

Principles of Ethanol Organosolv Lignin Precipitation: Process Simulation and Energy Demand

Felix Weiwurm^{*a}, Adela Drljo^a, Tania L. S. Silva^b, Anton Friedl^a

^aVienna Univ. of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166-2, 1060 Vienna, Austria;

^bMinho University, Department of Biological Engineering, Campus de Gualtar, 4710 - 057 Braga, Portug

felix.weiwurm@tuwien.ac.at

This study focuses on ways to precipitate lignin, and how the choice of pre-concentration technique affects an ethanol organosolv (EOS) processes' energy and chemicals demand. Experiments were performed in order to precipitate lignin from an EOS treatment liquor by a) direct precipitation with sulphuric acid, b) vacuum-assisted evaporation and acid precipitation, and c) concentration by nanofiltration and acid precipitation. Utilizing the process simulation tool ASPEN Plus®, supported by experimental data, energy and chemical demand were calculated. It was shown that chemicals demand decreased significantly by preconcentration and that the energy demand for the nanofiltration case was considerably lower than in the evaporation case.

1. Introduction

For quite some time now, a lot of research is aimed to substitute fossil raw materials with renewable sources. Biorefinery concepts are investigated to produce transportation fuels which could increasingly replace their fossil counterparts. In addition to fuels, newer biorefinery concepts also offer the possibility to produce chemicals on a sustainable basis. Besides sugars, bioethanol and fibbers, lignin is a promising product of biorefineries. To fractionate lignocellulosic biomass, which is the feedstock of choice to produce this spectrum of chemicals, several processes are investigated in literature. One of them that appears to yield high quality lignin is the ethanol organosolv (EOS) process, that utilizes ethanol in the pulping liquid. As a result of ethanol organosolv treatment, a cellulose rich solid fraction, and a liquor containing the cleaved lignin as well as some hemicellulose derived sugars and sugar degradation products are generated. In order to obtain the lignin, it has to be precipitated from this matrix of several compounds selectively. In some cases, this was achieved by selective precipitation through acidification by sulphuric acid or addition of water. Fractionation of different molecular weight lignins by ultrafiltration with subsequent precipitation was also investigated.

Previous studies, including our own, have also shown that lignin solubility depends on the ethanol content of the solution, therefore lignin precipitation can also be performed by reducing the ethanol content and/or removing liquid to bring the lignin concentration to its solubility limit. After precipitation, the lignin can then be recovered by filtration and/or centrifugation. Conventionally, the lignin which was removed in pulp and paper processes was incinerated for process heat. But lignin is a promising substance for many other uses, such as platform products, e.g. syngas products, hydrocarbon derivatives, or specialties as polymer alloys, nutraceuticals/drugs or adhesives and resins (Menon and Rao, 2012). Several groups have investigated classification in the liquid phase (Toledano et al., 2010), or lignin properties and purity (Buranov, 2010). At some point in a process, the energy and chemicals demand to obtain this product will be an issue towards a commercial process.

2. Materials and Methods

2.1 Materials

Sulfuric acid 98 % (by mass, %w), was purchased from Merck, Germany, all other chemicals from Sigma-Aldrich, St. Louis, MO, USA. The straw was harvested in autumn of 2009 in the region of Dürnkrot, Lower Austria and stored dry until use. It was reduced in size in a cutting mill, equipped with a 4 mm mesh.

2.2 Lignin preparation

The organosolv treatments were carried out in a HDA 9/16 high pressure autoclave (Zirbus, Germany) with a volume of 1 L. 30 g of milled straw were introduced in the reactor and 330 g of a 60/40 (w/w) mixture of Ethanol and MQ Water were added. The reactor was sealed and electrically heated up to 190 °C over a time span of 60 min. After that, the reactor was cooled by tap water to 30 °C and the products were removed. The liquors were separated from the straw by hand pressing and collected in a sealable bottle.

Precipitation batch a)

Concentrated sulphuric acid was added slowly to the liquor of three consecutive ethanol organosolv experiments in order to adjust the pH for precipitation while the pH was monitored with a pH electrode. From a starting pH of 6, the pH was reduced first to a 2 and then to 1. The liquors were centrifuged in a Sigma 4K15 (Sigma, Germany) centrifuge at 5,100 rpm for 10 min. The supernatant was collected and filtered through filter paper. The solids were dissolved in ethanol/water mixture again and also filtered through filter paper. To increase the lignin yield, the liquors were diluted with roughly 2 parts (by weight) acidified Water (pH1) and filtered. All filter cakes were dried in a convection oven at 40 °C over night.

Precipitation batch b)

The liquors from three consecutive experiments were centrifuged at 5,100 rpm for 10 min. Roughly two parts of acidified water (pH2) were added slowly to precipitate the lignin. The liquid was then centrifuged again, the solids were collected, suspended in MQ water, filtered through filter paper and dried at 40 °C over night. For the following experiments, both lignin fractions were combined.

2.3 Solubility limit determination

The lignin prepared by method a) was used to determine the solubility limit. An excess amount of lignin was placed in test tubes and placed in an ultrasonic bath for 20 min. The lignin concentration in the supernatant after centrifugation at 5,100 rpm for 40 min was determined by UV/Vis absorption at 279 nm against a calibration curve made with commercial low-alkali lignin.

2.4 Solvent removal by evaporation and nanofiltration

After determining the lignins solubility limit and precipitation without pre-concentration, we investigated possibilities to increase the lignin concentration in the solution. Since we wanted to avoid changes of the lignins structure, composition and properties due to elevated temperatures, we chose vacuum assisted evaporation and membrane separation. Lignin fractionation and concentration by membrane separation processes have already been studied by others and seem a viable option. Since, at this point, we do not seek to fractionate different molecular weight lignin fractions, we opted for nanofiltration to concentrate the lignin. 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). In general, membrane filtration processes seem advantageous for lignin concentration because they do not alter the solvent composition of the mother liquor, which means that, in theory, the lignin concentration could be increased close to the solubility limit. Reaching or exceeding the solubility limit should be avoided to prevent deposition of lignin in the equipment, which results in product loss and increased cleaning effort.

Evaporation

Roughly two grams of ethanol organosolv lignin were dissolved in 1.8 kg of 60/40 (w/w) ethanol–water mixture to create the mother liquor for the solvent removal experiments. Fifty grams of the mother liquor were taken and placed in a flask for evaporation. Using a rotary evaporator at 200 mbar and 60 °C, solvent was removed from the sample until the liquid appeared cloudy. The remaining liquor was centrifuged to remove suspended particles. The lignin concentration in the supernatant of the centrifugation and the mother liquor was measured by UV/Vis absorption as before.

Nanofiltration

The remaining mother liquor was used for cross-flow nanofiltration experiments. The membrane set-up consisted of a temperature controlled double mantle tank, a piston pump, a flat sheet membrane module

with an active area of 8 x 20 cm, and a rotameter to measure the retentate flow rate. The feed stream to the membrane cell and the applied pressure can be regulated by a bypass and a pressure retention valve. The permeate was collected in a bottle which was continuously weighed to determine the permeate mass flow. The set-up is shown in Figure 1.

The pressure was first adjusted to 10 bar, and was increased when the permeate flow decreased. The retentate flow rate was kept in the upper middle range of the rotameter, which had a scale from 1 to 5 L/min. Samples were taken repeatedly for lignin concentration measurement by UV/Vis spectroscopy.

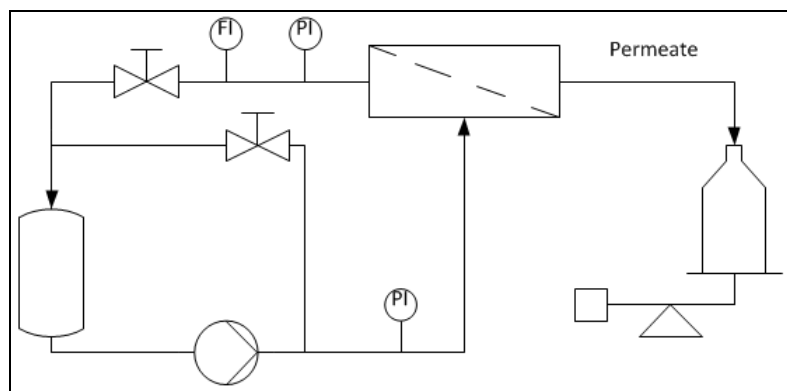


Figure 1: Membrane Equipment

2.5 Process Simulation

Based on the experimental results, organosolv process variants have been simulated in the flow sheeting simulation program Aspen Plus (V7.3.2, Aspen Technology Inc., 2012). Overall process is designed and scaled up to a realistic plant scale that could be located in the Lower Austrian region and supplied with wheat straw harvested in this region. Simulation in Aspen Plus was operated by using NRTL-RK (Non-Random Two-Liquids Redlich-Kwong) method to calculate the thermodynamic properties of the mixtures. Mass and energy balances calculated in this way are based on the wheat straw input of 12.5 t/h. The whole process is illustrated in Figure 2. Wheat straw was harvested and analyzed for the main composition for previous studies, the values are given in Table 1 (Silva, 2012).

Straw is pre-treated with water-ethanol solution (60 %w) at elevated pressure and temperature and a solid/liquid ratio of 1/10. Not all analyzed components from the wheat straw exist in the Aspen Plus database. Lignin and cellulose were defined by physical properties from the installed in-house NREL database. For protein and extractive components, ZYMO was chosen and all other components have

Table 1: Wheat straw composition

	Glucan %w	Xylan %w	Arabinan %w	Lignin %w	Ash %w	Protein %w	Extractives %w	Rest %w
Wheat straw	35.1	21.6	3.4	22.6	5.5	3.2	4.3	4.3

been simulated based on the predefined components in the installed Aspen Plus database.

For the simulation of the pre-treatment, an equilibrium reactor model RStoic from ready-made Aspen Plus models was used. After the pre-treatment, the solid and liquid phase are separated in a filter-press unit. The solid cake with 50 % moisture, containing mostly cellulose fraction, is washed and separated as a final product. Washing is simulated as a two-stage counter-current washing. The first stage is a water-ethanol washing, performed to wash all dissolved lignocellulosic matter out. The second washing stage is a pure water washing, performed to prevent ethanol loss in the washing procedure. In general, washing is simulated as displacement (ideal) washing which would mean that all liquor is ideally replaced by washing liquid.

The liquid phase is sent to lignin precipitation and isolation, where 70 %w of the lignin are assumed to be precipitated and recovered. The remaining liquid is directed to the distillation to recover water-ethanol at 60 %w ethanol and recycle it back to the process. For the simulation of distillation process, the RadFrac model is used and set up to recover the solvent under optimal conditions (At temperatures lower than 70 °C and the appropriate vacuum, according to Drljo et al. (2012)).

Nanofiltration

Due to the required liquid volume for operation of the membrane filtration and the rather low lignin yields by precipitation, the starting concentration was 1.63 g/kg, which is very low compared to real organosolv liquors. During operation, the maximum transmembrane flux was 9.5 kg/m²h, which declined to 1.5 kg/m²h. The average transmembrane flux was 4.1 kg/m²h. The behaviour of accumulated permeate mass and transmembrane flux over time is shown in Figure 3.

Judging by the behaviour of the transmembrane flux, fouling is an issue which has to be addressed in further studies. With this flux, the solubility limit could not be reached in reasonable time, and the experiment was stopped at a concentration of 1.81 g/kg in the tank. The values obtained in an earlier study (Silva, 2012) were used to have a more realistic separation efficiency in the process simulation.

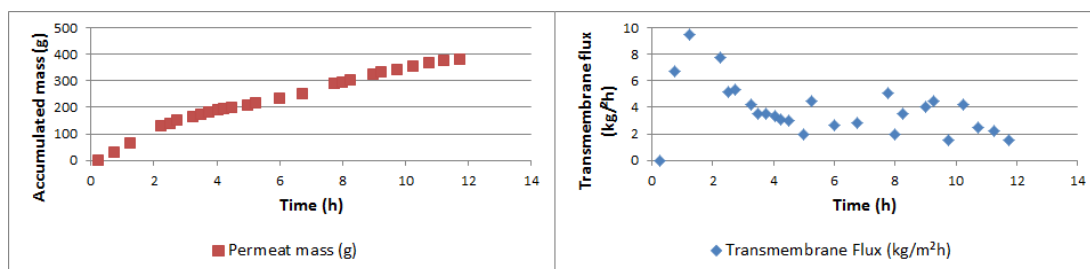


Figure 3: Nanofiltration progression

3.3 Chemicals and Energy Demand

By process simulation of the process variation mentioned above, the following results were obtained. The lignin concentration in the liquor coming out of the reactor is 10.7 g/kg, which also serves as the starting value for the preconcentration and precipitation procedures. Since the washing step is simulated ideally, as described above, the lignin and ethanol concentration do not decrease when the streams from the press and the washing unit are combined. The lignin concentrations at the inlet of the precipitation unit were determined experimentally for the evaporation and the nanofiltration process case. It was assumed that the ethanol concentration is not affected by the nanofiltration step. For the evaporation process case, the change in ethanol concentration was simulated as described above. In terms of heat demand for evaporation, 37.5 kJ/kg of heat were needed per kg of precipitated lignin.

$$P_{el} = \frac{1}{\eta} \cdot \frac{\dot{m}}{\rho} \cdot \Delta p \quad (1)$$

Using the simulated mass flow of 31.06 kg/s, a Δp of 10 bar which was used in the experiments, and a pump efficiency of 0.85, the electric power demand per kg of precipitated lignin was 1.31 kJ using Eq(1). A summary of the results is presented in Table 2. It seems evident, that the pre-concentration step via nanofiltration seems to be the better option of pre-concentration. The energy and chemical demand is significantly lower in our simulation. On the other hand, the evaporation unit utilizes thermal energy, which might result in an economically more feasible process, depending on how much additional energy is needed to provide the vacuum, which was not considered yet. Depending on the energy and chemicals cost, finding the most feasible process is an optimization task to be taken on in future studies.

Table 2: Process simulation results

Process case	Base case, no pre-concentration	Vacuum assisted evaporation	Nanofiltration
Lignin concentration at precipitation inlet (g/kg)	10.7	13.1	15.1
Ethanol concentration at precipitation inlet (%w)	58.0	53.0	58.0
Heat demand for evaporation per kg lignin (kJ)		37.5	
El. power demand per kg lignin (kJ)			1.31
Sulphuric acid use (g/kg lignin)	96.6	79.8	69.2

4. Conclusions

The comparison of different options to do or not to do pre-concentration prior to lignin precipitation in an ethanol organosolv process shows mainly that chemical use can be significantly reduced. In terms of energy demand, finding the optimum between energy form, availability and cost will be crucial for the feasibility of the product lignin.

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