# Lignin Concentration by Nanofiltration and Precipitation in a Lignocellulose Biorefinery

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In the presented work, some findings of three separate studies were combined. These experimental and process simulation works included one study regarding the production of organosolv liquors to investigate lignin and carbohydrate solubilisation and the precipitation of lignins, one study investigating the nanofiltration behaviour of organosolv liquors, which were approximated with synthetic solutions of Kraft lignin and glucose, and third, a process simulation of the whole organosolv process to investigate possibilities for process integration and energy and chemicals savings. Here, we want to concentrate on the possibilities of concentrating the organosolv liquor by nanofiltration for lignin separation and production. A liquor with a lignin concentration of 9.1 g/L and a total monomeric sugar concentration of 61.8 mg/L was produced by ethanol organosolv treatment at 180 °C. The synthetic liquor which resembled these conditions the most had concentrations of 1.1 %w lignin and 0.1 %w glucose. With this liquor, a lignin rejection of ca. 99 % was reached. In the process simulation, which was done at an earlier stage, a lignin rejection of 90 % was used. This could mean a much lower "loss" of lignin to the permeate and a higher lignin yield in the precipitation step.

## 1. Introduction

Lignocellulose based biorefineries, analogous to conventional refineries, aim to produce value-added products from renewable, lignocellulosic resources through a series of operations. Their products are raw materials for the chemical industry, food and feedstuff production or biofuels. The advantages of lignocellulose based biorefineries is that their feedstock is often cheap and easily available as a byproduct from agriculture or forestry, and that they offer a broad range of products (Kamm and Kamm, 2004). There are different paths to utilizing the biomass. Some use the whole biomass (e.g. biogas or syngas production), others aim to deconstruct it and convert the resulting fragments to produce a variety of chemicals (de Jong et al., 2012). Lignocellulosic biomass is made up of three major components - cellulose, hemicellulose and lignin – which have to be separated in order to process them into specific products. The cellulose, if it is of sufficient quality, can be sold as fiber. C5 and C6 carbohydrates can be fermented to various organic acids, or chemically converted to furfural, hydroxymethylfurfural or other chemicals. Lignin could be a precursor for for phenolic platform chemicals (e.g. benzene, substituted phenols, aromatic acids) or polymer products like resins, fillers, binders or adhesives (de Jong et al., 2012). There are different treatments to fractionate the biomass. For example, it can be cooked with water at elevated temperatures (160 to 240 °C) under pressure (Liquid hot water treatment), cooked with diluted acid or in alkaline conditions. Also, good fractionation has been accomplished with methods that combine cooking with a sudden pressure release, causing the moisture in the biomass to expand and thereby break up its structure (Mosier et al., 2005). Organosolv is a promising method to achieve high delignification of the biomass (Wörmeyer et al, 2011) and obtain relatively high purity lignin (Alvira et al., 2010), and at the same tame retain lower formation of sugar degradation products and cellulose. The lignin can be precipitated from the liquor by means of lowering the pH, reducing the concentration of the organic solvent (Fernando et al., 2010), lowering the temperature (Buranov et al., 2010), or a combination of those (Huijgen et al., 2010). Yet, chemically diversified second generation biorefineries are not ready for the market. Therefore, several studies were carried out to investigate these steps and combine the findings.

Organosolv treatment of wheat straw was carried out with the aim of investigating the fractionation of the straw. The amount of released saccharides, degradation products and dissolved lignin in the resulting liquor was investigated. To improve the performance of lignin isolation by precipitation, nanofiltration was evaluated with the goal of cleaning process liquors for recycling, and to concentrate the lignin solution before precipitation. For this, model solutions of ethanol organosolv liquors were prepared to resemble the lignin and saccharide concentrations of the produced organosolv liquor and filtrated in a bench-scale filtration set up. Empiric models for transmembrane flux and rejection were created. For mass- and energy balances, an overall organosolv process flowsheet was simulated using ASPEN Plus (V7.3.2, Aspen Technology Inc., 2012). The simulation assumptions and results were validated against the latest experimental results in terms of lignin precipitation effectivity, chemicals demand and membrane separation efficiency.

## 2. Methods

### 2.1 Organosolv Liquor Production

The raw material was milled in a cutter mill to pass through a 4 mm screen and 30 g were transferred into a high pressure autoclave (Zirbus, Germany) with a volume of 1 L. 330 g of 60 % (by weight) aqueous ethanol were added. A custom made distance keeper was set in place to ensure that straw stays covered in liquid at all times. The mixture was heated to 180 °C and the pressure rose to 15 bar. The target product temperature was reached after 60 min and the reactor was cooled down to ensure safe removal of the products. After the treated straw and liquor were gathered from the reactor, the solid and liquid fractions were separated by decantation of the coarse straw pieces and following pressure filtration in a stirred cell to remove fine suspended particles. For these studies, only the liquid fraction was relevant and used for further analyses and experiments. If not otherwise stated, the analytical procedures were performed according to the Laboratory Analytical Procedures (LAPs) provided by the US National Renewable Energy Laboratory (NREL, 2015). Monomeric sugars were determined after mixing the sample with 0.1 mol/L NaOH in a 1:9 ratio with a Dionex ICS-5000 system with a pulsed amperometric detector and a PA1 and a guard column. The flow rate was 0.26 mL/min of water with a post-column addition of 0.13 mL/min of 200 mmol/L NaOH. For the determination of the total sugar content in the organosolv liquor, a liquor sample was hydrolysed in the presence of 4 % sulphuric acid at 120 °C for 60 min. After being cooled to room temperature, the pH of the solution was adjusted by mixing with 0.4 molar NaOH in a 1:9 ratio. The pH-adjusted were filtered through 0.2 µm syringe filters into HPLC vials. The lignin concentration in the liquid samples was measured with a Shimadzu UV-1800 UV/Vis-Spectrophotometer at 280 nm after appropriate dilution with 60/40 (w/w) ethanol/water mixture.

### 2.2 Nanofiltration

For the nanofiltration, model liquors were prepared to resemble the organosolv liquors from earlier experiments. The investigated concentration range should cover fresh liquor, but also liquors from which the lignin or sugars were separated. To cover a large scale with few experiments, Design of Experiments (DoE) was employed. A central composite design (CCD) was created for the factors lignin content and sugar content. The high and low levels were 0.2 and 1.1 % (mass) for lignin and 0.02 and 0.1 % (mass) for glucose. The ethanol content was kept constant at 60 % (mass). The full chosen CCD is shown in Figure 1(a).
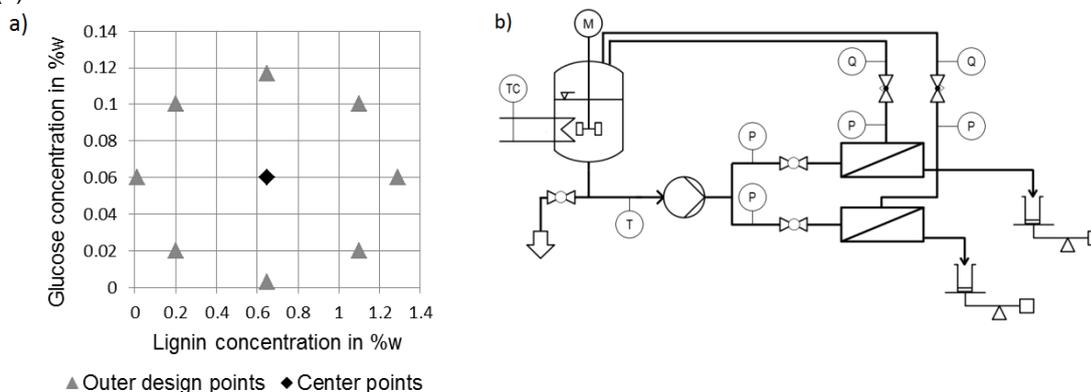


Figure 1: a) Central Composite Design for the model organosolv liquors used for nanofiltration. b) Flow diagram of the filtration setup (after Waldmüller, 2014).

Commercial Kraft lignin (low sulfonate content, Sigma-Aldrich, Germany) and glucose were chosen to represent the organosolv lignin and the dissolved carbohydrates, which were not readily available. The membrane set-up consisted of a temperature controlled stirred feed tank, a gear pump, flat sheet membrane modules with an active areas of 8 x 20 cm, and rotameters to measure the retentate flow rate. The feed flow rate to the membrane cell and the applied pressure can be regulated by frequency converter and a pressure retention valve. The flow diagram of the filtration apparatus is shown in Figure 1b).

The permeates were collected in separate cylinders which were continuously weighed to determine the permeate mass flow and recycled back periodically to the feed container to keep the concentrations constant. The retentate was continuously recycled. Based on earlier studies (Silva, 2012) the Filmtec NF270 membrane (Dow Water and Process Solutions, Michigan, USA) was chosen. It is a thin film composite membrane, consisting of a polyamide selective layer on a polysulfone support (Nghiem and Hawkes, 2007) with a nominal cut-off of 150-300 Dalton (Dolar et al., 2013). The preconditioning has substantial influence on the performance of ultrafiltration (Shukla and Cherian, 2002) and nanofiltration (Tsui and Cheriyan, 2004) membranes. The membranes were placed in 60 %w aqueous ethanol for 24 h. The pure water flux at 10 bar was measured, then the feed was changed to the model organosolv liquors and the filtration was carried out until the transmembrane flux was constant. The pressure was kept at 10 bar and the retentate flow rate at 15 L/min for all filtration experiments. Samples were taken repeatedly for lignin concentration measurement by UV/Vis spectroscopy. The rejection coefficient for lignin was calculated by Eq(1).

$$R = (1-w_p/w_F)*100 \tag{1}$$

### 2.3 Process Simulation

To calculate mass- and energy balances, a flowsheet (Figure 2) for an overall organosolv process was created and simulated using ASPEN Plus (V7.3.2, Aspen Technology Inc., 2012). Assumptions for the unit operations were based on earlier experimental studies for straw pretreatment and membrane filtration in dead-end mode and precipitation (Silva, 2012) and cross-flow filtration (Weinwurm et al., 2014) and scaled up for a straw input of 100.000 kt/y. The overall process, the simulation and integration of the process will be covered in a separate publication, which is under revision at the time this manuscript was submitted. Here, the simulated nanofiltration step will be compared with the latest experimental results.
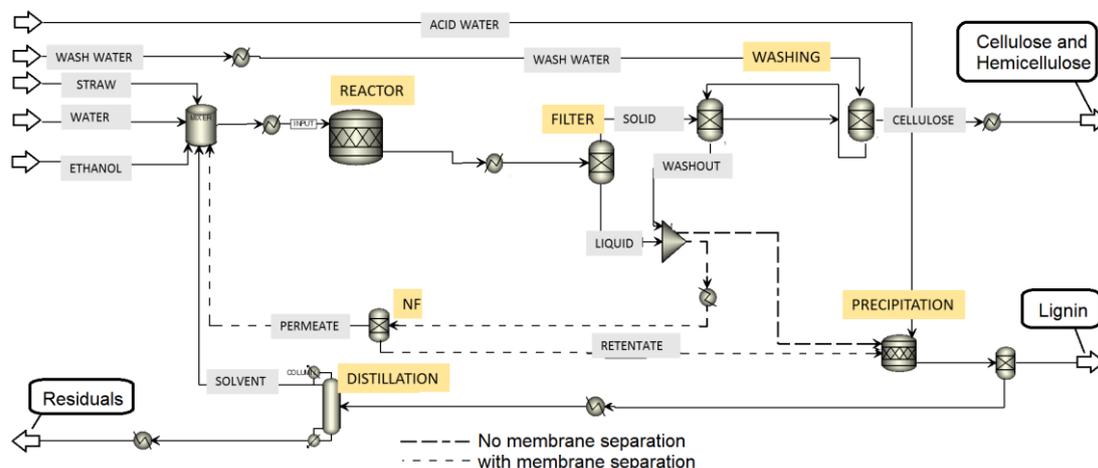


Figure 2: Organosolv process flowsheet. Base case without membrane separation: long dashes, Process case with membrane separation: short dashes

In the simulation, the NRTL-RK (Non Random Two Liquids Redlich Kwong) property method was used for the calculation of equilibrium and thermodynamic properties. In the simulated process, the solid residue from the organosolv treatment is washed and the wash liquid is combined with the organosolv liquor. 70 % of the dissolved lignin are precipitated by addition of diluted sulphuric acid. The simulation investigates, how a pre-concentration of the combined liquids prior to precipitation affects the energy and chemicals demand of the process. For this, several stage cuts (Eq(2)) of the membrane unit are used (15 %, 50 % and 80 %).

Stage cut: 
$$\theta = \frac{m_{Permeate}}{m_{Feed}}$$
(2)

The nanofiltration was simulated as a FILTER Sep unit, with the following split factors, which were adapted from the results of Silva (2012). For ethanol and water, no rejection was assumed, so the split factor was equal to the stage cut. For lignin, ash, and proteins, split factors of 10 %, 50 % and 1 % of the stage cut were assumed. For the main sugars Xylose, Arabinose and Glucose, the used split factors were 77.3 %, 80.6 % and 52.6 % of the stage cut.

## 3. Results

### 3.1 Lignin and Carbohydrate extraction

After organosolv treatment, 41 % of the straws lignin and 9.93 % of the total saccharides were dissolved in the liquid. The lignin concentration in the liquor was 9.1 g/L and the monosaccharide concentration was 61.8 mg/L. Silva (2012) reported an average of 45 % lignin solubilisation, 0.2 % of the carbohydrates dissolved in monomeric form and 2.0 % of the carbohydrates dissolved in total with a target temperature of 190 °C and a residence time of 60 min.

### 3.2 Nanofiltration

The membrane flux of the NF 270 membrane showed a somewhat inconclusive behaviour. At the lowest lignin concentrations, the flux was approximately the same as at the second highest lignin concentration. Apart from that, the flux tends to decline with increasing lignin concentration. The results at the repeated centerpoint conditions suggest that there is substantial variation in the flux, probably caused by irregularities of the membrane samples. The lignin rejection was, except for the run with the lowest lignin concentration, always higher than 98 %. In theory, a lower concentration would mean a lower driving force and thus less transport to the permeate side. Arsuaga et al. (2008) observed similar behaviour with malonic acid and phenol when they used the Filmtech NF 90 membrane, which is made from the same material with a higher degree of crosslinking. They concluded that this phenomenon is caused by solute-membrane interactions. Lignin rejection and transmembrane flux for NF 270 are pictured in Figure 3.
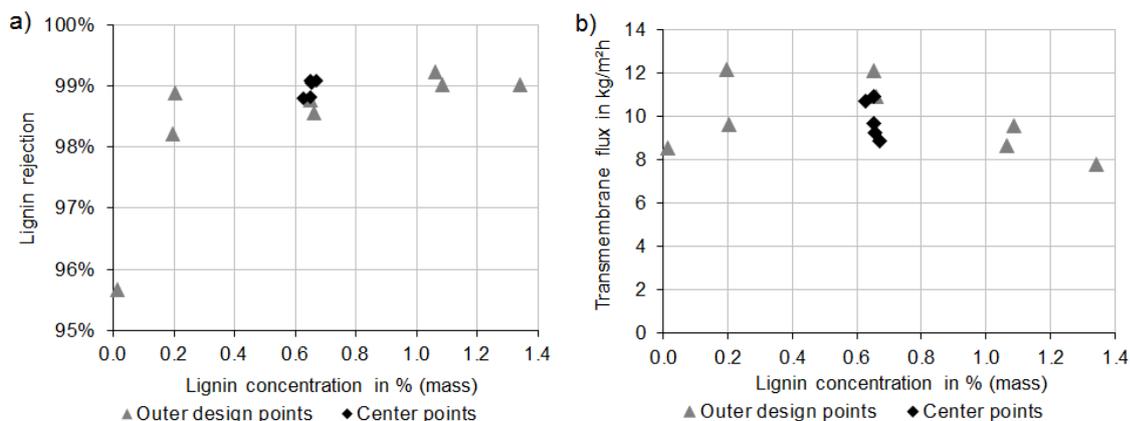


*Figure 3: Lignin rejection (a) and transmembrane flux (b) in the nanofiltration experiments, depending on the lignin concentration in the feed. Grey triangles represent the outer design points, black diamonds represent the repeated centerpoint conditions of the CCD from Figure 1 (adapted from Waldmüller, 2014)*

For the calculation of an empiric model for the lignin rejection coefficient, the value at a lignin concentration of 0.014 % was treated as an outlier. Still, the obtained model did not have a satisfactory R² value, so the mean value was chosen as the predictor for the rejection coefficient with a value of 98.9 %. The lignin concentration of the produced organosolv liquor lies in the range of the model liquors. Judging from that, a rejection of 99 % could be reached with the NF270 membrane. The monomeric sugar content of the model liquors exceeds the values of the organosolv liquor by far. Since no connection of the glucose content and lignin rejection was observed (data not shown) in the nanofiltration experiments, the effect of the monomeric sugars on the lignin rejection is expected to be negligible. But since there are also oligomeric saccharides, degradation products, lignin fragments and most likely lignin-carbohydrate compounds (Huijgen et al., 2010) in the liquor, fouling will take place when the organosolv liquor is concentrated by membranes without prior treatment. This fouling behaviour was observed in an earlier study (Weinwurm, 2014).

### 3.3 Simulation

In the simulation, the pre-precipitation EOS liquor was concentrated using nanofiltration, starting from a lignin concentration of 11.3 g/kg to 13.1, 20.9 and 51.8 g/kg, depending on the stage cut. The increase of the lignin concentrations corresponds to lignin rejection factors of 89.7 %, they differ only a little from the assumptions made for the split factors. Depending on the stage cut, certain amounts of lignin are "lost" to the permeate (they do not reach the precipitation unit), but also the amount of diluted sulphuric acid needed to precipitate 70 % of the lignin is reduced (Table 1). It is evident, that the operating cost, not only for the chemicals, but also for appliances and heat, can be substantially reduced as a result of much lower volumes that reach the precipitation unit.

*Table 1: Simulation results*

| Stage cut | 15 % | 50 % | 80 % |
|---|---|---|---|
| Lignin "loss" | 1.54 % | 5.13 % | 8.21 % |
| Sulfuric acid reduction | 15.2 % | 48.4 % | 77.6 % |

The lignin and sugar concentrations that were used in the simulation are similar to the ones covered in the nanofiltration tests (Table 2), so it is interesting, what the change in lignin rejection would mean for the simulation results. Compared to the assumptions made for the simulation, the new results from the nanofiltration experiments show a much higher rejection of about 99 %, which means that the lignin "loss" would decrease to roughly 1 %, if constant rejection is assumed.

*Table 2: Composition of the liquids*

| | Ethanol | Lignin | Glucose | Arabinose | Xylose | Total monomeric sugars |
|---|---|---|---|---|---|---|
| Organosolv liquor (produced) | Ca. 60 %w | 9.1 g/L | 7.52 mg/L | 46.4 mg/L | 3.72 mg/L | 61.8 mg/L |
| Model Liquor (Nanofiltration) | Ca. 60 %w | 0.014 -1.29 %w | 0.003 -0.117 %w | | | 0.003 -0.117 %w |
| Organosolv liquor (Simulation) | 58.31 %w | 1.13 %w | | 0.32 %w | 1.19 %w | 1.51 %w |
| Permeate (Simulation) | 59.83 %w | 0.12 %w | | 0.27 %W | 0.94 %w | 1.21 %w |
| Retentate (Simulation) | 56.86 %w | 2.09 %w | | 0.37 %w | 1.42 %w | 1.80 %w |

## 4. Conclusions

In this paper, we presented results from three moderately linked studies. One aimed to produce lignin from straw by an organosolv pretreatment and precipitation. Since some results are not yet available, the precipitation part was left out. The second part was dedicated to nanofiltration of solutions, which resemble organosolv liquors to investigate the behaviour of membranes. Third, a simulation study of the overall process was done, which is covered in a separate publication. Some results from the simulation were compared with the experimental work presented here.

With these studies, we wanted to gain knowledge about how the different unit operations that could be a part of a biorefinery process can be combined in order to promote the development of lignocellulosic biorefinery processes. With this and a previous study (Weinwurm, 2014) we showed that nanofiltration is a promising option to concentrate lignin. On average, a rejection of 98 % could be reached, which is a significant improvement over the assumptions for the simulation. Other groups have also successfully tried to separate and fractionate (Toledano et al., 2010) lignin with membrane processes. As the simulation showed, concentration of the lignin would lead to a high reduction of the chemical demand for lignin precipitation (up to 78 %). Open questions regarding the achieved lignin rejection are the difference in the molecular weight distribution of the commercial and our organosolv lignin and membrane fouling. If the lignin that was produced would exhibit a much lower molecular weight, the high cut offs that were determined in this study will most likely not be achieved with a real liquid. Our earlier study showed rapid flux decline when a fresh organosolv liquor was used in nanofiltration due to fouling. This could mean, that high stage cuts, which were used in the simulation, would require a more elaborate pretreatment and consequently higher energy demand and costs. Also, solute-membrane interactions might pose additional problems, since organosolv lignins have different functional groups than kraft lignins (El Mansouri and Salvadó, 2007) which could be a part of the explanations for the differences to the rejections of Silva

(2012). The organosolv treatment itself was found to be reproducible, since the dissolved lignin and carbohydrate values were in the same range as earlier values and other groups (Gonzalez et al., 2008).

In terms of lignin concentration, the produced liquor, the nanofiltration model liquors, and the simulated liquors are similar. Ethanol organosolv treatment, membrane preconcentration and precipitation is a viable combination of unit operations for a lignocellulose biorefinery process, provided the issues mentioned before (Fouling and lignin loss at higher concentrated liquors in the nanofiltration step) can be tackled successfully.

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