Solvent in (Dissolution)	8.32	2 49.5	5 101	204019.016	13.99904327	85.9941197	7.131E-07	0.006365294	4.15182E-10	0.000471054		0	0	0	0
Solvent recovered	8.25	3 7(0 101	203202.0102	13.99820994	85.9889978	1.33423E-06	0.0119096	7.76815E-10	0.000881353		0	0	0	~
Solvent make-up	0.05	5 2!	5 101	1208.228228	14	86	0	0	0	0		0	0	0	~
Heated stream before dissolution	11	1 8(0 101	159712.8157	23.20029529	63.6649156	12.33581649	0.459483274	0.006404889	0.013160271	0.31992419	6	0	0	~
Steam in	0.66	5 15(0 45C	1806.443497	100	0	0	0	0	0		0	0	0	<u> </u>
Condensate out	0.81	1 51.(0	2092.69368	100	0	0	0	0	0		0	0	0	<u> </u>
Pure steam condensate	0.65	5 147.5	9 45C	407.7041697	100	0	0	0	0	0		0	0	0	~
Wastewater out	0.84	4 73.5	5 101	259.2313288	99.99985301	0	0	0	0	0	0.00014695	5	0	0	~
Dope out	9.51	1 12(0 101	159716.2354	10.00000071	74.9197019	14.516562	0.540711467	0.007537156	0.015486765		0	0	0	6
SPINNING AND WASHING	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Dopein	9.51	1 12(0 101	159716.2354	10.0000071	74.9197019	14.516562	0.540711467	0.007537156	0.015486765		0	0	0	\sim
Pure washwater in	11.25	5 1(0 101	474.0135246	100	0	0	0	0	0		0	0	0	~
Recycled processwater in	45.61	1 1(0 101	1921.898521	100	0	0	0	0	0		0	0	0	~
Cooling demand	97.75		5 101	2066.842252	100	0	0	0	0	0		0	0	0	~
Processwater out	61.70	3 15.00026	3 101	206066.0724	88.41596418	11.5343656	0.04474243	0.002520197	2.33445E-05	0.002384286		0	0	0	<u> </u>
Wet fibre out	4.65	3 10.0970	1 101	28029.63669	69.84996896	0.1500003	28.91907175	1.065914659	0.015013593	3.10067E-05		0	0	0	6
DRYING	[kg/s]	[Celsius]	[kPa]	kW	W ater-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Wet fibre in	4.65	3 10	1 101	28029.63669	69.84996896	0.1500003	28.91907175	1.065914659	0.015013593	3.10067E-05		0	0	0	
Dry fibre out	1.55	9 64.5	5 10C	27832.21565	11.47269867	0.01734082	85.3111626	3.14444593	0.044290052	9.14698E-05		0	0	0	~
RECOVERY STEP 1	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	_
Processwater in	61.70	11:	5 101	206059.89	88.4159642	11.5343655	0.04474243	0.002520197	2.33445E-05	0.002384286		0	0	0	~
Processwater out	61.23	1	5 101	205503.0063	88.36912545	11.6249587	0.001803755	0.001728049	1.05019E-06	0.002383023		0	0	0	~
Wastewater out	0.45	3 1:	5 101	561.7180641	94.37886208	0.00123123	5.511133964	0.10336608	0.002861562	0.002545086		0	0	0	_
RECOVERY STEP 2	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	_
Processwater in	61.23	1 1;	5 101	205503.0063	88.36912545	11.6249587	0.001803755	0.001728049	1.05019E-06	0.002383023		0	0	0	
Processwater out	61.23	1	5 101	205503.0063	88.36912547	11.6249587	0.001803755	0.001728049	1.05019E-06	0.002383023		0	0	0	~
Wastewater out	5	11	5 101	. 0	0	0	0	0	0	0		0	0	0	_
		1	2		0	>	>	0	>	2		2	>		2

Table C-3 Process data for Concept 2 Flotation, Ion exchange & Evaporation, part 1

RECOVERY STEP 3	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Processwater in	61.21	15	101	205503.0063	88.36912547	11.6249587	0.001803755	0.001728049	1.05019E-06	0.002383023		0	0	0	C
Processwater out	61.21	15	101	205506.7894	88.37282517	11.6254454	1.80383E-07	0.001610141	1.05023E-10	0.000119156		0	0	0	0
Wastewater out	0.009	25.4	101	1.737356017	5.734614822	0	12.02947345	0.786874194	0.006245832	15.09955928		0	0 66.342	174 0	0
RECOVERY STEP 4	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-%	Aci d-%	Enzyme-%	
Processwater in	61.21	15	101	205506.7894	88.37282517	11.6254454	1.80383E-07	0.001610141	1.05023E-10	0.000119156		0	0	0	0
Processwater out	8.28	70	101	203202.011	13.99820678	85.9890009	1.33423E-06	0.011909601	7.76815E-10	0.000881353		0	0	0	0
Wastewater out	34.75	78.8	101	11466.49793	100	0	0	0	0	0		0	0	0	0
Steam in	20.17	150	450	55426.78432	100	0	0	0	0	0		0	0	0	0
Steam out	18.29	43.3	S	47206.77323	100	0	0	0	0	0		0	0	0	0
Pure steam condensate	20.0713	147.9	450	12509.51448	100	0	0	0	0	0		0	0	0	0
LLE 1 process water feed	80.12	19.3	101	251105.0476	88.37282444	11.6055608	2.25083E-06	0.020091453	1.31048E-09	0.001486833		0 3.42199	E-05	0	0
LLE 1 accept	87.09	19.4	101	662556.9993	0	8.00794119	2.07078E-12	1.84843E-08	1.07517E-15	1.3679E-09		0 91.99197	748	0	0
LLE 1 reject	73.15	80	101	69996.99682	96.78775025	3.17766217	2.46514E-06	0.022004509	1.43526E-09	0.001628406		0 0.010952	203	0	0
Recycled solution to LLE 1 feed	18.91	33.1	101	45598.2582	88.37282206	11.5411898	8.95334E-06	0.07991983	5.21283E-09	0.005914328		0 0.000144	866	0	0
LLE 2 process water feed	1.23	33.1	101	2973.799468	88.37282206	11.5411898	8.95334E-06	0.07991983	5.21283E-09	0.005914328		0 0.000144	866	0	0
LLE 2 accept	1.34	30.0	101	10202.44779	0	7.96705749	8.24084E-12	7.35598E-08	4.27873E-15	5.44367E-09		0 92.03286	109	0	0
LLE WW	1E-07	25	101	1.04899E-05	100	0	0	0	0	0		0	0	0	0
Organic solvent in	81.35	20	101	533068.8079	0	0	0	0	0	0		0 99.9991	305	0	0
Organic solvent recovered	80.99	20	101	530692.015	0	0	0	0	0	0		0 99.9991	162	0	0
Organic solvent make-up	0.36	20	101	2376.792979	0	0	0	0	0	0		0	100	0	0
TOTAL	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-% H	emicellulose-%	Lignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-%	Aci d-%	Enzyme-%	
Pulp in	1.56	25	101	28252.21558	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0	0
Fibreout	1.59	64.5	100	27832.21565	11.47269867	0.01734082	85.3111626	3.144444593	0.044290052	9.14698E-05		0	0	0	0
Solvent make-up	0.05	25	101	1208.228228	14	86	0	0	0	0		0	0	0	0
Organic solvent make-up	0.36	20	101	2376.792979	0	0	0	0	0	0		0	100	0	0
Freshwater in	12.56	10	101	529.094336	100	0	0	0	0	0		0	0	0	Ĉ
Steam in	20.8297	150	450	57233.22782	100	0	0	0	0	0		0	0	0	0
Steam pure condensate out	18.85	99.9	101	7891.01733	100	0	0	0	0	0		0	0	0	0
Evaporated condensate out	20.97	30	101	2636.584482	100	0	0	0	0	0		0	0	0	0
Wastewater to purification	57.05	60.3	101	14925.76917	99.93745977	1.0377E-05	0.048382213	0.000997735	2.52435E-05	0.002450417	2.16946	<u>-06</u>	0 0.0106	21 (0
Treated wastewater for re-use	45.61	60.3	101	11511.47775	100	0	0	0	0	0		0	0	0	Ĉ
Wastewater out	11.44	60.3	101	3414.291413	99.68807913	5.1754E-05	0.241307408	0.004976226	0.000125903	0.012221512	1.082021	5-05	0 0.0532	272 0	0

Table C-4 Process data for Concept 2 Flotation, Ion	exchange & Evaporation, part 2
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DISSOLUTION	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	temicel lulose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Pulp in (pre-treatment)	1.56	5 25	101	28252.25	5 7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0 0	
Mixing water in (pre-treatment)	1.31	1 10	101	55.08	100	0	0	0	0	0		0	0	0	
Solvent in (Dissolution)	8.3	2 49.5	101	204019.55	13.9990302	85.994148	0	0.006472764	4.53054E-11	0.000349081		0	0	0	
Solvent recovered	8.25	3 69.99997	101	203203.37	7 13.99818549	85.9890507	0	0.01211066	8.47671E-11	0.000653137		0	0	0	
Solvent make-up	0.0	5 25	101	1207.77	14	86	0	0	0	0		0	0	0	
Heated stream before dissol ution	11.15	9 80	101	159713.33	3 23.20028781	63.6649312	12.33581898	0.459563349	0.00640489	0.013069518	0.3199242	77	0	0 0	
Steam in	0.66	5 150	450	1806.44	100	0	0	0	0	0		0	0	0	
Condensate out	0.8	1 51.0	5	2092.70	100	0	0	0	0	0		0	0	0	
Pure steam condensate	0.65	148	3 450	407.70	100	0	0	0	0	0		0	0	0	
Wastewater out	0.8	4 73.53	101	259.23	99.99985301	0	0	0	0	0	0.0001469	95	0	0	
Dope out	9.5	1 120	101	159716.75	9.999991422	74.9197207	14.51656502	0.540805702	0.007537157	0.015379969		0	0	0 0	
SPINNING AND WASHING	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-%	lemicel lul ose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Dope in	9.51	1 120	101	159716.75	9.999991422	74.9197207	14.51656502	0.540805702	0.007537157	0.015379969		0	0	0 0	
Pure washwater in	11.24	1 10	101	473.47	100	0	0	0	0	0		0	0	0	
Recycled processwater in	45.6	3 10	101	1922.45	100	0	0	0	0	0		0	0	0 0	
Cooling demand	97.73	5	101	2066.84	100	0	0	0	0	0		0	0	0 0	
Processwater out	61.7(15	101	206066.91	1 88.41596699	11.5343648	0.044742372	0.002534661	2.33444E-05	0.002367845		0	0	0	
Wet fibre out	4.6	3 10.1	101	28029.68	8 69.84996928	0.14999993	28.91907127	1.065915139	0.015013593	3.07929E-05		0	0	0 0	
DRYING	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-%	temicel lul ose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Wet fibre in	4.68	3 10.1	101	28029.68	8 69.84996928	0.14999993	28.91907127	1.065915139	0.015013593	3.07929E-05		0	0	0 0	
Dry fibre out	1.55	9 64.5	100	27832.25	5 11.47270722	0.01734083	85.31115357	3.144445729	0.044290047	9.08389E-05		0	0	0 0	
RECOVERY STEP 1	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	lemicel lul ose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Processwater in	61.7(D 15	101	206060.73	88.41596701	11.5343648	0.044742372	0.002534661	2.33444E-05	0.002367844		0	0	0 0	
Processwater out	61.6(5 15	101	205512.42	2 88.45577201	11.5407638	0	0.001710944	1.13768E-07	0.001753177		0	0	0	
Wastewater out	÷0.0	3 15	101	548.30	16.66634428	0	80.69412708	1.487308058	0.041897283	1.110323295		0	0	0 0	
RECOVERY STEP 2	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	lemicel lul ose-%	Lignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%	
Processwater in	61.66	5 15	101	205512.42	2 88.45577201	11.5407638	0	0.001710944	1.13768E-07	0.001753177		0	0	0 0	
Processwater out	61.6(5 15	101	205512.42	2 88.45577203	11.5407637	0	0.001710944	1.13768E-07	0.001753177		0	0	0	
Wastewater out	0.0	0 15	101	0.00	0	0	0	0	0	0		0	0	0	

Table C-5 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 1

RECOVERY STEP 3	[kg/s]	[Celsius]	[kPa]	ŚW	Water-%	Solvent-%	Cellulose-%	Hemi cellul ose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Processwater in	61.66	Ĩ	5 101	205512.42	88.45577203	11.5407637	0	0.001710944	1.13768E-07	0.001753177		0	0	0
Processwater out	61.66	Ħ	5 101	205531.51	88.45732107	11.5409658	0	0.001625425	1.1377E-11	8.76604E-05		0	0	0
Wastewater out	0.01	26.	7 101	-14.99	6.520071603	0	0	0.881797211	0	17.16771061		0	0 75.429248	0
RECOVERY STEP 4	[kg/s]	[Celsius]	[kPa]	Ŵ	Water-%	Solvent-%	Cellulose-%	Hemi cellul ose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Processwater in	61.66	Ħ	5 101	205531.51	88.45732107	11.5409658	0	0.001625425	1.1377E-11	8.76604E-05		0	0 0	0
Processwater out	8.28	7	101 0	203203.27	13.99811592	85.9891203	0	0.012110673	8.47672E-11	0.000653138		0	0	0
Wastewater out	35.04	78.5	8 101	11564.18	100	0	0	0	0	0		0	0	0
Steam in	20.34	15(9 450	55897.40	100	0	0	0	0	0		0	0	0
Steam out	18.44	43	3 5	47602.70	100	0	0	0	0	0		0	0 0	0
^p ure steam condensate	20.24	147.5	9 450	12615.73	100	0	0	0	0	0		0	0 0	0
LE 1 process water feed	88.50	20.1	5 101	269763.91	88.45732173	11.5092547	0	0.031658062	2.21594E-10	0.001707401		0 5.80903E-	05 0	0
LLE 1 accept	95.49	20.4	4 101	718109.43	0	7.33310241	0	2.93394E-08	0	1.58235E-09		0 92.666815	58 0	0
LE 1 reject	81.50	8	101 0	89649.73	96.04765079	3.90526271	0	0.034374517	2.40608E-10	0.001853909		0 0.0108580	75 0	0
Recycled solution to LLE 1 feed	26.84	33	1 101	64232.40	88.45732323	11.4363918	0	0.100664278	7.04611E-10	0.005429093		0 0.0001915	65 0	0
LE 2 process water feed	1.00	33	1 101	2382.99	88.45732323	11.4363918	0	0.100664278	7.04611E-10	0.005429093		0 0.0001915	65 0	0
LLE 2 accept	1.07	30.1	101 0	8081.00	0	7.29005253	0	9.3335E-08	0	5.0338E-09		0 92.709865	35 0	0
TLE WW	0.00	2:	5 101	00.0	100	0	0	0	0	0		0	0 0	0
Organic solvent in	89.49	21	0 101	586411.45	0	0	0	0	0	0		0 99.999912	83 0	0
Organic solvent recovered	89.10	21	0 101	583846.17	0	0	0	0	0	0		0 99.999669	96 0	0
Organic solvent make-up	0.39	2(101	2565.28	0	0	0	0	0	0		0	0 00	0
TOTAL	[kg/s]	[Celsius]	[kPa]	Ŵ	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	-ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
oulp in	1.56	21	5 101	28252.25	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0 0	0
cibre out	1.59	64.	5 100	27832.25	11.47270722	0.01734083	85.31115357	3.144445729	0.044290047	9.08389E-05		0	0 0	0
Solvent make-up	0.05	2:	5 101	1207.77	14	86	0	0	0	0		0	0 0	0
Organic solvent make-up	0.39	2(0 101	2565.28	0	0	0	0	0	0		0	0 00	0
^c resh water in	12.54	11	0 101	528.55	100	0	0	0	0	0		0	0 0	0
Steam in	21.00	15(0 450	57703.85	100	0	0	0	0	0		0	0 0	0
Steam pure condensate out	19.00	: 66	9 101	7955.90	100	0	0	0	0	0		0	0	0
Evaporated condensate out	21.14	36	0 101	2657.81	100	0	0	0	0	0		0	0	0
Wastewater to purification	57.07	1.03	6 101	15014.53	99.94024689	0	0.048369978	0.00098396	2.52371E-05	0.00246511	2.1689E-	96	0 0.0079067	0
Treated wastewater for re-use	45.63	60.1	6 101	11584.02	100	0	0	0	0	0		0	0 0	0
Wastewater out	11.44	60.1	6 101	3430.52	99.70194684	0	0.241273217	0.004908067	0.000125885	0.012296162	1.08187E-	05	0 0.039439	0

Table C-6 Process data for Concept 3 Filtration, Ion exchange & Evaporation, part 2

DISSOLUTION	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Sol vent-%	Cellulose-%	Hemicellulose-%	.ignine-%	Inorganics-%	Deg. Solvent-%	Org. Si	olvent-% Ac	cid-%	Enzyme-%	
Pulp in (pre-treatment)	1.55631	25	101	28252.29916	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0	0	0
Mixing water in (pre-treatment)	1.3073	10	101	55.08097435	100	0	0	0	0	0		0	0	0		0
Solvent in (Dissolution)	7.23133	37.564282	101	203847.2005	0.500498281	99.0000235	0	6.24974E-08	8.44961E-12	1.27623E-07		0	0.499478059	0	0	0
Solvent recovered	7.18812	49.99	101	203035.5676	1.61456E-05	99.000047	0	1.25117E-07	1.69158E-11	2.55496E-07		0	0.999936487	0		0
Solvent make-up	0.04321	25	101	1218.035917	H	66	0	0	0	0		0	0	0	0	0
Heated stream before dissolution	10.0949	80	101	160272.3215	14.52770902	70.9169175	13.67227058	0.504014173	0.007098791	0.014197672		0	0.357792282	0	0	0
Steam in	0.15778	150	450	433.5293609	100	0	0	0	0	0		0	0	0		0
Condensate out	0.37129	45.857417	5	1029.757012	95.66465124	0	0	0	0	0		0	4.335348755	0		0
Pure steam condensate	0.15699	147.92804	450	97.84514623	100	0	0	0	0	0		0	0	0	-	0
Wastewater out	0.17381	61.046322	101	150.4476462	90.38682618	0	0	0	0	0		0	9.613173823	0		0
Dope out	9.55063	120	101	160445.8678	9.999997311	74.9585807	14.45147411	0.532738709	0.007503361	0.015006819		0	0.034699036)	0	0
SPINNING AND WASHING	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Sol vent-%	Cellulose-%	Hemicellulose-%	.ignine-%	norganics-%	Deg. Solvent-%	Org. S	olvent-% Ac	cid-%	Enzyme-%	
Dope in	9.55063	120	101	160445.8678	9.999997311	74.9585807	14.45147411	0.532738709	0.007503361	0.015006819		0	0.034699036			0
Pure washwater in	11.0035	10	101	463.6166437	100	0	0	0	0	0		0	0		0	0
Recycled processwater in	45.9822	10	101	1937.388586	100	0	0	0	0	0		0	0	U	0	0
Cooling demand	98.0373	2	101	2073.358235	100	0	0	0	0	0		0	0	0	0	0
Processwater out	61.8592	15.001787	101	207107.5613	88.38427189	11.5617476	0.044624152	0.00166115	2.32828E-05	0.002314679		0	0.00535729	0	0	0
Wet fibre out	4.67719	10.096771	101	28029.67162	69.84997002	0.14999995	28.91912588	1.065860503	0.015013621	3.00302E-05		0	0	0	0	0
DRYING	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Sol vent-%	Cellulose-%	Hemicellulose-%	.ignine-%	Inorganics-%	Deg. Solvent-%	Org. Si	olvent-% Ac	cid-%	Enzyme-%	
Wet fibre in	4.67719	10.096771	101	28029.67162	69.84997002	0.14999995	28.91912588	1.065860503	0.015013621	3.00302E-05		0	0	0	0	0
Dry fibre out	1.58549	64.461644	100	27832.25416	11.4726997	0.01734082	85.31132408	3.144284899	0.044290136	8.8589E-05		0	0	0	0	0
RECOVERY STEP 1	[kg/s]	[Celsius]	[kPa]	kW	W ater-%	Sol vent-%	Cellulose-%	Hemicellulose-%	.ignine-%	norganics-%	Deg. Solvent-%	Org. S	olvent-% Ac	cid-%	Enzyme-%	
Processwater in	61.8592	14.991787	101	207101.3732	88.38427191	11.5617475	0.044624152	0.00166115	2.32828E-05	0.002314679		0	0.00535729		0	0
Processwater out	61.825	14.991787	101	206552.9219	88.42394406	11.5681431	0	0.000839262	1.13467E-07	0.00171381		0	0.005359695	0	0	0
Wastewater out	0.0342	14.991787	101	548.4512677	16.66549831	0	80.71556554	1.487459877	0.041908414	1.088557696		0	0.001010156	0	0	0
RECOVERY STEP 2	[kg/s]	[Celsius]	[kPa]	kW	W ater-%	Solvent-%	Cellulose-%	Hemicellulose-%	.ignine-%	norganics-%	Deg. Solvent-%	Org. S.	olvent-% Ac	cid-%	Enzyme-%	
Processwater in	61.825	14.991787	101	206552.9219	88.42394406	11.5681431	0	0.000839262	1.13467E-07	0.00171381		0	0.005359695	0	0	0
Processwater out	61.825	14.991787	101	206552.9219	88.42394408	11.568143	0	0.000839262	1.13467E-07	0.00171381		0	0.005359695	U	-	0
Wastewater out	0	15.011803	101	0	0	0	0	0	0	0		0	0	0	0	0

Table C-7 Process data for Concept 4 Filtration & LLE (Butanol), part 1

RECOVERY STEP 3	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	ignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Processwater in	61.825	14.991787	101	206552.9219	88.42394408	11.568143	0	0.000839262	1.13467E-07	0.00171381		0.0053596	5	0
Processwater out	61.825	14.991787	101	206552.9219	88.42394408	11.568143	0	0.000839262	1.13467E-07	0.00171381		0.0053596	5	0
Wastewater out	0	26.750813	101	0	0	0	0	0	0	0		0	0	0
RECOVERY STEP 4	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cel lul ose-%	Hemicellulose-%	ignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Processwater in	61.825	14.991787	101	206552.9219	88.42394408	11.568143	0	0.000839262	1.13467E-07	0.00171381		0.0053596	5	0
Processwater out	7.18813	49.99	101	205173.1661	2.66262E-07	98.9999516	0	2.09005E-07	2.82573E-11	4.26798E-07		1.0000475	7	0
Wastewater out	35.307	76.891122	101	12096.47452	99.87318743	0.10128291	0	0.001469566	0	0.003000925		0.0210589	9	0
Steam in	36.8042	150	450	101126.1792	55.3978911	0	0	0	0	0		0	0	0
Steam out	20.3841	35.111997	2	62978.04055	98.46283725	0	0	0	0	0		1.5371627	4	0
Pure steam condensate	36.6202	147.92804	450	22823.6117	100	0	0	0	0	0		0	0	0
LLE 1 process water feed	88.8833	20.511407	101	270627.1987	88.42393103	11.5167459	0	0.016318782	2.20628E-06	0.033323684		0.0096783	80	0
LLE 1 accept	95.9205	20.306067	101	3358723.653	0	7.33687373	0	1.51215E-08	0	3.08789E-08		92.663044	6	0
LLE 1 reject	81.846	80	101	89627.82338	96.02679518	3.9084308	0	0.017721886	2.39598E-06	0.036188884	-	0.0108608	9	0
Recycled solution to LLE 1 feed	27.0583	33.123063	101	64074.27675	88.42390123	11.3993097	0	0.05168759	6.98811E-06	0.105548371		0.01954610	5	0
LLE 2 process water feed	1.00385	33.123063	101	2377.123252	88.42390123	11.3993097	0	0.05168759	6.98811E-06	0.105548371		0.01954610	5	0
LLE 2 accept	1.08262	27.99878	101	37941.79398	0	7.2668286	0	4.7927E-08	0	9.7869E-08	-	92.733089	9	0
LLE WW	34.8209	76.952953	101	11982.23431	99.88638064	0.10269687	0	0.001490097	0	0.003042844		0.0063893	.2	0
Organic solvent in	89.8871	20	101	3256190.713	0	0	0	0	0	0		99.999912	2	0
Organic solvent recovered	100.73	20	101	3242267.508	0	0	0	0	0	0		88.854031	5	0
Organic solvent make-up	0.38413	20	101	13923.20528	0	0	0	0	0	0		10	0	0
TOTAL	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cel lul ose-%	Hemicellulose-%	ignine-%	norganics-%	Deg. Solvent-%	Org. Solvent-%	Acid-%	Enzyme-%
Pulp in	1.55631	25	101	28252.29916	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0
Fibre out	1.58549	64.461644	100	27832.25416	11.4726997	0.01734082	85.31132408	3.144284899	0.044290136	8.8589E-05		0	0	0
Solvent make-up	0.04321	25	101	1218.035917	ti ti	66	0	0	0	0		0	0	0
Organic solvent make-up	0.38413	20	101	13923.20528	0	0	0	0	0	0		10	0	0
Freshwater in	12.3108	10	101	518.697618	100	0	0	0	0	0		0	0	0
Steam in	36.962	150	450	101559.7086	100	0	0	0	0	0		0	0	0
Steam pure condensate out	33.4441	99.899913	101	14002.52006	100	0	0	0	0	0		0	0	0
Evaporated condensate out	24.0885	30	101	14358.93111	98.63240311	0	0	0	0	0		1.3675968	2	0
Wastewater to purification	57.8707	58.820633	101	17556.50367	99.32091917	0.06179289	0.047699629	0.001775613	2.48874E-05	0.002474163		0.5653136	80	0
Treated wastewater for re-use	45.9822	58.820633	101	11323.84406	100	0	0	0	0	0		0	0	0
Wastewater out	11.8885	58.820633	101	6232.659607	96.69438698	0.30079392	0.232191086	0.008643287	0.000121146	0.012043672		2.7518199	e.	0

Table C-8 Process data for Concept 4 Filtration & LLE (Butanol), part 2

DISSOLUTION	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% Ht	amicel lulose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-9	% Acid-%	Enzyme-%	
Pulp in (pre-treatment)	1.5563	25	101	28252.20892	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0	0
Mixing water in (pre-treatment)	1.30729	10	101	55.08079842	100	0	0	0	0	0		0	0	0	0
Solvent in (Dissolution)	7.2313	37.564289	101	203846.5648	0.500497914	98.999992	0	6.18911E-08	8.44968E-12	1.27626E-07		0 0.4995	09911	0	0
Solvent recovered	7.1881	49.99	101	203035.0489	1.61448E-05	98.999984	0	1.23904E-07	1.69159E-11	2.55501E-07		0 0.999	99952	0	0
Solvent make-up	0.0432	25	101	1217.868083	-	66	0	0	0	0		0	0	0	0
Heated stream before dissolution	10.0949	80	101	160271.825	14.52770556	70.9169013	13.67226746	0.504014058	0.007098789	0.014197669		0 0.3578	15131	0	0
Steam in	0.15778	150	450	433.5275419	100	0	0	0	0	0		0	0	0	0
Condensate out	0.37129	45.857404	5	1029.760528	95.66438564	0	0	0	0	0		0 4.335	61436	0	0
Pure steam condensate	0.15699	147.92804	450	97.84473567	100	0	0	0	0	0		0	0	0	0
Wastewater out	0.17381	61.046084	101	150.4540928	90.38626365	0	0	0	0	0		0 9.6137	36348	0	0
Dope out	9.5506	120	101	160445.3569	9.999998459	74.9585778	14.45147357	0.532738688	0.007503361	0.015006819		0 0.0347	01264	0	0
SPINNING AND WASHING	[kg/s]	[Celsius]	[kPa]	kw	Water-%	Solvent-%	Cellulose-% Ht	amicel lulose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-9	% Acid-%	Enzyme-%	
Dopein	9.5506	120	101	160445.3569	9.999998459	74.9585778	14.45147357	0.532738688	0.007503361	0.015006819		0 0.0347	01264	0	0
Pure washwater in	11.0035	10	101	463.6169929	100	0	0	0	0	0		0	0	0	0
Recycled processwater in	45.9822	10	101	1937.386879	100	0	0	0	0	0		0	0	0	0
Cooling demand	98.0369	S	101	2073.350685	100	0	0	0	0	0		0	0	0	0
Processwater out	61.8591	15.001788	101	207106.9511	88.38429937	11.5617279	0.044624064	0.001653081	2.32827E-05	0.002314675		0 0.0053	57623	0	0
Wet fibre out	4.67719	10.096771	101	28029.68823	69.84997003	0.14999994	28.91902304	1.065963391	0.015013568	3.00302E-05		0	0	0	0
DRYING	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% Ht	amicel lulose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-5	% Acid-%	Enzyme-%	
Wet fibre in	4.67719	10.096771	101	28029.68823	69.84997003	0.14999994	28.91902304	1.065963391	0.015013568	3.00302E-05		0	0	0	0
Dry fibreout	1.58549	64.461608	100	27832.27068	11.47271837	0.01734084	85.31100274	3.144587757	0.044289969	8.8589E-05		0	0	0	0
RECOVERY STEP 1	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% Hi	emicel lulose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-9	% Acid-%	Enzyme-%	
Processwater in	61.8591	14.991788	101	207100.7626	88.38429939	11.5617279	0.044624064	0.001653081	2.32827E-05	0.002314675		0 0.0053	57623	0	0
Processwater out	61.8249	14.991788	101	206552.312	88.42397154	11.5681234	0	0.000831108	1.13467E-07	0.001713807		0 0.0053	60027	0	0
Wastewater out	0.0342	14.991788	101	548.4506404	16.66549979	0	80.71542109	1.487604538	0.041908339	1.08855603		0 0.0010	10219	0	0
RECOVERY STEP 2	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-% Hu	emicel lulose-%	ignine-%	Inorganics-%	Deg. Solvent-%	Org. Solvent-9	% Acid-%	Enzyme-%	
Processwater in	61.8249	14.991788	101	206552.312	88.42397154	11.5681234	0	0.000831108	1.13467E-07	0.001713807		0 0.0053	60027	0	0
Processwater out	61.8249	14.991788	101	206552.312	88.42397156	11.5681234	0	0.000831108	1.13467E-07	0.001713807		0 0.0053	60027	0	0
Wastewater out	0	15.011804	101	0	0	0	0	0	0	0		0	0	0	0

Table C-9 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 1

RECOVERY STEP 3	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	Inorgani cs-%	Deg. Solvent-%	Org. Solve	int-% Acid-%	Enzym	e-%
Processwater in	61.8249	14.991788	101	206552.312	88.42397156	11.5681234	0	0.000831108	1.13467E-07	0.001713807		0.0	05360027	0	0
Processwater out	61.8249	14.991788	101	206552.312	88.42397156	11.5681234	0	0.000831108	1.13467E-07	0.001713807		0.0	05360027	0	0
Wastewater out	0	26.751267	101	0	0	0	0	0	0	0		0	0	0	0
RECOVERY STEP 4	[kg/s]	[Celsius]	[kPa]	kW	W ater-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	Inorgani cs-%	Deg. Solvent-%	Org. Sol ve	:nt-% Acid-%	Enzym	e-%
Processwater in	61.8249	14.991788	101	206552.312	88.42397156	11.5681234	0	0.000831108	1.13467E-07	0.001713807		0.0 0.0	05360027	0	0
Processwater out	7.18808	49.99	101	203034.3918	1.6145E-05	986666.86	0	1.23904E-07	1.69159E-11	2.55501E-07		0 1.0	00003468	0	0
Wastewater out	35.307	76.89119	101	12096.41708	99.87320204	0.10128267	0	0.001455305	0	0.00300098		0.0	21058805	0	0
Steam in	23.929	150	450	65749.33844	85.20498729	0	0	0	0	0		0	0	0	0
Steam out	19.8123	34.000585	5	52037.6885	98.55186754	0	0	0	0	0		0 1.4	48132459	0	0
Pure steam condensate	23.8094	147.92804	450	14839.25707	100	0	0	0	0	0		0	0	0	0
LLE 1 process water feed	80.9803	19.279936	101	252019.4035	88.42397812	11.5401595	0	0.010363619	1.41489E-06	0.021370767		0.0	04126541	0	0
LLE 1 accept	87.9844	19.4383	101	668901.2905	0	7.96611762	0	9.53861E-09	0	1.96695E-08		0 92.	03380097	0	0
LLE 1 reject	73.9761	80	101	70091.74417	96.79611108	3.15820106	0	0.011344861	1.54886E-06	0.023394196		0.0	10947252	0	0
Recycled solution to LLE 1 feed	19.1554	33.120137	101	45467.09148	88.4239993	11.4499049	0	0.041130243	5.6153E-06	0.084814524		0.0	00145406	0	0
LLE 2 process water feed	1.24926	33.120137	101	2965.246063	88.4239993	11.4499049	0	0.041130243	5.6153E-06	0.084814524		0.0	00145406	0	0
LLE 2 accept	1.35642	30.054407	101	10318.65276	0	7.90902599	0	3.7881E-08	0	7.81142E-08		0 92.	09089245	0	0
LLE WW	35.307	76.89119	101	12096.41708	99.87320204	0.10128267	0	0.001455305	0	0.00300098		0.0	21058805	0	0
Organic solvent in	82.2255	20	101	538805.43	0	0	0	0	0	0		0 99.	99991299	0	0
Organic solvent recovered	81.8665	20	101	536427.241	0	0	0	0	0	0		0 99.	99991264	0	0
Organic solvent make-up	0.36295	20	101	2378.189075	0	0	0	0	0	0		0	100	0	0
TOTAL	[kg/s]	[Celsius]	[kPa]	kW	Water-%	Solvent-%	Cellulose-%	Hemicellulose-%	Lignine-%	Inorganics-%	Deg. Solvent-%	Org. Sol ve	int-% Acid-%	Enzym	e-%
Pulp in	1.5563	25	101	28252.20892	7.907907908	0	88.68468468	3.269269269	0.046046046	0.092092092		0	0	0	0
Fibre out	1.58549	64.461608	100	27832.27068	11.47271837	0.01734084	85.31100274	3.144587757	0.044289969	8.8589E-05		0	0	0	0
Solvent make-up	0.0432	25	101	1217.868083	1	66	0	0	0	0		0	0	0	0
Organic solvent make-up	0.36295	20	101	2378.189075	0	0	0	0	0	0		0	100	0	0
Freshwater in	12.3108	10	101	518.6977913	100	0	0	0	0	0		0	0	0	0
Steam in	24.0868	150	450	66182.86598	100	0	0	0	0	0		0	0	0	0
Steam pure condensate out	21.7943	99.899913	101	9124.946509	100	0	0	0	0	0		0	0	0	0
Evaporated condensate out	22.3556	30	101	4761.115635	98.64461149	0	0	0	0	0		0 1.3	55388505	0	0
Wastewater to purification	57.8707	58.820693	101	17556.43746	99.32092816	0.06179278	0.047699534	0.001766999	2.48873E-05	0.002474197		0 0.5	65313439	0	0
Treated wastewater for re-use	45.9822	58.820693	101	11323.84557	100	0	0	0	0	0		0	0	0	0
Wastewater out	11.8885	58.820693	101	6232.591886	96.69442959	0.30079351	0.232190705	0.008601357	0.000121146	0.012043839		0 2.7	51819858	0	0

Table C-10 Process data for Concept 5 Filtration & LLE (Dichloromethane), part 2	Table C-10 Process of	ata for Concept 5	5 Filtration & LLE	(Dichloromethane),	part 2
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Appendix D – Technical analysis

Flotation

The surface area of the flotation unit can be calculated from the following equation

$$A_{Surface\ area}\ [m^2] = \frac{\dot{Q}\ [m^3/h]}{v_t\ [m/h]}$$

Where v_t is the vertical rise speed of suspended solids and \dot{Q} is the total flowrate. The equation can be used in combination with the next one to obtain depth and retention time for the flotation unit

$$v_T [m/h] = \frac{Depth [m]}{Retention time [h]}$$

Common design values for flotation units are 3-8 [m/h], which would give the following result for retention at 30 minutes, 60 minutes and 90 minutes. An incoming mass flow of 65 kg/s is used as a design value.



Figure D-1 Flotation unit surface area and depth as a function of vertical speed of suspended solids.

Air-to-solids ratios are system specific, but normal process values are 5-60 [l/kg]. A ratio of 35 l/kg would result in an air demand of 92.7 m³/d.

<u>Filtration</u>

Membrane area required for a specific flow is given by the following general equation, which is based on the flux through the membrane

$$A_{Membrane} [m^2] = \frac{\dot{V}_{Tot} [m^3/h]}{Flux [m^3/m^2/h]}$$

Spiral-wound modules have a standard membrane area of $41m^2$, which means that the number of filtration modules needed can be calculated. Common flux values for ultrafiltration units at 15-150 [l/m²/h] are used to approximate the area. An incoming mass flow of 65 kg/s is used as a design value.



Figure D-2 Membrane area and number of modules as a function of transmembrane flux.

Table D-1 Calculated membrane area and number of modules for specific transmembrane fluxes

	Filtration	
Flux [l/m2/h]	A [m2]	Modules
15	14880	362.9
30	7440	181.5
45	4960	121.0
60	3720	90.7
75	2976.0	72.6
90	2480	60.5
105	2125.7	51.8
120	1860	45.4
135	1653.3	40.3
150	1488.0	36.3

Ion exchange

The operating capacity of a resin is expressed as equivalents per litre resin (eq/l), which the incoming inorganic flow has to be converted to. Equivalent is a unit and it corresponds to mole per valence of the incoming flow. The incoming flow can be converted by using the following formula

$$eq = \frac{m [g] \cdot \text{ion valence number}}{M [g/mole]}$$

The size of the resin bed is dictated by the operating time and resin capacity per litre. When the amount of equivalents in the incoming flow is known, it can be used to calculate the corresponding equivalents capacity for the resin bed. The molecular weight and ion valence number are calculated based on the distribution of ions in PHK TCF dissolving pulp according to Blechschmidt *et al.* (2006) (see Table D-2).

	ppm	g/mol	Valence
Mn	1	54.94	2
Fe	5	55.85	2
Mg	50	24.31	2
Са	20	40.08	2
Si	24	28.09	2

Table D-2 Distribution of ions in TCF PHK Dissolving pulp

The design calculations for a resin bed in Concept 1, 2 and 3 are presented in Table D-3, a resin charge value of 1.1 eq/l and a period of 24h are used.

Table D-3 Design calculations for ion exchange units in Concept 1, 2 and 3

Concept	1	2	3
Ion mass flow [g/s]	1.3974	1.386	1.0267
Ion mean molar mass [g/mol]	30.2545	30.2545	30.2545
Ion valence number	2	2	2
Ion charge flow [eq/s]	0.092376341	0.091622734	0.067870895
Bed charge demand [eq/24h]	7981.315837	7916.204201	5864.045349
Acid molar mass [g/mol]	98.1	98.1	98.1
Acid valence number	2	2	2
Acid mass flow (100%) [g/s]	4.531059512	4.494095093	3.329067411
Acid mass flow (100%) [kg/d]	391.48	388.29	287.63
Resin [eq/l]	1.1	1.1	1.1
Resin demand for 24h [m3]	7.256	7.197	5.331

Evaporation

The evaporator unit areas are approximated by using the following equation

$$A_{Evap} = \frac{\dot{Q}}{U\Delta T}$$

Where U is overall heat transfer coefficient for the evaporator, \dot{Q} is heat flux required for evaporating a specific amount of incoming liquid and ΔT is the temperature difference between incoming and outgoing vapour.

More accurate results can be obtained by describing heat and mass transfer in detail, but these types of approximations require more extensive calculations (Lopez-Toledo, 2006). Because detailed equipment design is not a central topic of this thesis, the more simple approach is opted for. The results are found in Table D-4.

Dissolution evap (1, 2 & 3)	1	2	3			
Thermal duty [kW]	1358.4	763.6	1254			
Delta_T[K]	49	25.6	29.6			
Area [m2]	15.4	16.6	23.5			
Concept 1 Recovery	1	2	3			
Thermal duty [kW]	43000	38650	42400			
Delta_T [K]	55.9	28.2	23.4			
Area [m2]	427.4	761.4	1006.6			
Concept 2 Recovery	1	2	3			
Thermal duty [kW]	42600	38300	42050			
Delta_T [K]	55.9	28.2	23.4			
Area [m2]	423.4	754.5	998.3			
Concept 3 Recovery	1	2	3			
Thermal duty [kW]	43000	38650	42400			
Delta_T [K]	55.9	28.2	23.4			
Area [m2]	427.4	761.4	1006.6			
Dissolution evap (4 & 5)	1	2	3			
Thermal duty [kW]	332	0	368			
Delta_T[K]	42	30.2	22			
Area [m2]	4.4	0.0	9.3			
Concept 4 Recovery	1 (H2O)	2 (H2O)	3 (H2O)	1 (Org.)	2 (Org.)	3 (Org.)
Thermal duty [kW]	41400	35850	42550	36390	14990	23300
Delta_T [K]	56.3	28.5	32.1	31	44.4	2.3
Area [m2]	408.53	698.83	736.41	652.15	187.56	5628.02
Concept 5 Recovery	1 (H2O)	2 (H2O)	3 (H2O)	1 (Org.)	2 (Org.)	3 (Org.)
Thermal duty [kW]	41755	36600	42390	8830	8330	11390
Delta_T[K]	56.4	28.5	32	108.8	43.4	2.5
Area [m2]	411.30	713.45	735.94	45.09	106.63	2531.11

Table D-4 Calculated values for evaporation units, where U=1.8 kW/m²K

Liquid/Liquid-extraction

The liquid/liquid-extraction equipment is assumed to operate as a packed bed. The design procedure for this type of equipment is taken from Couper, Penney and Fair (2012).

A packed bed operates by utilizing two immiscible liquids with different densities. The lighter of the two phases is injected from the bottom of the bed and is dispersed into droplets before starting to ascend to the top. The heavier phase enters from the top of the column from where it flows down through the packing material and interacts with the dispersed phase. Both the dispersed and the continuous phase have to be described to obtain the dimensions of a packed bed. The dispersed phase is described by the size of its droplets and their velocity. The size of the droplets can be described by the Sauter mean drop diameter, which is calculated by the following equation

$$d_{vs} = 1.15 \cdot n \cdot \sqrt{\frac{\sigma}{\mathsf{g} \cdot \Delta \rho}}$$

Where n = 1.0 if mass transfer occurs from the continuous phase to the dispersed phase, and n = 1.4 for the opposite. Gravity is denoted by g, the interfacial tension is represented by σ , and the difference in density by $\Delta \rho$. The drop diameter can be used to calculate the characteristic drop velocity according to

$$U_{so} = \frac{N_{RE} \cdot \mu_c}{d_{vs} \cdot \rho_c}$$

Where μ_c represents the viscosity of the dispersed phase and ρ_c is the density of the dispersed phase. The Reynolds number N_{RE} is calculated by

$$N_{RE} = (0.94 \cdot H^{0.757} - 0.857) \cdot P^{0.149}$$

when $H \leq 59.3$, or

$$N_{RE} = (3.42 \cdot H^{0.441} - 0.857) \cdot P^{0.149}$$

when H > 59.3. The dimensionless numbers *P* and *H* are obtained by using the two following formulas

$$P = \frac{\rho_c^2 \cdot \sigma^3}{\mu_c^4 \cdot g \cdot \Delta \rho}$$
$$H = \left(\frac{4 \cdot d_{vs}^2 \cdot g \cdot \Delta \rho}{3 \cdot \sigma}\right) \cdot \left(\frac{\mu_w}{\mu_c}\right)^{0.14} \cdot P^{0.149}$$

Where μ_w is a reference value for viscosity (0.009 P). The resulting drop velocity U_{so} is then used to obtain the flooding velocity U_{cf} from

$$\frac{1}{U_{cf}} = \frac{5.63}{\varepsilon \cdot U_{so}} + \frac{5.21 \cdot \left(\frac{Q_d}{\dot{Q}_c}\right)}{\varepsilon \cdot U_{so} \cdot \cos^2\left(\frac{\pi \cdot \zeta}{4}\right)}$$
$$\zeta = \frac{a_p \cdot d_{vs}}{2}$$

Where ε denotes porosity, a_p is the specific surface area of the packing material, and ζ is a dimensionless coefficient. The volumetric flows are expressed as \dot{Q}_c and \dot{Q}_d . The flooding velocity is used as a reference point to determine the superficial velocity U_c of the continuous phase. The velocity is used as a design value for the bed and is obtained by multiplying the flooding velocity with a certain factor

$$U_c = x_f \cdot U_{cf}$$

The factor is denoted by x_f and would for example be 0.6 when designing for 60% of flood. The superficial velocity is required for calculating the area of the bed and bed diameter, which is done by

$$A_{cross} = \frac{\dot{Q}_c}{U_c}$$
$$D_{Bed} = \sqrt{\frac{4 \cdot A_{cross}}{\pi}}$$

The height of the packed tower H is calculated from the following formula

$$H_{Bed} = N_t \cdot HEPT$$

Where *HETP* is the theoretical plate height and N_t is the number of theoretical plates. The theoretical plate height is calculated by

$$HETP = f_1 + f_2$$

Where f_1 and f_2 are defined as

$$f_1 = A \cdot B \cdot \left(\frac{U_c}{U_d}\right)^{0.8} \cdot \left(\frac{\sigma^2}{e^{\sqrt{a_p}} \cdot \Delta \rho}\right)^{0.25} \cdot \left(\mu_d^{0.5} \cdot \mu_c^{0.35}\right)$$
$$f_2 = Z_p \cdot \left[1 - exp\left(-C \cdot \left(\frac{D}{42}\right)^{0.3} \cdot \left(\frac{\mu_c^{0.5}}{a_p}\right) \cdot \left(\frac{U_d}{U_c}\right)\right)\right]$$

The symbols A, B and C are dimensionless constants. D stands for bed diameter, and Z_p for the packed height between redistributors. The superficial velocity of the

dispersed phase U_d is calculated by dividing the dispersed volumetric flow by the bed cross area

$$U_d = \frac{\dot{Q}_d}{A_{cross}}$$

The calculation results for Concept 4 and 5 are gathered in Table D-5.

	Concept 4 Butanol, dispersed Water, continuous		Concept 5 Water, dispersed Dichloromethane, continuous	
	LLE 1	LLE 2	LLE 1	LLE 2
Q_d (dispersed phase) [cm3/s]	100000.000	1604.938	83505.155	1340.206
Q_c (continous phase) [cm3/s]	83505.155	1340.206	60902.256	977.444
roh_d [g/cm3]	0.81	0.81	0.97	0.97
roh_c [g/cm3]	0.97	0.97	1.33	1.33
density difference [g/cm3]	0.16	0.16	0.36	0.36
Sigma [dynes/cm]	10	10	10	10
n (coefficient for d_vs))	1	1	1.4	1.4
d_vs [cm]	0.290	0.290	0.271	0.271
viscosity_w (reference) [cP]	0.9	0.9	0.9	0.9
viscosity_d [cP]	2.57	2.57	0.89	0.89
viscosity_c [cP]	0.89	0.89	0.413	0.413
Р	955420272	955420272	17215972773	17215972773
H (Butanol < 59.3; Dichl. > 59.3)	38.465	38.465	129.153	129.153
N_RE	305.726	305.726	948.920	948.920
U_so [cm/s]	9.664	9.664	10.876	10.876
a_p [cm2/cm3]	2.07	2.07	2.07	2.07
epsilon	0.94	0.94	0.94	0.94
zeta	0.300	0.300	0.280	0.280
1/U_cf	2.667	2.667	1.251	1.251
U_cf [cm/s]	0.375	0.375	0.799	0.799
U_c (60% flood) [cm/s]	0.225	0.225	0.480	0.480
Cross area (=Q_c/U_c) [cm^2]	371151.131	5956.747	127007.698	2038.395
Diameter, D_Bed [cm]	687.43	87.09	402.13	50.94
A (60 or 85)	60	60	85	85
В	1.5	1.5	1.5	1.5
С	0.3	0.3	0.3	0.3
D Bed [cm]	687.433	87.088	402.133	50.945
U_c [cm/s]	0.225	0.225	0.480	0.480
U_d [cm/s]	0.269	0.269	0.657	0.657
Z_p [cm]	305	305	305	305
f1 [cm]	418.43	418.43	195.36	195.36
f2 [cm]	96.16	56.23	67.82	38.60
HETP [cm]	514.59	474.66	263.18	233.96
N_t	1	1	1	1
Height, H Bed [cm]	514.59	474.66	263.18	233.96

Table D 5	Coloulations	forIIE	nantrad hada	in Concor	t 1 and 5
Table D-J	Calculations	IOF LLE	packed beds	in Concep	n 4 and 3