Organosolv using Wheat Straw

Dissolving Pulp Production and Process Simulation

Master’s thesis in Innovative and Sustainable Chemical Engineering

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Cover: Photograph of wheat straw and dissolving pulp after organosolv and bleaching. To the left, wheat straw. To the right, dissolving pulp.

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Abstract

The society today faces a lot of challenges when it comes to the reformation into a more sustainable way of living. One industry that requires this type of transformation is the textile industry. Textile production processes need to be modified to reduce its environmental impact and new raw materials have to emerge in order to make this shift possible. One alternative is the usage of manmade cellulosic fibers. These are usually produced from dissolving pulp, meaning that the pulp has to fulfill certain criteria such as a high cellulose content. Manmade cellulosic fibers can be produced from different raw materials such as wood but also wheat straw. Wheat straw is an agricultural residue from the wheat grain production.

In addition to the choice of raw material, the process of producing dissolving pulp also has to be evaluated and modified in order to make it more sustainable. Processing of lignocellulosic biomass, such as wheat straw, often results in different types of pollutants. One promising method of producing dissolving pulp with less environmental impact is the organosolv treatment. This treatment uses an organic solvent in the delignification process.

In this thesis, the possibility of producing dissolving pulp for textile production using organosolv treatment of wheat straw is investigated. The organic solvent used was ethanol or acetone together with water and sulfuric acid. Some of the produced pulps were also bleached. The objective was to identify important process parameters in the organosolv treatment of wheat straw. Experimental data of the product was obtained in order to investigate the possibility of producing dissolving pulp using this treatment as well as to study the effect of varying process parameters. A process simulation was also done to investigate the scale-up in terms of chemical consumption and water usage. The simulation also included a recovery of the organic solvent, water and acid from the spent liquor.

The results from the thesis showed the possibility of producing dissolving pulp using an organosolv treatment of wheat straw. The process simulation showed that a recovery of the spent liquor is feasible. However, since no techno-economical assessment is conducted, it is difficult to draw other conclusions about the scale-up.

Keywords: textile, dissolving pulp, scale-up, cellulose fibres, organosolv, wheat straw, agricultural residue.

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1

Introduction

In 2021, the global fiber production reached a level of 113 million tonnes [1]. This means almost a doubling compared to 58 million tonnes year 2000. Polyester constitutes 54% of the market share, were only 14.8% is made of recycled fibers. Cotton is the second most produced fiber, constituting 24% of the market [1]. Even though cotton fibers are made of a renewable material, the production still results in environmental issues. Cotton cultivation consumes 10% of the worldwide usage of pesticides and 25% of insecticides [2]. The pesticides and insecticides can pollute freshwater sources. Cotton is also a crop that depletes the soil resources and requires a lot of agricultural land, which can damage the biodiversity in the areas where it is grown. Alongside this, cotton cultivation consumes large amounts of water. In order to produce 1 kg lint, 644 L of irrigation water is required [2]. If the textile industry continues like this, it will not stay within the 1.5°-pathway stated in the Paris Agreement. Therefore, it is necessary to reform the textile industry and find new alternatives [1].

One alternative to synthetic fibers and cotton fibers is manmade cellulosic fibers, so called MMCFs. These have more than doubled since 1990 and now constitutes 6% of the market share. Two examples of MMCFs are viscose and lyocell, where viscose has a market share of 80% of all MMCFs. These fibers are currently mostly produced from wood, and less than 1% is made from other feedstocks [1]. One alternative to wood could be lignocellulosic residues, such as wheat straw. Wheat straw are one of the major by-products from agriculture. Today, it is not used as an industrial raw material except for a minor part as animal feed, household fuel or raw material for the paper industry [3]. Some are also used to enrich the soil, but it is estimated that 30-60% can be exported from farms without creating problems with the soil quality. In EU only, 144 million tonnes of wheat straw is accumulated per year [4]. Alongside this, wheat straw and wood are similar in chemical composition suggesting it could be a good substitute [3].

MMCFs are usually produced from dissolving pulp. This pulp has a high cellulose content and will be further described in section 2.6. 65% of the dissolving pulp is produced from the acid sulfite process and 25% from the prehydrolysis kraft process. Organosolv is another treatment that has been emerging for the past decades since it offers several advantages. It is more environmentally friendly and the viscose produced from organosolv has an improved strength compared to viscose from sulfite pulping. Organosolv can also be applied to small plants and different lignocellulosic biomass [5].

1.1 Scope

The goal of this project was to investigate if it is possible to produce dissolving pulp with wheat straw as a raw material, using an organosolv treatment. This was done by testing different parameters and then analyzing to see if the cellulose content was high enough. The intrinsic viscosity of pulp in cupriethylenediamine, CED, was also investigated to determine if the pulp is suitable as dissolving pulp. Alongside this, a process simulation was conducted in order to investigate opportunities for a large-scale production.

1.2 Limitations

Due to a limited time span for the project, some limitations had to be made. Wheat straw was the only lignocellulosic biomass used in this project. Also, ethanol and acetone were the only organic solvents used and sulfuric acid was the only catalyst investigated. Another limitation is that the thesis only considers dissolving pulp and its properties and do not investigate the production of fibers.

2

Theory

In this chapter, theory about wheat straw and its biomass components will be stated. Dissolving pulp and its criteria will also be explained. Alongside this, theory about organosolv treatment as well as bleaching, washing and chemical recovery will be described. Upscaling of a lab pulping process will also be explained in order to understand the difference between experimental trials and process simulation. A description of previous studies will be included in order to connect this thesis to previous research within the area. Lastly, a description of ethical and social aspects regarding the usage of wheat straw will be stated.

2.1 Lignocellulosic biomass

Lignocellulosic biomass can be classified either as non-wood or wood. In general, wood lignocellulosic involves hardwood and softwood. Meanwhile, non-wood lignocellulosic consists of biomass derived from other plant-based sources such as agricultural residues and other plant fibers, for example cotton and sugarcane [6]. The lignocellulosic biomass has a global production of 181.5 billion tonnes per year, thus making it the most abundant biomass on Earth. Out of this, around 4.6 billion tonnes are originated from agricultural waste [7]. The major components from lignocellulosic biomasses are cellulose, hemicelluloses and lignin. In recent years, lignocellulosic biomass has gained interest as a renewable resource for bio-materials since it has a wide availability and can be cost-effective when it comes to processing [8].

2.1.1 Wheat straw

Wheat straw, also called cereal straw, is the stem of the wheat crop and is a byproduct from grain production after the husks of the plant has been removed. The straw consists of around half of the dry weight of the crop. In general, for every ton grain produced, around 1.5 tons of straw are generated as a by-product [9]. The straw consists of a stalk and leaves. The stalk has two important functions, namely as a mechanical support for the plant as well as to transport nutrients and water. The stalk is a hollow cylinder partially interrupted by transverse septa called nodes, where the areas between the nodes are called internodes [10].

Wheat straw consist of cellulose, hemicelluloses and lignin as well as waxes, ash and other water-soluble compounds such as salts and sugars. However, the composition is strongly affected by factors such as weather condition, soil quality, stage of maturity and the type of fertilizer used. The composition also varies between the different sections of the straw, where the cellulose content tends to be higher in the internodes and lignin content is higher in the nodes. Ash, including silica, is more frequently found in the leaves of the straw [10].

Some of the main drawbacks of using non-wood lignocellulosic is that it is difficult to collect, transport and store [10]. This is due to the fact that wheat straw is a low-density material that has a high transportation cost. In addition to this, storage facilities are required in order to provide a year-round supply [11]. Straw also contains a lot of silica which can potentially cause problems regarding chemical recovery and processing due to, for example, blunting cutting machinery and interfere with chemical processes [10]. One advantage of using wheat straw for organosolv treatment is that wheat straw, in comparison to other non-wood biomass, has a higher conversion of lignin due to its weak inter- and intra-molecular linkages [12].

2.2 Cellulose

Cellulose is the most abundant renewable polymer on earth. It consists of glucose connected with β-1,4-glycosidic bonds. The glucose has three hydroxyl groups that can form hydrogen bonds within and between the cellulose molecules. These bonds make the cellulose insoluble in water and poorly soluble in organic solvents [13]. The repetitive unit can be seen in Figure 2.1. Cellulose has a hierarchical structure, where 18-36 cellulose chains forms one elementary fibril through hydrogen bonds. These elementary fibrils are packed together to form larger microfibrils and then macrofibrils. These, together with hemicelluloses and lignin, form the cell walls [13].

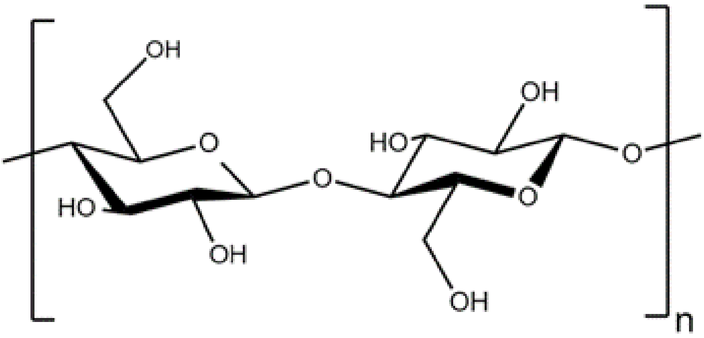

Figure 2.1: Molecular structure of cellulose

The cellulose microfibril consists of crystalline regions and amorphous regions. The crystalline regions are structured and closely packed forming a dense structure, while the amorphous regions are disordered and the cellulose chains are randomly entangled [13]. The cellulose in wheat straw has a rather low crystallinity [14].

2.3 Hemicelluloses

Hemicelluloses are polysaccharides with amorphous structures represented in the cell wall. They are associated with cellulose and lignin by covalent bonds, hydrogen bonds, ionic interactions and hydrophobic interactions. Hemicelluloses are hydrophilic and highly branched resulting in a lower chemical and thermal stability compared to cellulose. This results in hemicelluloses being more soluble and sensitive to hydrolysis [15]. Hydrolysis is the reaction where water is used in order to break the glycosidic bonds and form two alcohols [16]. Therefore, hemicelluloses will to a larger extent than cellulose be removed from the pulp during pulping. The hemicellulose monomers can be further treated to generate valuable products by for example fermentation to ethanol and xylitol [17].

Hemicelluloses are composed of a variety of different monosaccharides such as xylose, arabinose, glucose, galactose, mannose and uronic acids. Uronic acids are a class of different acids such as glucuronic acid and galacturonic acid. The distribution of monosaccharides depends on the plant specie [15]. In wheat straw, arabinoxylan and uronic acids are the main hemicelluloses [18]. Xylan mainly consist of xylose residues bonded by β-1,4-linkages forming a linear polysaccharide [15].

2.4 Lignin

After cellulose, lignin is the second most abundant natural macromolecule. In the cell wall, lignin adds strength and stability by fixating hemicelluloses and cellulose. The lignin molecule is a polyphenolic polyether that has a complex macromolecular structure. The amount of lignin, as well as the chemical composition, varies between different types of lignocellulosic biomass. In wheat straw the lignin monomers structures are p-hydroxyphenyl, guaiacyl and syringyl units. These structures are then randomly linked into a large macromolecule called lignin [19].

2.5 Ash

Ash consists of inorganic elements such as minerals [20]. Of the total mineral content in wheat straw, around 65-70% consists of silicon dioxide (SiO_2). In the plant, silica is important for the insect and fungi resistance. In the pulping process however, silica tends to cause problems and are considered an impurity [9]. The major problem is in the chemical recovery section, where silica tend to cause scaling. In dissolving pulp processing, silica also affect the conversion into high-value products. It has also been shown that silica can cause complications in the processing of water streams, such as scaling of the pipes and membrane fouling [21]. The ash content also consists of other minerals such as sodium (Na) and phosphorus (P) as well as minor contents of iron (Fe) and zinc (Zn) [9].

2.6 Dissolving Pulp

Dissolving pulps are a starting material for producing cellulose derivatives and textile fibers [22]. There are different processes for producing textiles from dissolving pulp, such as the viscose and lyocell process [23]. The dissolving pulp requires a cellulose content of more than 90% and a hemicellulose content of less than 6% [17, 22]. Compared to paper-grade pulp, the cellulose content is higher for dissolving pulp [17]. The dissolving pulp should also only contain trace amounts of lignin and other impurities [17].

The intrinsic viscosity is another important property of dissolving pulp. It is a measurement of the size of the polymer in the solution and hence proportional to the molecular weight [24]. If it is too low, it can cause a gel-like swelling and make filtration difficult. A low intrinsic viscosity also indicates a low physical strength of the pulp. However, if it is too high it can cause inhomogeneity. Usually it is desired to be between 400-600 mL/g and then reduced to 200-250 mL/g during the textile making process [17].

Another requirement is that the cellulose reactivity is high [17]. This means that the cellulose has a high capacity to partake in diverse chemical reactions [25]. If it is too low, it can cause problems during the textile making process such as plugging spinning nozzles or decrease the product yield. This is negative from both an economic and environmental perspective as well as for the product quality. A high accessibility and reactivity can be achieved if the dissolving pulp has a high porosity, large pore size and high surface area. The reactivity can depend on the raw material, but it can be improved by mechanical, chemical or enzymatic treatment [17].

A uniform molecular weight distribution of the dissolving pulp is also desirable. This is the case since it ensures homogeneous reactions during the textile making process [17]. Another property of interest is the ISO brightness. This is required to be between 89-93% for viscose fibers [26].

2.7 Pulping processes

Generally, all pulping processes consists of cooking, washing and bleaching. The cooking can take place in many different ways using different equipment, chemicals and cooking parameters. Following this, pulp washing is done to purify the pulp. The spent liquor from this is sent to chemical recovery to recover cooking chemicals and energy. After the washing, a bleaching step takes place [26].

As mentioned in section 1, the acid sulfite (AS) method and the prehydrolysis kraft (PHK) process are the most common ways of producing dissolving pulp. The objectives in these processes are to eliminate lignin and extractives without extensively degrading the carbohydrates. The PHK process produces stronger pulps and allows for an efficient chemical recovery which minimize release of pollutants. It is also more flexible in terms of raw material and require a shorter cooking time. On the other hand, the selectivity is higher for the AS method [26]. This means that lignin is more selectively removed without an as severe cellulose degradation [27]. Alongside this, the pulp is easier to bleach when using the AS method [26].

An alternative to the PHK and AS processes is the organosolv treatment, which will be described in section 2.8. This process has gained much interest due to environmental and economic concerns regarding the PHK and AS processes. The organosolv treatment generates by-products of greater quantity and quality. It also generates fewer pollutants and requires less water [26].

2.8 Organosolv treatment

The organosolv treatment has been known for over 100 years and consists of organic solvent and water, which are used in the fractionation of lignocellulosic biomass at elevated temperatures [28]. During organosolv treatment, several reactions occur. One desired reaction is delignification, meaning that the internal bonds in lignin as well as the lignin-hemicellulose bonds are cleaved to form lignin fragments. Another reaction occurring is the hydrolysis of hemicelluloses where hemicelluloses are dissolved as sugars and then degraded to furfural [29]. There are also undesired reactions occurring during the organosolv treatment such as lignin condensation, meaning that lignin fragments form intermolecular bonds with the lignin residue which prevents the depolymerization of lignin [30]. Another undesired reaction is the degradation of cellulose. The degradation reactions are strongly correlated to how severe the organosolv treatment is, where a more severe treatment results in a more significant degradation [31].

The organosolv treatment can be used with or without a catalyst, where the catalyst often consists of an acid. Another catalyst could be different metal complexes. In organosolv, one or several organic solvents are also used. One of the most common organic solvents in the treatment are alcohols, both high boiling point ones such as glycerol and ethylene glycol as well as low boiling point alcohols such as ethanol and methanol. It is also possible to use other organic solvents, such as acetic acid and formic acid that can be operated at atmospheric pressure, as well as acetone and dimethylformamide (DMF). Studies regarding different types of organic solvents in organosolv treatment can be found in Appendix A [28].

Organosolv has several advantages, mainly since cellulose is kept rather intact during the treatment and thus yield high-purity cellulose. It has also been shown that, in comparison to traditional pulping methods, hemicelluloses are more effectively fractionated. In addition to this, there is also a possibility to recover the organic solvent using a chemical recovery system and recycle the streams into the process again [28]. This is further described in section 2.10. Organic solvents with low boiling points are easier to recover compared to organic solvents with high boiling point. However, the high boiling point organic solvents are less volatile and flammable wherefore the pressure required for the treatment is lower and the investment for the process equipment is lower as well [32]. Previous studies have also shown that different organosolv treatments have different effects on the lignocellulosic biomass and its macromolecular structure [33].

2.8.1 Washing

Washing of the pulp is performed after the cooking step. This is important to remove chemicals and impurities adsorbed on the fibers. Ideally, this step would lead to a complete washing of fibers but this is not practically possible. Due to this all chemicals and impurities might not be removed during washing [34]. The pulp forms clumps of fibers, referred to as flocs, due to particle-particle interactions. These flocs constrain the free motion of undesirable matter. However, using a disintegrator, these flocs are separated leading to a more freely movement [35]. Therefore, even though the waste water appear as clean before the disintegrator, more chemicals can be released during the disintegration. Hence, it is important with a washing step after the disintegration as well.

2.9 Bleaching

After the organosolv treatment and washing are done, the pulp can be bleached to increase its brightness, increase the cellulose content and remove lignin and hemicelluloses. This can improve the quality of the pulp and thereby make it more suitable for textile fiber production. The bleaching step will also affect the cellulose chain length [36]. Too harsh bleaching treatments creates a risk of cellulose degradation, which makes the bleaching step a trade-off between cellulose content and pulp strength [37].

There are a number of different ways to bleach the pulp and these can be divided into elemental chlorine (EC), elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching. TCF means that all chlorine-based compounds are replaced with oxygen-based compounds. TCF does not contribute to formation of halides and therefore has a lower environmental impact. However, the selectivity is lower and it is more expensive compared to EC and ECF bleaching [36]. OQP is a sequence used in TCF bleaching where the first stage (O) is oxygen bleaching, Q is an acidic stage with chelating agents and the last stage (P) is an alkaline stage with hydrogen peroxide [38].

2.9.1 O - Oxygen bleaching

The first bleaching step uses oxygen gas to oxidize and solubilize lignin. It is done under alkaline conditions to make lignin form carboxylates and thereby enhance the reaction with oxygen. It is important to choose appropriate parameters for the oxygen bleaching. An elevated temperature is required, however a too high temperature will cause increased cellulose degradation since more undesirable side reactions will occur. The alkali charge should be relatively high in order to increase the oxidation, however if it is too high it will also accelerate side reactions and thereby decrease the cellulose yield and physical strength. It is also very important with a proper mixing and a high pressure to increase the concentration of oxygen gas in the liquid and thereby achieve a reasonable reaction rate [38].

2.9.2 Q - Acidic stage with chelating agents

Before the hydrogen peroxide stage, it is important to inactivate and remove heavy metals from the pulp. These heavy metals are naturally present in the pulp from the raw material and will cause side reactions leading to chain cleavage causing a decreased pulp strength. They can also cause chromophore formation [39]. These are groups of atoms and electrons that are part of an organic molecule and cause it to be colored [40]. The result of the chromophore formation is that the bleachability and brightness stability of the pulp will be decreased. In order to deactivate these metal ions, chelating agents such as ethylenediaminetetraacetic acid (EDTA) can be added to the pulp [39]. The chelating agents tightly bind to the metal ions and forms stable cages around them. They are efficient in removing metals such as calcium, magnesium and iron [38]. The metal complexes will then be removed from the pulp by washing. A concern about the usage of EDTA though is that the formed complexes with metal ions will be persistent in water and soil and thereby EDTA is considered an environmental pollutant. Research regarding alternative chelating agents are therefore ongoing [39]. The Q stage needs to be slightly acidic since many metal ions form insoluble hydroxides in alkaline conditions and thereby are not available for the formation of complexes with chelating agents [38].

2.9.3 P - Hydrogen peroxide bleaching

The last stage of the OQP bleaching sequence is the usage of hydrogen peroxide under alkaline conditions. Under alkaline conditions, hydrogen peroxide is in equilibrium with the perhydroxyl anion according to reaction 2.1 [38].

$$H_2O_2 + OH^- \leftrightarrow H_2O + HOO^- \tag{2.1}$$

The perhydroxyl anion act as a nucleophile and eliminates the side chains from lignin. High temperature and high hydrogen peroxide concentrations make this step more effective but also result in a decreased intrinsic viscosity [38]. The main reason to do hydrogen peroxide bleaching is not the removal of lignin but to increase the brightness by removing chromphoric groups in lignin. Therefore, this step does not have a significant impact on the yield of the pulp [41].

This stage also contains the addition of magnesium sulfate, since that reduces the rate of peroxide decomposition by deactivating transition metals. However, it can be seen that this only create a marginal improvement if the hydrogen peroxide bleaching is preceded with a chelating step [42].

2.10 Chemical recovery

One of the main advantages of the organosolv treatment is that the usage of organic solvents enables a feasible and practically possible chemical recovery of the spent liquor. The recovery system for the organosolv spent liquor mainly consists of three parts; partial recovery of the spent liquor by flashing, lignin precipitation by water dilution and lastly organic solvent recovery through distillation. After the reactor, the pulp is separated and the spent liquor stream enters the flash. In the flash, some of the organic solvent, acid and water are recovered and some are sent to the following lignin precipitation step. This stream with hemicelluloses, lignin and cooking chemicals are then sent to the lignin precipitation stage where the high molecular lignin are being precipitated using water [43].

It has been proven that different organic solvents in the reactor will generate different lignin structures with regards to functional groups and molecular weight. Thus, the lignin precipitation step is dependent on which organic solvent that is used in the treatment. The outlet stream from the lignin precipitation, containing mostly organic solvent, water and hemicelluloses, are mixed with soda and sent to the distillation. Here, the organic solvent as well as the by-products are recovered. Soda is added before the distillation column to prevent lignin precipitation in the stripping section, where the alcohol concentration becomes low [43]. The soda is added since the lignin macro structure contain weakly acidic groups which in alkaline conditions becomes ionized. Thus, the lignin is soluble in the alkaline solution preventing precipitation [44]. The addition of soda also neutralizes the organic acids, which can then be recovered as organic salts in this stage. The low molecular lignin, sugars, water and other by-products are then removed from the process, while the organic solvent and water is mixed with the stream from the flash and sent back to the reactor together with new organic solvent, acid and water [43].

2.11 Upscaling of a lab pulping process

Upscaling of chemical processes is a crucial area in the field of chemical engineering. When scaling from a small laboratory work to a larger process, there are numerous things to take into considerations. First of all, the equipment used in the laboratory trials will differ from the equipment used in the industrial scale process [45]. For example, the vacuum filtration in the laboratory process will in the industry be replaced with a press. This is a more economically viable option than drying and after the press a dry content of 53-57% can be reached [46]. If the fiber production is located adjacent to the pulp production, a dry content of 40 % would be enough (E-mail Å Östlund 2023-03-21), wherefore a press alone is sufficient to dry the pulp. Another example is the disintegration used in the laboratory process. This will not be used in the real process since the pressure drop during the unloading of the reactor will create shear stress and therefore separate the fibers of the pulp, thus having the same effect as the disintegrator (E-mail M Viikilä 2023-03-30). Another important matter to consider is the heat recovery in the process, that can be integrated in the process using heat exchangers. Also other process related matters has to be taken into account, for example transport of materials using pumps as well as facilities for storing raw materials and products [45].

Comparing laboratory scale and industrial scale, the equipment used in the latter is often more complex and do often differ from the laboratory trials. In the laboratory organosolv treatment, a small autoclave can be used for the cooking of pulp [47, 48, 49], while in reality a large reactor is used [32]. Thus, the fluid dynamics and the transport properties will differ and cause changes in the reaction dynamics [50]. When having chemical reactions in a process, these reactions are scaled in a linear way from small scale to large scale, even if the reactants are in excess. In the smaller scale, the process is often conducted in batches, while on industrial scale the process is often a continuous or semi-continuous process [32]. This will also have an impact on the reaction dynamics with regards to fluid dynamics and transport properties [50].

It is also crucial to investigate the utilities used on the laboratory scale in comparison to the larger scale. Regarding the washing step, the amount of water used in the laboratory trials to wash the pulp may, in comparison to the amount of pulp, be very large. If the same ratio is used on industrial scale, it would lead to an infeasible high amount of washing water [45].

2.12 Previous studies

On the topic of producing dissolving pulp using an organosolv treatment there are multiple studies conducted. Some of the relevant articles are presented in Appendix A. However, compared to this thesis, most of the studies are investigating either different type of raw materials or process equipment. The majority of the studies in the research area are investing wood lignocellulosic, where studies has proved to successfully produce dissolving pulp using various type of organic solvents [31, 47, 51]. Also other agricultural residues than wheat have been studied, such as oat husks [52], rice straw [48, 53, 54], rye straw [51] and corn stalk [55]. Different agricultural residues have different composition and structure [9], which in turn will have different effects on the organosolv treatment and its outcome [56]. Another thing that distinguishes this thesis from other related studies is the main product. For example, one of the primary goals of many studies is to extract lignin-based products [49, 52, 57], which in this thesis are only considered as a waste. There are also several studies that are using organosolv treatment for production of paper-grade products with a lower cellulose content [58], which is less relevant in this project.

2.13 Ethical and Social Aspects

When using agricultural products as a raw material, it is always important to consider the ethical and social aspects. There is a competition for agricultural land today, since the agricultural land is needed to produce many things such as food for humans, feed for animals, fuels and textiles. In 2018, around 13% of all global cropland was used to produce biofuels and textiles [59]. At the same time, one of ten people is undernourished [60]. Therefore, it is important to minimize the share of agricultural land used to produce other products than food. However, considering the situation today, wheat-straw is a by-product with a large share being accumulated each year. The utilization of it does therefore not contribute to a larger agricultural land use. If the wheat straw need would become larger than the wheat grain need it would be necessary to reconsider the ethical and social aspects. Except for land use, other ethical and social aspects are relevant. The usage of wheat straw would create an additional value stream for farmers and also create more jobs in rural areas [4].

3

Methods

This chapter will start with an explanation of the literature review of previous studies, which was the basis in designing the laboratory work. Following this, the raw materials used will be stated. Then there will be a description of the methods used in the laboratory work. An explanation of the design of the process simulation will also be included.

3.1 Literature review of previous studies

To begin with, previously made studies regarding organosolv were investigated. A selection of 34 different setups was made where the cellulose content in the dissolving pulp was relatively high. This can be seen in Appendix A. More focus was put on studies using wheat straw or other agricultural residues. However, some studies using wood were added as well since some of them showed good dissolving pulp properties.

After this first selection, a second selection of nine different studies to further analyze was made. The experiments chosen were number 1, 5, 11, 17, 20, 22, 24, 25 and 30 from Appendix A. The selection was made in order to choose both some ethanol-based treatments, an acetone based treatment and some acid based treatments. Also, a lactone-based treatment was chosen since it was an interesting non-toxic organic solvent that gave good results in terms of cellulose content, intrinsic viscosity and ISO-brightness for dissolving pulp. The other selections were chosen because they resulted in a pulp with distinctively high cellulose content. Also, six of the studies stated that they had a good quality for dissolving pulp or viscose. Following this, studies using metals as catalysts were not included in the second selection. This is the case since metal catalysts have many disadvantages such as high costs and harmful environmental impacts [61].

The laboratory work was then designed according to experiment 5. This choice was made because the laboratory equipment was similar to what was available in the lab, and also ethanol as an organic solvent was already available. Further on in the process, one experiment was also designed according to experiment 17 with acetone as an organic solvent because acetone was also available and it was of interest to compare different organic solvents.

3.2 Raw material

Wheat straw was cut in 2-3 cm pieces before the cooking. Both leaves and stalks were included in the cooking and are referred together to as wheat straw. The cooking chemicals were 99.96% ethanol purchased from VWR Chemicals, distilled water and 99.95% acetone purchased from Sigma-Aldrich. The acid used in the cooking was 95-97% sulfuric acid from Supelco. For the bleaching step 40 g/L sodium hydroxide was used, together with oxygen gas, EDTA, sulfuric acid, 35 % hydrogen peroxide from Merck and magnesium sulfate heptahydrate from Merck.

3.3 Organosolv

A flowchart of the experimental trials including the organosolv treatment, bleaching, washing and drying steps can be seen in figure 3.1.

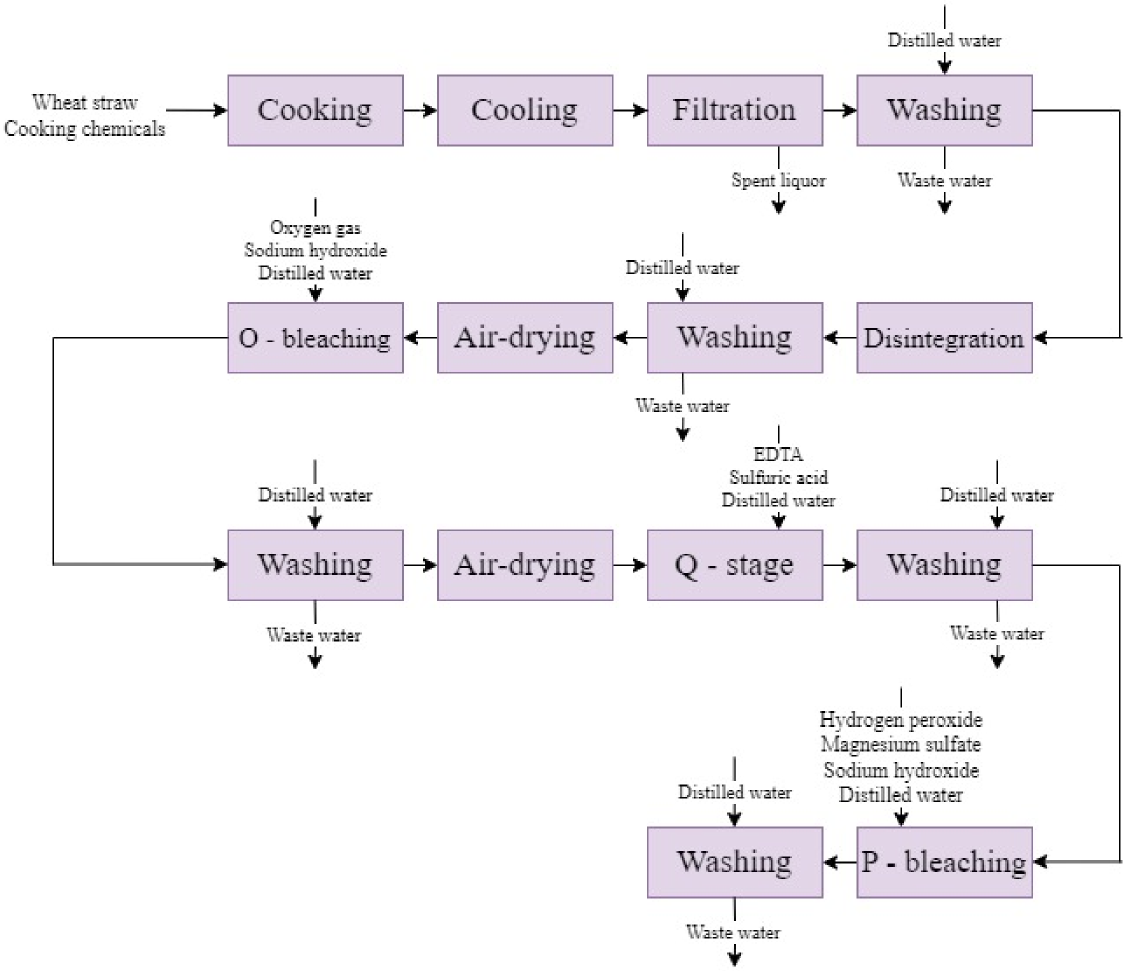

Figure 3.1: Flowchart of experimental trials

22-55 g of wheat straw was mixed with the different cooking chemicals in a 1.5 L steel autoclave. The autoclave was then inserted in a polyethylene glycol bath in an autoclave cooker that rotated with a speed of 15 rpm. The different experimental setups and how the parameters varied for each experiment can be seen in Appendix B.

After the treatment was done, the autoclave was put in a cold water bath for 5 minutes in order to handle it. Then the pulp was vacuum filtered twice using a Büchner funnel. The filter cake was then washed with an excess of distilled water. After the washing, the filter cake was put in a pulp disintegrator together with 1 L of distilled water and ran for 30 000 revolutions. It was then filtered using a Büchner Funnel and a filter paper, where the filter paper was weighed beforehand. After the filtration, the filter cake was washed using an excess of distilled water. After this, the filter cake was air dried in room temperature overnight before it was weighed and put in a plastic bag for storage. If the sample were to be bleached, it was stored in a plastic bag in the fridge.

3.4 Bleaching

The bleaching of the pulp was divided into three different sequences: oxygen bleaching (O) followed by a chelating stage (Q) and lastly a hydrogen peroxide stage (P). The first step was oxygen bleaching, which was conducted in the same autoclave cooker as the organosolv treatment. A portion of the organosolv treated filter cake was inserted into a plastic bag together with distilled water and sodium hydroxide. The amount of sodium hydroxide and water was based on the dry weight of the pulp, the calculations can be seen in Appendix C. The mixture was then blended in the bag until the pulp was thoroughly soaked in water and sodium hydroxide. The soaked pulp was placed into the autoclave, which then was sealed. Following this, the vessel was filled with oxygen gas until the pressure in the autoclave reached 4 bar. The autoclave cooker was then kept at a temperature of 60°C for 2 hours. After the cooking was done, the autoclaves were cooled down to room temperature using a water bath. Similar to section 3.3, the pulp was washed with distilled water in a Büchner Funnel and then disintegrated together with 1 L of distilled water for 30 0000 revolutions. The disintegrated pulp was then washed again, until the waste water reached a pH of 5. The samples were then left to dry in room temperature.

In the second stage, Q, EDTA was used as a chelating agent. On the basis of dry pulp, 0.5 weight% EDTA (5 g/L) was added together with 0.3 weight% sulfuric acid (5 g/L). The solid to liquid ratio in this step was 1:20, and the remaining liquid to reach this ratio consisted of distilled water. The solutions were added to a plastic bag together with the oxygen bleached pulp that had dried overnight. These bags were then kept in a 60°C water bath for 60 min. After the Q-step, the bags were removed and then filtered using a Büchner Funnel. The pulp was washed until the pulp reached a pH of 5 since the pH of the distilled water was 5. This will be further explained in section 4.4.

The last step, P, was conducted in the same bags as previously. To this bag, the Q-bleached pulp was added together with a bleaching solution consisting of hydrogen peroxide, sodium hydroxide, magnesium sulfate and distilled water. 3 weight% of magnesium sulfate was used, together with 3 weight% of hydrogen peroxide. As previously, these amounts were based on the dry weight of the pulp. The solid to liquid ratio was 1:20 in this step as well. Since the liquid ratio was large and the bleaching solution mainly consisted of water, it was assumed that the content had the same density of water. This, together with the dry weight of the pulp, was used to calculate the total volume of the solution. This solution includes the pulp and the mentioned bleaching chemicals. This total volume was used in order to calculate the amount of sodium hydroxide. In the solution, sodium hydroxide was added until the concentration reached 0.01 M. The plastic bags were then inserted once more into the 60°C water bath and kept there for 2 hours.

3.5 Analysis

Different methods were used to determine properties and composition of the pulp as well as content in the spent liquor. The methods for these analyses will be described in this section.

3.5.1 Dry content

A small piece of the filter cake was removed in order to calculate the dry substance content. This was done by weighing the part and then placing it in an oven at 105 °C overnight. Thereafter it was left to cool down in a desiccator. When the piece reached room temperature it was weighed again. The moisture content was calculated by dividing the weight of the oven-dried piece with the weight before it was placed in the oven. The oven-dried piece was stored in a plastic bag afterwards.

3.5.2 Hydrolysis

First of all, a hydrolysis step is performed in order to prepare the samples for Klason lignin analysis, UV/VIS analysis and the High-performance anion exchange chromatography (HPAEC). The filter cake was ground to 1 mm pieces. The ground sample was then dried in an oven at 105°C overnight. Following this, 200 mg of the oven-dried sample was weighed out to a 150 mL beaker. 3 mL 72% sulfuric acid was added and the sample was stirred with a glass rod. The beakers were kept under vacuum for 15 min, and then placed in a water bath for 60 minutes. After one hour the samples were diluted with 84 g of distilled water, covered with aluminum foil and placed in an autoclave. After the autoclave reached 125 °C, the samples were kept there for 60 minutes. After one hour the autoclave was turned off and when the temperature was below 90°C, the first sample was removed from the autoclave. The sample was filtered through 25 mm preweighed glass filters using vacuum filtration. The glass filter was removed and dried in an oven at 105 °C overnight. The filtrate was poured in to a 100 mL volumetric flask and the filter flask was washed with warm distilled water and added to the volumetric flask as well. The sample was left to cool down while the procedure was repeated for every sample. After cool-down the filtrate was diluted to 100 ml and stirred. Thereafter, 5 mL of the hydrolysate was added to a 50 mL volumetric flask using an automatic pipette. Following this, 2 mL of 200 mg/L fucose solution was added to some of the volumetric flasks as an internal standard for the HPAEC. It was then diluted to 50 mL. The 50 mL volumetric flasks were stored in the fridge before analysis.

3.5.3 Klason lignin

There were two different types of analytical lignin analyzed in this report: Klason lignin and acid soluble lignin. Klason lignin is the insoluble residue remaining after the hydrolysis described above [62]. This was filtered out and determined gravimetrically. The filter cake was put in an oven at 105 °C overnight and then weighed. This Klason lignin can also contain other insoluble substances than lignin such as proteins, fat, waxes, other polymers and ash [63].

3.5.4 Acid soluble lignin

The acid soluble lignin (ASL) was dissolved in the filtrate and was quantified using an UV/VIS spectrometer. The analysis was done by measuring the absorbance at a wavelength of 205 nm in a Specord 205, Analytic Jena. The absorptivity constant was assumed to equal 110 $dm^3g^{-1}cm^{-1}$ [64]. The concentration of acid soluble lignin was determined using Lambert-Beer law, see Appendix C.

3.5.5 Carbohydrates

After the hydrolysis, 1.5 mL of the diluted filtrate was filtered into smaller vials using a syringe filter. These vials were then inserted into a HPAEC of type ICS-5000, Dionex DC with a CarboPacTM PA1 column. The eluents used were milli-Q water, milli-Q water and sodium hydroxide as well as milli-Q water, sodium hydroxide and sodium acetate. The HPAEC was used to quantify the content of different sugars, namely arabinose, galactose, xylose, glucose and mannose. These amounts were used to calculate the purity according to Appendix C.

3.5.6 Ash

The ash content was determined using a Nabertherm furnace. The ground sample was oven-dried at 105 °C overnight and then 0.5 g of each sample was put in a crucible and inserted to the oven. The oven was heated from room temperature to 525 °C and then kept there for 3 hours. After this, the oven was cooled to 150 °C after which the samples were removed to cool down to room temperature in a desiccator. After completely cooled down, the samples were weighed and everything left in the crucible was assumed to be ash. Some of the ash will end up in what is referred to as Klason lignin, while some will be acid soluble and not quantified in the HPAEC [65].

3.5.7 Intrinsic viscosity of pulp in CED

The relative viscosity was determined using a capillary viscometer with addition of cupriethylenediamine (CED). The ground sample was oven-dried at 105 °C overnight.

200-250 mg of the dried sample was poured into a 50 mL polyethylene bottle. 25 mL of distilled water was then added together with a small copper cylinder. The bottle was shaken for 2 minutes, thereafter 25 mL of the CED solution was added. Air was pressed out from the bottle. The bottle was then shaken again for 2 minutes, before it was put in a 25 °C water bath for 30 minutes. Once again, the bottle was shaken firmly before the solution was inserted into the viscometer. The time it took for the solution to drain was measured. Using this drain time, the intrinsic viscosity of pulp in CED was calculated using the formulas in Appendix C.

3.6 Process simulation

The process simulation of the organosolv treatment was modelled using Aspen Plus software version 12.1. The simulated process was based on another similar simulation using soda pulping [66], which in this thesis was adjusted in order to simulate the organosolv treatment. The flowchart of the process can be seen in Figure 3.2. Specific settings and stream information can be found in Appendix D.

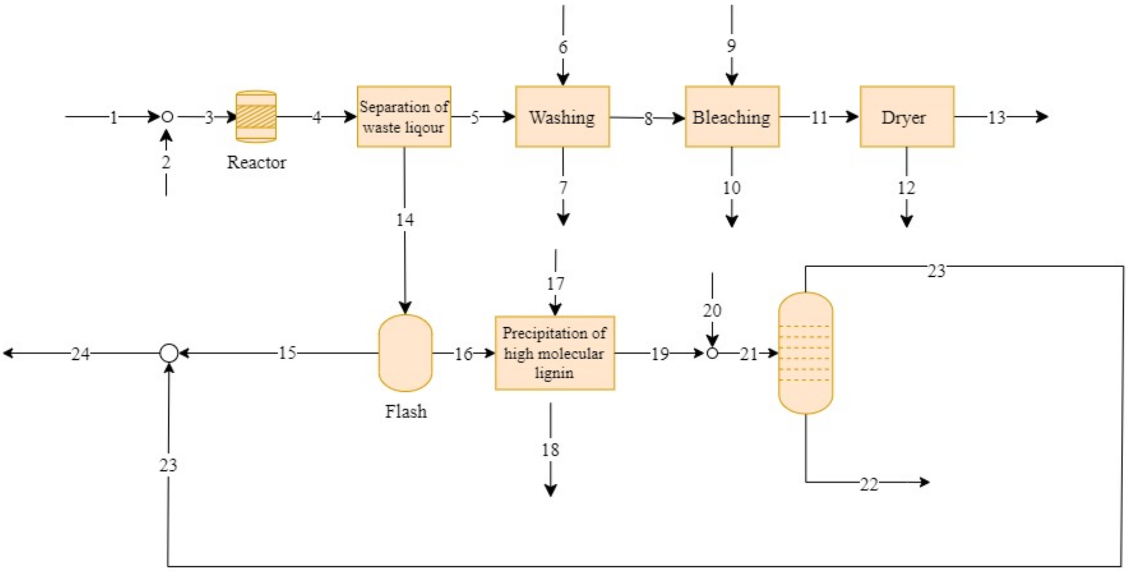

Figure 3.2: Process scheme

The components in wheat straw were glucose, xylose, galactose, arabinose, mannose, water, Klason lignin (simply named lignin in the simulation), acid soluble lignin (ASL), ash and other. According to previous studies, the amount of ash in Klason lignin in wheat straw is around 8.5 %. Thus, 8.5 % of the Klason lignin were subtracted from the simulation after the cook [67]. The remaining amount of ash is excluded from "other". The components called "other" are components that are not quantified in the analysis.

All of the above mentioned carbohydrates were specified using the data bank in Aspen that defined the properties of each of the components. Here, ash was defined as silicon oxide since the majority of ash in wheat straw consists of silica as described in section 2.5. Klason lignin and ASL were defined as vanillin since these components were not available in the data bank. Manually defined specifications are shown in Table D.1. The properties for the biomass components are approximated using solid models. The remaining components, such as the chemicals and water used in the process, are conventional components and can thus partake in a liquid-vapor equilibrium. To investigate the pH of the liquid phase, the feature called "Electrolyte Wizard" was also used in the property set. In this feature, the dissolution mechanism of sulfuric acid in water was simulated. The composition used for wheat straw in the process is presented in Table 4.1.

Property method had to be defined in Aspen in order to compute thermodynamic and transport properties. In this thesis, the electrolyte non-random two-liquid, NRTL, method was used. The NRTL method is an activity coefficient model widely used in phase equilibrium. It provides good data for non-ideal mixtures and partially immiscible systems [68]. In this thesis the electrolyte NTRL method is used since the simulation involves polar substances with salts, acids and bases [69]. In the simulation, the streams will contain both liquid from the cooking chemicals as well as solids from the biomass. Therefore, a predefined stream class called MIXCISLD stream class was selected to handle this issue and include conventional solids without any defined particle size distribution. This stream class includes two different substreams, Mixed and conventional inert, CI, solid. In the Mixed substream, the components partake in vapor liquid phase equilibrium. The conventional components appearing in solid phase, and hence not participating in phase equilibrium, are included in the CI solid substream.

The process parameters used in the simulation were specified according to experiment 16 in B.1. The reason for why experiment 16 was chosen was because it gave the best dissolving pulp properties after bleaching, discussed in section 4.1.4. Alongside this, the chemical recovery section was based on a study using ethanol as organic solvent, explained in section 3.6.3, wherefore it was expected that the chemical recovery section would change if the organic solvent was changed to acetone. The idea behind the simulation is to do a scale up in order to investigate the possibility to conduct a large scale organosolv treatment. Therefore, the input of chemicals and raw materials are larger in comparison to the laboratory experiment. In the simulation, the mass flow of wheat straw was chosen to 15 694 kg/h in order to compare with previous made studies [66]. The process flows and process units in the following sections can be seen in Appendix D.

3.6.1 Cooking

The solid components in the inlet were defined as CI solids, while the water in the wheat straw was defined as Mixed. In the cooking chemical stream, all the components were defined as Mixed. The cooking step was simulated using a Stoichiometric reactor called RStoic, which is based on known fractional conversions of the reactions. The fractional conversions used in this thesis are presented in Table D.4. The data presented in this table are defined using the experimental data from the experiments and calculated according to Equation D.1. In the reaction, the stoichiometry of all reactants was assumed to be 1:1, going from CI solid to Mixed and thus simulating the hydrolysis and dissolution of the biomass components in the treatment. In organosolv treatment, earlier studies has shown that the ash content in ethanol treated wheat straw Klason lignin was around 0.1 % [70]. Thus, 0.1 % of the Klason lignin were subtracted from the simulation after the cook. The remaining amount of ash is excluded from "other" in the same way as described earlier. After the stream exits the reactor, the pulp is separated from the spent liquor. The specifications for this can be seen in Table D.5.

3.6.2 Washing, bleaching and drying

After the separation of the spent liquor from the pulp, the stream entered a cooler. This cooling step is different from the laboratory experiments, where the feed was cooled down to room temperature to make it possible to handle. In the industry, it is assumed that this cooling step is not used since there are no need for cooling. However, in order to conduct a washing of the pulp in Aspen the cooler was needed since the SWash process unit in Aspen does not consider the presence of a vapor phase. In industry however, this cool-down is achieved by heat losses in the process.

After this, the stream was sent to the washing equipment. This procedure was in the laboratory setup conducted in two different stages, once before the disintegration and once after as described in section 3.3. However, as mentioned in section 2.11, in the real pulping process this disintegration step is not used and the washing is in the industry done in one step. In the simulation however, it can be seen that the washing step is conducted in two different equipment: one wash and one separator. This is due to the issue of handling a two-phase system in Aspen, since it is not possible to withdraw solid components in the first washing step. Thus, the first step is simulating the water consumption and liquid separation of the washing and the separator is the step that separates the solid components in the stream. According to previous studies, the ash content in Klason lignin is around 0,02 % [71]. Thus, 0.02 % of the Klason lignin were subtracted from the simulation after the cook. The remaining amount of ash is excluded from "other" in the same way as described earlier.

The mass flow of water into this washing step was controlled using the pH and design spec in Aspen. Thus, the water in the inlet was increased until the pH of the outlet stream reached 6.5. In the washing equipment, the liquid to solid mass ratio was determined from experiments. Here, the filter cake was weighed right after washing and once again after it was dried overnight. The weight of the wet cake was then subtracted by the dry weight to quantify the amount of water in the filter cake right after washing. The ratio of this water and the dry filter cake is defined as the liquid-to-solid mass ratio and can be seen in Table D.8. In the following step, the separator, some of the solids are being separated. The split fractions of these components are based on the experiments and are presented in Table D.10. Water is also separated out and shown in Table D.9.

After the washing, the stream enters the bleaching step. Here, it is mixed with the bleaching chemicals. Due to simplification of the process, the bleaching step is conducted in a single step using a separation in Aspen. Since this is the case, the washing step in the bleaching is also neglected. In reality, a washing step is conducted between each bleaching unit. Thus, all the bleaching chemicals are mixed together, which are sodium hydroxide, EDTA, water, hydrogen peroxide and magnesium sulfate. This is conducted in three steps in the real processes. It was assumed that the amount of ash in the Klason lignin was equal to the amount after washing, as described above. A split was added to the bleaching step as well and the values are given in Table D.11 and D.12. The bleached pulp was then dried using a separator unit in aspen, specified in Table D.13.

3.6.3 Chemical recovery

The aim of the chemical recovery is to recycle the organic solvent, water and acid. The process steps used in this thesis was based on a previous study of a chemical recovery system in an organosolv treatment using ethanol as an organic solvent [43]. After the spent liquor had been separated from the pulp, the spent liquor stream entered a flash column. This flash was used to reduce the pressure and at the same time recover some of the ethanol, acid and water. The rest of the stream, containing biomass components, water, organic solvent and acid was sent to the lignin precipitation step. In this part, as mentioned in section 2.10, the high molecular lignin is precipitated using water. However, to simplify the process, it was assumed that the lignin had a uniform molecular weight and literature values were used to approximate how much is removed in the lignin precipitation. A higher amount of water used in the precipitation step gives a higher yield of lignin. Although, in order to make the downstream distillation more feasible, a dilution ratio of 1:1.68 was proven to be the most optimal option. This dilution ratio gives a precipitation yield of 67% and the split fraction can be seen in Table D.16 [43].

Before the distillation column, soda was added to the system using a mixer. The amount of added soda was 0.13 times the total mass flow of spent liquor from the reactor, since this was proven to be the optimal amount [43]. The distillation column used was a RadFrac distillation column. The specific settings of this column can be seen in Table D.17. After the distillation, the bottom stream was identified as a waste stream. The distillate, containing organic solvent, water and acid, was then mixed with the stream from the flash. To match the inlet temperature of the cooking chemicals, a cooler was used in order to cool down the stream to 25°C. In reality, this cooler might not be necessary since this stream will be heated up together with the make-up cooking chemicals.

4

Results & Discussion

In this section, the results from the laboratory work and process simulation will be presented together with a discussion. Lastly, suggestions for future work will also be presented.

4.1 Composition of pulp & Intrinsic viscosity

During the thesis work there were problems with the HPAEC producing inconsistent results. Table 4.1 shows the content detected using the HPAEC. Experiment 1-8 were done using an external standard while experiment 9-17OQP and wheat straw were determined using an internal standard. Experiments 1-8 were measured in the same run, 9-15 together with wheat straw were measured in a second run and experiment 16-17OQP were measured in the last run. This should be kept in mind when comparing the results, and in this thesis comparisons between runs were avoided to the best possible extent. The *Experiment* number refers to the same number as in Table B.1. The experiment named wheat straw is referring to the analysis of pure wheat straw. 16OQP and 17OQP refers to experiment 16 and 17 bleached with the OQP sequence. *Glu* shows the glucose content in w% and represents the cellulose content. *Ara* is the arabinose content in w%, *Gal* is the galactose content in w%, *Xyl* is the xylose content in w% and *Man* is the mannose content in w%. The values of *Ara, Gal, Xyl* and *Man* together are the hemicellulose content. *Klason* is the amount of Klason lignin in w% and *ASL* is the acid soluble lignin in w%. *Ash* is the amount of ash in w%. *Other* shows what was not detected during the analysis. Ash was not included in the calculation of total amounts according to the explanation in section 3.5.6.

Table 4.1: Biomass content

Experiment	**Glu**	**Ara**	**Gal**	**Xyl**	**Man**	**Klason**	**ASL**	**Ash**	**Other**
Wheat straw	41.73	3.10	1.03	23.17	1.15	19.91	3.38	4.73	6.53
1	57.41	0.09	n/a	1.11	1.04	13.37	0.97	3.18	26.01
2	51.30	0.11	n/a	1.98	1.10	12.05	0.85	2.39	32.61
3	54.27	0.11	0.09	1.30	1.08	14.54	1.08	2.43	27.53
4	48.61	0.09	n/a	1.03	1.00	22.18	1.33	3.03	25.76
5	44.36	0.09	n/a	0.96	0.98	26.72	1.72	3.28	25.17
6	45.49	0.09	n/a	0.98	0.99	30.15	1.16	2.54	21.14
7	53.44	0.10	n/a	1.39	1.12	16.14	1.17	2.56	26.64
8	55.49	0.10	0.09	1.31	1.07	15.93	1.08	2.44	24.93
9	46.56	3.33	1.20	23.19	1.41	18.14	2.56	2.96	3.61
10	60.01	0.67	0.16	21.65	0.99	16.75	1.94	1.46	-2.17
11	90.10	0.15	0.04	4.51	1.00	14.49	1.08	2.53	-11.37
12	51.90	1.89	0.61	24.99	1.19	19.80	2.40	1.61	-2.78
13	99.47	0.08	n/a	1.77	0.92	12.92	0.98	3.30	-16.14
14	92.61	0.11	0.03	6.78	1.10	13.82	1.08	2.05	-15.53
15	64.09	0.50	0.12	19.42	0.95	13.31	1.86	1.29	-0.25
16	92.49	0.10	n/a	8.40	0.90	10.22	0.89	0.82	-13.00
17	85.32	0.21	0.07	16.16	1.04	13.06	1.30	1.94	-17.16
16OQP	121.15	0.04	n/a	4.33	1.04	0.85	0.61	0.28	-28.02
17OQP	126.08	0.08	0.07	6.32	1.20	2.50	0.85	0.18	-37.1

As can be seen in Table 4.1 some experiments had a rather large amount of undetected components while some experiments quantified more than 100%, which can be seen by a negative value for *Other*. The experiments with large amount undetected were done with external standard while the experiments that quantified more than 100 % were run with internal standard. The experiments for which more than 100% was detected were then normalized according to the description in section C.2. The normalized values can be seen in Table 4.2. The values for *Klason*, *ASL* and *ash* were not normalized and therefore not shown in Table 4.2. This was the case since they were not analyzed using the HPAEC.

Table 4.2: Normalized carbohydrate content

Experiment	Glu	Ara	Gal	Xyl	Man
10	58.45	0.65	0.16	21.09	0.97
11	79.41	0.13	0.03	3.98	0.88
12	50.10	1.82	0.59	24.13	1.15
13	83.76	0.07	n/a	1.49	0.78
14	78.32	0.10	0.03	5.73	0.93
15	63.90	0.50	0.12	19.36	0.94
16	80.69	0.09	n/a	7.33	0.78
17	71.08	0.18	0.06	13.46	0.87
16OQP	94.33	0.03	n/a	3.37	0.80
17OQP	91.11	0.06	0.05	4.57	0.87

Another important aspect for dissolving pulp was the intrinsic viscosity. The values of the intrinsic viscosity of pulp in CED for each experiment were calculated according to section C.3 using the cellulose content in Table 4.1. The values are displayed in Table 4.3. The viscosity was measured in mL/g. It was not measured for experiment 9 and 12. This was the case since experiment 9 and 12 still contained pieces of wheat straw that could be difficult to dissolve in the solution used in the viscosity measurement, and hence it would not be possible to determine the viscosity.

Table 4.3: Intrinsic viscosity of pulp in CED [mL/g]

Exp.	1	2	3	4	5	6	7	8	10	11	13	14	15	16	17	16OQP	17OQP
Visc.	165	313	197	117	101	153	274	207	988	213	166	350	830	573	733	516	628

For experiment 1-8, rather large amounts of *Other* can be seen in Table 4.1. Literature shows that there are several compounds from the alcohol organosolv treatment that are not quantified by the analysis methods used in this thesis. This includes degradation products such as furfural, hydroxymethyl tetrahydrofuran and acetic acid [28]. There could also be uronic acids in the sample which, as explained in section 2.3, are one of the main hemicelluloses in wheat straw. Uronic acids are also not detected by the analysis methods used. The reason for why there were large amounts of undetected components could also have been due to the usage of external standard and problems with the HPAEC, as mentioned earlier.

4.1.1 Effect of sulfuric acid concentration

It was discovered during the laboratory work that the sulfuric acid concentration had a large effect on the pulp wherefore this was the parameter that was most extensively varied. Experiment 9 was conducted with no acid added. By comparing the values in Table 4.1 for experiment 9 and wheat straw it can be seen that the cook had little effect on the content. The cellulose content was slightly increased and the Klason lignin and ASL content was slightly decreased. However, the hemicellulose content was the same. Studies have shown that it is possible to efficiently do organosolv treatment without a catalyst, but then cooking temperatures above 185 °C are required in order to release acetyl groups from the hemicellulose hydrolysis and thereby acidify the cooking liquor [28]. It can also be seen in Table 4.1 that some of the ash was removed during the cook without added acid. However, it was difficult to determine if this was due to the cooking or washing step. This will be further discussed in section 4.3.

For experiment 10, 16 and 11, the acid concentration was increased from 0.1% to 0.3% while other parameters were kept the same. In Table 4.2 it can be seen that the glucose content increased from 58% to 81% when the acid content was increased from 0.1% to 0.2%. The same trend can be seen when using the values in Table 4.1. In Table 4.1 it can also be seen that the Klason lignin, ASL and ash content decreased when the acid content was increased from 0.1% to 0.2%. However, when the acid concentration was increased from 0.2% to 0.3%, the opposite was true. When comparing the case of 0.1% and 0.3%, it could be seen that the glucose content was higher for the 0.3% case. Studies have shown that sulfuric acid is an efficient catalyst for delignification in organosolv but that it also results in a large sugar degradation [28]. Therefore, it is necessary to use a sulfuric acid content that is not too low since that gives low fractionation, but at the same time not too high so that the sugar degradation is kept low.

The acid content also had a large effect on the intrinsic viscosity of pulp in CED. This can be seen in Figure 4.1 where an almost linear decrease was seen for viscosity when the acid concentration was increased for ethanol. A decrease can be seen for the acetone experiments as well. The viscosity is proportional to the degree of polymerization [64]. A high degree of polymerization means that there are many repeating units in the cellulose polymers [72]. Hence, the same reasoning as above can be used, a higher sulfuric acid content results in a larger degradation of cellulose.

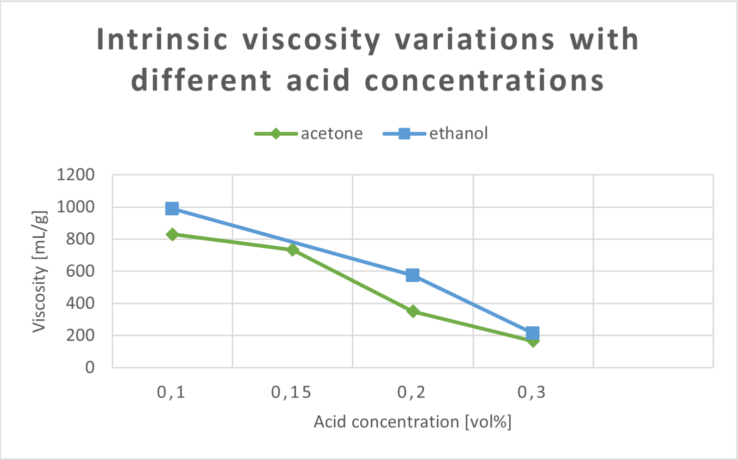

Figure 4.1: Intrinsic viscosity at different acid concentrations using ethanol or acetone as organic solvents

4.1.2 Effect of time & temperature

By comparing experiment 5 and 7 in Table 4.1, it can be seen that the glucose content was higher when the temperature was set to 160 °C compared to 175 °C. The Klason lignin, ASL and ash content were also lower at 160 °C, but the total hemicellulose content was higher. The intrinsic viscosity of pulp in CED, shown in Table 4.3, was higher for the cook at 160 °C.

The effect of the severity can also be seen when comparing experiment 3, 4 and 5 in Table 4.1 that were cooked at 175 °C with increased time from 35 min to 90 min. Here, the apparent glucose content decreased with prolonged cooking time, while the Klason lignin, ASL and ash content increased. The viscosity, shown in Table 4.3, was also decreased, showing a degradation of cellulose. However, when considering experiments 7 and 8 in Table 4.1 where a lower temperature of 160 °C was used, the opposite trends for the content of the pulp can be seen when time was increased from 90 min to 120 min. The viscosity still decreased when time was increased which can be seen in Table 4.3.

Previous studies have shown that the degree of polymerization of cellulose decreases when higher temperature and longer cooking times are applied [73]. Studies have also shown that severe conditions are good for delignification and hemicellulose removal, but at the same time causes significant degradation of the cellulose [31, 73]. This corresponds to the trends seen when comparing experiment 7 and 8. However, it does not correspond to the comparison between experiment 3, 4 and 5 or the comparison between experiment 5 and 7. An explanation for this can be seen by comparing the amount of dried pulp received in the experiments. This is shown in Table 4.4, where it can be seen that the dry weight of the filter cake decreased when the time or temperature was increased. This was probably due to the increased cellulose degradation. When considering Table 4.4 it can be seen that the amount of Klason lignin decreased between experiment 3 and 5 as well as between experiment 7 and 5 even though the share in the pulp increased. Unexpectedly, this was not shown for experiment 4. This can however be due to problems in the laboratory work such as not removing all of the pulp from the autoclave or problems with the filtration.

Table 4.4: Dry weight and Klason lignin amount for the filter cake

Experiment	**3**	**4**	**5**	**7**
Dry weight (g)	7.36	5.64	3.69	4.20
Klason lignin (g)	1.07	1.25	0.98	0.68

A conclusion that could be drawn from this section was that it was important for the treatment to use a temperature and time that were not too severe or too mild in order to get a pure cellulose and a intrinsic viscosity between 400-600 mL/g.

4.1.3 Effect of organic solvent concentration

The effect of organic solvent concentration can be studied by comparing experiment 5 and 6 in Table 4.1. Here, only a minor increase in glucose content could be seen when the organic solvent concentration was decreased from 65% to 50%. The Klason lignin content was higher when the organic solvent concentration was reduced. Similar trends have been seen in previous studies, where an organic solvent concentration increase have enhanced the delignification while not increasing the cellulose degradation [74].

4.1.4 Dissolving pulp

There are different criteria important for dissolving pulp. These are explained in section 2.6. In this thesis, the composition of the pulp as well as the intrinsic viscosity of pulp in CED have been investigated. By considering experiment 16OQP and 17OQP in Table 4.2, it can be seen that both of the bleached pulps had a cellulose content over 90% and a hemicellulose content lower than 6%. This was according to the criteria for dissolving pulp. Regarding the lignin and ash, as explained in section 2.6, it should only be traces of these components. In Table 4.1 it can be seen that the amounts of Klason lignin, ASL and ash were small. It can also be seen that the Klason lignin and ASL amount were smaller for experiment 16OQP than for 17OQP but that the opposite was true regarding the ash content.

The intrinsic viscosity was another criteria mentioned in section 2.6 and it should be between 400-600 mL/g for dissolving pulp. In Table 4.3 it can be seen that the viscosity for experiment 16OQP was within this given interval. However, for experiment 17OQP this value was slightly too high. This probably means that the conditions for experiment 17OQP could have been made a bit harsher by increasing the acid concentration, temperature or time slightly. This would probably then have resulted in a higher glucose content, lower hemicellulose and lignin content as well as an intrinsic viscosity within the given range. It would be important though to choose conditions carefully since too harsh conditions could result in cellulose degradation and thereby a lower cellulose purity.

4.2 Choice of organic solvent

During this thesis, both acetone and ethanol were used as organic solvents. The differences between these organic solvents can be seen by comparing both experiment 10 with 15 and 11 with 13 from both Table 4.1 and Table 4.2. Here, it can be seen that the usage of acetone resulted in a higher cellulose content and a lower lignin content. However, the intrinsic viscosity of pulp in CED was lower when using acetone compared to ethanol. The fact that acetone was more efficient at lignin removal and had a higher cellulose content at 160 °C than ethanol has also been showed by previous studies [75]. The connection between choice of organic solvent and viscosity could however not be found in literature.

Another important thing to consider for the choice of organic solvent were the boiling points, as explained in section 2.8. For acetone the boiling point is 56 °C while for ethanol it is 78 °C [30]. This means that the chemical recovery probably will be easier when using acetone, while the investment for the process equipment probably will be higher.

4.3 Washing

As explained in section 2.8.1, washing of the pulp was important to remove both chemicals and impurities. Table 4.5 shows how the content of the pulp varied before and after the washing step. These values are shown without normalisation for experiment 16 and 17. As can be seen, there was differences in the glucose content before and after washing. This have been confirmed by previous studies [76], and shows that the washing step was important. Notable is also that the ash content in the pulp before washing was approximately the same as in wheat straw, displayed in Table 4.1. However, during washing large amounts of ash were removed. Previous studies have shown that the ash content in Klason lignin after organosolv is significantly smaller compared to the values for kraft and soda pulping when using wheat straw as a raw material [70]. As explained in section 2.5, wheat straw ash mainly contains silica meaning that during the washing step large amounts of silica was washed away and removed from the pulp.

Table 4.5: Biomass content before and after washing

Organic Solvent	**Sample**	**Glu**	**Ara**	**Gal**	**Xyl**	**Man**	**Klason**	**ASL**	**Ash**
Ethanol	Before wash	64.90	1.52	0.45	15.18	0.99	13.65	3.06	4.68
	After wash	92.49	0.10	0	8.40	0.90	10.22	0.89	0.82
Acetone	Before wash	63.52	1.14	0.40	17.56	1.00	13.99	2.60	4.52
	After wash	85.32	0.21	0.07	16.16	1.05	13.06	1.30	1.94

In this thesis, the waste from the wash was removed from the process and not considered for chemical recovery even though it contained cooking chemicals. This was the case since the water content was so large that it was assumed to be unfeasible to recover the chemicals. Alongside this, the content of silica in the wash stream could cause problems during a chemical recovery step as explained in section 2.5.

4.4 Distilled water

During the laboratory work it was discovered that the distilled water was not neutral and had a pH of around 5.5. This can be the case since distilled water has a very small buffering capacity and therefore is extremely sensitive to contamination.

Therefore, distilled water tends to absorb carbon dioxide from the atmosphere which can lower the pH from 7 to 5.8 in a few hours. Alongside this, the addition of up to 30% ethanol to distilled water can increase the solubility of carbon dioxide which further on can decrease the pH of the solution. However, when more ethanol is added, the pH is again increased since ethanol has a higher pH. However, it is also stated that it is difficult to correctly measure the pH of both ethanol and distilled water due to their low electrical conductivity [77]. Acetone also has a neutral pH of 7 [78], wherefore it can be expected that it will, as described for ethanol, neutralize the solution when more acetone is added. It was therefore assumed that the lower pH of the distilled water had no effect on the cooking conditions. Distilled water was also used in the washing phase during the laboratory work, which made the washing water slightly acidic. However, acid hydrolysis only occurs for dilute acids at high temperature and pressure [79], wherefore it was expected that no additional acid hydrolysis occurred in the washing phase.

4.5 Bleaching

As explained in section 2.9, the bleaching step decreased the cellulose chain length and thereby decreased the intrinsic viscosity of pulp in CED. Since the usage of acetone resulted in a lower viscosity compared to ethanol, as shown in section 4.2, the acetone pulp used for bleaching was cooked with a lower amount of sulfuric acid. This was done in order to not get an intrinsic viscosity too low for the dissolving pulp requirements explained in section 2.6.

The recalculated results after the bleaching step can be seen for experiment 16OQP and 17OQP in Table 4.2. Here it can be seen that the glucose content was higher than 90% and that the hemicellulose content was lower than 6% for both experiments. This aligned with the dissolving pulp criteria. In Table 4.3 it is seen that the intrinsic viscosity for experiment 16OQP was within the range of intrinsic viscosity required for dissolving pulp. However, for experiment 17OQP the intrinsic viscosity was a bit too high, showing that the conditions for the pulping could potentially have been a bit harsher. This could for example have been achieved by a slightly increased time, temperature or acid concentration. By comparing experiment 16OQP and 17OQP it can also be seen that the glucose content was higher in the 16OQP pulp and that the lignin content was lower. The difference between the samples can also be seen in Figure 4.2.

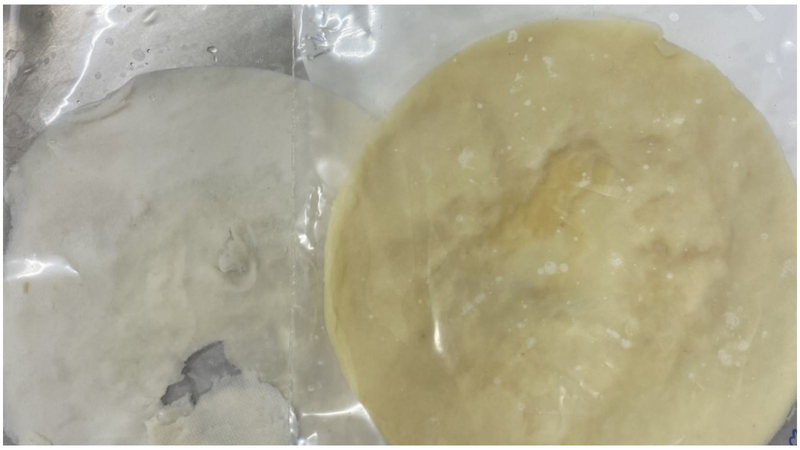

Figure 4.2: Bleached pulp

In Figure 4.2, experiment 16OQP is to the left while experiment 17OQP is to the right. Experiment 17OQP showed a more yellow color meaning that it contained more chromophoric groups from impurities, as explained in section 2.9. This can also be seen by the fact that the cellulose content was higher in experiment 16OQP and thereby the content of lignin, hemicellulose and other impurities were lower. Since both the acid concentration and organic solvent were not the same for experiment 16OQP and 17OQP it was not possible to say if the usage of acetone resulted in a pulp that was less bleachable compared to if ethanol was used.

4.6 Process simulation

In this section, the results from the process simulation are presented. This simulation was based on experiment 16 which, after bleaching, showed satisfactory dissolving pulp qualities. The inlet of wheat straw was 15 694 kg/hr. The streams mentioned in this section refer to Figure 3.2. The total production of dissolving pulp was 0.23 kg dissolving pulp per kg wheat straw.

4.6.1 Chemical consumption

The consumption of cooking and bleaching chemicals as well as washing water are presented in Table 4.6. The difference between *water* and *washing water* is that *water* refers to the water inlet in stream 2, 9 and 17. *Washing water* refers to the water inlet in the washing step, stream 6. In the laboratory experiments, oxygen gas was used in the oxygen bleaching step. However, since the amount of gas used in the experiment was difficult to determine this was neglected in the estimation of consumed chemicals.

Table 4.6: Consumption of chemicals and washing water per kg wheat straw

Component	Consumption [kg/kg wheat straw]
Water	28.51
Ethanol	5.84
Sulfuric acid	0.049
Sodium hydroxide	2.69
EDTA	0.0048
Magnesium sulfate	0.0029
Washing water	36.86
Hydrogen peroxide	0.029

Table 4.6 shows that consumption of ethanol and water were the largest, along with the consumption of sodium hydroxide. The consumption of water was largest in the washing step since the scale up of washing often is incorrect, as described in section 2.11. It is also worth noticing that, as mentioned in 3.6.2, the washing water of the bleaching step was neglected. In the washing unit after cooking however, the amount of washing water was expected to be large since the washing column in the simulation washed until the outlet had a pH of 6.5. In this outlet stream, most of the sulfuric acid was dissociated in the water causing the pH to decrease. It could therefore be the case that the consumption of water was high since some of the water was also used to dilute the washing water stream, causing the pH to raise to 6.5, rather than to wash away impurities in the pulp. Another chemical that could possibly have been reduced was the magnesium sulfate. As explained in section 2.9.3, this chemical might not be needed since the P-bleaching was preceded with a chelating step.

4.6.2 Chemical recovery

Other interesting result from the process simulation was the chemical recovery section. In Table 4.7, the percentages of the recovered chemicals in relation to the inlet of the reactor are presented.

Table 4.7: Recovered chemicals in the recovery section

	Ethanol	Water	Acid	Total
Flash stage	60.00	60.40	3.40	59.90
Distillation	0.00007	7.20	0.00007	2.91
Total	60.0	67.60	3.40	62.80

The data in Table 4.7 shows that most of the cooking chemicals were recovered in the flash. In the case of ethanol, a very small amount was recovered in the distillation column while 60% was recovered in the flash. The same trend can be seen for water, where a smaller amount was recovered in the distillation process. Overall, the recovery of sulfuric acid was limited. In total, most of the cooking chemicals were recovered in the flash while only around 3% was recovered in the distillation. The heat duties from this column can be seen in Table 4.8.

Table 4.8: Heat duties in distillation column

Specification	**Value**	**Unit**
Heat duty condenser	5665	kW
Heat duty reboiler	5904	kW

Here, it can be noticed that the energy consumption was 5904 kW in the reboiler and the heat duty from the condenser was 5665 kW. The main objective regarding the distillation was to recover the remaining ethanol in stream 19, that is after the lignin precipitation. However, as seen in Table 4.7, the main distillate product was water. Since the amount of recovered chemicals from this column were very small, one option in this chemical recovery section could be to remove the distillation column. This would also have resulted in a decrease in the consumption of sodium hydroxide in the process since half of the total amount of sodium hydroxide was added in this step. In this thesis however, the recovery of valuable by-products such as lignin and hemicelluloses were not considered. Since the distillation column, according to section 2.10, also could have recovered substances such as furfural and lignin, the distillation column could theoretically be a good implementation in the chemical recovery if these by-products would have generated a revenue. Although without any techno-economical evaluations, it was difficult to draw any conclusions regarding this matter.

Another aspect that was investigated was the feasibility of implementing the recovered chemicals into the feed stream into the reactor. In Table 4.9, the composition and flow of stream 2 and 24 are presented.

Table 4.9: Composition and flow of inlet of cooking chemicals and recovered cooking chemicals

	Mass fraction			
Stream	**Ethanol**	**Water**	**Acid**	**Flow [kg/h]**
2	0.59	0.40	0.0047	154 902
24	0.57	0.44	0.00	97 280

As seen in Table 4.9, the composition of the two streams were quite similar to each other. According to this, as well in order to adjust the composition of the flow to match the cooking liquor composition, some additional cooking chemicals had to be added. Thus, in order for the recovered stream to be fully implemented into the process, 20 280 kg/h make-up water together with 36 639 kg/h make-up ethanol and 727 kg/h make-up sulfuric acid would have to be added to stream 24.

4.7 Future work

There are things left to investigate in order to determine if this process is suitable for producing dissolving pulp or not. As explained in section 4.1.1, it might be possible to do the organosolv treatment without the addition of sulfuric acid if higher temperatures were to be used. This was not possible to investigate in this thesis due to temperature limitations of the autoclave cooker but would be interesting to investigate in the future. This might also affect the profitability and environmental impact of the process. It would also be interesting to use acetone instead of ethanol in the process simulation and investigate how this would change the process, especially in the chemical recovery section. Another thing worth considering is a potential chemical recovery of the waste water from the washing step. This water contained cooking chemicals but, as explained in section 4.3, it might be unfeasible and difficult to recover those chemicals. This would need more thorough investigation since it affects both the environmental impact and profitability of the process. Regarding the bleaching step, further studies are required in order to be able to split it into three different steps and analyze what was removed in each step. It is also important to study the consumption of washing water in the bleaching step. Alongside this, it should be investigated what the difference is when magnesium sulfate is not used in order to determine if it can be eliminated from the bleaching process or not.

Throughout the process, a heat integration should also be investigated in order to determine how much energy is needed since this also will affect the environmental impact and profitability of the process. To determine how well the process works, the product and by-products from it should be analyzed. There are several things mentioned in section 2.6 regarding the criteria for dissolving pulp that is yet to be analyzed. This includes the cellulose reactivity, molecular weight distribution and ISO brightness. It would also be interesting to investigate if the hemicelluloses and lignin from the process are valuable in order to determine the profitability of the process. Alongside this, a techno-economic assessment of the process should also be done to provide valuable insights regarding if it is an appropriate method of producing dissolving pulp.

5

Conclusion

During this thesis, the production of dissolving pulp from wheat straw using the organosolv treatment has been investigated. This has been done by both laboratory experiments and analysis and by a process simulation for the upscaling. It was found that it was important to carefully choose conditions in terms of acid concentration, time and temperature in order to produce a pulp that both had high cellulose content and an appropriate intrinsic viscosity of pulp in CED. It was also found that both ethanol and acetone could be used as organic solvents in the organosolv treatment for producing dissolving pulp. Another thing discovered during the laboratory work was the importance of a washing step after the organosolv treatment. Here, large amounts of hemicelluloses, Klason lignin, acid soluble lignin and ash are removed. It could also be seen that a bleaching step was necessary to increase the cellulose content and remove other biomass components.

It is difficult to draw major conclusions from the process simulation since no techno-economic assessment was done. However, it can be seen that the recovered cooking chemicals seem to be useful as inlet cooking chemicals due to the rather similar compositions of the streams and the large flow. However, chemicals need to be added to the inlet stream. Further investigation as well as optimization of the process need to be done to determine the profitability and environmental impacts.

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A

Previous experiments

In this Appendix previous experiments are presented. Some of these studies are a basis of the laboratory set-up and are a selection of articles relevant to this thesis. The experiments are divided into five different categories, where different organic solvents are used. The classes are divided according to: ethanol-based treatments in Table A.1 and other alcohols, that is other alcohols than ethanol, in Table A.2. The acid-based treatments can be found in Table A.3 and A.4, where acetic acid and formic acid are used separately or combined. In Table A.5, other types of organic solvents that does not classify as either alcohol or acid can be found.

The tables consist of a number of the experiments. The column *No.* constitutes a numbering of the experiments in order to make it more comprehensive to refer to, the column *Raw material* defines the raw material used in the study. *Solvent* defines which organic solvents and acids that are used. Along with this, the concentration of the organic solvents and acids are presented in column *Solvent conc.* The abbreviation v/v means the volume percentage and w/w means the weight percentage. The temperature is presented in column *Temp (°C)* and time of the cooking step in column *Time (min).* The solid to liquid ratio is defined in column *S/L ratio.* The abbreviation w/v refers to weight solid per volume liquid and w/w refers to weight solid per weight liquid. The equipment used for the cooking step are specified under the column *Equipment* together with potential information about the treatment. In the *Result* column of the tables, the results relevant for this study are presented. This means that some results from the studies may be left out if it is not relevant for this project. In the column *Summary and comments* a brief overview of the article is presented together with some important comments made by the authors. Lastly, the source or sources where information about the study or process is received from is referred to in column *Source.*

Table A.1: Previous experiments based on ethanol as an organic solvent

Ethanol based process											
No.	**Raw material**	**Solvent**	**Solvent conc.**	**Temp. (°C)**	**Time (min)**	**S/L ratio**	**Equipment**	**Additional steps**	**Results**	**Summary and comments**	**Source**
1	Wheat straw	Ethanol	55% ethanol	180	120	1:10 (w/v)	Not mentioned	**Before treatment:** Dried in oven and smashed into powder for use. The powder was hydrolyzed using 1.5 % sulfuric acid at 125C for 2 h with a solid to liquid ratio of 1:8 (g/ml). Then filtered and washed before treatment with ethanol. **Bleaching step:** The obtained pulp was reacted with 1% sodium peroxide and 3% hydrogen peroxide at 70 C for 6 hours with a solid to liquid ratio of 1:20 (g/ml).	83.61% cellulose purity	This is originally a method for producing CMC from the isolated cellulose, but the purity of cellulose before the CMC synthesis is high and thus this method is investigated.	[80]
2	Oat husks	Ethanol, oxalic acid or phosphoric acid	50% ethanol, 0.01428% acid (w/w)	210	90	1:2 (w/v)	150 ml Swagelok reactors (tubular stainless steel) and oil bath under static conditions	After oil bath transferred to container with ice to cool, poured into a sieve (0.25 mm2 pore size) to separate into solid and liquid phases. The solid phase was washed with 28.3 mL of solvent/g of dry sample. The effect on amount of solvent and water used for glucan recovery was investigated. All fractions were kept in refrigerator at 4C until use.	Glucan purity around 65-70% when using phosphoric acid or oxalic acid.	The article is a comparison of using sulfuric acid, phosphoric acid and oxalic acid and how this affects the ethanol organosolv process. The acids were primarily investigated in terms of lignin and glucan quality.	[76]
3	Giant populus — short rotation forestry (hardwood)	Ethanol, carbon dioxide	25% (v/v) ethanol	220	240	1:6.6	Soxhlet extractor, 600 ml autoclave equipped with gas valve, thermowell and cooling coil (cooling flow rate 1 l/min). Collecting cup and extraction cup with a syphon that unloads directly into the collection cup placed inside the autoclave. Also added a heterogeneous catalyst (Pd/C) in the extraction cup. Pressure: 25-30 barg at 220C by adding 8 barg of inert nitrogen gas at room temperature.	Sawdust was used in the experiments. Automatic disintegrator to release fibers from each other. **Bleaching:** elemental chlorine-free bleaching using sodium chlorite and a sodium hydroxide/acetic acid buffer	91% ISO-brightness, 90.58% cellulose purity. 442 mL/g viscosity, DP=610, complies with requirements for lyocell production.	Organosolv method using high pressure extractor and carbon dioxide as an acid source. The carbon dioxide is both mild and recyclable.	[47]

Table A.1 Continued.

4	Oat husks	Ethanol, sulfuric acid	50% (v/v) ethanol, 2M sulfuric acid	210	120	1:20 (w/v)	150 ml Swagelok reactors (tubular stainless steel) placed in a hot oil bath.	pH was adjusted to 3.0 using sulfuric acid. After the cooking, the reactors were cooled in an ice bath. The slurries were poured into sieves (0.25 mm2) to recover glucan rich fraction.	86.5%± 4.8% glucan purity	Milling-free ethanol organosolv using low amount of acids for delignification of oat husks. Focusing on three different streams: glucan-rich, lignin-rich, and hemicellulosic compound-rich streams. Lot of attention on lignin and enzymatic hydrolysis.	[52]
5	Hemp Hurd (byproduct from hemp fiber production, constitutes a large share of the hemp stalk)	Ethanol and water, hydrochloric acid	65% ethanol, 1% hydrochloric acid	175	180	1:13 (w/v)	20 mL stainless steel reactor	**After treatment:** After the reaction, the reactor was cooled down and the pulp was filtrated. The filtrated slurry was then disintegrated and homogenized. **Bleaching:** Bleached using 6.0 g pulp/600 mL of bleaching solution (sodium chloride, sodium hydroxide and acetic acid)	**Before bleaching:** 82% cellulose purity **After bleaching:** 95% cellulose purity. Also high viscosity (898 mL/g) and high ISO-brightness (90.2%) which makes it suitable for viscose production.	The source involves a description of organosolv pulping that was bleached to produced dissolving pulp for nanocellulose and textile fiber applications.	[81]
6	Wheat straw	Ethanol	50% (v/v) ethanol, 1% (w/w) sulfuric acid	160	50	1:10 (w/v)	High-temperature and high-pressure stainless steel reactor (Greenwood Instruments, USA). Fixed temperature ramp-up at 45 min.	**Before treatment:** Washing the straw using distilled water, then dried and cut. **After treatment:** Collection of wheat straw using filtration. **Alkaline pretreatment:** Using 13% (w/w) sodium carbonate in a 500 mL Erlenmeyer flask in a water bath with shaking. Time of procedure: 85 min.	**Organosolv treatment:** (ethanol at 50 min) purity of 63% glucan. **Alkaline treatment:** 74.8 ± 0.8% glucan purity.	Two stage process: alkaline pretreatment and organosolv Sequential two-stage pretreatment process using ethanol and alkaline pretreatment in order to convert the carbohydrates of wheat straw into bioethanol and recover the lignin and silica. The pretreatment was followed by an enzymatic hydrolysis with the aim of recover silica and lignin at a high purity. The report covers four different solvents: ethanol, methanol, acetone and toluene.	[82]

Table A.1 Continued.

7	Rice straw	Ethanol, acetic acid and sodium hydroxide in alkaline treatment	50% ethanol, 0.1M acetic acid.	160	240	1:6.6 (w/v)	Acid digestion vessel, 45 mL thick-walled PTFE liner from Parr equipped with a pressure safety disc. Vessel was placed on a hot magnetic stirrer, and was stirred during procedure.	**Before treatment:** Sample was soaked in distilled water overnight. Sample was then dried and grounded. **Base treatment:** Removal of extractives using ethanol, then the sample was dried. The dried sample was suspended in base solution (100 mg straw, 0.07 M base).	**Organosolv treatment:** 67.3% S-ICEL purity (silica inter-twined cellulose). **After alkaline treatment:** 78% cellulose purity.	Two stage process: alkaline pretreatment and organosolv Efficient removal of silica and separation of main components of rice straw: cellulose, hemicellulose and lignin. This is a two-step process consisting of first organosolv treatment followed by base treatment. The opposite sequence is also investigated, showing less ability to fractionate the straw.	[53]
8	Wheat straw	Ethanol, sulfuric acid	33% (v/v) ethanol, 0.5% (w/w) sulfuric acid	150	360	1:10 (w/v)	500 mL stainless steel autoclave.	**Before treatment:** Straw was extracted using toluene/ethanol mixture to remove impurities.	76.4% cellulose purity	Cellulose and lignin isolation using two stage process. In the first stage, cellulose is obtained at a lower temperature and acid concentration. At the second step, the sample is treated at a higher temperature and acid concentration. In this second step, the focus is isolation of lignin. The potential usage of isolated compounds was investigated as well.	[49]
9	Rice straw	Ethanol, sulfuric acid	50% (v/v) ethanol, 0.05 M sulfuric acid	150	360	1:10 (w/v)	100 mL stainless steel autoclave	**Before treatment:** The cut straws was washed with hot water and then dried and smashed into powder. Toluene and water was then used on this powder to remove further impurities. **Bleaching:** 2 g crude cellulose was added into a round-bottom flask (100 mL) together with 20 mL Na2CO3 (8 wt%) and hydrogen peroxide mixed solution (2 wt%). Heated at 60 C for 10 h.	**Before bleaching:** 67.3 wt% cellulose purity **After bleaching:** 90.1 wt% cellulose purity	Preparation of microcrystalline cellulose (MCC) out of rice straw using organosolv process together with bleaching.	[48]

Table A.1 Continued.

10	Beech wood (hardwood) pulp and pine (softwood) pulps	Ethanol	50% (w/w) ethanol	175	120	1:10 (w/v)	Autoclave reactor The time (120 min) involves the operation time at the desired temperature (175 C) Initial pressure of O2: 16 barg (0.99 atm) at room temperature	**After treatment:** Solid fraction separated using vacuum-filtration. The pulp was then washed with distilled water and dried.	82.6% glucose purity for beech wood, 79.6% glucose purity for pine	**Oxiorganosolv process** Acid-free and mildly oxidative organosolv process. Uses oxygen gas to depolymerize and remove the lignin. Focusing on enzymatic hydrolysis and conversion of cellulose to glucose.	[83]
11	Rye straw	Ethanol, sulfuric acid	50% (w/w) ethanol, with 0.25M sulfuric acid	166,85	35	1:10 (w/w)	Fixed-bed reactor (50 mL), liquid flow rate of 4 mL/min Pressure: 35 bar	Residual biomass is flushed and cooled to avoid inhibition of enzymatic hydrolysis by residual ethanol	84.9% glucose purity	Comparison between liquid hot water (LHW) treatment, ethanol organosolv and soda pulping process.	[51]

Table A.2: Previous experiments based on acetone or other alcohols than ethanol as organic solvents

Various alcohol based processes											
No.	**Raw material**	**Solvent**	**Solvent conc.**	**Temp. (°C)**	**Time (min)**	**S/L ratio**	**Equipment**	**Additional steps**	**Results**	**Summary and comments**	**Source**
12	Wheat straw	Butanol, oxalic acid	50% (v/v) butanol, 7.5% (w/w) oxalic acid	180	90	1:20 (w/v)	300 mL Parr reactor, stirred at 400 rpm, then cooled down and depressurized. Solid load of 5 wt%.	Poured into a beaker and filtered. Washed and then dried at 60C in an oven overnight.	64% cellulose fraction purity	Wheat straw and eucalyptus is pretreated in a biphasic system with butanol and 2-methyltetrahydrofuran. The fractionation was divided into three different streams; the aqueous phase with hemicellulose, organic phase with lignin and solid residue with cellulose. The cellulose was then hydrolyzed using enzymes and the cellulose digestibility was investigated. The report also cover optimization of the process conditions. The article showed that 2M-tetrahydrofuran gave too low purity and that eucalyptus gave a higher purity.	[84]
13	Wheat straw	Methanol, sulfuric acid	66% (v/v) ethanol, 0.5% (w/w) sulfuric acid	150	360	1:10 (w/v)	500 mL stainless steel autoclave.	**Before treatment:** Straw was extracted using toluene/ethanol mixture to remove impurities.	78.8% cellulose purity	Cellulose and lignin isolation using two stage process. In the first stage, cellulose is obtained at a lower temperature and acid concentration. At the second step, the sample is treated at a higher temperature and acid concentration. In this second step, the focus is isolation of lignin. The potential usage of isolated compounds was investigated as well.	[49]
14	Wheat straw	Acetone	50 % acetone	220	60	1:14.2 (w/v)	0.5 L autoclave reactor	Wheat straw was cut before treatment.	73.4% glucan purity	Acetone-based organosolv process with the aim of producing sugars and lignin in a biorefinery. Reaction time, solvent concentration and enzymatic digestibility are some parameters investigated.	[85]

Table A.2 Continued.

15	Rice straw	"Ethylene glycol (EG), aluminum chloride"	90% (v/v) ethylene glycol, 0.055M aluminum chloride	160	30	1:20 (w/v)	Three-necked round bottom flask with heating and mechanical stirrer. Condenser at the neck of the flask in order to reflux the vapors.	**After treatment:** The temperature was slowly decreased in order to avoid foam formation. Solid residue was separated using filtration through a sand core funnel and then washed with distilled water and dried.	79.25 ± 0.36% cellulose purity	Rice straw treated with ethylene glycol (EG) and aluminium chloride for enzymatic hydrolysis. Lewis acids, as metal salts, were used in acidic pretreatment for their less corrosivity to equipment, non toxicity and low-cost instead of conventional acids that is more often used.	[54]
16	Beech wood (hardwood) pulp and pine (softwood) pulps	Acetone	50% (w/w) acetone	175	120	1:10 (w/v)	Autoclave reactor The time (120 min) involves the operation time at the desired temperature (175 C) Initial pressure of 100% oxygen: 16 barg (0.99 atm) at room temperature	**After treatment:** Solid fraction separated using vacuum-filtration. The pulp was then washed with distilled water and dried.	86.1% glucose purity for beech wood, 89.9% glucose purity for pine	**Oxiorganosolv process** Acid-free and mildly oxidative organosolv process. Uses oxygen gas to depolymerize and remove the lignin. Focusing on enzymatic hydrolysis and conversion of cellulose to glucose.	[83]
17	Wheat straw	Acetone	50% (v/v) ethanol, 1% (w/w) sulfuric acid	160	50	1:10 (w/v)	High-temperature and high-pressure stainless steel reactor (Greenwood Instruments, USA). Fixed temperature ramp-up at 45 min.	**Before treatment:** Washing the straw using distilled water, then dried and cut. **After treatment:** Collection of wheat straw using filtration.	**Organosolv treatment:** Purity of 64.1% glucan.	Two stage process: alkaline pretreatment and organosolv Sequential two-stage pretreatment process using ethanol and alkaline pretreatment in order to convert the carbohydrates of wheat straw into bioethanol and recover the lignin and silica. The pretreatment was followed by an enzymatic hydrolysis with the aim of recover silica and lignin at a high purity. The report covers four different solvents: ethanol, methanol, acetone and toluene.	[82]

Table A.3: Previous experiments based on acetic acid as organic solvent

Acetic acid based process											
No.	**Raw material**	**Solvent**	**Solvent conc.**	**Temp. (C)**	**Time (min)**	**S/L ratio**	**Equipment**	**Additional steps**	**Results**	**Summary and comments**	**Source**
18	Wheat straw	Acetic acid	87% acetic solvent	146,43	180	1:25	1 L handmade stainless steel reactor	**After treatment:** the pulp was disintegrated with an overhead stirrer, washed first with hot 87% acetic acid solution and then with distilled water	Viscosity value of 430.05 ml/g. 94.3% holocellulose content, which is the sum of cellulose and hemicellulose [86]	The aim is to produce paper pulp.	[73]
19	Sugarcane straw	Acetic acid, hydrochloric acid	93% (v/v) acetic acid, 0.05-0.2% hydrochloric acid	110	240	1:30 (w/v)	Not mentioned	Washed the pulps with acetic acid and then water until wash water had a neutral pH. **Bleaching step:** Enzymatic biobleaching with xylanases.	Glucan content was 63%.	**Acetosolv** Combined organosolv treatment (acetosolv) of sugar cane straw and enzymatic bleaching. The article also studied ethanol/water pulping and bagasse as a raw material. Acetosolv pulping of bagasse and sugarcane straw have the same glucan purity (63%)	[87, 88]
20	Wheat straw	Acetic acid, nitric acid	80% acetic acid, 8.5% nitric acid	120	20	1:20 (w/v)	30 mL Pyrex tubes inserted into a hot oil bath. These tubes were sealed using Teflon liners.	**Minimizing sample loss:** the loss was minimized by adding some extra liquid extraction and flushing the sample downwards. **After treatment:** Reagent was decanted off and the residue was washed with distilled water and ethanol to remove the nitric acid. The sample was then dried for 16 h.	Approximately 96% cellulose purity	Wheat straw is delignified using a totally chlorine-free method using acetic acid and nitric acid. The effect of temperature and nitric acid concentration was investigated.	[57]
21	Wheat straw	Acetic acid, sulfuric acid	90% (v/v) acetic acid, 4% (w/w on straw) sulfuric acid	105	180	1:10	2 L round-bottom, wide-mouth boiling flask equipped with a condenser.	**After treatment:** The reactor was cooled down and then the crude pulp was separated by using filtration. The crude pulp was disintegrated and screened. **Bleaching step:** E/P - D -P sequence (E/P - alkaline extraction using peroxide, D - chlorine dioxide bleaching, P - peroxide bleaching)	66.5% glucose content.	Fractionation of wheat straw using an atmospheric acetic process. Focus on producing pulp made for paper production	[89]

Table A.3 Continued.

22	Birch, but the process can be used for Hardwood, softwood, annual plants (such as flax and grasses)	Acetic acid, phosphinic acid	80% acetic acid, 3.5% phosphinic acid	150	120-240	1:5	Air bath digester fitted with 6 autoclaves (1 L) Temperature was raised to cooking temperature for 60 min and then treated at cooking temperature.	**Before treatment:** Before cooking, the chips are extracted with alkali by treating the chips with NaOH at 95C and solid to wood ratio of 1:5 for 60 min. Then washed twice with water and pressed to solid contents with a FREX press. Unextracted chips were also pressed to solids. Cooking was done for both extracted and unextracted chips. **After treatment:** Separation of the pulp using filtration. The solid residue was then washed and screened. **Bleaching step:** Bleached with ODEDED sequence (O - oxygen delignification, D - chlorine dioxide bleaching, E - extraction step)	High cellulose content (65-86% after cooking depending on cooking conditions), after bleaching it has potential as dissolving pulp due to high cellulose reactivity. Preliminary results indicate that it can be used as triacetates [90] (compound used to create fibers in clothing [91]).	**Lignofibre process** Lignofibre is an organosolv process able to use different solvents, and depending on which solvent used the fractions can be applied to different biomaterials. The process involved cooking at elevated temperatures using organic solvents and organic acids. Mention that one were not able to progress to commercialization due to high process cost, energy consumption and fluctuation of fossil oil prices. The catalyst is expensive.	[31, 90]

Table A.4: Previous experiments based on either formic acid or acetic and formic acid as combination as organic solvents

Formic acid based processes											
No.	**Raw material**	**Solvent**	**Solvent conc.**	**Temp. (C)**	**Time (min)**	**S/L ratio**	**Equipment**	**Additional steps**	**Results**	**Summary and comments**	**Source**
23	Non-wood plants; tall fescue, reed canary grass , goat's rue and common reed	Step 1a: Formic acid (impregnation step)	83% formic acid	Not mentioned	30	1:5	Not mentioned.		**Tall fescue:** 120C, 60 min, 5% hydrogen peroxide → 0,89% lignin. **Reed canary grass:** 100C, 120 min, 5% hydrogen peroxide → 1,68% lignin. **Goat's rue:** 110C, 120 min, 4% hydrogen peroxide → 3,39% lignin	**Milox process:** Cooking with formic acid alone then followed by a reaction with formic acid and hydrogen peroxide. The report investigates how different cooking time and temperatures affects the pulp, as well as two-stage or three stage cooking of the pulp. The Milox method provides an alternative for pulping non-wood raw materials, where a high-quality pulp can be achieved without disturbing silicon compounds.	[87, 92]
		Step 1b: Formic acid	83% formic acid	100-120	45-180		Not mentioned.	Spent liquor was removed by filtration, and then the grass was defibrated in a laboratory blender. This defibrated grass was then inserted into next step.			
		Step 2: Formic acid, hydrogen peroxide	83% formic acid, 0-5% hydrogen peroxide	80	60	1:4	90 min heating 60 min at 80C	Bleaching step: bleaching with alkaline peroxide			
Formic and acetic acid based processes											
24	Straw (wheat, rye and oats), bagasse, bamboo, cotton, wood etc. Generally, most non-wood material.	Formic acid, acetic acid and furfural	40-80% (w/w) formic acid, 8-35% (w/w) acetic acid and 2.5-7.5% (w/w) furfural	105-140	20-120	1:2.5-1:10	Tube reactor, preferable 1<L/D<15. Lined with a zirconium or teflon coating		Dissolving pulp, up to 90% cellulose purity	**Chempolis process:** The chempolis process can be applied to any lignocellulosic material using formic acid. This patent contains different methodologies for the same process.	[32, 93]

Table A.4 Continued.

25	Eucalyptus	Acetic acid, formic acid	76.5% (v/v) acetic acid, 8.5% (v/v) formic acid	170	90	1:5	Autoclaves	**Bleaching:** Ozone bleaching in a round bottom flask at high consistency (40%) at pH 2.5 The report also describe the viscose production from the isolated cellulose, including steeping, preparation and production of viscose.	96.1% glucan content compared to other carbohydrates. Article states that the viscose quality from the formacell process was good, as well as the strength of the fibers which turned out to be better for the organosolv processes than for sulfite.	The report covers a detailed analysis of the three different kinds of organosolv pulping processes, namely Milox, Acetosolv and Formacell process. These processes are compared to the acid magnesium sulfite process that is commonly used. The described experiment in this table is the formacell process since it, according to the article, gave best results regarding glucan purity and viscose properties.	[94]
26	Corn stalk	Acetic acid and formic acid, hydrochloric acid	30% (v/v) acetic acid, 60% (v/v) formic acid, 10% (v/v) hydrochloric acid	90	180	1:5 (w/v)	100 mL autoclave reactor (Parr 4590). The reactor was sealed and stirred during procedure and heated at a rate of 10C/min.	**After treatment:** After the reactor had cooled down, the slurry was poured into a beaker. The filter cake from this slurry was then, after 15 min, rinsed with ethyl acetate and thereafter with distilled water. After the washing, the cake dried in an 105C oven. The filtrate was evaporated.	Slightly above 80% cellulose purity	This study investigate the fractionation of corn stalk using different solvents, catalysts, temperature and residence time in terms of yield, purity and chemical composition. The experiments showed that there was a very small difference between the trials with catalyst and without catalyst.	[55]

Table A.4 Continued.

27	Corn stalk	Acetic acid and formic acid with hydrochloric acid	30% (v/v) acetic acid, 60% (v/v) formic acid, 10% (v/v) hydrochloric acid	90	210	1:5 (w/v)	101 mL autoclave reactor (Parr 4590). The reactor was sealed and stirred during procedure and heated at a rate of 10C/min.	**After treatment:** After the reactor had cooled down, the slurry was poured into a beaker. The filter cake from this slurry was then, after 15 min, rinsed with ethyl acetate and thereafter with distilled water. After the washing, the cake dried in an 105C oven. The filtrate was evaporated.	Around 85% cellulose purity	This study investigate the fractionation of corn stalk using different solvents, catalysts, temperature and residence time in terms of yield, purity and chemical composition. The experiments showed that there was a very small difference between the trials with catalyst and without catalyst.	[55]
28		Acetic acid and formic acid with sulfuric acid	30% (v/v) acetic acid, 60% (v/v) formic acid, 10% (v/v) sulfuric acid		180				Slightly above 80% cellulose purity		
29		Acetic acid and formic acid	33% (v/v) acetic acid, 60% (v/v) 66% formic acid		180				Slightly above 80% cellulose purity		

Table A.5: Previous experiments based on other organic solvents than mentioned in Table A.1, A.2, A.3 and A.4.

Gamma-valerolactone based processes											
No.	**Raw material**	**Solvent**	**Solvent conc.**	**Temp. (C)**	**Time (min)**	**S/L ratio**	**Equipment**	**Additional steps**	**Results**	**Summary and comments**	**Source**
30	Eucalyptus	Gamma-valerolactone (GVL)	50% (w/w) GVL	180	180	1:10 (w/v)	225 mL bombs heated in a silicon oil-bath reactor or 2.5 L bombs heated in an air-bath reactor	**Before treatment:** Impregnation step. **After treatment:** The pulp was separated using filtration and then washed. **Bleaching:** The bleaching was done in plastic bags that was heated by steam in a water bath. If bleaching is used, the cooking time reduced to 150 min	**Unbleached pulp:** 92.7% cellulose purity, viscosity of unbleached pulp was 456 mL/g **Bleached pulp:** 93.6% cellulose purity. ISO-brightness of bleached pulp was 86%, viscosity for bleached pulp was 470 mL/g.	Fractionation of eucalyptus as wood chips (woody biomass) using gamma-valerolactone. In the report, it is shown that the eucalyptus is successfully disintegrated in a single step showing high cellulose purity. The pulp was spun to produce cellulosic fibers that could be compared to man-made fibers on the market.	[95]
Dioxane based processes											
31	Wheat straw	1,4-dioxane, sulfuric acid	67% (v/v) 1,4-dioxane , 1% (w/w) sulfuric acid	150	360	1:10 (w/v)	500 mL stainless steel autoclave.	**Before treatment:** Straw was extracted using toluene/ethanol mixture to remove impurities.	86,8% cellulose purity	Cellulose and lignin isolation using two stage process. In the first stage, cellulose is obtained at a lower temperature and acid concentration. At the second step, the sample is treated at a higher temperature and acid concentration. In this second step, the focus is isolation if lignin. The potential usage of isolated compounds was investigated as well.	[49]

Table A.5 Continued.

Amide based processes											
32	Rice straw	Dimethylformamide (DMF), aniline	25% (v/v) DMF, 25% (v/v) aniline	95	360	1:20 (w/v)	Three-necked flask equipped with a reflux condenser	**Before treatment:** The straws were cut and then shredded before entering the process. **Steam explosion pretreatment:** Pretreatment with steam explosion before cooking, executed in a pilot-scale equipment. The residue was after the steam explosion treated with solvents. **Bleaching:** The solid residue from the solvent treatment was bleached using hydrogen peroxide at 50C for 12 h. The bleached pulp was then washed with distilled water and dried.	95.58 % cellulose purity	Efficient and clean method of isolating cellulose from rice straw using steam explosion with recyclable solvents, followed by bleaching with hydrogen peroxide. The most efficient steam explosion process parameters were investigated as well as the delignification degree of the different solvent systems.	[96]
Ether based processes											
33	Beech wood (hardwood) pulp and pine (softwood) pulps	Tetrahydrofuran	50% (w/w) tetrahydrofuran	175	60 for beech wood, 120 for pine	1:10	**Autoclave reactor** The time (120 min) is the operation time at the desired temperature (175 C) Initial pressure of O2: 16 barg (0.99 atm) at room temperature	**After treatment:** Solid fraction separated using vacuum-filtration. The pulp was then washed with distilled water and dried.	85.3% glucose purity for beech wood, 71.3% glucose purity for pine	**Oxiorganosolv process** Acid-free and mildly oxidative organosolv process. Uses oxygen gas to depolymerize and remove the lignin. Focusing on enzymatic hydrolysis and conversion of cellulose to glucose.	[83]
Phenol based processes											
34	Wheat straw	Phenol	65%	200	120	1:40	750 ml Berghof rector	Disintegrate pulp in a laboratory blender, wash with a hot phenol-water mixture and then wash with hot distilled water	To get high holocellulose and alpha-cellulose contents and low lignin and ethanol-benzene extractable contents, 200 degrees, 120 min cooking time and 65% phenol concentration is best (around 90% holocellulose).	Several experiments	[97]

B

Experimental setup

Table B.1: Experimental setup for organosolv treatment

Exp.	**Organic solvent**	**Organic solvent conc. (vol%)**	**Acid conc. (vol%)**	**Temp. (°C)**	**Time (min)**	**S:L ratio (w/v)**
1	Ethanol	65	1	175	35	1:12
2	Ethanol	65	1	175	20	1:12
3	Ethanol	65	0.5	175	35	1:12
4	Ethanol	65	0.5	175	70	1:12
5	Ethanol	65	0.5	175	90	1:12
6	Ethanol	50	0.5	175	90	1:12
7	Ethanol	65	0.5	160	90	1:12
8	Ethanol	65	0.5	160	120	1:12
9	Ethanol	65	0	160	90	1:12
10	Ethanol	65	0.1	160	90	1:12
11	Ethanol	65	0.3	160	90	1:12
12	Acetone	50	0.06	160	50	1:10
13	Acetone	65	0.3	160	90	1:12
14	Acetone	65	0.2	160	90	1:12
15	Acetone	65	0.1	160	90	1:12
16	Ethanol	65	0.2	160	90	1:12
17	Acetone	65	0.15	160	90	1:12

C

Calculations

C.1 Acid soluble lignin

Acid soluble lignin concentration was determined using Lambert–Beer law according to Equation C.1 [98].

$$C = \frac{\epsilon * l}{A} \tag{C.1}$$

In this expression, A is the absorbance and ϵ is the absorptivity constant. l is the optical path length, which was 1 cm in the analysis. The concentration, C, is the concentration of the acid soluble lignin given in mg/L.

C.2 Carbohydrate quantification

The quantification of glucose content was based on the detected sugar monomers in the HPAEC analysis. The amounts of monomers were also corrected by withdrawing water. In the case of pentoses, the detected values were multiplied by a factor of 0.88. For the hexoses, the detected values were multiplied by a factor of 0.9 [64].

The content of each of the carbohydrates in the pulp are then calculated according to Equation C.2.

$$C = \frac{a * f * 10}{m * 10} \tag{C.2}$$

,where C is the content, a is the amount detected in the HPAEC in mg/L, f is the factor according to the description above and m is the mass of the oven-dried sample weighed out for hydrolysis in mg. The other values are used to correct for the dilution steps occurring in the hydrolysis of the sample.

The carbohydrate composition was also corrected using the hydrolysis yield. These value have been determined experimentally based on the hydrolysis of pure monosaccharide standards according to: arabinose 93.1%, galactose 92.9%, glucose 91.8%, xylose 78.6% and mannose 90.2% [99]. The values given from the analysis were divided by the above mentioned factors in order to get the real carbohydrate composition.

Some runs resulted in an overestimation of the content wherefore a correction factor had to be used. This correction factor, cf, was calculated according to Equation

C.3.

$$cf = \frac{100 - C_{Klason} - C_{ASL}}{C_{Glu} + C_{Ara} + C_{Gal} + C_{Xyl} + C_{Man}} \tag{C.3}$$

,where C_i is the content of Klason lignin, acid soluble lignin, glucose, arabinose, galactose, xylose and mannose respectively. If the calculated correction factor was higher than 1, showing that less than 100% was quantified, it was set to 1. The correction factors were then multiplied with the detected cellulose and hemicellulose compositions. The resulting values can be seen in Table 4.2.

C.3 Intrinsic viscosity of pulp in CED

The viscosity constant h_n is estimated to 0.102. Using this, and the average drain time t_n, the relative viscosity,η_{rel}, is then approximated according to Equation C.4.

$$\eta_{rel} = h_n * t_n \tag{C.4}$$

$[\eta]$*C is determined using the relative viscosity [100]. $[\eta]$ is the intrinsic viscosity and C is the mass concentration of cellulose. This concentration is determined according to Equation C.5.

$$C = \frac{\text{Cellulose content} * \text{Mass of ground sample}}{V} \quad [\text{g/cm}^3] \tag{C.5}$$

,where V is the volume of the viscosity measurement, in this report 50 mL of CED solution and water is used. The intrinsic viscosity of pulp in CED is then determined by Equation C.6.

$$[\eta] = \frac{[\eta] * C}{C} \quad [\text{cm}^3/\text{g}] \tag{C.6}$$

C.4 Bleaching

The amount of sodium hydroxide used in the oxygen bleaching step was based on the dry weight of the pulp, determined using the dry content. 12% of the bleaching mixture, that is the pulp, water and sodium hydroxide, should constitute of dry pulp. This gives the basis for the calculations, according to Equation C.7.

$$\text{dry pulp (\%)} = 12\% * \text{total content (g)} \tag{C.7}$$

In turn, 12% of this total content should consist of sodium hydroxide. The added water into the solution is determined by Equation C.8.

$$\text{Water amount (g) = Total content - Pulp (g) - Sodium hydroxide (g)} \tag{C.8}$$

In the expression above, pulp refers to the air-dried filter cake.

D

Aspen

In this section, specifications in the Aspen simulation are stated. In order to properly model Klason lignin and acid soluble lignin, some user defined properties had to be defined in Aspen since these could not be found in the included databases. These settings can be seen in Table D.1. The user defined specifications are *DHSFRM* showing the heat of formation at 25 °C and *CPSPO1* showing the solid heat capacity coefficients [66].

Table D.1: User defined specifications for lignin

Component	**DHSFRM [cal/mol]**	**CPSPO1 [kJ/kmol-K]**
Lignin	-108248	C1=-0.472915, C2=0.79267

The different sections of the simulation are divided into three different sections: cooking, bleaching, washing and drying and chemical recovery. In contrary to Figure 3.2 containing information about the names of the streams, the Figures presented in this section also show all the sub-streams. For example, the inlet feed stream 3, does in the simulation in fact include stream 3A and 3B with different temperature and pressure. 7-1 and 7-2 are the outlet water stream from the washing step. As mentioned before, the washing is in reality conducted in one step. These two streams could therefore be considered as one stream.

D.1 Cooking section

The first part of the simulation, the cooking section, can be seen in Figure D.1. In this Figure, stream 5A is sent to the washing step (Figure D.2) while 14 continues to the chemical recovery (Figure D.3).

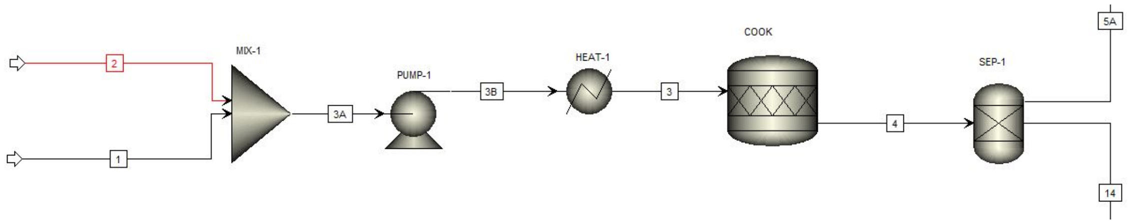

Figure D.1: Process simulation of the cooking section

The process flows in the cooking section are displayed in Table D.2. The *Stream* refers to the same name as in Figure D.1. *Content* explains what is included in the stream. *T* shows the temperature of the stream in °C and *P* shows the pressure in bar. *Flow* shows the mass flow of the stream in kg/h.

Table D.2: Process flows in the cooking section of the Aspen simulation

Stream	**Content**	**T(°C)**	**P(bar)**	**Flow (kg/h)**
1	Inlet of wheat straw	25	1	15 694
2	Inlet of cooking chemicals	25	1	154 902
3A	Cooking chemicals and wheat straw	25	1	170 596
3B	Cooking chemicals and wheat straw	25	9	170 596
3	Cooking chemicals and wheat straw	160	9	170 596
4	Pulp and spent liquor	160	9	170 596

The different process units used in the simulation are presented in Table D.3. In the first column, *Name* is referring to the process unit name in Figure D.1. The second column, *Type*, refers to which type of equipment this corresponds to in Aspen and *Aim* refers to what the step accomplish in the process. *Industrial unit* refers to which equipment this step is included in on a larger scale.

Table D.3: Process units used in the cooking section

Name	**Type**	**Aim**	**Industrial unit**
MIX-1	Mixer	Mix wheat straw with cooking chemicals	Reactor
PUMP-1	Pump	Increase pressure	Reactor
HEAT-1	Heat exchanger	Increase temperature	Reactor
COOK	RStoic Reactor	Cooking	Reactor
SEP-1	Separator	Separation of solid pulp	Filter

The fractional conversion in the reactor is calculated according to Equation D.1.

$$X = 1 - \frac{m_{in}}{m_{out}} \tag{D.1}$$

,where X is the fractional conversion, m_{in} is the mass flow of the specific component in to the reactor and m_{out} is the mass flow of the same component out of the reactor. This calculation is done for glucose, arabinose, galactose, xylose, mannose, Klason lignin, acid soluble lignin, ash and others. The values are shown in Table D.4.

Table D.4: Fractional conversion specification in the RStoic reactor

Component	**Fractional conversion**
ASL	0.38
Lignin	0.49
MAN	0.41
XYL	0.55
CELL	0.00
ARA	0.67
GAL	0.70
ASH	0.33
Other	1.00

The split fraction in the separation SEP-1 is specified according to Table D.5. This split fraction shows how large fraction of each component in the MIXED substream in stream 4 that is sent to stream 5 [66].

Table D.5: Split fraction for SEP-1

Component	**Split fraction**
CELL	0.15
XYL	0.15
GAL	0.15
ARA	0.15
LIGNIN	0.15
ASL	0.15
ASH	0.15
MAN	0.15
OTHERS	0.15
H20	0.4
H2SO4	0.4
ETHANOL	0.4

D.2 Washing, bleaching and drying section

The washing, bleaching and drying step can be seen in Figure D.2. The stream 5A in this Figure is the outlet stream from SEP-1, seen in Figure D.1.

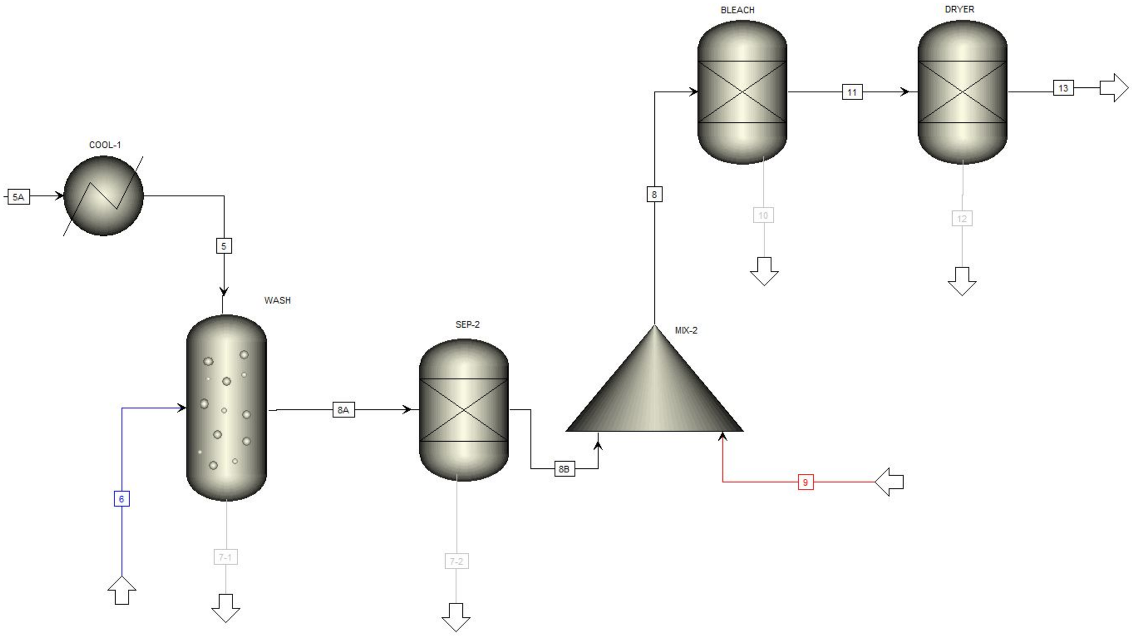

Figure D.2: Process simulation of the washing, bleaching and drying section

The process flows in the washing, bleaching and drying section are displayed in Table D.6. The definition *waste* means that the stream is exiting the process simulation.

Table D.6: Process flows in the washing, bleaching and drying section of the Aspen simulation

Stream	**Content**	**T (°C)**	**P (bar)**	**Flow (kg/h)**
5A	Filter cake containing some spent liquor	160	9	72 937
5	Filter cake containing some spent liquor	63	1	72 937
6	Inlet of water	25	1	578 511
7-1	Waste stream of water	29	1	607 765
7-2	Waste stream of biomass components and cooking chemicals	29	1	13 381
8A	Washed pulp	29	1	43 853
8B	Washed pulp	29	1	30 472
8	Washed pulp and bleaching chemicals	25	1	437 284
9	Inlet of bleaching chemicals	25	1	406 812
10	Waste from bleaching	25	1	426 568
11	Bleached pulp	25	1	10 716
12	Waste stream of water	25	1	7 054
13	Dried pulp	25	1	3 662

The process units used in this section are defined in Table D.7. *N.e* indicates that this equipment is not used in industry.

Table D.7: Process units used in the bleaching, washing and drying section

Name	**Type**	**Aim**	**Industrial unit**
COOL-1	Heat exchanger	Cool down the stream into liquid phase	N.e
WASH	SWash	Wash the pulp using water	Washing
SEP-2	Separator	Remove remaining cooking chemicals and some biomass components	Wash
MIX-2	Mixer	Mix washed pulp with bleaching chemicals	3 reactor units with intermediate washing
BLEACH	Separator	Bleach the pulp	3 reactor units with intermediate washing
DRYER	Separator	Dry the pulp	Press

The cooler before the washing unit was adjusted using design specification, shorten design spec, in Aspen. By using a design spec, it allows for specifications of certain variables and could be compared to a feedback controller. For each of the design specifications, a block or stream variable is adjusted in order to reach the specified target. In this cooler the specification was set to a molar vapor fraction of 0. To reach this value, the temperature in COOL-1 was allowed to be varied between 60 and 90°C. As seen in stream 5 in Table D.6, the temperature satisfying this molar vapor fraction was 63°C. Following the cooler, the specification of the washing unit is presented in Table D.8. *Liquid-to-solid mass ratio* is defined as the liquid to solid mass ratio in the outlet solid stream.

Table D.8: Specifications in the washing unit

Specification	**Value**
Liquid-to-solid mass ratio	3
Mixing efficiency	0.9
Pressure	1 bar

In the case of the washing unit, a design spec was also set for the amount of washing water needed. The target variable in this unit was the pH of the MIXED liquid phase in stream 7-1. The target was set to 7, with a tolerance of 0.5. This means that when the pH reached 6.5, the solution will converge. To reach this specification, the mass flow of water in stream 6 was allowed to vary between 1000 and 900 000. The mass flow of water in stream 6 is shown in Table D.6. After the washing unit, a separator is used. The moisture content, MC, of the filter cake is used to specify the split fraction of the water in this unit. This content is determined according to Equation D.2.

$$MC = \frac{m_w - m_{a.d.} * DS}{m_w} \tag{D.2}$$

,m_w refers to the weight of the filter cake immediately after washing which is 123.33g. $m_{a.d}$ refers to the weight of the air dried filter cake which is 32.00 g. DS refers to the dry substance content of the air dried filter cake which is 0.50. This shows that the moisture content of the filter cake is 74.06% immediately after washing and a design spec is used to determine the split fraction that correspond to this. In this design spec, mass flow of water was defined as a stream variable in stream 8B. The total content of the stream was defined as a stream variable in terms of total MIXED together with CISOLID mass flow. By dividing the water variable with the total content, the total mass fraction of water in the outlet stream could be defined and was set to 0.746 as a target specification. The split fraction in order to reach this target is presented in Table D.9, which represents the split fraction of water from stream 8A to 8B.

Table D.9: Split fraction for SEP-2 of mixed component

Component	Split fraction
H20	0.78

The split fraction for the CISOLID sub stream is presented in Table D.10. These values are adjusted using a design spec in aspen to give amounts in stream 8B according to experiment 16 in Table 4.2.

Table D.10: Split fraction for SEP-2 of solid components

Component	Split fraction
CELL	1.00
XYL	0.36
GAL	0.50
ARA	0.04
LIGNIN	0.49
ASL	0.19
ASH	0.12
MAN	0.60
OTHERS	0.00

A split is also used in the bleaching step. Table D.11 shows the values for mixed components from stream 8 to 11. It is assumed that all bleaching chemicals are removed by washing. The water value is received using a design spec. This design spec was defined in the way as mentioned before, by defining the water mass flow as well as the total mass flow in stream 11. The specification of this design spec was then set to 0.2091, which was the laboratory determined moisture content of the pulp.

Table D.11: Split fraction for BLEACH of mixed components

Component	**Split fraction**
H2O	0.02
NaOH	0
H2O2	0
EDTA	0
MgSO4	0
H2SO4	0

The split fractions for the solid components from stream 8 to 11 are displayed in Table D.12. These are determined using a design spec. This design spec for the BLEACH column was set in order to vary the split fraction in the BLEACH separation column from 0 to 1. The specification for each of the components are presented in Table 4.2, experiment 16OQP.

Table D.12: Split fraction for BLEACH of solid components

Component	**Split fraction**
CELL	0.33
XYL	0.13
GAL	0.00
ARA	0.10
LIGNIN	0.03
ASL	0.22
ASH	0.11
MAN	0.29

A dry content of 40% is enough, as explained in section 2.11. To reach this value, a design spec was used for the dryer to determine how much water was to be split from stream 11 to 13, referred to as the dryer. This design spec was defined in the way as mentioned before for SEP-2 MIXED components. The split fraction of the separator to stream 12, the waste water stream, was allowed to be varied between 0 and 1. The split fraction in this separation then turned out according to Table D.13.

Table D.13: Split fraction for DRYER

Component	Split fraction
H2O	0.17

D.3 Chemical recovery section

Lastly, the chemical recovery is presented in Figure D.3. The inlet stream is the spent liquor stream from SEP-1 in Figure D.1.

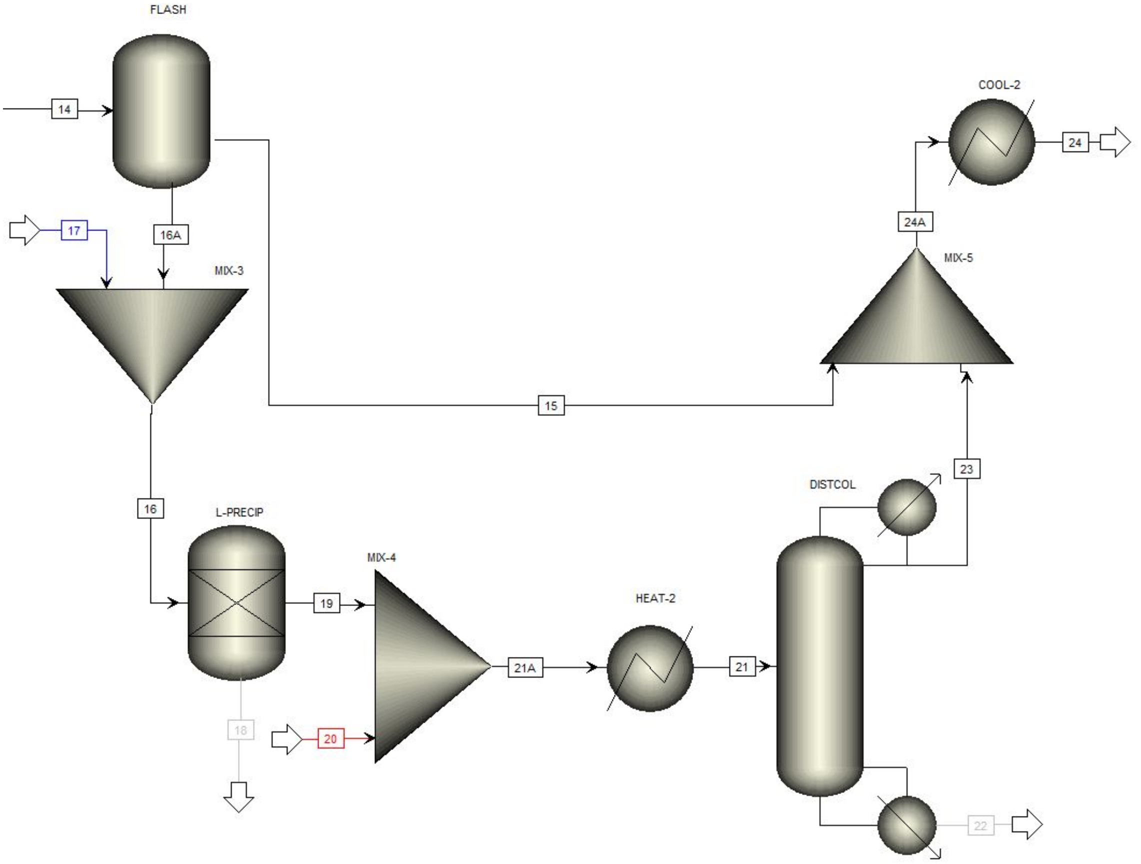

Figure D.3: Process simulation of the chemical recovery section.

The process flows in the chemical recovery section are displayed in Table D.14.

Table D.14: Process flows in the chemical recovery section of the Aspen simulation

Stream	**Content**	**T (°C)**	**P (bar)**	**Flow (kg/h)**
14	Biomass components and cooking chemicals	160	9	97 659
15	Recovered cooking chemicals	160	1	92 780
16A	Biomass components and cooking chemicals	160	1	4 879
16	Biomass components, cooking chemicals and water	43	1	13 077
17	Inlet stream of water	25	1	8 197
18	Waste stream of lignin	43	1	867
19	Biomass components, cooking chemicals and water	43	1	12 210
20	Inlet stream of soda	25	1	12 696
21A	Biomass components, cooking chemicals, water and soda	37	1	24 906
21	Biomass components, cooking chemicals, water and soda	58	1	24 906
22	Waste stream of biomass components, cooking chemicals, water and soda	108	1	20 406
23	Recovered cooking chemicals	99	1	4 500
24A	Recovered cooking chemicals	101	1	97 280
24	Recovered cooking chemicals	25	1	97 280

The process units used in this section are presented in Table D.15

Table D.15: Process units used in the chemical recovery section

Name	Type	Aim	Industrial unit
FLASH	Flash2	Recover some cooking chemicals	Flash
MIX-3	Mixer	Dilution with water	Lignin precipitation
L-PRECIP	Separator	Remove 67% of lignin	Lignin precipitation
MIX-4	Mixer	Mix with sodium hydroxide inlet	Mixer
DISTCOL	RadFrac	Recover remaining ethanol, together with some water and acid	Distillation column
HEAT-2	Heat exchanger	Increase temperature of distillation inlet	Heat exchanger
MIX-5	Mixer	Mix outlet of cooking chemicals from flash with outlet of cooking chemicals from distillation	Mixer
COOL-2	Heat exchanger	Cool down flow of cooking chemicals to 25°C	Heat exchanger

A split is used for the lignin precipitation showing how much of stream 16 that goes to stream 18. These values are used according to the description in section 3.6.3. The values are displayed in Table D.16.

Table D.16: Split fraction for L-PRECIP

Component	Split fraction
Lignin	0.67
ASL	0.67

The specifications of the distillation column are presented in Table D.17. These were adjusted in order to distil as much ethanol as possible and at the same time minimize the energy consumption in the reboiler.

Table D.17: Specifications in the distillation column

Specification	**Value**
Number of trays	8
Distill rate (kg/h)	4500
Reflux ratio	1

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