

## Analysis of the Performance of Membrane Ultrafiltration in the Biorefinery by Aspen Plus<sup>®</sup> Simulation

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The liquid fraction obtained from the alkaline fractionation of apple tree pruning was treated in a laboratory scale ultrafiltration plant with different cut-off membranes. The obtained fractions were analyzed and the lignin content was chemically characterized to evaluate the purity of the samples. Furthermore, the system pressure drops were measured (valve, membranes and pipes pressure drops) in order to simulate the system using Aspen Plus<sup>®</sup> software and determine the energy consumption. For the estimation of the process economic viability, the system was scaled up and the ultrafiltration cost was evaluated. As a conclusion, it could be stated that the UF process allowed the efficient concentration of the liquid fraction and its fractionation for the lignin separation. The chemical composition of the fractionated lignin samples, especially the lowest molecular size fraction, revealed very little contamination indicating the lignin suitability for higher added value applications, which could support the slightly higher price of the obtained lignin in comparison to the commercial lignin one.

### 1. Introduction

Separation technologies, for the recovery and purification of products, are key stages in any production process, but especially in the biorefinery, where the recovery of products results fundamental for the appropriate exploitation of lignocellulosic components. Separation processes are usually size and cost-intensive stages, clearly susceptible to be improved by the process intensification (PI) principles application (Reay, 2008). The membrane technology is an interesting process easily implementable at industrial scale that has the potential to accomplish the selective and efficient transport of specific components (increasing selectivity and purity) (Pal et al., 2012). UF technology has been widely investigated within biorefinery processes for the separation and purification of different products (Hellstén et al., 2013) as well as for process stream concentration (Jönsson and Wallberg, 2009). For the industrial implementation of the membrane technology as a separation and purification stage, it is very important to evaluate the technology performance (energy efficiency, separation capacity, selectivity and capital investment). For this purpose, the simulation of the process is a very helpful tool for the establishment of the system energy consumption and the process scale-up (García et al., 2013).

In this study, the liquid fraction obtained from the alkaline (soda) fractionation of apple tree pruning was treated in a laboratory scale ultrafiltration plant. The obtained fractions were analyzed (yields and composition) and the lignin content was chemically characterized in terms of inorganic matter, acid insoluble lignin, acid soluble lignin, glucose, xylose and arabinose contents with the aim of evaluating the purity of the samples. Right after, the process was characterized in terms of system pressure drops (valve, membranes and pipes pressure drops) and liquid flows to carry out a simulation using Aspen Plus<sup>®</sup> software. Several user defined modules were developed to define the membranes performance and, once the simulation was correctly established, the process energy requirements were calculated. Finally, in order to obtain an estimation of the process economic viability, the system was scaled up and the ultrafiltration costs were evaluated.

## 2. Materials and methods

### 2.1 The UF laboratory plant

A set of four tubular multichannel (7 channels of 2 mm of hydraulic diameter each) ceramic membranes (external diameter: 10 mm, length: 250 mm, transfer area/ membrane: 110 cm<sup>2</sup>) of different molecular weight cut-offs, MWCO (5, 15, 50, 300 kDa) manufactured by Industrial Biotech Membranes, Germany was used during the experiments. The UF equipment used was a Pall Membralox XLab5 pilot unit equipped with a 3 L 316L stainless steel tank, with a water jacket for temperature control, a progressing cavity pump (PCM, France) and a control valve (Saunders diaphragm valve) for the adjustment of the UF system pressure drop. The maximum operating pressure in the UF circuit was 4 bar. For the simulation study, it was necessary to characterize the experimental process, including flows, general system pressure drops, pressure drops associated to the membranes, to the valve (at different opening percentages), permeate flows with different membranes, etc.

### 2.2 The raw liquid fraction

The alkaline liquid fraction was carried out in an atmospheric glass reactor with 7.5 % NaOH w/w aqueous solution as solvent at 90 °C, during 90 min, with a solid to liquid ratio (S/L) of 1:10. After reaction, the solid and liquid fractions were separated by simple filtration and the liquid fraction, named AS (apple pruning-soda), was physico-chemically characterized determining pH, density, total dissolved solids (TDS), inorganic matter (IM), organic matter (OM) and lignin (LIG) (González Alriols et al., 2010). The AS liquid fraction was first ultrafiltrated with the 300 kDa ceramic membrane for mayor impurities removal. The resulting permeate, AS-UFp300, containing the UF rejected dissolved compounds, was then passed through the 50 kDa MWCO membrane. The generated retentate (liquid fraction with particle sizes smaller than 300 kDa and bigger than 50 kDa), AS-UF300, was collected and the corresponding permeate (AS-UFp50) was fed to the 15 kDa membrane, obtaining the retentate with particle sizes smaller than 50 kDa and bigger than 15 kDa (AS-UF50 sample) and the permeate (AS-UFp15) that was finally treated in the 5kDa membrane and gave the 15-5 kDa retentate (AS-UF15 sample) and 5 kDa permeate (AS-UFp5 sample). The UF experiment temperature was kept constant at 50 °C. In all experiments, the permeate yield respect to the initial sample volume for each used membrane was determined. All the collected samples (permeates, retentates and initial liquid fractions) were characterized (TDS, IM, OM and LIG contents, pH and density).

### 2.3 Physicochemical characterization of UF lignin samples

For a better evaluation of the UF process success, the purifying performance of the membrane technology was studied in terms of the composition and purity of the UF resulting lignin fractions. For this purpose, lignin samples (AS-L, AS-UF300L, AS-UF50L and AS-UF15L) precipitated from the resulting liquid fractions were characterized determining the chemical composition. Ash and moisture contents were thermogravimetrically quantified by TGA/DTG analysis. The acid insoluble and soluble fraction and sugars contents were determined on the basis of the work of Gosselink et al. (2004). Mono- and polysaccharides concentration in the obtained filtrate was measured by HPLC following a HPLC technique similar to the described in the NREL protocol (Sluiter et al., 2004).

## 3. Process definition in Aspen Plus®

### 3.1 Components definition

The chemical structure and physicochemical properties of cellulose, lignin and hemicelluloses were defined using data presented by the NREL (National Renewable Energy Laboratory, reference number BF521004). Regarding the thermodynamic model, ELECT-NRTL (non-random, two liquids) model was selected due to the presence of electrolytes generated in the dissociation of soda in the presence of water.

### 3.2 Simulation modules

The simulation process was established with the aim of calculating the energy requirements of the UF equipment by the evaluation of the pressure drop of the simulated UF system. For this purpose, the experimental equipment was defined in Aspen Plus® using different modules. The thickness of the pipes was 2.5 mm and the material stainless steel 316L. Straight pipe sections of the UF equipment were simulated with the PIPE module of Aspen Plus® that allows to specify diverse parameters (material, pipe section, length, inclination, roughness, inner diameter, join type ...). Using this data, the program calculates the friction losses associated to each defined section. To represent elbow sections, modified PIPE module was used specifying a fluid direction change of 90°. A MIXER module was used to represent the deposit of the UF equipment. The liquid fraction (with a defined composition, flow and present phases) is fed to this unit at a specified pressure and temperature. The control valve of the UF experimental plant

was simulated as a VALVE module, specified by its operation opening percentage. Different valve parameters were also defined: the experimentally determined correlation between valve opening and valve coefficient  $C_v$ , the pressure drop ratio factor  $x_T$  and the pressure recovery factor  $F_L$  (assumed values of 0.6 and 0.7, respectively, according to literature (Nesbitt, 2011)). For the simulation of the pump a PUMP module was used in Aspen Plus, specifying a standard efficiency of 0.85 and using a performance curve to determine discharge conditions. The curve was defined by tabular experimental data, previously determined, specifying the measured pressure change across the pump for different studied flows. A combined SEPARATOR-PIPE module was used to represent the UF membranes for the simulation. For each used membrane cut-off, several characterized operating parameters were defined. In the SEPARATOR module, permeate/retentate flows and component split ratios were defined, whereas in PIPE module experimentally determined friction losses were used for represent membranes pressure drop.

## 4. Results and discussion

### 4.1 Results of the experimental UF process of the alkaline black liquor

Table 1 and Figure 1 show the results in terms of composition of the raw liquid fractions, permeates and retentates obtained by the applied UF processes. No clear differences were observed between pH and density values respect to the raw liquid fraction. As the UF processes enable the separation of different molecular size components (Menon and Rao, 2012), it would have been expected that the retention of certain acidic species (as low molecular weight lignin) would led on the obtaining of lower pH values permeates, but this parameter remained considerably constant indicating that the separation was not as strong as to influence the acidity of the media. The TDS content of the obtained permeates gradually increased as the membrane pore size was larger (from 9.48 to 12.87 %). This trend was also observed in the OM percentages. Nevertheless, small differences in the inorganic matter content of the analyzed liquid samples were detected, which varied in the range of  $8.47 \pm 1.05$  %. This fact was also observed by Jönsson (Jönsson et al., 2008) that found that the retention of the main inorganic elements during UF of kraft cooking liquor was very low regardless of the membrane cut-off, due to their small size. Similar results were observed for the lignin contents of the obtained liquid fractions.

Figure 1 displays the volume recovery ratio (%) in each UF, i.e. the percentage of permeate recovered respect to the processed liquid in the different steps. As observed, the collected permeate volume decreased as the membrane cut-off was smaller. When 300 kDa membrane was used, the 91 % of the original black liquor was recovered as permeate. Subsequently, with the UF performed with 50 kDa membrane, the 65 % of the 300 kDa permeate was recovered. Similarly, a recovery of 22 % and 10 % were achieved with 15 and 5 kDa membranes, respectively. Since the pump flow and process temperature were kept constant during the two experiments, the fact of obtaining less permeate volume at lower MWCO could be associated to the inherent resistance of the liquors to be ultrafiltrated. In this sense, it was clear that greater permeate recovery rates could be achieved by applying specific operating conditions for each membrane, e.g. by increasing the liquid fraction feed flow rate or the temperature and pressure during the UF process (Jönsson et al., 2008).

*Table 1: Results of the physicochemical characterization of the analyzed liquid fractions (raw liquor, retentates from UF with membranes of 300, 50, 15 and 5 of MWCO and permeate resulted from UF with 5 kDa membrane)*

Sample	Fraction	pH	Density (g/mL)	TDS (%)	IM (%)	OM (%)	LIG (g/L)
AS	Raw liquor	12.39±0.05	1.066±0.081	14.3±0.8	8.47±0.08	5.81±0.91	4.4±0.2
AS-UF300	<300 >50 kDa	12.37±0.04	1.047±0.061	12.9±0.2	7.91±0.07	5.11±0.24	1.1±0.2
AS-UF50	<50 >15 kDa	12.37±0.03	1.054±0.045	11.9±0.4	7.42±0.15	3.96±0.40	0.8±0.1
AS-UF15	<15 >5 kDa	12.50±0.02	1.048±0.048	11.2±1.0	7.69±0.07	3.26±0.93	0.6±0.1
AS-UF5	< 5 kDa	12.31±0.02	1.053±0.032	9.48±0.31	7.65±0.04	1.83±0.30	0.7±0.2
AS	Raw liquor	12.39±0.05	1.066±0.081	14.3±0.8	8.47±0.08	5.81±0.91	4.4±0.2

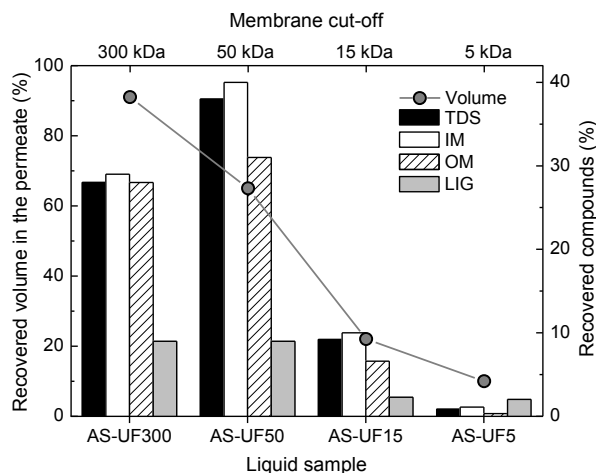


Figure 1: Results of the applied UF processes: percentage of collected volume of permeate after each UF experiment (referred to the liquor fed to each UF step) and recovery of components in the resulted permeates (referred to the initial raw liquor)

Figure 1 displays as well the component recovery ratios in the resulting liquid fractions. In general, the collection yield of the substances dissolved in the liquid fraction was directly related to the obtained liquid fraction volume. Thus, the recovered amounts of TDS, OM and IM resulted higher for greatest MWCO membranes (300 and 50 kDa). The highest compound recovery ratios corresponded to AS-UF300 and AS-UF50 fractions, which contained 28 % and 38 % of the initial TDS content, 29 % and 40 % of initial IM content, 28 % and 31 % of initial OM content, respectively. Regarding to the lignin recovery, both AS-UF300 and AS-UF50 liquid samples contained 9 % of the lignin contained in the initial raw liquors, whereas only 2.3 % and 2.0 % of lignin was recovered in AS-UF15 and AS-UF5 fractions, respectively, leading to a clear fractionation of this component. Thus, the applied UF process resulted effective in terms of fractionation extent, obtaining less polydisperse lignins. Nevertheless, low lignin quantity was obtained in the smaller cut-off fractions and the majority of the lignin was recovered in AS-UF300 and AS-UF50 fractions. Therefore, according to the obtained results, it could be stated that UF process allowed the efficient concentration of the liquid fraction besides the fractionation of liquid fractions for lignin separation. Table 2 presents the lignin samples chemical composition results. The fractionation processes significantly influenced the composition of the lignin samples, particularly referred to the acid insoluble lignin and carbohydrates contents. The purity of the samples, i.e. the sum of acid insoluble and soluble lignin contents (AIL and ASL, respectively), resulted quite variable, ranging from 27.7 % to 84.2 % w/w of the dry sample. The ASL contents of the analyzed samples, corresponding to the lignin fraction that results more easily removable by simple water or weak acid- washing, ranged from 1.72 to 2.21 % w/w, being in agreement with those found by other authors (Buranov et al., 2010). The hemicelluloses content (sum of GLU, XYL and ARA contents) found in the smaller molecular size fractions was 3.1 %, which means that low polysaccharides contamination was associated to these lignins. Thus, it could be said that the AIL fraction of apple tree pruning alkaline samples was improved after the ultrafiltration process, especially, less sugar and ash contaminated lignin samples were obtained when low cut-offs were used. The obtained results are in concordance with others published in the literature (Jönsson et al., 2008) confirming the purifying effect of the membrane technology.

#### 4.2 UF process simulation results

The simulation using Aspen Plus<sup>®</sup> software of the mentioned process was carried out with the aim of evaluating the energy consumption associated to the membranes and the economic viability of the technique. The density and viscosity of the liquid fractions was defined as the average value, 1.055 g/cm<sup>3</sup> and 0.009 g/cm. Table 3 presents the pressure drop results obtained by simulation and the

Table 2: Chemical composition (inorganic matter IM, acid insoluble lignin AIL, acid soluble lignin ASL, glucose GLU, xylose XYL and arabinose ARA, in % w/w dry basis) of the lignins obtained from raw liquor and different ultrafiltered liquid fractions

Sample	IM	AIL	ASL	GLU	XYL	ARA
AS	47.1±0.9	21.8 ±0.65	1.75 ±0.03	2.24±0.06	20.9±0.21	2.55±0.05
AS-UF300L	37.5±0.6	25.5 ±0.73	2.21 ±0.06	2.27±0.09	20.6±0.10	1.04±0.02
AS-UF50L	12.5±0.7	78.7 ±0.52	1.72±0.04	1.71±0.06	1.61±0.06	0.23±0.07
AS-UF15L	9.12±0.5	82.4 ±0.31	1.81±0.05	2.03±0.08	0.77±0.03	0.30±0.08

Table 3: Simulated and experimental pressure drop comparison

Pump capacity (%)	F total (cm <sup>2</sup> /s <sup>2</sup> )	Simulated ΔP (Pa)	Simulated ΔP (bar)	Experimental ΔP (bar)
2	36,348	3624	0.04	-
3	56,526	5636	0.06	-
4	152,311	15,186	0.15	0.18
5	245,845	24,512	0.24	0.28
6	3,341,225	33,314	0.33	0.35
7	502,633	50,116	0.49	0.47
8	650,720	64,882	0.64	0.61
9	793,367	79,105	0.78	0.74
10	795,440	79,311	0.78	-

Table 4: Assumptions for cost estimates and the calculated cost estimates for the ultrafiltration process

Assumptions for cost estimates				Cost estimates		
Parameter	Value	1.	Units	Parameter	Value	Units
Investment cost	3,300	€ / m <sup>2</sup>	memb. area	Investment cost	122,500	€
Annuity factor	0.1			Capital cost	12,250	€ / y
Membrane cost	1,000	€ / m <sup>2</sup>		Electricity cost	270	€ / y
Membrane lifetime	6	years		Memb. replacement cost	650	€ / y
Pump efficiency	0.82			Cleaning cost	1,960	€ / y
Cleaning cost	50	€ / m <sup>2</sup>		Maintenance cost	650	€ / y
Maintenance cost	5	% cap. cost / y		Operating costs	3,530	€ / y
Operating time	8,000	h / y		Total costs	15,780	€ / y
Membrane area	33	m <sup>2</sup>		Lignin production	350	t / y
Electricity price	0.04	€ / kWh		Production cost	45	€ / t of lignin
Electricity consum.	0.13	kWh				

ones measured for the experimental system. The results are quite similar, indicating that the simulation units were successfully designed to represent the pressure drops related to the ultrafiltration system, which would allow the estimation of the costs associated to the purification process and the evaluation of its profitability.

The cost estimation of the simulated ultrafiltration process (Table 4) was calculated considering the electricity consumption calculated by Aspen Plus<sup>®</sup>, the efficiency of the pump that was estimated and some assumptions reported by other authors (Jönsson and Wallberg, 2009). In order to obtain an approximation of the costs associated to the process at industrial scale, the system was scaled up and a liquid flow of 2,000 L/h were considered. Supposing an average flux of 58 L/m<sup>2</sup> h, a total membrane area of 33 m<sup>2</sup> was estimated. The costs associated to these assumptions are presented as well in Table 4. As a result, a total cost of 15.78 k€ / y was obtained, which implied a production cost of the lignin fractions of 45 € / t of product. This value is higher than the kraft lignin one (Jönsson and Wallberg, 2009), (33 € / t of lignin) but lower than the organosolv lignin one (González Alriols et al., 2010), (52 € / ton of lignin). Considering the purity of the samples, especially those of the smallest particle size fraction, the found price was considered acceptable.

## 5. Conclusions

The concentration of the processed streams was achieved by ultrafiltration, demonstrating that membrane technology could replace the evaporation operation (used in P&P mills), which generally results cost-intensive. In addition, a clear fractionation of the dissolved components was found, particularly of the broadly size distributed lignin. The chemical composition of the lignin samples, especially the lowest molecular size fraction one, was quite pure. In this sense, this technology could provide different liquid fractions, with narrower and well defined molecular weights components, considered as higher added

value biorefinery products. The final price calculated for the lignin was considered acceptable and the interest of the intensification process was confirmed.

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