

# Fractionation of Spent Sulphite Liquor into Monomeric Sugars and Lignosulphonates by an Ultrafiltration Series System

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Spent sulphite liquor (SSL) is the main byproduct of acid sulphite pulping. Its main components are lignosulphonates (LS) and monomeric sugars. SSL is typically intended as binder, emulsifier or additive in concretes due to its high amount of LS. Sugars can be converted into high value-added products such as xylitol, PHB or biofuels among others; by means of fermentation processes. However, a separation step to remove the compounds that can act as fermentation inhibitors, as LS, is needed.

Membrane technology allows the separation of sugars and LS from the SSL because of their different size of molecular weight. In the present study, ceramic membranes with different cut-offs (15 kDa, 5 kDa and 1 kDa) were used. 15 kDa membrane offered the best results according to LS concentration in the retentate stream, 5 kDa membrane the highest LS removal in permeate stream, and 1 kDa membrane the minimum sugar losses in the permeate stream. Because of this, the combination of the three membranes in a series system was proposed. In this way, an increase in LS removal in the final permeate was achieved (72.78 %), but also an increase in the sugar losses (26.80 %). Hence, further studies will determine the optimal configuration system of this process.

## 1. Introduction

The traditional Pulp and Paper industry (P&P) is going through a current difficult situation due to economic and environmental constraints. The emerging trend in the production of bio-based products can offer a great option to transform these traditional factories into innovative multiproduct biorefineries (Lundberg et al., 2013).

Woody biomass is used as raw material in these industries, which is composed by three major components: cellulose (41 - 49 %), hemicellulose (23 - 34 %) and lignin (20 - 31 %). The traditional portfolio of this kind of industry is focused on the cellulose platform neglecting, in large part, the options that both hemicelluloses and lignin could offer (Christopher, 2013)

Dissolving pulp, a high purity pulp, is one of the main products that can be obtained in the P&P industry. It is composed by a high  $\alpha$ -cellulose content (95 - 98 %) and relatively low hemicellulose (1 - 10 %) and lignin (<0.05 %) content, which is used for the production of specialty cellulose derivatives such as cellulose acetate, cellulose nitrate, viscose, rayon and many others. Two main chemical processes are used to manufacture dissolving pulp: prehydrolysis Kraft (PHK) or acid sulphite pulping.

The pulping with usual sulphite process is carried out at high temperature (135 - 140 °C) under acidic conditions (pH: 1.2 - 1.5) using a cooking liquor that contains sulphite and bisulphite acids, produced by the mixture of sulphur dioxide (SO<sub>2</sub>) and an alkali. A large portion of the lignin and the majority of the hemicellulose in the wood are dissolved into the cooking liquor during the process (Rueda et al., 2015). Spent sulphite liquor (SSL) is the main byproduct of this process and, after its concentration by evaporation, is commercialised because of its high amount of lignosulphonates (LS). Despite the exact

structure of LS has not been elucidated, LS can be defined as a tridimensional polyelectrolytic macromolecule, composed by phenylpropane units with a high amount of ionic groups. Because of the coexistence of hydrophilic and hydrophobic groups, LS usually are used in different applications due to their high surface activity, such as dispersants for concrete, pesticides, etc. (Li et al., 2014). But recently, some studies have been published based on some innovative applications for intending LS. For example, as precursors for carbon fibres or as plywood adhesives, replacing phenol from petrol (Holladay et al., 2007).

Nonetheless, besides the LS, SSL contains other interesting compounds like monomeric sugars. In comparison to Kraft pulping, acid sulphite pulping not only dissolves hemicelluloses, but also reduces them until their monomeric structure in the spent liquors. Hence, these monomeric sugars are able to be transformed by means of fermentation processes into high value-added products such as xylitol, polyhydroxybutyrates (PHB's) and many others (Rueda et al., 2014). However, the fermentation of these sugars can be damaged by the inhibitor action induced mainly by the phenolic groups from LS. Therefore, a detoxification stage, with which sugars would be separated from LS, is needed to achieve a proper yield during the sugars transformation (Ajao et al., 2015).

Many techniques have been studied for this type of processes, among which, the membrane processes play a remarkable role because of their advantages base on their physical and chemical stability, reproducible performance, selectivity and high surface area per unit volume (Alriols et al., 2014). Mainly, the membrane processes in P&P industries have been applied to the treatment of wastewater streams, in which the spent liquors have traditionally been intended as energy supplier and burned base on their high carbon content (Pizzichini et al., 2005). In an ordinary membrane process as the ultrafiltration, the separation is based on the different molecular size of the solutes that have to be separated. In this case, ultrafiltration adjusts to the requirements because of the different molecular size that exists between LS (from 200 g/mol up to 250,000 g/mol) and monomeric sugars (150 - 180 g/mol) (Restolho et al., 2009).

In this study, the fractionation of the spent sulphite liquor from acid sulphite pulping was carried out by an ultrafiltration process. A pilot-scale equipment was used to achieve the LS concentration and the fermentable sugars purification. Ceramic membranes of different pore sizes were tested for this purpose. The aim of this study was not only the purification of the monomeric sugars contained in SSL, but also the LS concentration, since they are the most plentiful components in the SSL. Hence, LS concentration also was considered as an important issue to facilitate their valorisation. To improve the performance of the separation process, sequential systems were also proposed.

## 2. Materials and methods

### 2.1 Raw material and equipment

SSL was supplied by Sniace S.A. (Torrelavega, Spain), an industry whose pulping process is based on the acid sulphite process. The SSL was pretreated in two steps. First, a dilution was carried out to reduce the viscosity of the stream and then, a filtration with cellulose filters of 0.45  $\mu\text{m}$  was conducted to remove the suspended solids.

The physico-chemical properties of the industrial SSL and the pretreated SSL are reported in Table 1.

The ultrafiltration equipment used in this study was a pilot unit (Pall Membralox XLab5), composed by a 3 L feed stainless tank with water jacket for temperature control, a diaphragm pump and the membrane module. Three ceramic membranes were used in this study with different cut-offs (15, 5 and 1 kDa) manufactured by IBMEM (Industrial Biotech Membranes, Germany). The membranes are made of  $\text{TiO}_2$ , in multichannel shape. The external and hydraulic diameters of the membranes were, 10 and 2 mm; the length was 250 mm and the surface area of each membrane was 110  $\text{cm}^2$ .

Table 1: Physico-chemical properties of industrial SSL and pretreated SSL

Parameter	Industrial SSL*	Pretreated SSL
Density (g/L)	1,300 $\pm$ 35.1	1,029 $\pm$ 15.2
Viscosity ( $\text{mm}^2/\text{s}$ )	296 $\pm$ 382	1.02 $\pm$ 0.011
pH	2.35 $\pm$ 0.51	3.30 $\pm$ 0.02
Dry matter (%)	58.5 $\pm$ 5.01	7.23 $\pm$ 0.42
Inorganic matter (%)	416 $\pm$ 55.3	41.1 $\pm$ 3.05
Lignosulphonates (g/L)	138 $\pm$ 37.35	23.31 $\pm$ 1.37
Monomeric sugars (g/L)	0.20 $\pm$ 0.05	0.0039 $\pm$ 0.004
Furfural (g/L)	8.01 $\pm$ 1.42	0.25 $\pm$ 0.27
Acetic acid (g/L)	12.5 $\pm$ 4.03	1.39 $\pm$ 0.71

\*Rueda et al., 2014

## 2.2 Experimental set up

The experiments were performed at constant temperature of 20 °C, controlled by means of the water circulation in the jacket of the feed tank. The transmembrane pressure, the driving force of the process, are created by the pump and controlled, around 180 - 200 kPa, with valves. The feed flow was established in 650 - 690 L/h.

The methodology of the ultrafiltration experiments is described in the schematic representation showed in Figure 1. The permeate stream was withdrawn of the system to the permeate tank, while the retentate stream was whole recirculated to the feed tank.

A strict cleaning procedure was applied after each experiment to the membrane, according to the method described by Colyar et al. (2009), that consisted in three steps: 1) Rinsing with distillate water for 30 min. 2) Cleaning with 0.1 N NaOH for 30 min. 3) Final rinsing for neutralising the membrane pH with distillate water.

## 2.3 Analytical methods

Dry matter content was determined gravimetrically after 24 h in a Selecta Stove at 105 °C. Ashes or inorganic matter were measured following Tappi 211 om-02 using a Selecta furnace.

The pH was measured by a Crison Kit 2012T pH-meter with 5012T electrode. Density was measured gravimetrically and viscosity by means of a Werner (Proton) viscometer in bath at 25 °C.

Monomeric sugars (glucose, xylose, arabinose, galactose and mannose), were measured by HPLC using CHO782 Pb Form Carbo & Biomass Analysis SS 300 mm x 7.8 mm column and refraction index detector according to Llano et al. (2013) method using 0.3 mL/min of ultrapure water as a mobile phase and 68 °C in the oven.

LS content were obtained following the standard UNE-EN 16109. First, a solution was prepared taking 0.15-0.2 grams of dry sample in a volume of 250 mL. From this solution, a dilution (3:100) was made (B) and adjusting to pH 4.0-5.0. UV-Vis Perkin Elmer Lambda 25 Spectrophotometer was used to measure the absorbance of the samples. LS content was measured from B solution at 232.5 nm of wavelength.

Resulting streams of membrane processes were subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate the average molecular weight (MW) of the solutes and also their molecular weight distribution (MWD), employing a JASCO instrument equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031Plus). Two PolarGel-M columns (300 x 7.5 mm) and PolarGel-M guard (50 x 7.5 mm) were employed. The flow rate was 0.7 mL/min and the analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

## 3. Ultrafiltration results.

### 3.1 Individual membrane assessment

Regarding the previously described process, membranes of 15 kDa, 5 kDa and 1 kDa, were tested for the SSL fractionation. The average permeate flux for each membrane was 55.45, 5.77 and 6.00 L/m<sup>2</sup>·h. Parameters related to the efficacy of the separation are represented in Table 2.

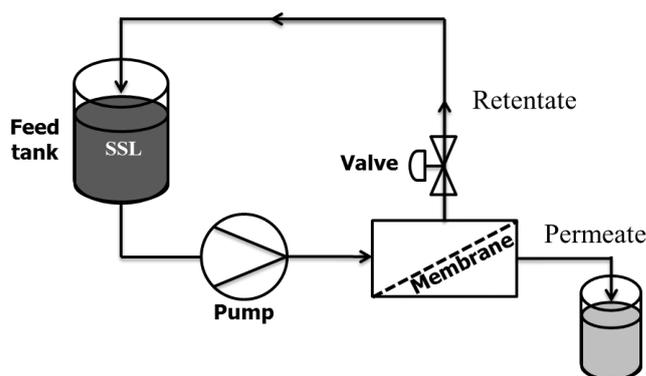


Figure 1: Schematic flowsheet of the ultrafiltration experiments.

Table 2: Composition of the streams produced with the membrane separation (monomeric sugars an LS contents, and average molecular weight (MW) and polydispersity (MWD) of the streams).

Pore size	Stream	Sugars (g/L)	LS (g/L)	MW (g/mol)	MWD
15 kDa	Initial	25.78	44.25	3,963	7.02
	Permeate	21.16	24.49	1,850	4.23
	Retentate	29.22	96.87	7,394	8.20
5 kDa	Initial	23.03	39.87	4,297	7.48
	Permeate	20.07	13.70	899	2.67
	Retentate	25.07	63.69	5,410	7.27
1 kDa	Initial	14.73	40.67	4,466	8.27
	Permeate	15.72	22.10	411	3.99
	Retentate	13.98	44.22	8,652	3.05

According to the sugars content during the ultrafiltration process, an unexpected fact occurred both in 15 kDa and 5 kDa membranes, since the sugars content in the permeate was lower than in the retentate streams. Monomeric sugars have a lower size than the pores of the membrane, hence, these sugars should have crossed the membrane towards the permeate stream, becoming this stream richer in these components. However, the opposite phenomenon occurred with these membranes. The reason of this fact was due to the additional resistance created by the LS rejection, which formed a gel layer in the proximity of the membrane when they were rejected. Thus, 1 kDa membrane offered the best conditions for the sugars purification due to the increase of 6.72 % in the concentration of the permeate stream. Conversely, the sugars losses with 15 kDa and 5 kDa were 17.92 % and 12.85 %.

Turning to LS separation, the reported results showed a proper separation for all the membranes, since every membrane presented a great reduction of LS in the permeate streams. The rejection value for LS was 44.66 %, 65.64 % and 45.66 %. Therefore, the membrane with best performance, according the LS rejection, was the 5 kDa membrane, whose level of the rejection was quite higher (around 20 %) than the other ones. Remembering that not only the sugar purification in the permeate stream was aimed, but also the LS concentration. In this sense, 15 kDa membrane offered the highest potential to concentrate the LS in the retentate stream with an increase in the concentration of 118.92 % with regard to the initial concentration. While in the 5 kDa and the 1 kDa membranes, the concentration of the LS reached 59.75 % and 8.73 %.

Furthermore, the molecular weight distribution of the involved streams during the separation process was studied. From Table 2, it can be observed that the MW of the permeate stream was significantly lower than those of the retentate streams, fact that confirmed the barrier effect of the membranes in function of the size of the solutes. In addition, this reduction was much sharper for the membrane with smallest pore size, being this parameter reduced until 411 g/mol in 1 kDa membrane, value quite smaller than the initial one (4,466). In contrast to the permeate streams, the MW was increased in the retentate streams, demonstrating that these streams were enriched in LS, the highest solute in the SSL.

On the other hand, the MWD was represented to know the homogeneity of the streams. According to the showed results in Table 2, this parameter was substantially reduced in the permeate streams in comparison with the initial liquor. This fact is predominant in the membrane processes since the fractionation is based on the molecular weight of the solutes. However, in the retentate streams the MWD barely varied. Thus demonstrated that the LS, components in which these streams were enriched, present a wide range of molecular weight in line with others authors (Bhattacharya et al., 2005).

With respect to the obtained results, each membrane presented more advantages than the rest depending on the studied parameter. Hence, the combination of these membranes was proposed to improve the performance of the separation process.

### 3.2 Series system of ultrafiltration.

Using the available membranes, a series system consisting in three stages was studied, where retentate streams were withdrawn of the system and the permeate streams were driven to the next stage.

In this system, a total of four streams were obtained, whose compositions are shown in Table 3.

The aim was to produce a final permeate stream with the highest purity in sugars, i. e., a stream with the minimum content in LS as possible and without accumulating a severe sugar loss. On the other hand, the rest of the streams would be valorised based on its predominant components. Besides their composition, the MW and MWD of each stream are also shown.

Table 3: Characteristics of the resulting streams from the series system (monomeric sugars and LS contents, and average molecular weight (MW) and polydispersity (MWD)).

Stream	Sugars (g/L)	LS (g/L)	MW (g/mol)	MWD
Initial	25.78	44.25	3,963	7,02
> 15 kDa	29.21	96.87	7,394	8,20
> 5 kDa	23.49	37.89	2,816	4,89
> 1 kDa	19.67	16.76	1,278	3,40
< 1 kDa	18.87	12.14	889	2,71

As in the previous section, in the first stage, the sugar concentration was increased in the retentate stream with regard to the initial concentration. The purified stream (" $<1$  kDa") showed a proper sugar concentration, with a global loss of 26.78 %. This value is higher than the losses obtained with the processes formed by only one membrane. However, the LS removal in this stream was upper than the obtained using processes with one membrane, with a total rejection of 72.56 %.

It was observed that the first retentate (" $>15$  kDa") was the unique stream whose concentration in LS was increased with regard to the SSL. Furthermore, its MW was significantly increased with regard to the initial SSL, which demonstrates that this stream was quite enriched in LS, components with the highest molecular weight. According to the intermediate stream, the composition of the " $> 5$  kDa" stream presented similarities to SSL in sugars and LS concentration, nevertheless, the MW and MWD decreased. Therefore, this stream was concentrated in the fraction of low molecular weight LS, remaining the fraction of high molecular weight LS in the first retentate stream (" $>15$  kDa"). The " $>1$  kDa" stream obtained a low concentration of LS without great loss of sugars. Thus, even this stream could be intended as sugar enriched stream. This fact indicated that the last stage barely caused impact on the process, with a rejection factor lower than in the previous stages. In Figure 3, the rejection factors for sugars and LS for each stage were represented to assess the impact of each membrane on the global process.

Referred to the LS rejection, the first stage (15 kDa membrane) offered the highest rejection factor (44.26 %), more than the 50 % of the global factor (72.56 %), the second stage (5 kDa membrane) 33.78 % and the last stage (1 kDa membrane) 25.12 %. Regarding sugars rejection, at the first stage 17.93 % sugars were rejected, 5.67 % in the second one, and 5.42 % at the last one. Thus, the rejection factors were decreased for the subsequent stages and, besides this, the real impact over the global process was lower than these indicated percentages. This fact, can be observed in the accumulate rejection represented in Figure 3.

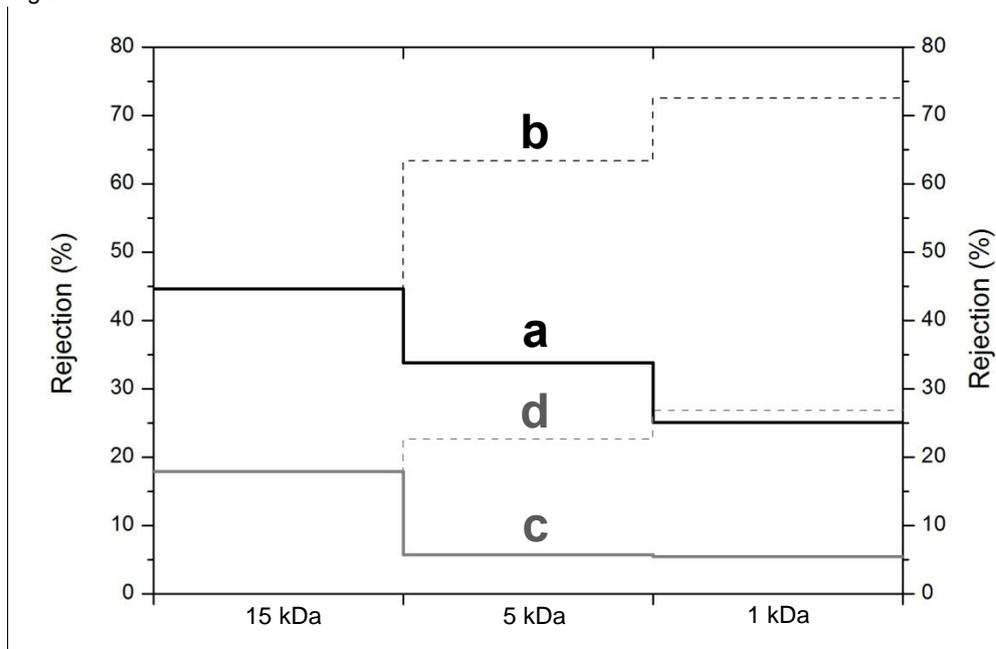


Figure 3: Evolution of the membrane rejection in each stage of the process ((a) LS rejection; (b) LS accumulate rejection; (c) sugars rejection; and (d) sugars accumulate rejection).

#### 4. Conclusions

The fractionation of the SSL into its main components (monomeric sugars and LS) was carried out by an ultrafiltration pilot-plant. Three ceramic membranes were tested (15kDa, 5 kDa and 1kDa). Each one presented advantages over the rest, depending on the studied parameter. 1 kDa membrane offered the minimum sugar rejection (the concentration increased in 6.72 %); 5 kDa membrane, the highest LS rejection (65.68 %); and 15 kDa membrane, the maximum concentration factor in LS in the retentate stream (118.92 %). Because of that, a series system, with the three membranes, was proposed. In this way, the total LS rejection increased up to 72.56 %, but also the sugar loss (26.78 %). Hence, the assessment of the global process according to the chemical characterisation of the resulting streams to evaluate their valorisation options and the economical study would be needed to determine the optimum combination for the separation process.

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