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Spent sulphite liquor fractionation into lignosulphonates and fermentable sugars by ultrafiltration

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ABSTRACT

Lignosulphonates (LS) and fermentable sugars are the main components of spent sulphite liquors (SSL) produced in acid sulphite pulping. Ultrafiltration (UF) technology allows the separation of these components from the SSL due to their different molecular size. In the present study, ceramic membranes with different cutoffs (15, 5 and 1 kDa) were used. The membranes were evaluated according to not only their efficiency parameters, but also their efficacy of separation as well as their physico-chemical properties. Each membrane offered the best conditions in function of the studied parameter. Hence, different membrane series systems were proposed. System 3 (15 and 5 kDa membranes) and System 4 (15, 5 and 1 kDa membranes) showed the best conditions taking into account all the studied parameters. The description in more detail of these systems was carried out to determine the possible potential of the resulting streams for their further valorisation by biorefinery processes.

1. Introduction

Currently, the future depletion of the fossil feedstock and the high dependence of the industries from these materials cause serious problems around the world. Biomass can be an option to substitute the fossil raw materials at the time of producing bioproducts within the biorefinery concept [1]. Biorefineries integrate biomass conversion processes and equipment for sustainable processing of biomass into a spectrum of value-added bio-based products, such as bioenergy and bioproducts (chemicals and materials). Nowadays, many studies are focused on biorefinery development to achieve a competitive level in the actual frame-market, led by oil-based products [2].

Pulp and paper industry (P&P) presents a quite potential to allow the integration of biorefinery units, adapting its traditional portfolio creating new bioproducts, energy and renewable materials and converting it into an Integrated Forest Biorefinery (IFBR) [3]. Considering the present economics, these new products should be derived from hemicelluloses and lignin, and not from cellulose, because the profits of cellulose derivatives are considered higher than the one of the bioproducts that could be manufactured by biorefinery processes, such as cellulosic ethanol and butanol [4].

Among the products that can be obtained from P&P industry, dissolving pulp is high purity pulp of cellulose. It 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: (i) prehydrolysis kraft, which involves a pre-extraction step of the hemicelluloses prior to the cooking stage; and (ii) the acid sulphite process, in which the digestion of the wood is carried out using a cooking liquor that contains sulphite and bisulphite acids, produced by the mixture of sulphur dioxide (SO_2) and an alkali [5].

The pulping in an usual sulphite process is carried out at high temperature (135–140 °C) under acidic conditions (pH: 1.2–1.5). A large portion of the lignin and the majority of the hemicellulose in the wood are dissolved into the cooking liquor during the process [6].

The main difference among SSL and black spent liquor is that during the sulphite pulping the hemicelluloses are hydrolysed up to their monomeric form as it was demonstrated by Llano et al. [7], while in the kraft method, the hemicelluloses are dissolved without undergoing a heavy fractionation; thus, they present a very high molecular weight [8].

Traditionally, SSL are concentrated by evaporation and finally dried by centrifugation. Therefore, no separation is produced regarding their dissolved components and they are commercialised as LS because of their high content in this component (55–70%) [9]. The principal use of these no-purified LS is as binder

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in concretes or as surfactant [10]. However, high amount of monomeric sugars (around 25–35% of the commercialised LS), that are also contained in the SSL from the hemicelluloses degradation, is not properly exploited, being integrated to the LS [9].

The monomeric sugars offer a large range of opportunities to convert them into high value-added bioproducts, e.g., as polyhydroxybutyrates (PHBs), succinic acid or xylitol, which can be obtained by fermentation process [11,12].

Hence, a separation of LS and monomeric sugars not only would allow the sugars valorisation, it would also let to obtain more purified LS that could open new alternatives of use in more innovative and value-added applications [13].

Prior to fermentation, a detoxification stage is necessary to remove the main yeast inhibitors present in the SSL (LS, phenolics, and others), in order to effectuate the valorisation of these sugars in a proper yield [14]. Many studies have been proposed for this separation, such as overliming adsorption among others [15,16]. However, the huge difference among the sizes of LS (1000–50,000 g/mol) [17] and fermentable sugars (150–180 g/mol) that exists in the SSL makes the membrane technology, whose principle of separation is based on the different sizes between solutes, a suitable technology for carrying out this separation.

UF has been traditionally applied to this type of separation; even being adopted by the industries. Borregaard Industries (Norway) possess the most important plant for LS concentration by UF since 1981. This plant allows producing a concentrate stream enriched in LS (approximately 95% of purity) with a low percentage of sugars and salts. High value-added products as vanillin can be obtained for this company from these LS after using an UF stage, demonstrating the benefits of this technique [18].

Although the membrane technology has been applied to LS purification since decades, the utilisation of membranes has been solely focused on the LS concentration. Some studies have been conducted by other authors for SSL fractionation [19,20]. The results in these previous studies vary significantly regarding LS rejection, e.g., from 59–63% [21] up to 85–92% [19,20]. In any case, the results depend on the liquor used as feedstock, since the composition and molecular weight distribution of the components within the liquor depend on the pulping process utilised.

However, the isolation of sugars from this stream for their further valorisation in high value-added products has not been considered until the recent years. Restolho et al. [22] carried out a SSL fractionation using the membrane technology, concretely UF and nanofiltration (NF). In UF stage retention of LS around 50–75% could be reached whereas in NF the best results were 68% of rejection of LS with only 3% of sugars rejection demonstrating that the separation of this type of liquor by means of this technology is feasible.

In any case, the previous studies have been developed taking into account the efficiency that could be achieved by UF technology to concentrate the LS or other lignins in order to study the feasibility of the scaling up of this technology in the P&P industries. Nevertheless, none of them has focused on the characteristics, properties, and structure of the different fractions of the obtained streams fractions.

In this study, fractionation of SSL from acid sulphite pulping process by UF treatment was carried out using ceramic membranes with different cutoffs (15 kDa, 5 kDa and 1 kDa). The pore sizes of the membranes were selected in consonance with the molecular weight of the LS as it was described above, and also based on the membranes used in other similar works [22,23]. The membrane separation in pilot-scale equipment was applied to achieve the LS concentration and the purification of the fermentable sugars contained in the SSL. Sequential systems were also tested with these membranes adopting several configurations. The membrane separation processes were not only evaluated taking into account the efficiency of the processes, but also the selectivity of the separation and the physico-chemical characteristics of the resulting streams after the treatment in order to establish the potential of each stream for their further valorisation by biorefinery methods into high valued-added compounds.

2. Materials and methods

2.1. Raw material and ultrafiltration equipment

Industrial SSL from acid sulphite pulping of *Eucalyptus globulus* were supplied by Sniace S.A. (Torrelavega, Spain) and used as raw material for this work. The samples were collected directly from the factory in different days; thus, a weak variation in the composition can appear.

The used UF equipment is a Pall Membralox XLab5 pilot unit, formed by 3L 316 stainless steel tank with water jacket for temperature control, recirculation diaphragm pump, a valve lash for the control of the pressure during the experimental procedure and a membrane module where the membrane is introduced.

Three membranes were used in this study with different cutoffs (15 kDa, 5 kDa and 1 kDa) manufactured by IBMEM (Industrial Biotech Membranes, Germany). The membranes were made of ceramic material (TiO_2), in multichannel shape. The external and hydraulic diameters of the membranes are 10 mm and 2 mm, respectively, while the length is 250 mm and the superficial area of each membrane is 110 cm^2.

2.2. Experimental procedure

Prior to the introduction of the SSL to the UF plant, a conditioning stage was needed. This pretreatment consisted in diluting the liquor ten times to reduce the high viscosity of the SSL that could dramatically slow down the rate of the process due to a bad diffusion along the membrane. In addition, a decrease of the energy consumption for pumping the initial solution is reached with this dilution. Secondly, a filtration step, using cellulose filters of 0.45 μm pore size, was carried out to remove the major suspended solids that could contribute to block the membrane pores, reducing the performance of the separation process.

Afterwards, the UF experiments can be started introducing the diluted SSL in the feed tank. The fractionation of the SSL is performed due to the pressure difference created between the two sides of the selected membrane. This pressure difference, named transmembrane pressure (TMP), is generated with the pump and adjusted manually with the valve lash, causing the driving force of the process. The feed stream is pumped towards the membrane module where it is divided into two streams: permeate and retentate. The retentate stream is recirculated while the permeate stream is withdrawn during the operational time until getting a determined volume of permeate in semi-batch separation process. This type of process is considered optimum for the retentate concentration in the heavy component and the permeate purification, aim of this study. A schematic representation of the UF experiments is shown in Fig. 1.

Experiments were carried out at constant temperature of 20 °C, controlled through the water circulation in the jacket of the feed tank.

The TMP was controlled around 180–200 kPa with a valve and the feed flow was established to 650–690 L/h.

After each experiment, a cleaning procedure was applied to the membrane to avoid the permanent flux decline, i.e., the membrane fouling. This method was structured in three steps, according to Colyar et al. [24]: (1) the membrane was flushed with distillate water during 30 min; (2) a solution of 0.1 N NaOH is pumped