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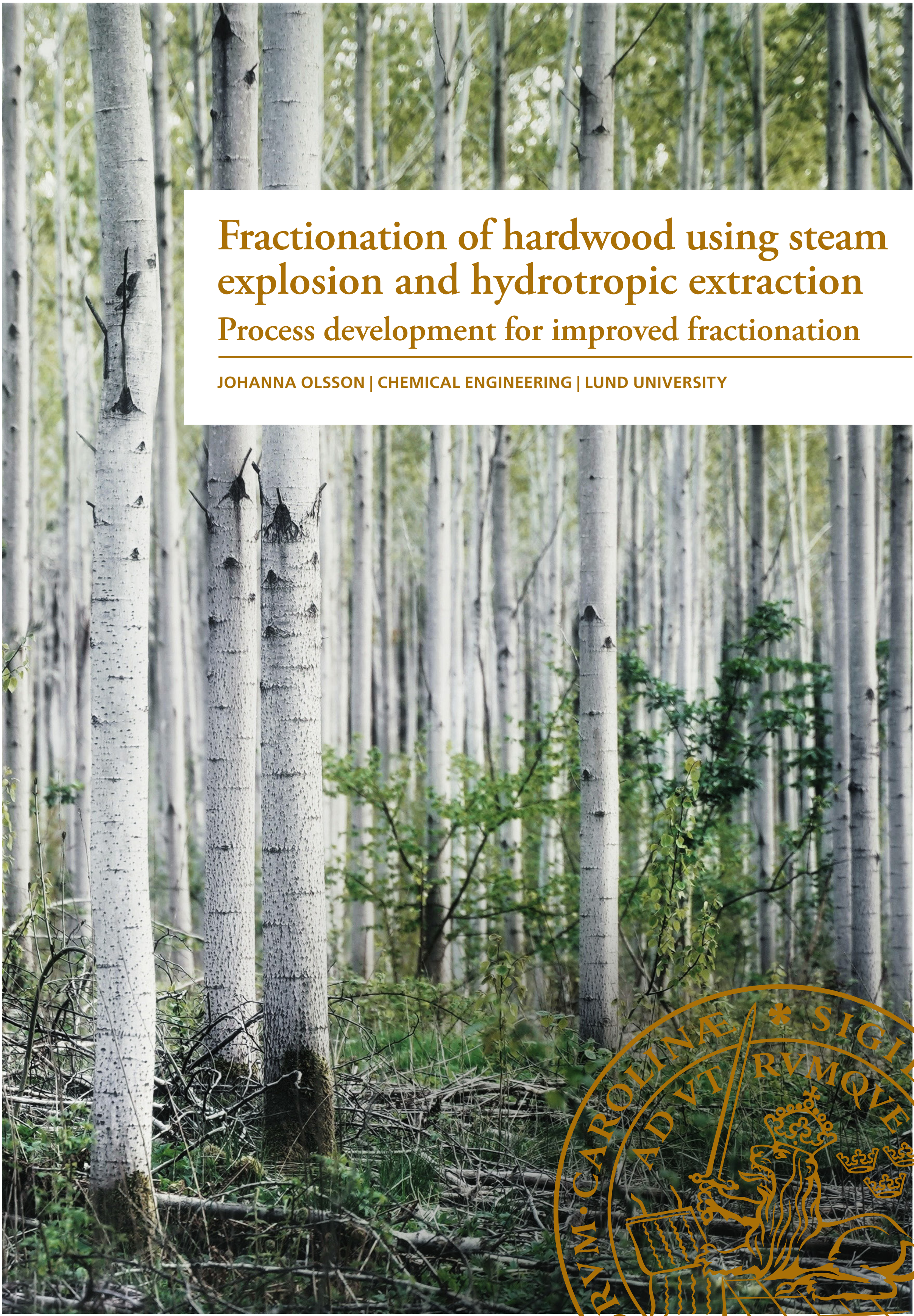

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Process development for improved fractionation

JOHANNA OLSSON | CHEMICAL ENGINEERING | LUND UNIVERSITY

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Process development for improved fractionation

Johanna Olsson

LUND
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Fractionation of hardwood using steam explosion and hydrotropic extraction – process development for improved fractionation

Abstract

The utilisation of biomass instead of fossil resources is an important alternative for the transition into a sustainable society. Biomass, owing to its primary constituents—cellulose, hemicelluloses and lignin—has the potential to replace many products that are produced from fossil resources today, including plastics, textile fibres and fuels. To fully exploit this potential, all of the components in the biomass matrix need to be used. To this end, efficient and environmentally friendly fractionation processes must be developed.

In the work that is described in this thesis, a two-stage process was examined for the fractionation of hardwood chips into cellulose, hemicelluloses and lignin. This process consists of an initial stage of steam explosion, in which hemicelluloses are recovered in the liquid fraction, and an extraction step, whereby lignin is removed from the solid fraction using a hydrotropic agent. Sodium xylene sulfonate, an environmentally friendly chemical that is commonly used in everyday products, such as shampoos and soaps, was used as the hydrotrope.

During the hydrotropic extraction, lignin was extracted into the liquid fraction, generating a solid fraction that was enriched in cellulose. Next, the lignin was recovered from the liquid fraction by diluting the solution with water, causing the lignin to precipitate. Over 70% of the hemicelluloses and approximately 50% of the lignin were recovered from the liquid fractions after steam explosion and hydrotropic extraction respectively. More than 90% of the cellulose was recovered in the solid fraction after hydrotropic extraction.

Next, the influence of process conditions during steam explosion and hydrotropic extraction was studied. Based on the findings, hydrotropic extraction could be performed even at ambient temperature with a short residence time, provided that the feedstock had been steam-pretreated prior to the hydrotropic extraction. The recycling of sodium xylene sulphonate was examined, and the results demonstrated that it could be reused several times without losing its efficiency. This property could be advantageous, because the regeneration of the used hydrotropic agent can be expensive and energy-demanding. Furthermore, it was shown that nanofiltration could be used to recover the diluted sodium xylene sulphonate solution, thus reducing the heat-energy demand of evaporation, which is commonly used for concentration.

Key words
Hydrotropic fractionation, steam explosion, hardwood, sodium xylene sulphonate, lignocellulosic biomass

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You don't expect to be at the top of the mountain
the day you start climbing

Ron Dennis, CEO McLaren

Abstract

The utilisation of biomass instead of fossil resources is an important alternative for the transition into a sustainable society. Biomass, owing to its primary constituents—cellulose, hemicelluloses and lignin—has the potential to replace many products that are produced from fossil resources today, including plastics, textile fibres and fuels. To fully exploit this potential, all of the components in the biomass matrix need to be used. To this end, efficient and environmentally friendly fractionation processes must be developed.

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Populärvetenskaplig sammanfattning

I framtiden ska förnybar råvara från jordbruk och skog inte bara förse jordens växande befolkning med föda utan även användas för att ersätta bränsle, kemikalier och andra produkter som idag framställs ur fossila råvaror. För att den förnybara råvaran ska räcka till allt detta måste vi inte bara återanvända och återvinna använda produkter utan också utveckla metoder så att vi kan ta till vara och dra nytta av alla biomassans olika beståndsdelar. Hur man kan göra detta på ett både miljövänligt och resurseffektivt sätt har studerats i detta arbete.

Användandet av fossila råvaror leder till en ökad koncentration av växthusgaser i atmosfären vilket leder till att medeltemperaturen på jorden nu ökar snabbare än normalt. För att vända på denna trend behöver vi hitta andra mer miljövänliga alternativ till fossila råvaror. Genom att ersätta fossila råvaror med råvaror från växtriket kan vi hålla kolets kretslopp intakt eftersom växter binder koldioxid genom fotosyntesen och är en del av det naturliga kretsloppet av kol. 70% av Sveriges yta är täckt av skog vilket gör skogsråvara till ett naturligt alternativ i Sverige för processer baserade på biomassa. Inte bara ved utan alla växter innehåller tre dominerande beståndsdelar; cellulosa, lignin och hemicellulosa. Forskning har visat att de kan användas som råvaror för att ersätta oljebaserade produkter som bränslen, plaster och textilier om vi bara kan utveckla kostnads- och energieffektiva metoder att separera, rena och koncentrera dem, vilket är precis vad jag gjort i detta arbete.

Jag har använt en tvåstegsprocess för att dela upp vedens huvudkomponenter i olika fraktioner. I processens första steg används vattenånga för att lösa ut hemicellulosan. Det återstående materialet behandlas sedan i en process där en billig och miljövänlig kemikalie (en hydrotrop), som länge använts i vanliga hushållsprodukter som tvål och schampo, utnyttjas för att lösa ut ligninet. Kvar blir då till slut cellulosan. Mitt arbete har främst varit inriktat på att klarlägga hur olika processparametrar i det andra processteget, den hydrotropa extraktionen, påverkar utbytet av lignin. Parametrar som jag undersökt var uppehållstid, temperatur, mängd biomassa i förhållande till mängd hydrotrop samt hydrotropens koncentration. Resultat från mina försök visar att hydrotrop extraktion kan användas för att separera hemicellulosa, lignin och cellulosa i björk- och bokved. Genom att behandla träflis med ånga under en kort tid kan man dessutom utföra den efterföljande hydrotropa extraktionen vid rumstemperatur vilket gör att energibehovet i processen därmed blir lågt.

För att erhålla ligninet späds den hydrotropa lösningen ut med vatten varpå ligninet, som i vanliga fall inte är lösligt i vatten, faller ut. När ligninet har filtrerats bort från lösningen måste hydrotropen koncentreras vilket enligt tidigare forskning har gjorts med indunstning. I denna avhandling visas att membranfiltrering skulle kunna användas för att ta bort 50% av vattnet från den utspädda hydrotropen. Vidare undersöktes också om man kunde återanvända hydrotropen till flera på varandra efterföljande extraktioner utan att regenerera den. De erhållna resultaten visar att det är möjligt och att hydrotropen kan återanvändas flera gånger utan att tappa sin effektivitet. Detta innebär i sin tur att dyra kostnader för rening och regenerering kan minskas.

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List of publications

The thesis is based on the following publications, which will be referred to in the text by their Roman numerals.

I. **J. Olsson**, V. Novy, F. Nielsen, O. Wallberg, M. Galbe, Sequential fractionation of the lignocellulosic components in hardwood based on steam explosion and hydrotropic extraction, *Biotechnology for Biofuels*, (2019) 12:1. Doi.org/10.1186/213068-018-1346-y

II. V. Novy, F. Nielsen, **J. Olsson**, K. Aïssa, J.Saddler, O. Wallberg, M. Galbe, Elucidation of changes in cellulose ultrastructure and accessibility in hardwood fractionation processes with carbohydrate-binding modules (CBMs), *ACS Sustainable Chemistry & Engineering* (2020). https://dx.doi.org/10.1021/acssuschemeng.9b07589

III. **J. Olsson**, M. Persson, M. Galbe, O. Wallberg, A.-S. Jönsson, An extensive parameter study of hydrotropic extraction of steam-pretreated birch, Submitted for publication.

IV. **J. Olsson**, M. Galbe, O. Wallberg, A.-S. Jönsson, Influence of concentration of sodium xylene sulphonate during hydrotropic extraction of hardwood, Manuscript.

V. **J. Olsson**, V. Novy, O. Wallberg, M. Galbe, A.-S. Jönsson, Consecutive extraction of hardwood using the hydrotrope sodium xylene sulphonate, Manuscript.

VI. **J. Olsson**, M. Galbe, O. Wallberg, A.-S. Jönsson, Membrane filtration of the hydrotropic agent sodium xylene sulphonate (SXS), Submitted for publication.

My contribution to the papers

I. I planned and performed the experiments together with Vera Novy. I wrote the paper together with the authors.

II. I co-planned the study together with Vera Novy and Fredrik Nielsen. I performed the experiments of steam explosion and hydrotropic extraction. I wrote the paper together with the authors.

III. I planned the study together with Michael Persson. I performed the experimental and analytical work. I wrote the paper together with the authors.

IV. I planned and performed the experiment. I wrote the paper together with the authors.

V. I planned and performed the study together with Vera Novy. I wrote the paper together with the authors.

VI. I planned and performed the study. I wrote the paper together with the authors.

Abbrevations

DES	Deep eutectic solvent
DI water	De-ionised water
DM	Dry mass
DoE	Design of experiment
HAc	Acetic acid
HEX	Hydrotropic extraction
IL	Ionic liquid
LF	Liquid fraction
NF	Nanofiltration
NREL	National Renewable Energy Laboratory
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
SF	Solid fraction
STEX	Steam explosion
SXS	Sodium xylene sulphonate
TMP	Transmembrane pressure

Table of Contents

1 Introduction

In December of 2015, parties to the United Nations Framework Convention on Climate Change accepted the Paris Agreement, which aims to strengthen and coordinate the global response to climate change. These activities are to be performed by keeping the global temperature rise below 2°C in comparison with pre-industrial levels, to avoid the irreversible effects of climate change. To achieve this goal, all parties will strive to reduce their CO_2 levels and greenhouse gas (GHG) emissions rapidly [1].

To implement the Paris Agreement, the European Union presented its new strategy for addressing climate change at the end of 2019. The European Green Deal aims to shift the European economy into one that is circular and bio-based and to make Europe the first climate-neutral continent by 2050 [2]. To this end, a new legislation proposal, called the European Climate Law, was presented in March of 2020. The climate law includes, among other mandates, a framework to assess the progress and render net-zero GHG emissions legally binding by 2050 for all member states [3].

As of January 2018, Sweden's Climate Act was enacted as a result of a new climate policy framework that was adopted in 2017. The framework builds upon three pillars: the Climate Act, specific climate goals and a climate policy council. To reach the goals in this framework, the Swedish government is obliged to present a climate report in the budget bill every year and a new action plan every fourth year [4]. The long-term climate goal in the framework stipulates that Sweden reach net-zero GHG emissions by no later than 2045. This target should be attained by cutting emissions by 85% compared with the levels in 1990 and thereafter through supplementary measures. One such suggested approach is to increase the CO_2 uptake by forests.

Approximately 70% of the Swedish land area is covered by forest, corresponding to 28 million hectares, of which 23.6 million is productive forest land [5]. Annually, 70 million m^3 of timber is harvested for the production of wooden goods, fibre-based products and renewable energy [6]. By substituting products that are made from fossil resources with ones that are derived from the forest, Swedish CO_2 emissions are estimated to decrease by 42 million metric tonnes of CO_2 equivalents yearly. Further, the rising growth of Swedish forest accounts for an increase in the annual

CO_2 uptake of 55 million metric tonnes of CO_2 equivalents. As stated in the Swedish climate policy framework, the CO_2 uptake by forests will play a key role in Sweden's road toward being the first country to reach net-zero emissions by 2045. To exploit the full potential of the forest in replacing fossil-based products, it is vital to utilise all of the components of wood, necessitating access to cost- and energy-efficient separation methods that make it possible to purify and concentrate these constituents.

1.1 Aim and outline of the thesis

The aim of the work in this thesis was two-fold: i) to evaluate the performance of a two-stage biomass fractionation process, consisting of pretreatment by steam explosion (STEX), followed by hydrotropic extraction (HEX), and ii) to study the influence of the operating conditions on the recovery of lignin during HEX. Hardwood was used in the experimental studies, and sodium xylene sulphonate (SXS) was the hydrotrope that was used during HEX.

A brief overview of the main components of wood is presented in Chapter 2. In Chapter 3, processes that are used to extract lignin are presented. The equipment and analytical procedures that were used in the experimental studies is described in Chapter 4. In Chapter 5, the results of the fractionation of hardwood using the two-stage process are presented (Papers I and II). The findings of the study of the influence of temperature, residence time and biomass loading during HEX (Paper III) and the concentration of SXS (Paper IV) are also summarised in Chapter 5. The conditions for reusing SXS in repeated extraction (Paper V) and for concentrating the diluted SXS solution by nanofiltration (Paper VI) are discussed in Chapter 6. In Chapter 7, the influence of operating conditions on the properties of the wood components are discussed. Finally, concluding remarks and suggestions for future work are provided in Chapters 8 and 9.

2 Lignocellulosic biomass

Lignocellulosic biomass is the most abundant renewable feedstock on earth, with an estimated annual production of approximately 180 billion tonnes [7], which can be compared with the total global production of crude oil of approximately 5 billion tonnes in 2020 [8]. Lignocellulosic biomass can be found everywhere throughout the planet, from forests and agricultural residues to energy crops and grasses. The three main components of lignocellulosic biomass are cellulose, lignin and hemicellulose, together accounting for roughly 95% of the total composition. Lignocellulosic biomass also contains small amounts of extractives and inorganics. Depending on the species, there are differences in the ratio of these components. The chemical compositions of a few lignocellulosic materials are presented in Table 1.

Table 1. Composition (%) of different lignocellulosic materials [9].

Material	Cellulose	Hemicelluloses	Lignin	Extractives
Softwood	40 – 44	25 – 29	25 – 31	1 – 5
Hardwood	43 – 47	25 – 35	16 – 24	2 – 8
Bagasse	40	30	20	10
Wheat straw	30	50	15	5

2.1 Cellulose

Cellulose constitutes most of the cell wall in plants. It is a linear polymer that comprises D-glucose units that are linked by β-(1-4)-glycosidic bonds (Figure 1). A single cellulose molecule can have a chain length of roughly 10,000 glucose units [10]. In plants, single cellulose chains are arranged in so-called microfibrils, which consist of cellulose chains that are held together by hydrogen bonds between the hydroxyl groups in the cellulose molecule. The structure within and between microfibrils causes cellulose to form a rod-like structure, which aids the stability of the plant.

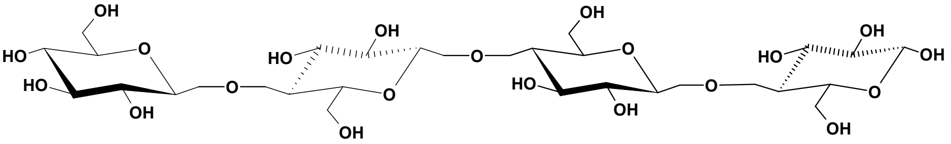

Figure 1. Schematic illustration of cellulose.

2.2 Hemicelluloses

Hemicelluloses are polysaccharides that add rigidity to the plant cell wall [10]. Hemicelluloses, unlike cellulose, are heteropolymers and can be both linear and branched. They are derived primarily from hexoses, such as glucose, mannose and galactose, and pentoses, such as xylose and arabinose [11]. Either monosaccharide can function as the backbone with various side groups. Hemicelluloses are smaller than cellulose, with a typical degree of polymerisation of approximately 40 to 200 [12].

In hardwood, xylan is the most predominant hemicellulose, with a backbone that consists of D-xylopyranose units that are irregularly arranged and mainly substituted by glucuronic acid groups [13]. Other side chains in hemicelluloses include acetic acid and hexuronic acids. Such side chains are responsible for the solubility of hemicelluloses in water or alkali [14].

2.3 Lignin

Lignin is the polymer that provides mechanical strength and facilitates transportation of water and nutrients in plants [15]. It is an aromatic heteropolymer that comprises primarily three phenylpropane units—p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [10, 15], as shown in Figure 2, differing in the number of methoxy groups that are attached to the aromatic ring, ranging from zero in p-coumaryl alcohol to two in sinapyl alcohol [16]. When these monolignols are polymerised through a reaction between phenoxyradicals [16] to form lignin, they are referred to as p-hydroxyphenyl, guaiacyl and syringyl lignin, respectively [17]. The ratio of the building blocks in the three-dimensional lignin polymer differs between species [17]. For example, hardwood contains both G- and S-units, whereas softwood is mainly composed of G-units [10].

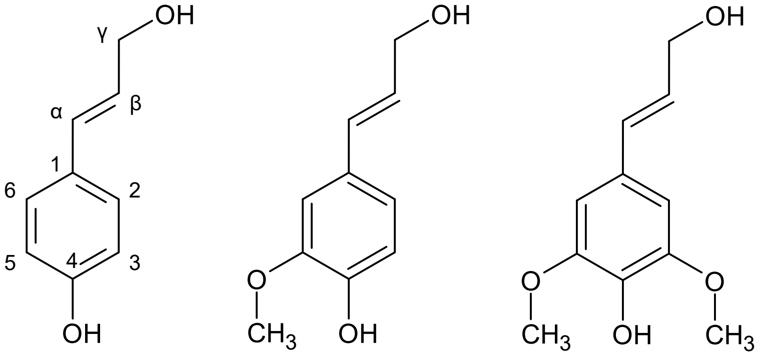

Figure 2. Coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

Single monolignols are linked together by covalent bonds, such as ether bonds, which appear somewhat randomly. The most common bond in hardwood lignin is the β-O-4 ether bond, followed by the β-5 bond [18], with the former reportedly accounting for 50% to 70% of the total bonds in lignin [15], versus 35% to 60% in softwood lignins. Other common bonds include α-O-4 and β-β, which appear at various ratios, depending on the source of the lignin [17].

The lignin molecule also contains several functional groups that affect its reactivity and offers various possibilities for chemical modifications [16, 19]. Such groups include hydroxyl groups, carbonyl groups, methoxyl groups and sulfonic acid [17]. Due to its versatility, lignin is a potential raw material for a variety of high-value-added products and chemicals, such as dispersants [20, 21], vanillin [22, 23], thermoplastics [24, 25] and fuels [26, 27].

3 Fractionation of lignocellulosic biomass

Sustainable utilisation of biomass requires that all components of the raw material are utilised. Hence, the fractionation of lignocellulosic biomass is an important step in many well-established processes around the world. However, many existing processes do not utilise the entire biomass, instead targeting one or two components. One such example is the most common pulping method, the kraft process, in which cellulose fibres with high mechanical strength have historically been the primary focus and the dissolved lignin has been burnt due to its excellent heating value. However, lignin can be used as a raw material for a wide variety of value-added products, as discussed, rendering this biopolymer a notable source of revenue. However, to utilise the lignin in biomass, cost- and energy-efficient methods of extracting it from biomass must be implemented. The most common methods for such purposes are presented below.

3.1 Pulping processes

Pulping processes are used to generate a fibrous mass (pulp) from lignocellulosic biomass. They are broadly classified as chemical or mechanical [28]. The aim of chemical pulping is to remove lignin, whereas mechanical pulping defibrillates wood using mechanical forces. Approximately 50% of the raw material (mainly lignin and some hemicelluloses) is dissolved in the cooking liquor during chemical pulping whereas only about 2% to 10% is dissolved in mechanical and thermomechanical pulping [18, 28]. Chemical pulping accounts for roughly 75% of the pulp that is produced worldwide [29]. The two most common chemical pulping processes are the kraft (sulphate) process and the sulphite process. They include an extraction stage in which a cooking solution is used at elevated temperatures to dissolve the lignin molecule to produce a lignin-weak pulp [18, 29]. The spent pulping liquors (containing cooking chemicals, dissolved lignin and hemicelluloses) are burnt in the recovery boiler, salvaging cooking chemicals and the heat value of dissolved organic substances.

3.1.1 The kraft process

In the kraft process, wood chips are treated with a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S) as cooking chemicals, making this process alkaline [30]. The cooking step is carried out in a pressurised digester at temperatures of 150–175°C [18] for 1–2 hours [30]. Next, the resulting pulp is washed and often bleached, and the cooking chemicals are regenerated and reused in the process. The pulp that is generated from the kraft process has high mechanical strength and can be bleached to obtain high-quality paper, such as white paper for printing [31].

The cooking chemicals and the lignin that is dissolved from the biomass are collectively called black liquor. This fraction is normally burnt in the recovery boiler to produce heat and electricity. However, utilising the lignin in this fraction is an important step toward converting a pulp mill into a biorefinery. One commercial process that targets this is the LignoBoost process. In this process, the black liquor is treated (preferably) by the addition of CO_2, causing the lignin to precipitate under acidic conditions. The lignin is then filtered off and re-suspended in H_2SO_4 before it is washed and dried [32]. Because it is applied commercially, LignoBoost-generated lignin is often used as a model compound for further upgrading and processing, for example, into liquid biofuels [33].

3.1.2 The sulphite process

Compared with kraft pulping, sulphite pulping utilises sulphurous acid and bisulphite ions, such as magnesium or calcium, as the cooking chemicals [34, 35]. This process is flexible in comparison to the kraft process, because it can be performed in a wide span of pH conditions, ranging from acidic sulphite pulping (pH 1–2) to neutral sulphite cooking (pH 7–9). The pulps from kraft and sulphite pulping have different properties—the pulp from the kraft process has higher strength, whereas sulphite pulp requires less bleaching [36]. Both pulping methods have a low pulping yield, although that of sulphite pulping is normally slightly higher than the corresponding value for kraft pulping [18, 34]. Due to the lower strength of sulphite pulps, they are typically used for the production of tissue and newspaper [31].

3.1.3 Dissolving pulp

Pulp is used primarily for paper and packaging, but the application of using cellulose to produce textile fibres has increased in recent years. When used to produce textile fibres, the cellulose must be free of not only lignin but also of hemicelluloses. Dissolving pulp can be produced through an acidic sulphite process or by adding an acidic prehydrolysis step to the kraft process [31]. Acidic conditions are applied to remove hemicelluloses, which stabilise somewhat under alkaline pulping conditions, from the pulp [34]. The resulting pulp, which is rich in cellulose, can be used for the production of regenerated cellulose fibres, such as rayon, viscose and lyocell [31, 37].

3.2 The organosolv process

Initially, organosolv processes were developed as an alternative to traditional chemical pulping processes due to issues with pollution from the bleaching stage and to avoid the need for expensive recovery boilers [38]. This process has also become an interesting option for the removal and recovery of lignin in biorefineries while at the same time making the remaining cellulose-rich fraction more susceptible to further processing, for example, by enzymatic hydrolysis [39, 40]. The fractionation is performed by treating lignocellulosic biomass with an organic solvent, such as ethanol or methanol, with or without a catalyst, such as organic [41] or inorganic acids [42-44]; one of the most common combinations being an ethanol/H_2SO_4 mixture [45]. Depending on the exact process, the temperatures and residence times during the extraction can vary greatly, from room temperature to 240°C [46] and 30-90 minutes [44].

During the extraction, the lignin and hemicelluloses in the material are degraded and dissolved in the solvent [46]. In the second stage, lignin is recovered by precipitation, often by the addition of water [47], and subsequently dried to form a high-quality lignin fraction [46]. There are several commercial processes using organosolv techniques, such as the Alcell process, which uses ethanol for fractionation [48], and the CIMV process, in which wheat straw is treated with a mixture of acetic acid, formic acid and water at proportions of 55:30:15 (w/w/w) [49] for 3.5 hours at 105°C [50]. Further research has also been put into combining organosolv with other pretreatment processes, such as steam explosion (STEX) [40]. When treating birch with the combined process, a solid fraction containing 78% cellulose, 9% hemicellulose and 7% lignin was produced [51]. The combined process was also reported to improve saccharification yields when treating the cellulose-rich fraction with enzymes [51].

3.3 Ionic liquids

Ionic liquids (ILs) are considered to be green solvents that, based on the discovery that they can be used to dissolve lignocellulose [52], have received increasing interest due to their unique properties. ILs are defined as organic salts with melting points below 100°C [53] and have several benefits compared with organic solvents, such as their low vapour pressure and high thermal stability [54]. ILs typically consist of a large organic cation and an inorganic or organic anion and can be designed to exist in a liquid state at room temperature [55]. Based on the possibility of tuning the properties of ILs by choosing various combinations of ions, they can be produced to target a specific molecule, such as lignin, in the biomass matrix. For example, Yan et al. found a group of amine-sulphonate ILs that, at a concentration of 5mM, can dissolve lignin in a model solution at 100°C, but did not dissolve either xylan or cellulose under the same conditions [56]. However, lignin that is embedded in the biomass matrix might be harder to extract. Furthermore, this group also showed that the same type of selective behaviour was seen when extracting lignin from bark at 120°C for 10 hours but with slightly higher dissolution of the hemicelluloses [56].

There are other ILs that have shown promising results with regard to the dissolution of kraft lignin in a model solution. For example, it has been reported that the solubility of lignin using pyridinium formate is as high as 70 wt% in a temperature range of 20-140°C [57]. To recover ILs, several processes are used, depending on the properties of the IL, including distillation, extraction with an organic solvent and separation using membranes [58].

3.4 Deep eutectic solvents

Deep eutectic solvents (DESs) are defined as solvents that, when mixed together, have a considerably lower melting point than the individual components [59]. DES are generally prepared by mixing a hydrogen bond donor (such as an acid, alcohol or amine) [60] or metal salt with a hydrogen bond acceptor, such as a quaternary ammonium or phosphonium salt [60, 61]. The first DESs were mixtures of urea and ammonium salts [59].

DESs have a number of similar physical properties to ILs, such as low flammability and vapour pressure, and it is possible to tune the DES by choosing the individual components [61, 62]. The major advantage of using DESs as compared to ILs is that they can be prepared easily from inexpensive compounds that are readily accessible and being convenient to handle as individual components [61]. By mixing the compounds often under moderate heating, the production process is inexpensive, allowing large-scale processing [61, 62]. In the case of fractionation of biomass with DES, the first promising results were reported by Francisco et al. in 2012 [63], showing that several DESs could be used for the selective extraction of lignin from a model solution that contains lignin, cellulose and starch. They also found that depending on the ratio of the constituents of the DES, they could dissolve more or less of the lignin, demonstrating that tuning the DES is important for optimising the process.

DESs have been examined in conjunction with other methods to improve the solubility of lignin, including microwave treatment and ultrasonic treatment of biomass [64]. Liu et al. [65] reported that 80% of the lignin in poplar can be extracted using a DES that consists of choline chloride and oxalic acid dehydrate. The samples were heated by microwave radiation at 800 W to 80°C for 3 minutes. It has also been shown that 50% of the lignin in a model solution can be solubilised using a DES (resorcinol-choline chloride) when applying ultrasonic radiation for 20 minutes at 90°C [66]. The desired molecule is often recovered by precipitation, most often with the addition of water in the case of biomass [67]. The diluted DES are then often recovered by evaporation, but due to the high energy intensity of this process, alternative methods are being researched, such as liquid-liquid extraction and sorption [67].

3.5 Hydrotropic extraction

3.5.1 Hydrotropes

Hydrotropes are molecules that increase the solubility of otherwise sparingly soluble compounds when used at sufficient concentrations in an aqueous solution [68-70]. These molecules are typically organic salts and have an amphiphilic structure—ie, they have both a hydrophobic and hydrophilic region, the former often being an aromatic ring [68, 71] and the latter being an ionic group [72]. Hydrotropes are similar to ordinary surfactants with respect to their amphiphilic structure, but they have a shorter hydrophobic tail [73].

The exact mechanism of hydrotropy remains incompletely understood, but several studies have reported that for a hydrotrope to be active, its concentration in solution must reach a specific threshold, often referred to as the minimum hydrotrope concentration [70, 74-76]. This property is similar to the critical micelle concentration for surfactants and has been defined as the point at which the concentration is sufficiently high for hydrotrope molecules to form associated structures [70, 77]. Due to this behaviour, the solute can be recovered easily from the hydrotropic solution by adding water, thus lowering the concentration of the hydrotrope [74]. Several suggestions have been proposed regarding the exact mechanism. For example, McKee [78] has opined that the hydrotropic effect is similar to that of the salting-in process of proteins, whereas Srinivas et al. [77] reported that hydrotropes form layered structures that provide microenvironments in which the hydrophobic solute can be solubilised. Recently, Abrances et al. [79] theorised that the hydrotrope gathers around the solute, driven by hydrophobic interactions between the hydrotrope and solute, which increase in the presence of water.

A variety of molecules are considered to be hydrotropes, the most commonly used of which are sodium salts of alkylbenzene sulphonates, such as sodium xylene sulphonate (SXS), sodium toluene sulphonate and sodium cumene sulphonate [80, 81]. Other hydrotropes that are used in various types of research include urea and nicotinamide [82, 83]. Some of the most common hydrotropes are shown in Figure 3.

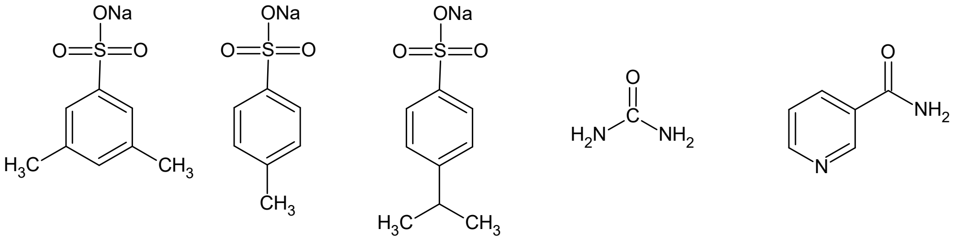

Figure 3. Typical hydrotropes, SXS, sodium toluene sulphonate, sodium cumenesulfonate, urea and nicotinamide

Based on their properties and the fairly easy recovery of the solute by dilution with water, the use of hydrotropes has been investigated in a wide variety of applications, such as in the pharmaceutical industry [83, 84], as additives in detergents [81] and for various industrial fractionation purposes, such as the fractionation of lignocellulosic biomass [85-89].

3.5.2 Hydrotropic fractionation of lignocellulosic biomass

Fractionation of lignocellulosic biomass using hydrotropes was first patented by McKee in 1943 [90], who reported that several hydrotropic agents, such as SXS, could be used for the selective recovery of lignin from woody and nonwoody biomass [90]. McKee treated the material at 150°C for 12 hours using SXS at a concentration of approximately 30% (w/w) [90]. In recent years, interest in using hydrotropes as delignification agents for lignocellulosic biomass has re-emerged. Woody biomass, such as eucalyptus, birch and spruce [86, 87, 91, 92], and nonwoody biomass, such as bagasse, cotton stalks and straw [85, 88, 89, 93], and their fractionation by a variety of hydrotropes, such as SXS, sodium cumene sulphonate, sodium benzoate and p-toluene sulfonic acid [88, 89, 94], have been examined. A variety of residence times, between 20 minutes to 12 hours [85, 91, 94, 95], and temperatures from 80°C–180°C [86, 93, 94] have been investigated. The concentration of the hydrotropic agent that is used in the fractionation is typically 30% to 40% [86, 88, 95, 96], but ranges of 10% to 80% have been evaluated in some cases [85, 91, 94]. After hydrotropic extraction (HEX), the lignin-rich hydrotropic solution is separated from the solid phase by filtration, for example [85]. The solid fraction is then washed with NaOH [87] or a weaker solution of hydrotrope [86] to prevent redeposition of lignin onto the cellulose fibres.

The reported results of the HEX have varied, with lignin extraction yields ranging between 40% to 93%, depending on the raw material [86, 91, 94, 96]. To further increase the efficiency of the process, Gabov et al. [87] added a catalyst, such as hydrogen peroxide and/or formic acid, during the HEX, showing that more lignin could be extracted and that the selectivity toward lignin increased with the addition of the investigated catalysts. Although the delignification increased, the total pulp yield declined with the addition of a catalyst, likely due to the more extensive degradation of the carbohydrates present in the material. In another study, Gabov et al. [96] found that the lignin that was recovered from the modified process was altered to a higher degree than that from hydrotropic extraction without an added catalyst.

To recover lignin from a hydrotropic solution, the lignin-rich liquid is diluted by simply adding water [86, 87, 96]. As the concentration of hydrotrope in the solution decrease, the lignin particles are no longer solubilised and thus precipitate. The lignin particles can then be filtered off or separated from the diluted hydrotropic solution by centrifugation [87, 96]. The precipitated lignin is then washed thoroughly with water [87, 89] or NaCl [86] to remove any remaining hydrotrope. The precipitated lignin has been reported to be pure, with a low sulphur content, compared with other technical lignins, such as those that originate from the kraft process. The impurities in HEX-generated lignin are often attributed to the hemicelluloses present in the raw material [87, 89].

3.6 Steam explosion

Steam explosion (STEX) is a common process for pretreating lignocellulosic biomass [44], for which there are several pilot plants for industrial or research applications worldwide [97, 98]. In this process, the biomass is subjected to high-pressure steam, typically at temperatures of 160–260°C for 1–20 minutes [44, 98]. The pressure is then decreased rapidly, causing explosive decompression of the biomass [44]. During STEX, hemicellulose bonds are hydrolysed, either by the release of organic acids from the material itself due to thermal degradation (autohydrolysis) or by the addition of a catalyst, such as H_2SO_4, HCl and SO_2 [98, 99]. Upon hydrolysis of the hemicelluloses, they become water-soluble and can thus be recovered in the liquid fraction, whereas the remaining solids are enriched in cellulose [100].

During STEX, the ultra-structure of the material changes, and its surface area and porosity increase, rendering the material more susceptible to further processing [100]. During STEX, the lignin is chemically modified by depolymerisation and subsequent repolymerisation, leaving the lignin more prone to be extracted, for example, by alkali [97, 101]. It has been reported that higher severities during STEX result in a loss of β-O-4 bonds in the lignin and greater repolymerisation [101, 102], due to the acidic environment that is created in the STEX process. One way to avoid this type of reaction is to use very mild conditions during the process [101].

To achieve complete fractionation of lignocellulosic biomass, this work proposed and examined a process that used STEX as the initial step to recover hemicelluloses, followed by HEX to recover lignin. This process resulted in three fractions of interest: a liquid fraction that is rich in hemicelluloses, a liquid fraction with lignin in solution and a solid fraction that is enriched in cellulose. The process and its implications are discussed in the following chapters.

4 Equipment and experimental procedures

The two-stage fractionation process that was studied in this work consists of pretreatment by STEX, followed by HEX. The lignin that is dissolved during HEX is precipitated by diluting the hydrotropic solution with water. The precipitated lignin and diluted SXS solution are then separated by centrifugation. Finally, the SXS solution is recovered by nanofiltration (NF). A schematic of the process is shown in Figure 4.

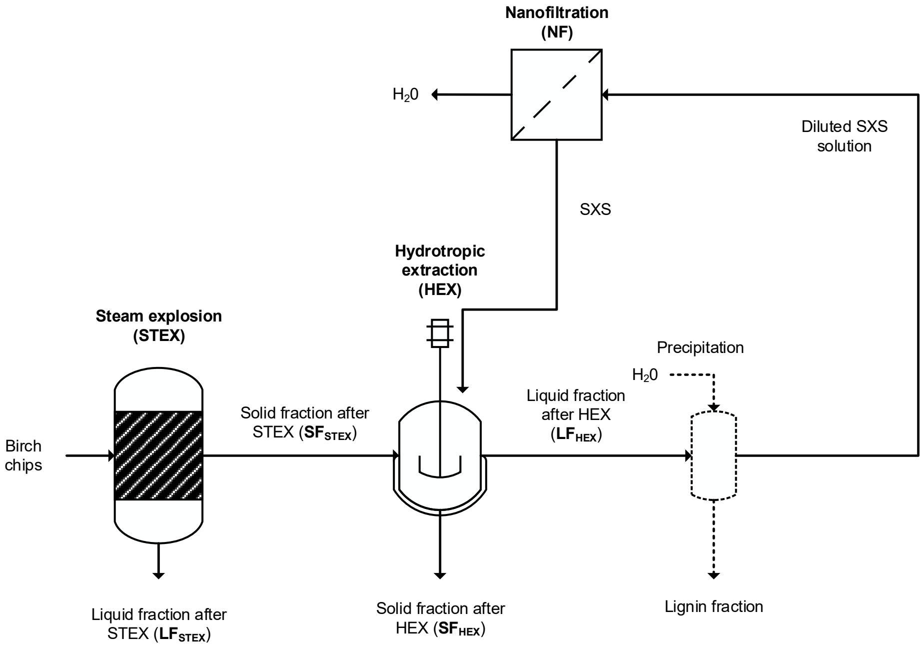

Figure 4. The investigated process for fractionation of hardwood.

4.1 Steam explosion

STEX was used as a pretreatment in Papers I-V. STEX was performed in a 10-L preheated pretreatment reactor that was equipped with a flash tank to collect the pretreated material, as presented in Figure 5. The reactor was connected to a steam boiler that provided steam at a maximum of 28 bar. Prior to STEX, the wood chips were milled and sieved to obtain a uniform size of 2-10 mm. The material was then impregnated with water to reach a DM content of approximately 50% and loaded into the reactor in batches of 750 g (DM). After STEX, the liquid and solid fractions were separated using a filter press. To remove solubilised hemicelluloses that adhered to the fibres, the solid fraction was washed with an excess of hot deionised (DI) water and agitated for 1 hour. After the wash, the solid and the liquid fraction were separated using a filter press at 6 bar.

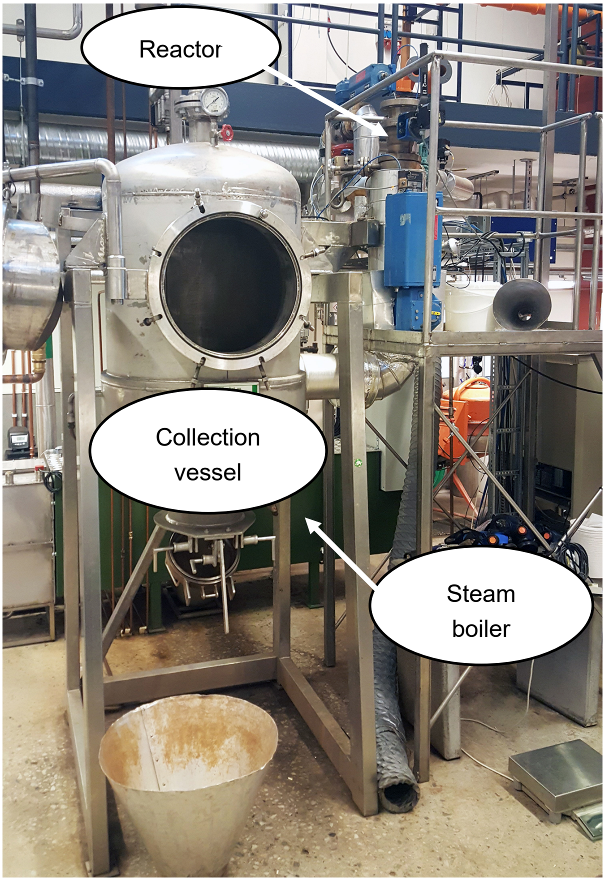

Figure 5. The STEX equipment used.

4.2 Hydrotropic extraction

The HEX was performed in a reactor (Papers I-III and V) or microwave oven (Paper IV). The reactor was a 2-L stirred batch reactor (Polyclave, Büchi AG, Switzerland) that was connected to a thermostat (Unistat T305, Kältenmaschinenbau AG, Germany), as shown in Figure 6. The reaction proceeded under constant agitation at 350 rpm. The SXS was prepared by mixing DI water with 93% pure SXS powder (Stepanate SXS-93, Alsiano, Denmark) to the desired concentration.

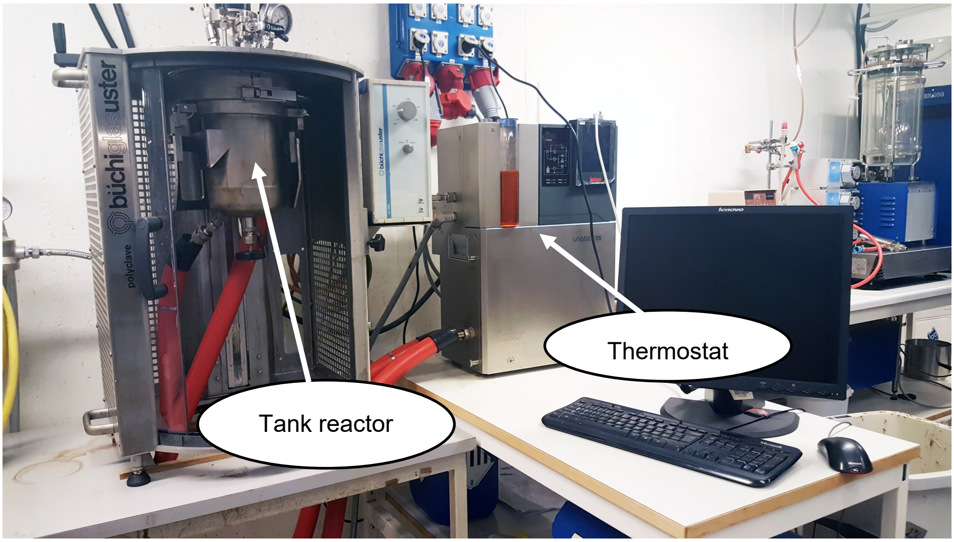

Figure 6. The reactor and thermostat used for HEX in Paper I-III and V.

The microwave experiment (Paper IV) was performed in an Ethos Plus laboratory microwave (Milestone Srl, Sorisole, Italy) with a maximum effect of 2.0 kW. The microwave was equipped with a tray and 6 separate compartments with a maximum volume of 200 ml each. One of the compartments was equipped with a temperature probe for control. To ensure a uniform temperature profile in all compartments, the tray was rotated, and the direction was reversed after one rotation (360°).

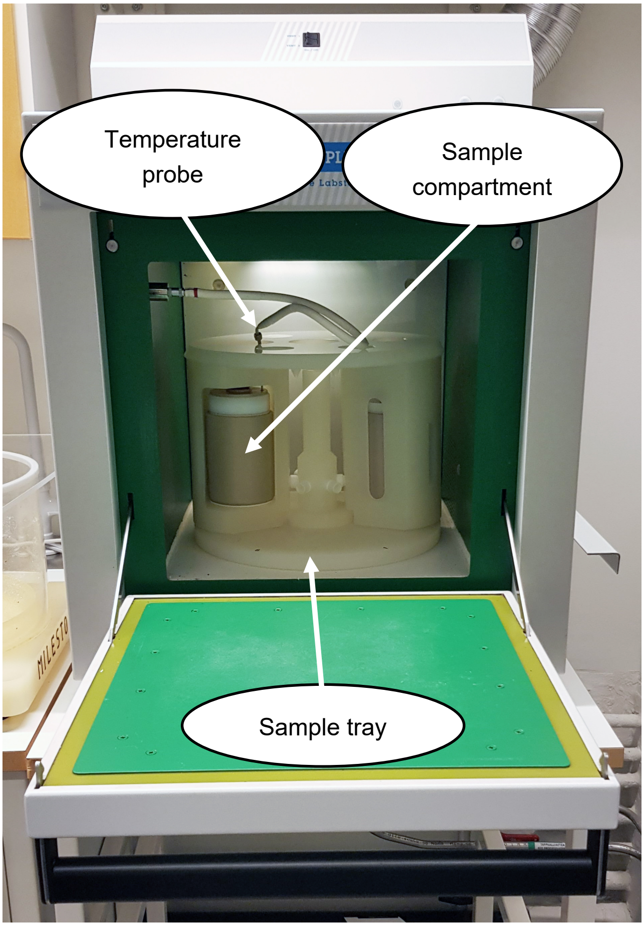

Figure 7. The microwave oven used in Paper V.

After HEX, the liquid fraction was separated from the solid fraction using a Büchner funnel that was connected to vacuum or by filtration using a small filter press. The solids were then washed sequentially with 0.1 M NaOH, 0.05 M NaOH and DI water to remove any residual SXS and lignin from the fibres. The lignin that was dissolved in the SXS solution was recovered by diluting the solution with DI water. The precipitated lignin was then separated from the diluted SXS solution by centrifugation.

4.3 Nanofiltration

In Paper VI, nanofiltration (NF), a pressure-driven membrane process, was used to concentrate the diluted SXS solution. The flux (ie, capacity) and retention of lignin of 5 membranes were examined, and the performance of the most promising membranes was evaluated in concentration studies. The experimental set-up for this study included a temperature-controlled feed tank and a displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, MN, USA). A flat-sheet membrane module with a membrane area of 0.00196 m^2 was used in the parameter studies, as shown in Figure 8. During the concentration studies, the same membrane was mounted in three modules that were connected in parallel yielding a total area of 0.00588 m^2. The permeate flux was measured using an electronic balance (PL6001-S, Mettler Toledo Inc., Columbus, OH, USA), and the temperature was controlled using a temperature regulator that was connected to a Pt-100 temperature probe. The pressure was measured at the outlet, before the retentate valve. The flow rate was controlled using a frequency converter (ELEX 4000, Bergkvist & Co AB, Gothenburg, Sweden) that was connected to the pump.

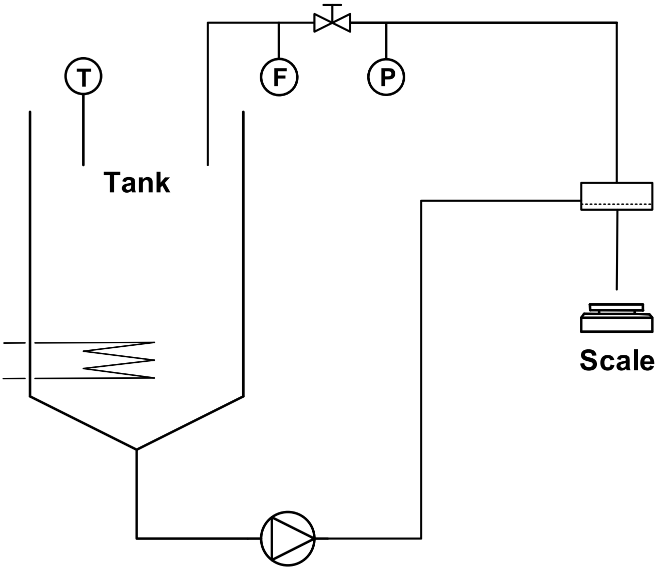

Figure 8. Experimental setup used in the NF experiments.

4.4 Analytical procedures

Much analytical work was conducted to evaluate the results of the various treatments, including many compositional analyses of different solid fractions and size exclusion chromatography and elemental analysis of the precipitated lignin.

4.4.1 Compositional analysis

To determine the lignin and carbohydrate content in the raw material (hardwood chips), the solid fraction after STEX (SF_{STEX}, Figure 4) and after HEX (SF_{HEX}, Figure 4) was subjected to acid hydrolysis and then analysed according to the NREL procedure [103]. The DM contents in the samples were measured as oven-dry weight at 105°C. The content of acid-insoluble lignin (often referred to as Klason lignin) was determined using a filter crucible with a maximum pore size of 16 µm to collect the solid residue after the acid hydrolysis. The solid residue was dried at 105°C overnight and then weighed. Carbohydrate monomers in the liquid hydrolysate were measured by isocratic high-performance anion-exchange chromatography with pulsed amperometric detection, using an ICS-3000 chromatography system (Dionex, USA) that was equipped with a Carbo Pac PA1 analytical column (Dionex, USA). Measurements were performed at 30°C using DI water as the eluent at a flow rate of 1 mL min^{-1}. The liquid fractions of a few selected samples were analysed in accordance to the NREL standard procedures for liquids [104]. Carbohydrate content was determined by high-performance liquid chromatography (HPLC) using a refractive index detector (RID-10A, Shimadzu, Kyoto, Japan), with an Aminex HPX-87H column for separation.

4.4.1.1 Reproducibility of the compositional analysis

The reproducibility of this analytical procedure was evaluated by analysing the same sample on three occasions over three months. The analysed sample was a hardwood mix of 80% birch and 20% beech that was steam-pretreated at 210°C for 5 minutes and then subjected to HEX at 150°C for 8 hours. As seen in Table 2, there were no major differences in the results between the three analyses performed. This is a clear indication that the reproducibility of the analysis is high.

Table 2. Composition (%) of the solid fraction after HEX at 150°C for 8 h. All three analyses were performed for the same sample on three occasions. BDL, below detection limit.

	1st analysis	2nd analysis	3rd analysis	Mean value
Carbohydrates	81.7 ± 1.6	83.2 ± 0.5	87.4 ± 1.1	84.1 ± 3.0
Glucan	73.1 ± 1.5	75.1 ± 0.4	76.8 ± 1.2	75.0 ± 1.9
Xylan	6.1 ± 0.1	6.0 ± 0.1	6.1 ± 0.2	6.1 ± 0.1
Mannan	2.6 ± 0.0	2.1 ± 0.0	4.5 ± 0.1	3.1 ± 1.3
Arabinan	BDL	BDL	BDL	BDL
Galactan	BDL	BDL	BDL	BDL
Lignin	12.9 ± 0.3	14.6 ± 0.7	13.8 ± 0.2	13.8 ± 0.9
Acid insoluble	10.9 ± 0.2	12.2 ± 0.6	11.6 ± 0.2	11.6 ± 0.7
Acid soluble	2.0 ± 0.1	2.4 ± 0.3	2.3 ± 0.1	2.2 ±0.2
Ash	BDL	BDL	BDL	BDL
Recovery	94.6 ± 1.2	97.7 ± 1.2	101.1 ± 1.1	97.8 ± 3.3

During the work of this thesis, STEX was performed several times. The variations in the composition of the steam-pretreated material could have been an issue had the several runs of STEX needed for a study not been performed at the same time. Thus, a new batch of STEX material was prepared for each study. However, because the same material was used in several studies, the composition of the material that had been subjected to STEX at 210°C and 5 minutes could be compared. As presented in Table 3, the composition did not vary significantly, despite the STEX being performed at different occasions. Notably, the differences in the composition of the material after STEX are in the same range, or even lower, than those for the HEX-treated material in Table 2, indicating that these differences are attributed more to the analysis than the treatment itself.

Table 3. Composition (%) of the solid fraction after STEX at 210°C for 5 minutes. STEX was performed on the same material on three occasions. BDL, below detection limit.

	1st STEX	2nd STEX	3rd STEX	Mean value
Carbohydrates	67.1 ± 1.1	66.7 ± 0.6	65.3 ± 0.2	66.4 ± 1.0
Glucan	59.2 ± 0.7	58.1 ±0.6	55.9 ±0.3	57.7 ± 1.7
Xylan	5.7 ± 0.0	6.7 ±0.1	7.8 ± 0.0	6.7 ± 1.1
Mannan	1.9 ± 0.0	1.9 ±0.0	1.7 ± 0.1	1.8 ± 0.1
Arabinan	BDL	BDL	BDL	BDL
Galactan	BDL	BDL	BDL	BDL
Lignin	30.4 ± 0.0	27.6 ±1.0	30.5 ± 0.9	29.5 ± 1.7
Acid insoluble	27.5 ± 0.1	25.1 ± 1.0	26.3 ± 1.0	26.3 ± 1.2
Acid soluble	2.9 ± 0.1	3.1 ± 0.1	4.2 ± 0.0	3.4 ± 0.7
Ash	BDL	BDL	BDL	BDL
Recovery	97.6 ± 1.1	94.2 ± 0.5	95.9 ± 0.7	95.9 ± 1.7

The raw material (hardwood chips) that was used in the studies was kept in a cold storage room at 6°C. The material was extracted with water and ethanol in accordance with NREL procedures and then analysed. Although the material was stored for two years, no differences in composition were observed, as seen in Table 4.

Table 4. Composition (%) of the raw material (80% birch and 20% beech) extracted on three occasions. BDL, below detection limit.

	1st extraction	2nd extraction	3rd extraction	Mean value
Carbohydrates	67.6 ± 1.4	65.5 ± 0.7	64.7 ± 0.2	65.9 ± 1.5
Glucan	39.4 ± 0.8	39.5 ± 0.5	39.7 ± 0.1	39.5 ± 0.2
Xylan	22.2 ± 0.6	21.9 ± 0.3	21.8 ± 0.1	22.0 ± 0.2
Mannan	3.7 ± 0.2	3.6 ± 0.0	2.5 ± 0.0	3.3 ± 0.7
Arabinan	0.6 ± 0.0	0.6 ± 0.0	BDL	0.4 ± 0.4
Galactan	1.8 ± 0.1	BDL	0.7 ± 0.0	0.8 ± 0.9
Lignin	27.2 ± 1.1	27.4 ± 0.4	28.6 ± 0.1	27.7 ± 0.8
Acid insoluble	20.7 ± 1.0	20.1 ± 0.5	21.2 ± 0.1	20.7 ± 0.6
Acid soluble	6.5 ± 0.0	7.3 ± 0.2	7.4 ± 0.0	7.1 ± 0.5
Ash	BDL	BDL	BDL	BDL
Recovery	94.9 ± 2.5	92.9 ± 0.4	93.3 ± 0.0	93.7 ±1.1

4.4.2 Size exclusion chromatography of lignin

The size distribution of the lignin that was extracted by HEX was determined using size exclusion chromatography (SEC) in Paper III. SEC was performed on an Alliance 2695 HPLC system (Waters, Milford, MA, USA) that was equipped with a 2487 UV detector (Waters, Milford, MA, USA) at 280 nm and a 2414 RI detector (Waters, Milford, MA, USA). Separation was conducted using two columns in series: a Superdex 200 Increase (300 x 10 mm, 9 µm) and a Superdex 30 (300 x 10 mm, 9 µm). The mobile phase was 0.1 M NaOH. The system was calibrated using poly-ethylene glycol standards with molecular weights of 200, 400, 1000, 4000, 10,000 and 35,000 Da. The lignin samples were dissolved in 0.5 % (wt/wt) NaOH to a concentration of approximately 1 g/L before analysis.

4.4.3 Combustional elemental analysis of lignin

An elemental analysis of lignin was performed in Paper III. Total carbon, hydrogen, nitrogen and sulphur content in the samples was determined on an elemental analyser (Vario MICRO cube, Elementar Analysensysteme GmbH, Langeselbold, Germany). Oxygen was assumed to constitute the remainder of the material.

5 Two-stage biomass fractionation process

One of the objectives of the work presented in this thesis was to investigate the fractionation efficiency of a two-stage process, consisting of STEX and HEX. Using STEX as pretreatment, a hemicellulose-rich liquid fraction that contained over 70% hemicelluloses was obtained, represented by the xylan content in Figure 9. The remaining solid fraction after STEX was further treated by HEX, resulting in a lignin-rich liquid that contained approximately 50% of the total lignin present in the hardwood that was used in the experiments, and a solid fraction that was enriched in cellulose (represented by the content of glucan), containing over 90% of the total amount of glucan in the raw material. As shown in Figure 9, all fractions were enriched in one of the three major wood components, demonstrating the efficient fractionation achieved using the studied process.

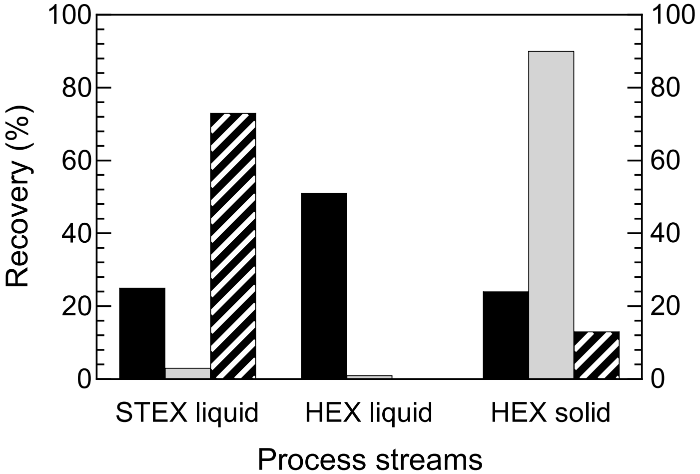

Figure 9. Recovery of lignin (black), glucan (grey) and xylan (striped) in hardwood in various process streams. Standard deviation is less than 2.5% in all cases. Adapted from Paper I.

The following subchapters focus on the influence of the operating conditions on process efficiency.

5.1 Influence of operating conditions during steam explosion

The influence of STEX on the subsequent HEX was studied in Papers II and III. Paper II examined three STEX conditions and their influence on the composition of the remaining solid fraction after STEX: “mild” STEX at 180°C for 5 minutes (denoted STEX_{180}), “moderate” STEX at 210°C for 5 minutes (STEX_{210}) and “harsh” STEX at 210°C for 10 minutes, with the addition of acetic acid (HAc) as a catalyst ($\text{STEX}_{210+\text{HAc}}$). The composition of the remaining solids after each treatment is presented in Table 5.

Table 5. The composition (%) of the raw material and the solid fraction after STEX under various process conditions. BDL: below detection limit. Adapted from Paper II.

	Raw material	**STEX_{180}**	**STEX_{210}**	**$\text{STEX}_{210+\text{HAc}}$**
Carbohydrates	64.7 ± 0.2	66.1 ± 0.6	66.6 ± 0.8	66.9 ± 1.5
Glucan	39.7 ± 0.1	48.3 ± 0.6	58.8 ± 0.8	62.4 ± 1.3
Xylan	21.8 ± 0.1	16.0 ± 0.1	7.0 ± 0.0	4.3 ± 0.1
Mannan	2.5 ± 0.0	1.4 ± 0.1	0.7 ± 0.0	0.2 ± 0.1
Arabinan	BDL	BDL	BDL	BDL
Galactan	0.7 ± 0.0	0.3 ± 0.0	BDL	BDL
Lignin	28.6 ± 0.1	29.4 ± 0.5	30.1 ± 0.2	30.9 ± 1.4
Acid insoluble	21.2 ± 0.1	24.2 ± 0.3	26.8 ± 0.0	28.1 ± 1.4
Acid soluble	7.4 ± 0.0	5.2 ± 0.2	3.3 ± 0.2	2.8 ± 0.0
Ash	BDL	0.2 ± 0.1	0.2 ± 0.1	BDL
Recovery	93.3 ± 0.0	95.7 ± 0.3	96.8 ± 0.6	97.8 ± 0.1

Glucan was enriched in the solid fraction after STEX as the severity of the treatment increased, as shown in Table 5. The glucan content rose from 48% to 62% between the mildest and harshest pretreatments, due primarily to more xylan being dissolved as the content of xylan decreased in the solid fraction from 16% to 4.3%, respectively. Small differences in total lignin content were observed between treatments, indicating good selectivity toward hemicelluloses during STEX.

HEX was performed under two process conditions, 150°C and 190°C for 4 hours (HEX_{150} and HEX_{190}, respectively) to determine how the severity of the STEX affects the performance of the subsequent HEX. Between the results of the two-stage treatment (STEX followed by HEX), minor differences in the composition of the solid fractions were seen. The largest deviation was observed for the material that was pretreated under the mildest STEX conditions and HEX at 150°C, as shown in Table 6. The most notable difference was the higher xylan content in this sample, attributed to the greater xylan levels after $STEX_{180}$, as shown in Table 5.

Table 6. Composition (%) of the material treated with STEX under various process conditions followed by HEX. BDL: below detection limit. Adapted from Paper II.

	$STEX_{180}$+ HEX_{150}	$STEX_{180}$+ HEX_{190}	$STEX_{210}$+ HEX_{150}	$STEX_{210}$+ HEX_{190}	$STEX_{210HAc}$+ HEX_{150}	$STEX_{210HAc}$+ HEX_{190}
Carbohydrates	77.8 ± 0.1	85.1 ± 0.3	84.0 ± 0.2	84.8 ± 0.8	81.2 ± 0.4	82.6 ± 0.5
Glucan	64.6 ± 0.1	80.3 ± 0.3	76.6 ± 0.2	80.4 ± 0.7	76.6 ± 0.3	79.7 ± 0.6
Xylan	11.9 ± 0.0	4.5 ± 0.0	6.6 ± 0.0	4.0 ± 0.0	4.3 ± 0.1	2.7 ± 0.1
Mannan	1.0 ± 0.0	0.3 ± 0.0	0.7 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
Arabinan	BDL	BDL	BDL	BDL	BDL	BDL
Galactan	0.2 ± 0.0	BDL	BDL	BDL	BDL	BDL
Lignin	17.7 ± 0.2	12.5 ± 0.5	14.4 ± 0.0	13.4 ± 0.2	15.6 ± 0.5	16.2 ± 0.8
Acid insoluble	14.0 ± 0.2	10.6 ± 0.5	11.7 ± 0.1	11.6 ± 0.2	13.4 ± 0.5	14.7 ± 0.8
Acid soluble	3.7 ± 0.1	1.9 ± 0.0	2.7 ± 0.0	1.8 ± 0.0	2.1 ± 0.0	1.5 ± 0.0
Ash	BDL	BDL	BDL	BDL	0.1 ± 0.1	0.4 ± 0.0
Recovery	95.5 ± 0.2	97.6 ± 0.2	98.7 ± 0.9	98.4 ± 0.9	96.8 ± 0.0	99.3 ± 0.2

The remaining solid fraction after HEX was further enriched in cellulose through the combination of STEX and HEX, as seen in Table 6, due to the simultaneous delignification and removal of xylan from the solid material during HEX. Furthermore, comparing the results of HEX at 150°C and HEX at 190°C at the medium- and higher-severity STEX conditions, implies that the temperature during HEX did not have a significant impact on the extraction, yielding similar compositions of the solid fraction after HEX.

In Paper III, the influence of pretreatment with STEX was examined further. Untreated and STEX-pretreated birch chips were subjected to HEX at 25°C and 250°C. STEX was performed at 210°C for 5 minutes, and the residence time during HEX was kept constant for 1 hour in all four experiments. The extraction of the individual components was calculated according to Equation 1:

$$Ex = \left(1 - \frac{m_{X,SFHEX}}{m_{X,SFSTEX}}\right) \cdot 100 \qquad (1)$$

where Ex is the extraction (%), $m_{X,SFHEX}$ is the mass of component X in the solid fraction after HEX and $m_{X,SFSTEX}$ is the mass of component X in the solid fraction before HEX (for abbreviations, see Figure 4).

The results show that using STEX as a pretreatment before HEX is paramount if HEX is to be performed at ambient temperature. As shown in Figure 10, no component was extracted at 25°C in the absence of pretreatment with STEX, whereas 50% of the lignin was extracted, even at room temperature, when the material was pretreated by STEX.

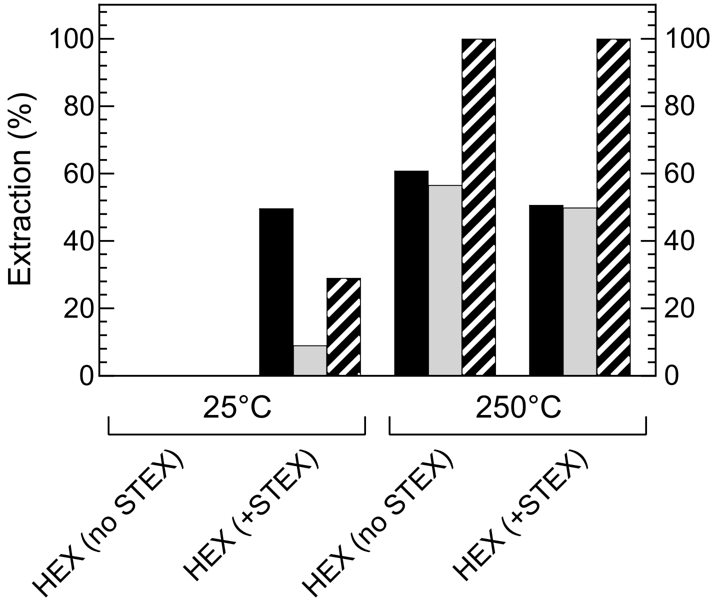

Figure 10. Extraction (%) during HEX of untreated and pretreated birch chips at 25°C and 250°C. Lignin: black bars, glucan: grey bars and xylan: striped bars. Standard deviations were less than 1.5% in all cases. Adapted from Paper III.

With HEX at 250°C, approximately the same amounts of lignin, xylan and glucan were extracted with and without pretreatment by STEX (Figure 10). This result indicates that if some form of hydrothermal treatment is applied, during STEX or within the HEX itself, 50% to 60% of the lignin present in the material can be extracted by HEX.

5.2 Influence of operating conditions during hydrotropic extraction

The influence of temperature and residence time during HEX was studied in Paper I. The raw material (80% birch and 20% beech) in these investigations was STEX-pretreated at 210°C for 5 minutes. HEX was performed at 150°C, 170°C, 180°C and 190°C with a residence time of 4 h. Temperature had no significant influence on the extraction of any component, as shown in Figure 11a. Between residence times of 0.5 h and 8 h during HEX at 150°C, a significant difference was observed only at 0.5 h (Figure 11b).

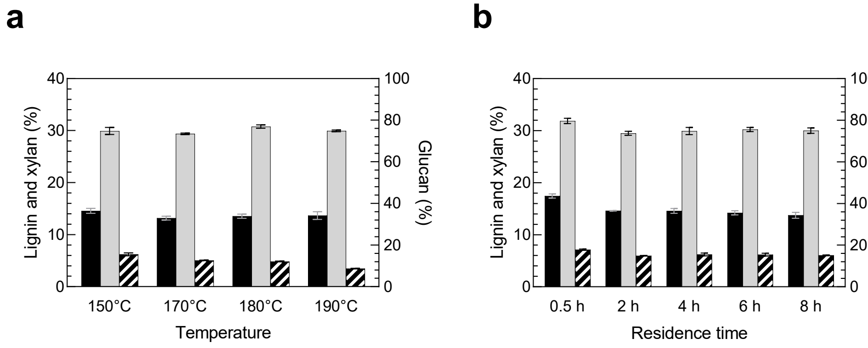

Figure 11. Composition (%) of the solid material after HEX at a) 4 h and various temperatures and b) at 150°C and various residence times. Glucan: grey, lignin: black and xylan: striped. Adapted from Paper I [105]. Infogad som png.

To systematically evaluate the influence of temperature, residence time and biomass loading on lignin extraction during HEX of STEX-pretreated birch, a design of experiments (DoE) methodology was applied in Paper III. The influence of temperature was determined between 100°C and 200°C, at residence times between 0 min and 1 h, and at biomass loadings of 5% to 10%. All parameters correlated positively with lignin extraction. To illustrate the effect of these parameters, response surfaces were created (Figure 12). Further, residence time also had a quadratic effect, indicating that a local maximum was achieved for lignin extraction at a residence time of approximately 45 min, as shown in Figures 12a and 12c.

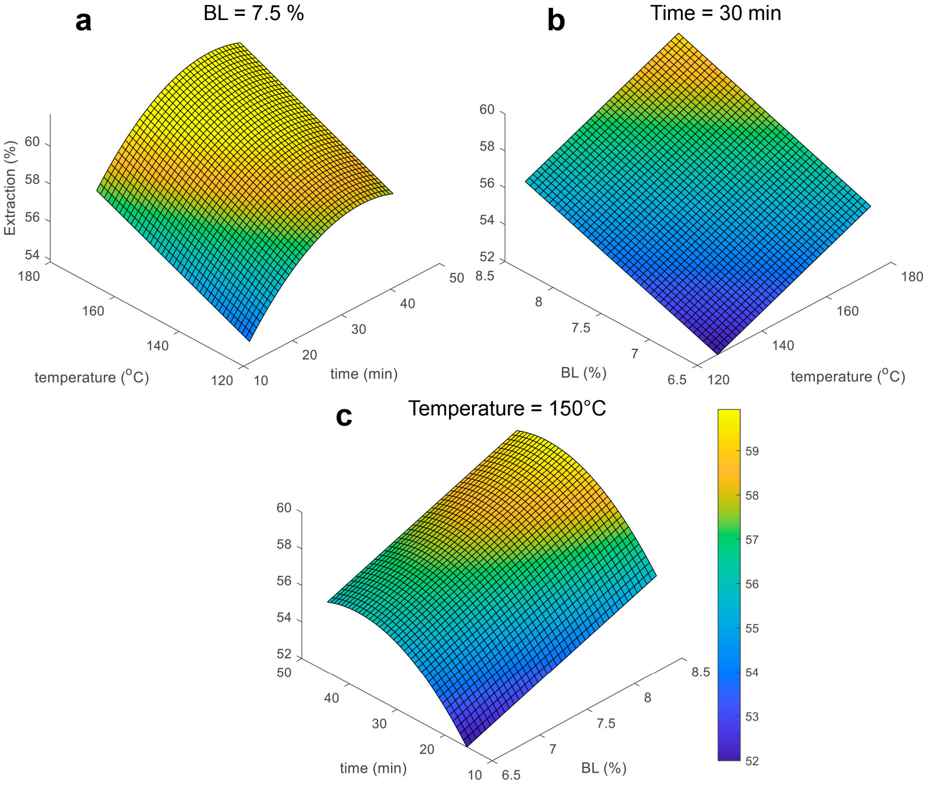

Figure 12. Response surfaces fitted to the experimental data in the DoE design. Response surface at a) a constant biomass loading (BL) of 7.5%, b) a constant residence time of 30 min and c) a constant temperature of 150°C. Adapted from Paper III.

The results of the DoE slightly contradict the findings in Paper I, in which temperature and time had little or no effect on lignin extraction. A possible explanation is that the extraction of lignin during HEX reaches a "steady state" at a sufficiently high temperature and residence time. The extraction of lignin plateaus as the residence time increases, as shown in Figure 13. This "steady-state" point was already attained at a residence time of 2 h, indicating that the process conditions in Paper I did not include sufficiently low temperatures and short residence times for the effects of these parameters to be visible.

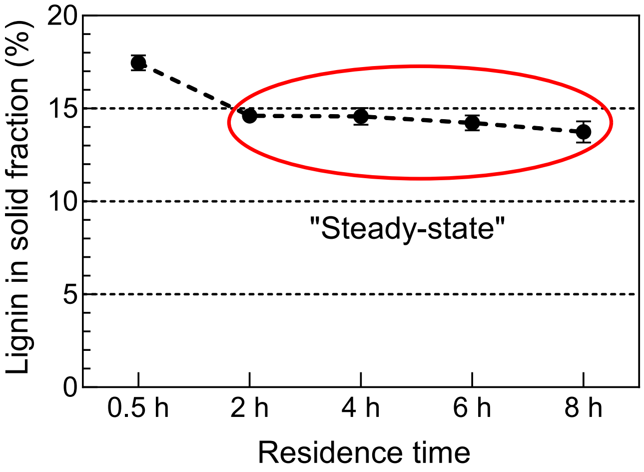

Figure 13. Lignin content in the solid fraction after HEX. Values are shown in Figure 11b. Standard deviations were less than 2.2% at all points. Adapted from Paper I.

In Paper III, the effect of temperature was also examined over a broader temperature span of 25°C to 250°C at a constant residence time of 1 h. The extraction of various components was calculated according to Equation 1. The extraction of lignin rose slightly with increasing temperature until 200°C, levelling off and decreasing at 250°C, as shown in Figure 14a.

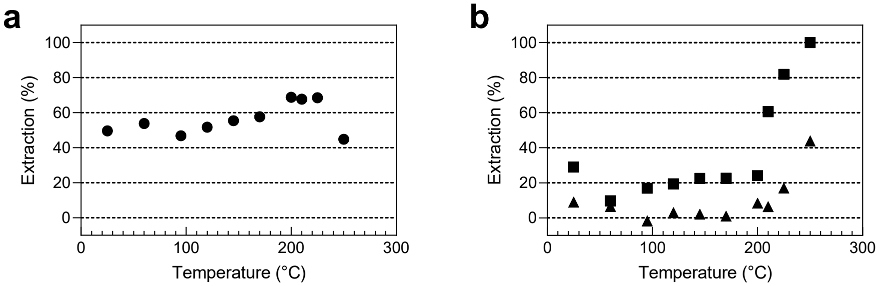

Figure 14. a) Extraction of lignin (●) and b) glucan (▲) and xylan (■) versus temperature during HEX. Standard deviations were less than 5.5% at all points. Adapted from Paper III.

The results from Paper III also show that the extraction of glucan and xylan increased above 200°C (Figure 14b), indicating that more extensive breakdown of the entire lignocellulosic structure occurred above this temperature. Furthermore, these data demonstrate that above 200°C, the selectivity toward lignin is lost, because glucan and especially xylan were extracted together with the lignin. The same behaviour was observed in Paper II, in which two HEX experiments were performed using untreated hardwood chips at 150°C and 190°C for 4 h. The results indicate that lignin and xylan were extracted together during HEX, especially at higher temperatures, as evidenced by the increase in glucan content in the solid fractions after HEX and the simultaneous decline in lignin and xylan content, as shown in Table 7. This result could have implications if pure lignin is desired.

Table 7. Composition (%) of hardwood chips and the solid fraction after HEX at 150°C and 190°C.

	Raw material	HEX_{150}	HEX_{190}
Carbohydrates	64.7 ± 0.2	73.2 ± 1.0	85.5 ± 0.3
Glucan	39.7 ± 0.1	53.6 ± 0.7	80.9 ± 0.3
Xylan	21.8 ± 0.1	17.5 ± 0.3	4.2 ± 0.0
Mannan	2.5 ± 0.0	1.7 ± 0.0	0.4 ± 0.0
Arabinan	BDL	BDL	BDL
Galactan	0.7 ± 0.0	0.4 ± 0.0	BDL
Lignin	28.6 ± 0.1	22.0 ± 0.1	12.4 ± 0.4
Acid insoluble	21.2 ± 0.1	17.0 ± 0.1	10.5 ± 0.4
Acid soluble	7.4 ± 0.0	5.0 ± 0.0	1.9 ± 0.0
Ash	BDL	0.1 ± 0.0	0.2 ± 0.0
Recovery	93.3 ± 0.0	95.4 ± 0.9	98.1 ± 0.7

The influence of the concentration of SXS on the delignification of hardwood was studied in Paper IV. The content of cellulose (represented as glucan) was markedly higher after HEX, even at the lowest SXS concentration, as shown in Figure 15. As the SXS concentration rose from 10% to 50%, the lignin content in the solid material decreased from 27.7% to 16.2%.

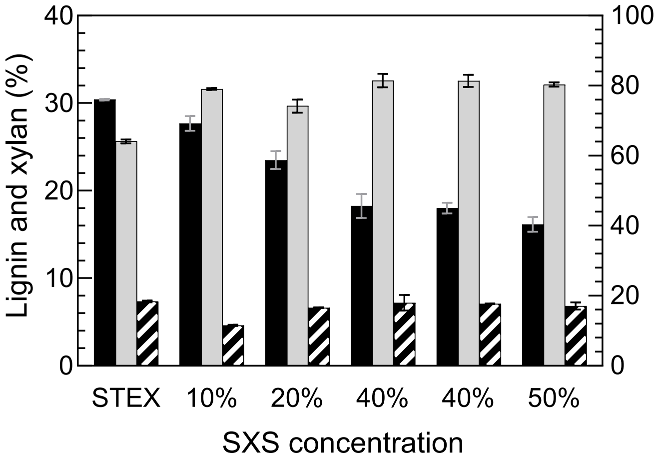

Figure 15. Composition (%) of the solid fraction after HEX at various SXS concentrations. Adapted from Paper IV.

The content of lignin in the solid fraction after HEX fell linearly with SXS concentration until 40% but slowly began to level off as the concentration increased to 50%, as shown in Figure 16. This could have implications on the process economy if the process is to be used industrially, because there would be a trade-off between the costs of increasing the SXS concentration against the gain in lignin that is extracted.

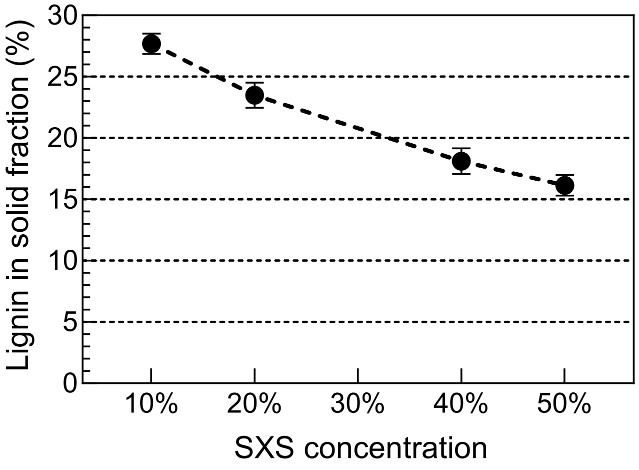

Figure 16. Influence of SXS concentration on the removal of lignin during HEX of STEX-pretreated hardwood samples. Adapted from Paper IV.

6 Reuse and recovery of the SXS solution

The use of HEX as a fractionation process has been examined in several studies, as presented in Chapter 3. However, if the process is to be implemented on a large scale, the recovery and regeneration of the SXS solution will be an important part of the complete process. To the best of our knowledge, the reuse and recovery of the SXS solution and its impact on process economy have not been studied further since McKee filed his patent in 1943 [90]. These topics are discussed in this chapter.

6.1 Reuse of the SXS solution

When HEX of lignocellulosic biomass was first patented by McKee in 1943 [90], a reported advantage of the process was the possibility of using the same hydrotropic solvent in several runs. It was also claimed that as the hydrotropic solvent became more concentrated with lignin in solution, it would become increasingly effective as a solvent for lignin. In Paper V, an experiment with a series of extractions using the same SXS solution was performed to test this hypothesis. The experiment was designed such that new STEX-pretreated material was used in each HEX. The HEX was performed at 150°C for 2 hours, after which the solid and liquid fractions were separated, with the latter advancing to the next stage, as illustrated in Figure 17.

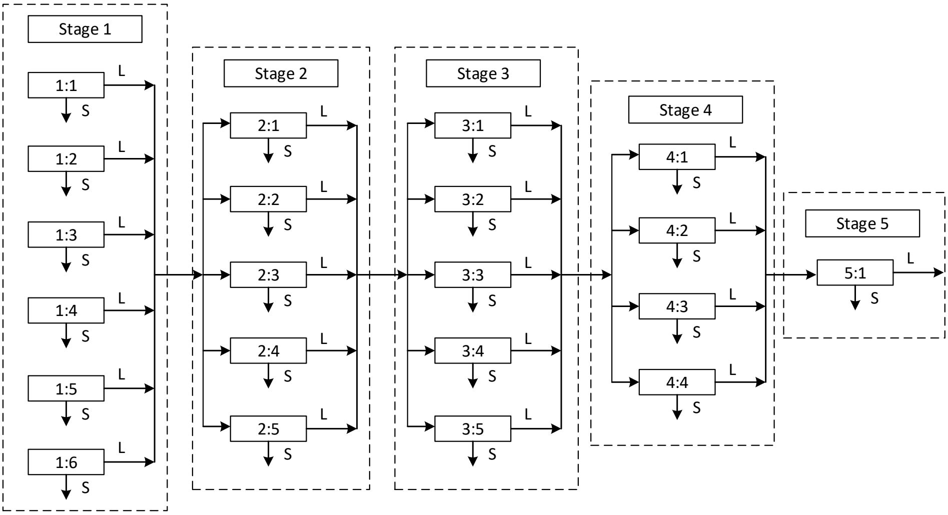

Figure 17. Schematic illustration of the sequential hydrotropic extraction. S and L denote solids and liquids, respectively. New STEX-pretreated material was used in each extraction. Each extraction is denoted "x:y", where x is the stage and y is the number of the extraction within the stage. Adapted from Paper V.

After each individual stage, the solid fractions after each HEX in the stage (1:1-1:6 and so on) were washed and mixed together. The compositions were analysed to determine if the efficiency of the SXS solution varied between stages. By using STEX-pretreated material from the same batch in every extraction, the composition of the solid fraction after HEX was a good indicator of whether the efficiency of the SXS solution changed between stages.

The glucan content increased from 59% in the solid fraction after STEX to roughly 75% in the solid fraction after each stage of HEX, as shown in Table 8, compared with lignin declining from 30% to approximately 15%, respectively. The lignin content remained constant at approximately 15% for all extractions except after the fourth stage, after which the lignin content was 18%. This lignin content of 15% is similar to that under the same HEX conditions in Paper I (14.6% in the solid fraction after HEX at 150°C for 2 hours), indicating that the variations during the HEX treatment itself are small.

Table 8. Composition (%) of material after STEX and each extraction stage and the calculated concentration of SXS (Paper V).

	STEX	HEX 1	HEX 2	HEX 3	HEX 4	HEX 5
Concentration of SXS after extraction [%]	-	37	34	32	29	27
Carbohydrates	67.1 ± 1.1	83.1 ± 0.4	83.4 ± 0.9	84.2 ± 2.1	82.4 ± 0.8	80.1 ± 6.2
Glucan	59.2 ± 0.7	76.0 ± 0.4	76.3 ± 0.8	77.0 ± 2.2	75.3 ± 0.6	73.3 ± 0.4
Xylan	5.7 ± 0.0	5.2 ± 0.1	5.2 ± 0.0	5.3 ± 0.1	5.2 ± 0.0	4.9 ± 0.4
Mannan	1.9 ± 0.0	1.9 ± 0.2	1.9 ± 0.2	1.9 ± 0.2	1.9 ± 0.2	1.9 ± 0.2
Arabinan	BDL	BDL	BDL	BDL	BDL	BDL
Galactan	BDL	BDL	BDL	BDL	BDL	BDL
Lignin	30.4 ± 0.0	14.9 ± 0.6	15.1 ± 0.3	15.9 ± 1.0	18.2 ± 0.6	15.2 ± 0.4
Acid insoluble	27.5 ± 0.1	12.7 ± 0.4	13.0 ± 0.2	13.9 ± 1.1	16.3 ± 0.2	13.2 ± 0.2
Acid soluble	2.9 ± 0.1	2.2 ± 0.5	2.1 ± 0.5	2.1 ± 0.5	2.0 ± 0.4	2.0 ± 0.5
Ash	BDL	BDL	BDL	BDL	BDL	BDL
Recovery	97.6 ± 1.1	98.0 ± 1.0	98.6 ± 0.8	100.1 ± 1.1	100.6 ± 0.6	95.3 ± 6.6

This study did not confirm the claim by McKee [90] that the efficiency of the SXS solution increases with lignin concentration. Instead, approximately the same amount of lignin (12 g) was dissolved in each stage, despite the concentration of lignin steadily increasing. A nearly linear rise in the total amount of lignin in the SXS solution was observed during the experiment, as shown in Figure 18. In total, 56 g of lignin was dissolved in the final liquid fraction after Stage 5, corresponding to roughly 65% of the total lignin that was added over the 5 stages.

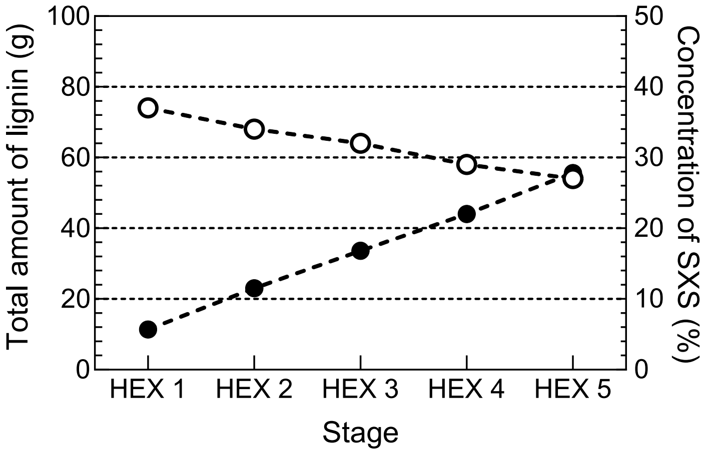

Figure 18. Total amount of lignin dissolved (black dots) in each stage of the HEX and the SXS concentration (white dots). Adapted from Paper V.

However, due to the moisture content in the STEX-pretreated material (approximately 40%), the SXS solution was diluted with each addition of new STEX material. In this study, approximately 84 g of water was added at each extraction, resulting in a nearly linear decrease in SXS concentration, from 40% in the first stage to 27% in Stage 5, as shown in Figure 14. Given the decrease in the delignification efficiency of the SXS solution with lower SXS concentrations, as seen in Figure 11, McKee's claim that the dissolving efficiency of SXS at higher lignin concentrations could still be correct. The dilution of the SXS solution in each stage could be compensated for by adding more SXS powder at each stage. However, doing so would increase the costs, and lignin is still extracted extensively in each stage, despite the concentration of SXS decreasing, which is an important process-related aspect to consider. Consequently, this dilution effect must be considered if this process is to be implemented on a larger scale.

6.2 Recovery of the SXS solution

The recovery of spent SXS solution has previously been performed by evaporation. However, this process is energy-intense and thus expensive. In Paper VI, an alternative method for recovering spent SXS solutions by nanofiltration was examined.

Five membranes with varying characteristics were evaluated in a screening study, in which their flux and retention were recorded as a function of transmembrane pressure (TMP). The initial concentration of SXS in the experiments was 4% (w/v). This concentration has been found to be appropriate when precipitating lignin from a used SXS solution [96] and confirmed by own, not published results. In this study, a model SXS solution was used. The performance of the individual membranes was determined in parameter studies at 45°C between TMPs of 1 to 35 bar. In general, the membranes with high flux had low retention, and vice versa. However, two membranes from General Electric (GE) that had a relatively high retention of SXS in the parameter study (87% for the HL membrane and 90% for the AL membrane) were assessed further in concentration studies.

In the concentration studies, a final concentration of SXS of approximately 8% was achieved with both membranes. A higher volume reduction (VR = permeate volume/initial feed volume) was needed to reach the final SXS concentration of 8.5% with the HL membrane due to its lower retention. The average retention for the HL and AL membranes were 70% and 96%, respectively. A VR of nearly 70% was needed to reach the final concentration with the HL membrane, versus 47% with the AL membrane, as shown in Figure 19. Despite the slightly lower mean flux of the AL membrane during the concentration (31 L/m^2 h compared with 41 L/m^2 h for the HL membrane), it remains the most advantageous choice due to its higher retention of SXS.

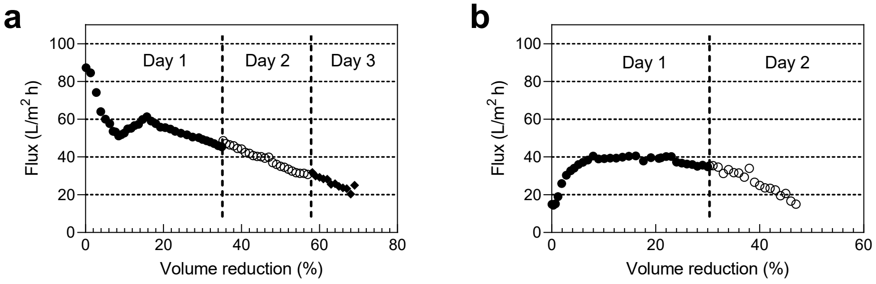

Figure 19. Flux during concentration of a 4% SXS solution with the a) HL membrane and b) AL membrane at 30 bar and 45°C. Adapted from Paper VI.

Although the flux remained above 0 at the final concentration of SXS in the experiments in Figure 19, the maximum concentration that can be obtained by nanofiltration is likely close to that in these experiments (approximately 8%). In the initial stage of the design of the nanofiltration experiments, the flux of a 10% solution was 0, likely due to the high osmotic pressure of the SXS solution.

According to the van't Hoff equation, the osmotic pressure of a 10% SXS solution is 25 bar at 45°C. Thus, at a pressure of 35 bar, as in this study, our result approximates the maximum concentration that is achievable with this setting. Further, despite the ostensibly minor increase in concentration from 4% to 8%, as much as 50% of the water has been removed at 8%, which will have a tremendous impact of the overall recovery cost.

6.2.1 Potential energy savings using membrane filtration

Removing water from a solution by evaporation is expensive. When the concentration of SXS is lowered to 4% to precipitate lignin, 9 m^3 of water must be added to each m^3 of 40% SXS solution. To restore the original concentration, the 9 m^3 of water that has been added needs to be removed again. Accurately estimating the energy savings that can be obtained using nanofiltration requires a more extensive evaluation of operating conditions and their effect on the membrane performance, including pilot plant studies. However, to get an understanding of the possible energy savings that could be made when SXS is treated with nanofiltration, a comparison between the commercial concentration of whey proteins using membrane filtration, and industrial evaporation were made. Whey was selected, because its molecular weight (382 Da) is similar to that of the SXS molecule (210 Da) and because its starting concentration in the process is approximately the same (5%) as the SXS solution in the study (4%).

It has been reported that the energy requirement to remove water during the membrane filtration of whey is 9-20 kWh/m^3 water removed [106]. With evaporation, these requirements vary between 209 kWh/m^3 removed water in a 3-effect evaporator to 90 kWh/m^3 in a 7-effect evaporator, estimated according to Ekbåge [107]. Because the concentration of SXS in our study was 8% when the experiment ended, some evaporation will be necessary to restore the SXS solution. However, as stated above, 50% of the water had already been removed, with a lower energy requirement. Thus, the energy savings could be considerable if the used SXS solution that is to be restored is pre-concentrated by nanofiltration before evaporation.

7 Discussion

Chapters 5 and 6 focused on the levels of each wood component that was obtained in each process stream after STEX and HEX under various operating conditions. However, lignin and hemicelluloses are not only polydisperse but also collective terms for a range of heteropolymers with various functional groups. This chapter discusses the influence of some important operating conditions on the properties of the wood components and what significance this may have in the further processing of the various substances.

7.1 Impact of steam explosion

The primary purpose of STEX is to extract hemicelluloses and open the wood structure to facilitate HEX. During STEX of hardwood chips, the extraction of hemicelluloses increases as the severity of STEX rises, as shown in Table 5, due to the higher acidity in the more severe treatments. As the severity increases, acetic acid is released from the material due to the hydrolysis of acetyl groups present in the biomass [108]. Acetic acid was added as a catalyst in one of the experiments, lowering the initial pH of this solution and promoting the extraction of more acid-soluble components. The amount of total lignin increased slightly at higher severities during STEX, as shown in Figure 20. Concurrently, the amount of acid-soluble lignin in the remaining solids after STEX declined, as expected, as the pH fell with increasing severity from 3.3 in the liquid fraction after the mild STEX to 2.4 in the liquid fraction after the high severity STEX. The operating conditions under STEX thus affect the ratio between the amount of acid-insoluble and acid-soluble lignin.

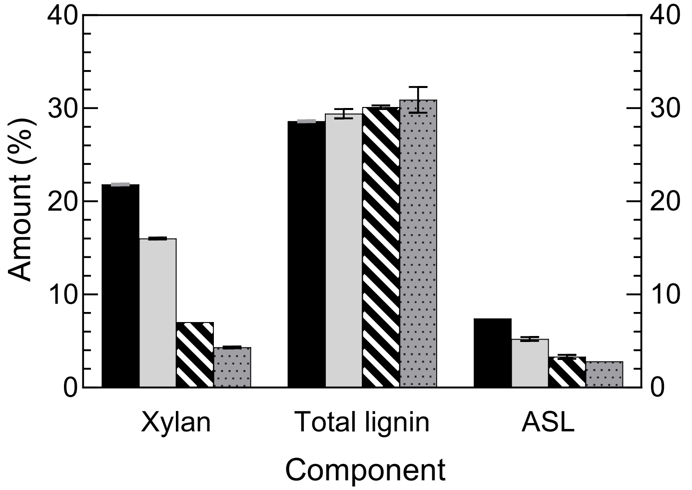

Figure 20. Amount of xylan (representing hemicelluloses), total lignin and acid-soluble lignin (ASL) in the raw material (hardwood chips) and the solid fraction after STEX under various operating conditions. Hardwood chips: black bars, $STEX_{180}$: grey bars, $STEX_{210}$: striped bars and $STEX_{210+HAc}$: grey dotted bars. Adapted from Paper II.

Another result of higher severities during STEX is that the lignin present in the material, which undergoes several subsequent de- and repolymerisation reactions during the treatment, might form more condensed structures (with increasing amounts of carbon-carbon bonds) at higher severities [101, 109, 110]. Thus, it might be harder to extract lignin during HEX due to the condensed structures. Consequently, even if performing STEX at a higher severity could be beneficial with regard to the greater solubilisation of hemicelluloses, the resulting lignin might be harder to extract. Therefore, the severity during STEX is a trade-off between extracting as much hemicelluloses as possible and the potential issue of removing condensed lignin structures from the fibres during the consecutive HEX.

7.2 Impact of hydrotropic extraction

When HEX was performed on the STEX-pretreated hardwood in Paper I, the differences in the composition between the solid fraction after HEX at 150°C for 8 h and 190°C for 4 h were small, as shown in Figure 11. However, the visual differences of the solids were profound. To better understand the ultrastructural changes, SEM images of two solid fractions after HEX were compared. A comparison of the solids after HEX at 150°C and 190°C (Figure 21 a1 and b1, respectively) shows that the structure has collapsed after HEX at the higher temperature. It is also clear that the fibrillose structure was visible in both cases, based on their magnified images (Figure 21 a2 and b2). However, pictures that are taken by SEM merely depict a small area of the entire sample. Thus, these images might not be representative of the entire sample.

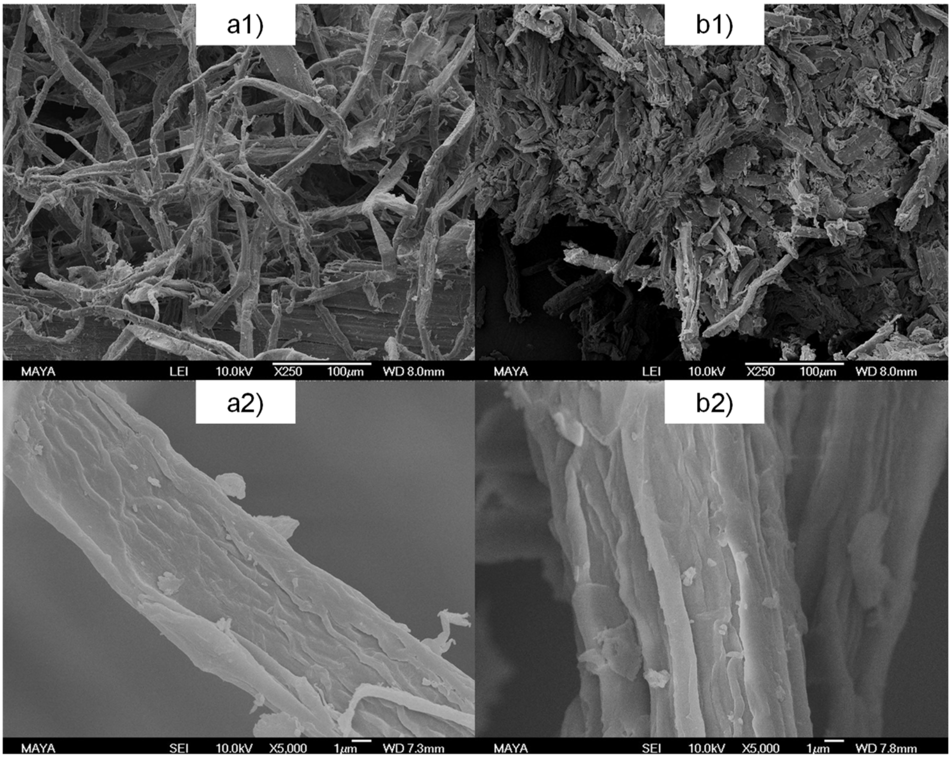

Figure 21. SEM images of the solid fraction after HEX at a) 150°C for 8 h and b) 190°C for 4 h. The magnification was 250x (a1 and b1) and 5000x (a2 and b2). Adapted from Paper I.

A trade-off between the purity and yield of lignin must be made when selecting the operating conditions during HEX. The results presented in this thesis clearly show that the extraction of lignin and xylan increases when the temperature and residence time rise beyond a certain threshold. This aspect must be considered, because the lignin that will be precipitated from the liquid fraction after HEX might be contaminated with xylan, which might have implications for the end use of the lignin. This risk also underscores the importance of incorporating STEX before HEX to remove as much xylan as possible before HEX.

Notably, in Paper III, the extraction of lignin decreased suddenly at 250°C (Figure 14a). However, previous studies have shown that the content of Klason lignin in biomass can be overestimated due to the formation of so-called pseudo-lignin [111]. Further, the generation of pseudo-lignin correlates with high severities during pretreatment, acidic conditions, and the presence of xylan [112, 113]. At high temperatures during HEX, the pH in the liquid decreased, as shown in Figure 22, perhaps indicating that the conditions at higher temperatures favour the formation of pseudo-lignin. Furthermore, the amount of xylan decreased in the liquid fraction after HEX at elevated temperatures (Figure 22). This finding contradicts the results in Figure 14b, in which the extraction of xylan clearly increased at higher temperatures. The observations in Figures 14b and 22 support the assumption that some xylan was transformed into pseudo-lignin at high temperatures during HEX, because it was not accounted for either in the solid, or liquid fraction after HEX.

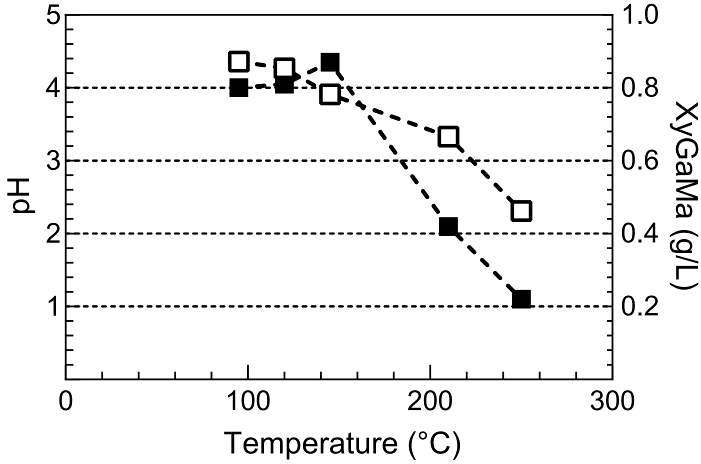

Figure 22. Influence of temperature during HEX on pH (white boxes) and the concentration of xylose+galactose+mannose (XyGaMa) (black boxes) in the liquid fraction after HEX. Adapted from Paper III.

In the study performed in Paper III, lignin was precipitated from the liquid fraction after HEX and analysed by size exclusion chromatography and elemental analysis. The results indicate that the lignin depolymerised at higher temperatures, as evidenced by the decrease in weight average molecular weight (Mw), as presented in Table 10. In the elemental analysis, oxygen content declined at higher temperatures (Table 10). It has been reported that the cleavage of ether bonds accelerates at temperatures above 160°C under acidic conditions [114]. As the cleavage of ether bonds is often hydrolytic, resulting in the formation of water, this could explain the lower oxygen content. Smaller lignin fragments are often considered to be beneficial for the further processing of lignin. However, if the creation of smaller lignin molecules is offset by reactive bonds being broken (such as aryl-ether bonds), which might occur with the lignin that is extracted at higher temperatures, possibly rendering the lignin undesirable for use in the production of other chemicals and products.

Table 10. Elemental and SEC analysis of lignin precipitated from the liquid fraction after HEX. Carbon and oxygen content is expressed as % dry matter. Mw is weight average molecular weight, Mn is number average molecular weight and PDI is poly dispersity index. Adapted from Paper III.

Sample	Carbon content	Oxygen content	Mw	Mn	PDI
25°C	61.4	31.8	5779	1947	3.0
60°C	60.9	31.4	5650	1844	3.1
120°C	61.2	31.2	5602	1864	3.0
145°C	61.1	31.4	5904	1956	3.0
200°C	63.3	29.4	4805	1963	2.4
250°C	66.3	26.9	3764	1550	2.4

To fully understand how lignin transforms during HEX, the produced lignin must be examined more comprehensively—for example, by H-NMR, QC-NMR and FTIR. Such a characterisation could also determine whether it is advantageous to perform HEX at lower temperatures, given that it was already possible to extract 50% of the lignin in the solid fraction after STEX at ambient temperatures during HEX, as shown in Figure 14a. Because many current lignin extraction processes involve high temperatures for longer periods, this “new” HEX-derived lignin could be interesting for further investigation and processing.

8 Concluding remarks

Hardwood can be divided into a hemicellulose-rich, a lignin-rich and a cellulose-rich fraction in a two-stage process that comprises pretreatment by STEX, followed by HEX. More than 70% of the hemicelluloses in the wood can be recovered in the liquid fraction after STEX, compared with 50% of the lignin in the liquid fraction after HEX, and over 90% of the cellulose is found in the solid fraction after HEX. When STEX is used as a pretreatment step, the subsequent HEX can be performed at ambient temperature with a short residence time of 1 hour, maintaining a high yield of 50%. These properties are important for the process economy (no extra heating required during HEX) and could have a positive impact on the structure of the extracted lignin.

HEX can be used as a "stand-alone" process, as well, without pretreatment by STEX. However, lignin and xylan will be extracted together in a one-stage, HEX-only process. This set-up can have a negative effect on the efficiency of the fractionation and the purity of the extracted lignin, which will be tainted by xylan. If a cost- and energy-efficient method to separate these two components in the HEX liquid were to be developed, pretreatment by STEX might be unnecessary. Unfortunately, it is not possible to avoid heating the material completely, because, as demonstrated in this work, some form of hydrothermal pretreatment is required to make the lignin available for HEX, whether the heating is performed during STEX or during HEX itself.

The hydrotropic solution can be reused several times without losing its efficiency. If the process is to be operated on a larger scale, this would be advantageous, because the regeneration of the used SXS solution could be quite expensive. However, when reusing the SXS solution, one must account for the dilution effect of the repeated addition of biomass, which usually has a high moisture content.

The extracted lignin is precipitated by diluting the SXS solution, which must be concentrated before it can be used again. It was shown that 50% of the water in the a diluted SXS solution can be removed by nanofiltration. Evaporation, a highly energy-demanding process, has been suggested for the recovery of SXS, but nanofiltration could potentially reduce the energy requirements in this part of the process. Notably, the reuse of the SXS solution, combined with the energy-efficient concentration of the used solution by nanofiltration, can have a significant impact on the overall economy of the process.

Finally, to transform our society from a fossil-based to a sustainable and bio-based one, we must find environmentally friendly and energy-efficient fractionation processes and use the available biomass wisely without unnecessary waste. In Sweden, branches and treetops that are generated during forestry operations constitute a largely unutilised biomass fraction that could be used in the STEX + HEX process. Another type of waste that can be treated in this process is agricultural residues (preliminary results). The use of environmentally friendly chemicals and the modest energy requirement of the process that was studied in this thesis render it an interesting alternative for treating residues from the forestry and agricultural industries.

9 Future work

The two-stage process that has been discussed in this thesis shows promise regarding the fractionation of the main components of lignocellulosic biomass. However, further research on the purification and upgrading of the various fractions is needed. Potential applications for this already exist: cellulose can be used as textile fibres, hemicelluloses are potential biopolymers and lignin is a valuable source of aromatics, for example. However, developing environmentally friendly and energy-efficient separation methods for further purification will be challenging.

The precipitated lignin that is obtained after HEX must be characterised to take advantage of its full potential. By better understanding how the process conditions during HEX affect the extracted lignin and its properties, the process could be tuned toward generating a more reactive lignin, depending on what is requested for further processing. It is likely that lignin that is extracted from HEX at low temperatures differs from that at higher temperatures. Through a complete understanding of these disparities, it is possible that the process will have even more advantages than those that have been presented in this thesis. A relatively pure liquid lignin fraction is obtained after HEX, but part of the original lignin remains in the solid cellulose-rich fraction. If the cellulose is to be used for the production of textile fibres, for example, the lignin must be removed, resulting in another lignin fraction with different properties that potentially can be used in other applications than the lignin that is extracted during HEX.

A greater understanding of the mechanisms during HEX is needed to improve the process, for example, by studying how the size of the wood chips affects the mass transfer. It is also important to investigate how the properties of the SXS solution is altered upon the addition of lignin in order to determine how long it can be reused. Furthermore, the combination of SXS with another solvent, such as ethanol, during HEX could be a compelling pursuit. This modified HEX and organosolv process, might affect both the lignin recovery and the properties of the produced lignin.

The recovery of the spent SXS solution by nanofiltration and the possibility of reusing the SXS solution will likely impact the overall process economy, necessitating further investigation of the reuse and recovery of the SXS solution. By performing nanofiltration of the spent SXS solution on a larger scale than the lab scale that was used in this work, a more well-founded estimation of the economy of this segment of the process can be made. Further, the actual spent SXS solution (after precipitation and subsequent filtration of the lignin) could be used to examine whether residual lignin particles affect the performance of the membranes. Additional experiments should be performed to evaluate whether the SXS solution becomes more effective when reused in several consecutive extractions. To account for the dilution effect, solid SXS could be added after each stage to revert the concentration to the target value.

The possibility of using raw materials other than hardwood should be assessed. Agricultural residues are interesting in this context, because the sugars in their hemicelluloses consist largely of pentoses, and the STEX + HEX process makes it possible to separate the pentoses of the hemicelluloses and the hexoses of the cellulose. Our preliminary results have shown that straw can be used as raw material instead of hardwood, meriting further investigation to identify new areas of use.

References

1. **Paris Agreement**. In.: The United Nations; 2015.
2. **The European green deal**. In: *COM(2019) 640 final.* The European Union; 2019.
3. **European Climate Law**. In. Edited by Commission TE; 2020.
4. **Klimatpolitiskt ramverk för Sverige**. In. Sweden; 2017.
5. Sciences SUoA: **Forest statistics 2020**. In.; 2020.
6. Holmgren P: **Så stort är skogsnäringens bidrag i klimatarbetet**. In.: Skogsindustrierna; 2019.
7. Dahmen N, Lewandowski I, Zibek S, Weidtmann A: **Integrated lignocellulosic value chains in a growing bioeconomy: Status quo and perspectives**. *GCB Bioenergy* 2019, **11**(1):107-117.
8. **Short-Term Energy Outlook**. In.: U.S. Energy Information administration; 2021: 1-21.
9. Koch G, Sixta H, Süss H, Potthast A, Schwanninger M, Krotscheck A: **Raw material for pulp**. In., vol. 1: Wiley-VHC Verlag GmbH and Co. Weinheim, Federal Republic of Germany; 2006: 21-68.
10. Sjöström E: **Wood chemistry : fundamentals and applications**, 2. ed. edn: Academic Press; 1993.
11. Fengel D, Wegener G: **Wood: chemistry, ultrastructure, reactions**: Walter de Gruyter; 2011.
12. de Jong E, Gosselink RJA: **Chapter 17 - Lignocellulose-Based Chemical Products**. In: *Bioenergy Research: Advances and Applications.* Edited by Gupta VK, Tuohy MG, Kubicek CP, Saddler J, Xu F. Amsterdam: Elsevier; 2014: 277-313.
13. Spiridon I, Popa VI: **Hemicelluloses: major sources, properties and applications**. In: *Monomers, polymers and composites from renewable resources.* Elsevier; 2008: 289-304.
14. Bobleter O: **Hydrothermal degradation of polymers derived from plants**. *Progress in Polymer Science* 1994, **19**(5):797-841.
15. Gellerstedt G, Ek M, Henriksson G: **Wood chemistry and biotechnology**; 2009.
16. Katahira R, Elder TJ, Beckham GT: **Chapter 1 A Brief Introduction to Lignin Structure**. In: *Lignin Valorization: Emerging Approaches.* The Royal Society of Chemistry; 2018: 1-20.

17. **Chapter 2 - Structure and Characteristics of Lignin**. In: *Lignin Chemistry and Applications.* Edited by Huang J, Fu S, Gan L: Elsevier; 2019: 25-50.
18. Suslick KS: **Pulp**. In: *Kirk-Othmer encyclopedia of chemical technology*

vol. 21: J. Wiley & Sons: New York; 1998: 517.

19. Laurichesse S, Avérous L: **Chemical modification of lignins: Towards biobased polymers**. *Progress in Polymer Science* 2014, **39**(7):1266-1290.
20. Aso T, Koda K, Kubo S, Yamada T, Nakajima I, Uraki Y: **Preparation of novel lignin-based cement dispersants from isolated lignins**. *Journal of Wood Chemistry and Technology* 2013, **33**(4):286-298.
21. He W, Gao W, Fatehi P: **Oxidation of Kraft Lignin with Hydrogen Peroxide and its Application as a Dispersant for Kaolin Suspensions**. *ACS Sustainable Chem Eng* 2017, **5**(11):10597-10605.
22. Fache M, Boutevin B, Caillol S: **Vanillin Production from Lignin and Its Use as a Renewable Chemical**. *ACS Sustainable Chem Eng* 2016, **4**(1):35-46.
23. Silva EABd, Zabkova M, Araújo JD, Cateto CA, Barreiro MF, Belgacem MN, Rodrigues AE: **An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin**. *Chem Eng Res Des* 2009, **87**(9):1276-1292.
24. Zhao S, Abu-Omar MM: **Renewable Thermoplastics Based on Lignin-Derived Polyphenols**. *Macromolecules* 2017, **50**(9):3573-3581.
25. Saito T, Brown RH, Hunt MA, Pickel DL, Pickel JM, Messman JM, Baker FS, Keller M, Naskar AK: **Turning renewable resources into value-added polymer: Development of lignin-based thermoplastic**. *Green Chem* 2012, **14**(12):3295-3303.
26. Chheda JN, Huber GW, Dumesic JA: **Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals**. *Angewandte Chemie - International Edition* 2007, **46**(38):7164-7183.
27. Bhat AH, Dasan YK, Khan I: **Extraction of Lignin from Biomass for Biodiesel Production**. In: *Agricultural Biomass Based Potential Materials.* Edited by Hakeem KR, Jawaid M, Y. Alothman O. Cham: Springer International Publishing; 2015: 155-179.
28. Brännvall E: **Overview of pulp and paper processes**. In: *Pulping chemistry and technology.* Edited by Ek M, Gellerstedt G, Henriksson G, vol. 2: Walter de Gruyter; 2009.
29. Bajpai P: **Chapter 2 - Wood and Fiber Fundamentals**. In: *Biermann's Handbook of Pulp and Paper (Third Edition).* Edited by Bajpai P: Elsevier; 2018: 19-74.
30. Gierer J: **Chemical aspects of kraft pulping**. *Wood Sci Technol* 1980, **14**(4):241-266.
31. Bajpai P: **Chapter 12 - Pulping Fundamentals**. In: *Biermann's Handbook of Pulp and Paper (Third Edition).* Edited by Bajpai P: Elsevier; 2018: 295-351.
32. Tomani P: **The lignoboost process**. *Cellulose Chemistry and Technology* 2010, **44**(1-3):53-58.

33. Kosa M, Ben H, Theliander H, Ragauskas AJ: **Pyrolysis oils from CO2 precipitated Kraft lignin**. *Green Chem* 2011, **13**(11):3196-3202.

34. Ragnar M, Henriksson G, Lindström ME, Wimby M, Blechschmidt J, Heinemann S: **Pulp**. In: *Ullmann's Encyclopedia of Industrial Chemistry.* 2004.

35. Bajpai P: **Basic Overview of Pulp and Paper Manufacturing Process**. In: *Green Chemistry and Sustainability in Pulp and Paper Industry.* Edited by Bajpai P. Cham: Springer International Publishing; 2015: 11-39.

36. Young RA: **Comparison of the properties of chemical cellulose pulps**. *Cellulose* 1994, **1**(2):107-130.

37. Schild G, Sixta H: **Sulfur-free dissolving pulps and their application for viscose and lyocell**. *Cellulose* 2011, **18**(4):1113-1128.

38. Johansson A, Aaltonen O, Ylinen P: **Organosolv pulping — methods and pulp properties**. *Biomass* 1987, **13**(1):45-65.

39. Zhao X, Cheng K, Liu D: **Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis**. *Applied Microbiology and Biotechnology* 2009, **82**(5):815-827.

40. Matsakas L, Raghavendran V, Yakimenko O, Persson G, Olsson E, Rova U, Olsson L, Christakopoulos P: **Lignin-first biomass fractionation using a hybrid organosolv – Steam explosion pretreatment technology improves the saccharification and fermentability of spruce biomass**. *Bioresour Technol* 2019, **273**:521-528.

41. Nitsos C, Rova U, Christakopoulos P: **Organosolv fractionation of softwood biomass for biofuel and biorefinery applications**. *Energies* 2018, **11**(1):50.

42. Zhao X, Cheng K, Liu D: **Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis**. *Applied microbiology and biotechnology* 2009, **82**(5):815.

43. Wang K, Yang H, Guo S, Tang Y, Jiang J, Xu F, Sun R-C: **Organosolv fractionation process with various catalysts for improving bioconversion of triploid poplar**. *Process Biochemistry* 2012, **47**(10):1503-1509.

44. Kumar P, Barrett DM, Delwiche MJ, Stroeve P: **Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production**. *Ind Eng Chem Res* 2009, **48**(8):3713-3729.

45. Thoresen PP, Matsakas L, Rova U, Christakopoulos P: **Recent advances in organosolv fractionation: Towards biomass fractionation technology of the future**. *Bioresour Technol* 2020, **306**:123189.

46. Zhang K, Pei Z, Wang D: **Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: A review**. *Bioresour Technol* 2016, **199**:21-33.

47. Ferreira JA, Taherzadeh MJ: **Improving the economy of lignocellulose-based biorefineries with organosolv pretreatment**. *Bioresour Technol* 2020, **299**:122695.

48. Pye EK, Lora JH: **The AlcellTM process: a proven alternative to kraft pulping**. *Tappi journal* 1991, 74(3):113-118.

49. Llovera L, Benjelloun-Mlayah B, Delmas M: **Organic acid lignin-based polyurethane films: synthesis parameter optimization.** *BioResources* 2016, **11**(3):6320-6334.
50. Delmas GH, Benjelloun-Mlayah B, Bigot YL, Delmas M: **Functionality of wheat straw lignin extracted in organic acid media.** *Journal of Applied Polymer Science* 2011, **121**(1):491-501.
51. Matsakas L, Nitsos C, Raghavendran V, Yakimenko O, Persson G, Olsson E, Rova U, Olsson L, Christakopoulos P: **A novel hybrid organosolv: Steam explosion method for the efficient fractionation and pretreatment of birch biomass.** *Biotechnol Biofuels* 2018, **11**(1).
52. Zhang Z, Song J, Han B: **Catalytic Transformation of Lignocellulose into Chemicals and Fuel Products in Ionic Liquids.** *Chemical Reviews* 2017, **117**(10):6834-6880.
53. **Introduction: Ionic Liquids.** *Chemical Reviews* 2017, **117**(10):6633-6635.
54. da Costa Lopes AM, João KG, Morais ARC, Bogel-Łukasik E, Bogel-Łukasik R: **Ionic liquids as a tool for lignocellulosic biomass fractionation.** *Sustainable Chemical Processes* 2013, **1**(1):3.
55. Stark A: **Ionic liquids in the biorefinery: a critical assessment of their potential.** *Energy & Environmental Science* 2011, **4**(1):19-32.
56. Yan P, Xu Z, Zhang C, Liu X, Xu W, Zhang ZC: **Fractionation of lignin from eucalyptus bark using amine-sulfonate functionalized ionic liquids.** *Green Chem* 2015, **17**(11):4913-4920.
57. Rashid T, Kait CF, Regupathi I, Murugesan T: **Dissolution of kraft lignin using Protic Ionic Liquids and characterization.** *Ind Crops Prod* 2016, **84**:284-293.
58. Mai NL, Ahn K, Koo Y-M: **Methods for recovery of ionic liquids—A review.** *Process Biochemistry* 2014, **49**(5):872-881.
59. Abbott AP, Capper G, Davies DL, Rasheed RK, Tambyrajah V: **Novel solvent properties of choline chloride/urea mixtures.** *Chemical Communications* 2003(1):70-71.
60. Poole CF: **Chapter 2 - Solvent Selection for Liquid-Phase Extraction.** In: *Liquid-Phase Extraction.* Edited by Poole CF: Elsevier; 2020: 45-89.
61. Smith EL, Abbott AP, Ryder KS: **Deep eutectic solvents (DESs) and their applications.** *Chemical reviews* 2014, **114**(21):11060-11082.
62. Van Osch DJGP, Kollau LJBM, Van Den Bruinhorst A, Asikainen S, Rocha MAA, Kroon MC: **Ionic liquids and deep eutectic solvents for lignocellulosic biomass fractionation.** *Physical Chemistry Chemical Physics* 2017, **19**(4):2636-2665.
63. Francisco M, van den Bruinhorst A, Kroon MC: **New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing.** *Green Chem* 2012, **14**(8):2153-2157.

64. Tan YT, Chua ASM, Ngoh GC: **Deep eutectic solvent for lignocellulosic biomass fractionation and the subsequent conversion to bio-based products – A review.** *Bioresour Technol* 2020, **297**.
65. Liu Y, Chen W, Xia Q, Guo B, Wang Q, Liu S, Liu Y, Li J, Yu H: **Efficient Cleavage of Lignin–Carbohydrate Complexes and Ultrafast Extraction of Lignin Oligomers from Wood Biomass by Microwave-Assisted Treatment with Deep Eutectic Solvent.** *ChemSusChem* 2017, **10**(8):1692-1700.
66. Malaeke H, Housaindokht MR, Monhemi H, Izadyar M: **Deep eutectic solvent as an efficient molecular liquid for lignin solubilization and wood delignification.** *Journal of Molecular Liquids* 2018, **263**:193-199.
67. Smink D, Kersten SRA, Schuur B: **Recovery of lignin from deep eutectic solvents by liquid-liquid extraction.** *Separation and Purification Technology* 2020, **235**:116127.
68. Hodgdon TK, Kaler EW: **Hydrotropic solutions.** *Current Opinion in Colloid and Interface Science* 2007, **12**(3):121-128.
69. Balasubramanian D, Friberg SE: **Hydrotropes–recent developments.** *Surface and Colloid Science* 1993, **15**:197-220.
70. Agarwal M, Gaikar VG: **Extractive separations using hydrotropes.** *Sep Technol* 1992, **2**(2):79-84.
71. Dhapte V, Mehta P: **Advances in hydrotropic solutions: an updated review.** *St Petersburg Polytechnical University Journal: Physics and Mathematics* 2015, **1**(4):424-435.
72. Kumar S, Parveen N, Kabir ud D: **Additive-induced association in unconventional systems: A case of the hydrotrope.** *Journal of Surfactants and Detergents* 2005, **8**(1):109-114.
73. Hopkins Hatzopoulos M, Eastoe J, Dowding PJ, Rogers SE, Heenan R, Dyer R: **Are Hydrotropes Distinct from Surfactants?** *Langmuir* 2011, **27**(20):12346-12353.
74. Balasubramanian D, Srinivas V, Gaikar V, Sharma M: **Aggregation behavior of hydrotropic compounds in aqueous solution.** *The Journal of Physical Chemistry* 1989, **93**(9):3865-3870.
75. Kumar S, Parveen N: **Additive-induced association in unconventional systems: A case of the hydrotrope.** *Journal of surfactants and detergents* 2005, **8**(1):109-114.
76. Subbarao CV, Chakravarthy IPK, Sai Bharadwaj AVSL, Prasad KMM: **Functions of Hydrotropes in Solutions.** *Chemical Engineering & Technology* 2012, **35**(2):225-237.
77. Srinivas V, Rodley G, Ravikumar K, Robinson WT, Turnbull MM: **Molecular organization in hydrotrope assemblies.** *Langmuir* 1997, **13**(12):3235-3239.
78. McKee RH: **Use of hydrotropic solutions in industry.** *Ind Eng Chem* 1946, **38**(4):382-384.

79. Abranches DO, Benfica J, Soares BP, Leal-Duaso A, Sintra TE, Pires E, Pinho SP, Shimizu S, Coutinho JAP: **Unveiling the mechanism of hydrotropy: evidence for water-mediated aggregation of hydrotropes around the solute.** *Chemical Communications* 2020, **56**(52):7143-7146.
80. Kunz W, Holmberg K, Zemb T: **Hydrotropes.** *Current Opinion in Colloid & Interface Science* 2016, **22**:99-107.
81. Burns RL: **Hydrotropic properties of some short-chain alkylbenzene- and alkylnaphthalene sulfonates.** *Journal of Surfactants and Detergents* 1999, **2**(1):13-16.
82. Coffman RE, Kildsig DO: **Effect of nicotinamide and urea on the solubility of riboflavin in various solvents.** *Journal of Pharmaceutical Sciences* 1996, **85**(9):951-954.
83. Beig A, Lindley D, Miller JM, Agbaria R, Dahan A: **Hydrotropic solubilization of lipophilic drugs for oral delivery: The effects of urea and nicotinamide on carbamazepine solubility-permeability interplay.** *Frontiers in Pharmacology* 2016, 7(OCT).
84. Kim JY, Kim S, Papp M, Park K, Pinal R: **Hydrotropic Solubilization of Poorly Water-Soluble Drugs.** *Journal of Pharmaceutical Sciences* 2010, **99**(9):3953-3965.
85. Ansari KB, Gaikar VG: **Green hydrotropic extraction technology for delignification of sugarcane bagasse by using alkybenzene sulfonates as hydrotropes.** *Chem Eng Sci* 2014, **115**:157-166.
86. Korpinen R, Fardim P: **Lignin extraction from wood biomass by a hydrotropic solution.** *O Papel* 2009, **70**(5):69-82.
87. Gabov K, Fardim P, da Silva Júnior FG: **Hydrotropic fractionation of birch wood into cellulose and lignin: A new step towards green biorefinery.** *BioResources* 2013, **8**(3):3518 - 3531.
88. Karthyani S, Pandey A, Devendra LP: **Delignification of cotton stalks using sodium cumene sulfonate for bioethanol production.** *Biofuels* 2017:1-10.
89. Gabov K, Hemming J, Fardim P: **Sugarcane bagasse valorization by fractionation using a water-based hydrotropic process.** *Ind Crops Prod* 2017, **108**(Supplement C):495-504.
90. McKee RH: **Recovery of cellulose and lignin from wood.** In.: Google Patents; 1943.
91. Vivian MA, da Silva Júnior FG, Fardim P, Segura TES: **Evaluation of yield and lignin extraction from *Eucalyptus grandis* × *Eucalyptus urophylla* wood chips with the hydrotropic compound sodium xylenesulphonate (SXS).** *BioResources* 2017, **12**(3):6723-6735.
92. Nelson PJ: **Hydrotropic pulping of *Eucalyptus regnans* wood.** *Appita* 1978, **31**(6):437 - 442.

93. Denisova MN, Budaeva VV, Pavlov IN: **Pulps isolated from Miscanthus, oat hulls, and intermediate flax straw with sodium benzoate.** *Korean Journal of Chemical Engineering* 2015, **32**(2):202-205.
94. Bian H, Chen L, Gleisner R, Dai H, Zhu JY: **Producing wood-based nanomaterials by rapid fractionation of wood at 80 °c using a recyclable acid hydrotrope.** *Green Chem* 2017, **19**(14):3370-3379.
95. Vivian MA, Siva J: **Effect of eucalyptus wood chips pretreatment with sodium xylenesulphonate (SXS) in the kraft cellulosic pulp quality.** *Scientia Forestalis* 2018(118):261-269.
96. Gabov K, Gosselink RJ, Smeds AI, Fardim P: **Characterization of lignin extracted from birch wood by a modified hydrotropic process.** *J Agric Food Chem* 2014, **62**(44):10759-10767.
97. Ramos LP: **The chemistry involved in the steam treatment of lignocellulosic materials.** *Química Nova* 2003, **26**(6):863-871.
98. Galbe M, Zacchi G: **Pretreatment: The key to efficient utilization of lignocellulosic materials.** *Biomass Bioenergy* 2012, **46**:70-78.
99. Kumar L, Chandra R, Saddler J: **Influence of steam pretreatment severity on post-treatments used to enhance the enzymatic hydrolysis of pretreated softwoods at low enzyme loadings.** *Biotechnol Bioeng* 2011, **108**(10):2300-2311.
100. Donaldson L, Wong K, Mackie K: **Ultrastructure of steam-exploded wood.** *Wood Sci Technol* 1988, **22**(2):103-114.
101. Li J, Henriksson G, Gellerstedt G: **Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion.** *Bioresour Technol* 2007, **98**(16):3061-3068.
102. Auxenfans T, Crônier D, Chabbert B, Paës G: **Understanding the structural and chemical changes of plant biomass following steam explosion pretreatment.** *Biotechnol Biofuels* 2017, **10**(1):36.
103. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker D: **Determination of structural carbohydrates and lignin in biomass.** In. Golden, CO: National Renewable Energy Laboratory; 2012.
104. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D: **Determination of sugars, byproducts, and degradation products in liquid fraction process samples.** In: *Laboratory analytical procedure.* Golden, CO: National Renewable Energy Laboratory; 2008.
105. Olsson J, Novy V, Nielsen F, Wallberg O, Galbe M: **Sequential fractionation of the lignocellulosic components in hardwood based on steam explosion and hydrotropic extraction.** *Biotechnol Biofuels* 2019, **12**(1).
106. Gésan-Guiziou G: **Dairy industry and animal products processing applications.** In: *Engineering Aspects of Membrane Separation and Application in Food Processing.* 2017: 93-148.

107. Ekbåge D, Nilsson L: **Potential energy improvements in a multiple-effect evaporation system: Case studies of heat recovery.** *Nord Pulp Pap Res J* 2016, **31**(4):583-591.

108. Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch M: **Features of promising technologies for pretreatment of lignocellulosic biomass.** *Bioresour Technol* 2005, **96**(6):673-686.

109. Trajano HL, Engle NL, Foston M, Ragauskas AJ, Tschaplinski TJ, Wyman CE: **The fate of lignin during hydrothermal pretreatment.** *Biotechnol Biofuels* 2013, **6**(1):110.

110. Li J, Gellerstedt G, Toven K: **Steam explosion lignins; their extraction, structure and potential as feedstock for biodiesel and chemicals.** *Bioresour Technol* 2009, **100**(9):2556-2561.

111. Hu F, Jung S, Ragauskas A: **Pseudo-lignin formation and its impact on enzymatic hydrolysis.** *Bioresour Technol* 2012, **117**:7-12.

112. Shinde SD, Meng X, Kumar R, Ragauskas AJ: **Recent advances in understanding the pseudo-lignin formation in a lignocellulosic biorefinery.** *Green Chem* 2018, **20**(10):2192-2205.

113. Kumar R, Hu F, Sannigrahi P, Jung S, Ragauskas AJ, Wyman CE: **Carbohydrate derived-pseudo-lignin can retard cellulose biological conversion.** *Biotechnol Bioeng* 2013, **110**(3):737-753.

114. Jasiukaitytė-Grojzdek E, Huš M, Grilc M, Likozar B: **Acid-Catalyzed α-O-4 Aryl-Ether Cleavage Mechanisms in (Aqueous) γ-Valerolactone: Catalytic Depolymerization Reactions of Lignin Model Compound During Organosolv Pretreatment.** *ACS Sustainable Chem Eng* 2020.

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