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Optimization and modeling of diananofiltration process for the detoxification of ligno-cellulosic hydrolysates - Study at pre-industrial scale

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ABSTRACT

In order to improve bioethanol production by yeast fermentation of lignocellulosic hydrolysates, sugar/inhibitor separation by nanofiltration was studied on a bench-scale unit equipped with a spiral-wound membrane. Therefore, a model solution containing 3 sugars and 4 inhibitors was treated with two previously selected membranes (NF270 from DOW Filmtec and DK from GE Osmonics). Both membranes led to high sugar rejection, especially at high permeate flux ($>90\%$ for glucose and arabinose and $>85\%$ for xylose). Although its water permeability was smaller, DK membrane was preferred for its higher transmission of the inhibitors, especially for the largest ones (vanillin and 5-hydroxymethyl furfural), ensuring a better detoxification level. Diafiltration was applied to improve sugar purity of the treated hydrolysate. With a diavolume equivalent to 1.25 times that of the feed, acetic acid concentration was divided by 5 and brought back to concentrations lower than 1 g L^{-1}. A simulation model was proposed to predict the diavolume to apply, depending on the initial concentrations. Finally, processed hydrolysates were tested for the fermentation ability with a *Pichia stipitis* species. Fermentation tests showed that diafiltration followed by concentration led to retentates as fermentable as an equivalent pure sugars solution.

1. Introduction

With advantages of sustainability in comparison with fossil energy sources, bioethanol production is more and more studied for replacing or supplementing the latter. It appears more environmental friendly [1] but with an equivalent-energy 68% lower than that of petroleum [2]. Using by-products of agricultural and forestry industries (lignocellulosic biomass) instead of sugars and corn as initial material is additionally an important breakthrough since it is a very cheap and available resource, presenting no conflict with human food resources [3]. Sugarcane bagasse, rice hull, willow, switch grass, softwood, rice straw, wheat straw, etc. can be used as lignocellulosic biomass for ethanol production with sugar recovery reaching 97% of the original material when cotton was used [4,5]. However, for most of these available raw materials, fermentable sugar recovery and production of ethanol is more complicated than from starch [6] due to their complex and compact structure including 30–50% cellulose, 15–35% hemicellulose and 10–30% lignin [7]. In most cases, fermentable sugar recovery is rather around 30% of the original material [5] and ethanol production can vary between 1.3 and 95.3 g/L [4] depending on the source and the pretreatment steps. In fact, the process of ethanol production includes several steps, in which acid hydrolysis or pretreatment by acid leads to cellulose destructuration before enzymatic hydrolysis, that releases fermentable sugars [4]. But at the same time, fermentation inhibitors are created, mainly by the degradation of lignins and the dehydration of free sugars. On the one hand, the most common sugars in these hydrolysates are glucose, xylose and arabinose. On the other hand, type and amount of inhibitors depend on the biomass type, pre-treatment and hydrolysis conditions (temperature, pH, etc), but are mainly carboxylic acids, furan derivatives or phenolic compounds. Among them, three major solutes are identified by several authors, whatever the type of the treated biomass and the applied hydrolysis process [8–10]: acetic acid, furfural and 5-hydroxymethyl

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furfural. Phenolic compounds are generally quantified globally, unless vanillin often appears.

In order to increase fermentation efficiency of those hydrolysates, detoxification methods are currently investigated. They can be physical, chemical, biological or combination of them, each method removing one or some types of inhibitors, rarely all of them. Besides, all of these methods have their own weaknesses. For example, over-liming which consists in alkali addition causes sugar loss [11] and biological detoxification has low efficiency [12]. Among physical treatments, ion exchange and adsorption on resins were first studied [13]. More recently membrane technology gained attention as a cleaner process [14,15]: it does not create by-products neither requires chemical addition (in most cases), and is quite straightforward to operate and scale-up. Due to the molecular weights of the solutes to separate (inhibitors molecular weights being inferior to 150 g mol^{-1} when those of sugars are above), membranes such as RO or tight NF of appropriate molecular weight cut-off (MWCO) were studied, especially during the past five years. These studies provide valuable information to target the best membranes to screen: NF90 and NF270 from Dow or DK from GE-Osmonics are often cited, as well as some RO membranes when sugar recovery is preferred to detoxification. But most of them deal with very simple model solutions [16–19] and when more complex or real hydrolysates are considered, dead-end device or very limited flat membrane area are used [20–23].

Before studying and optimizing lignocellulosic hydrolysate detoxification on a bench-scale device (2540 spiral-wound module) and significant filtration area, we conducted a preliminary study on a flat-sheet device with a complex model hydrolysate containing 3 sugars (glucose, xylose and arabinose) and 4 inhibitors (acetic acid, furfural, 5-hydroxymethyl furfural (HMF) and vanillin) [24]. This study, performed with ten NF and RO membranes, led to the selection of two nanofiltration membranes (NF270 – Dow Filmtec (USA) and DK– GE Osmonics (USA)) allowing simultaneously a high transmission of the inhibitors (above 95%) and a very good sugar recovery (between 82% and 95% depending on the sugar). However, even 100% transmitted through the membrane, a solute is still in the retentate at a concentration equivalent to feed concentration. Purification is then expected to occur through concentration mode or diafiltration. Concentration mode leads to the removal of the smallest solutes (inhibitors) in the permeate while the biggest ones (sugars) are rejected and concentrated in the retentate stream, increasing their purity [25,26]. But doing so, formation of polarization concentration and fouling by accumulation of the rejected species occurs, justifying the choice of diafiltration [16,20]: during permeate removal, solvent (water) is added to the feed stream to maintain sugars in the retentate at a quite constant concentration while washing out the inhibitors. This method improves the purity of the retentate and ensures an economically acceptable permeation flux. This mode can be continuous or discontinuous and its efficiency depends on the relative rejections, the volume dilution ratio or volume concentration ratio [27,28]. Eventually, some of the eliminated inhibitors recovered in the permeate, such as furfural, can be valorized depending on their concentration.

The objectives of the present work are to optimize the sugars/inhibitors separation performances at a pre-industrial scale and to estimate the detoxification efficiency by fermentation tests on the purified retentates produced. Therefore, operating parameters (pressure, feed flow-rate) are studied as well as purification effect through a concentration mode and a diafiltration mode. A solution-diffusion modeling approach is further used to simulate the rejections obtained through diananofiltration.

Sugar sorption on the membranes, highlighted during this study, is also quantified.

2. Experimental

2.1. Model hydrolysate solution and solutes analyses

A solution containing glucose (10 g L^{-1}), xylose (15 g L^{-1}) and arabinose (5 g L^{-1}) as sugars; acetic acid (5 g L^{-1}), HMF (1 g L^{-1}), furfural (0.5 g L^{-1}) and vanillin (0.05 g L^{-1}) as inhibitors, was chosen as model hydrolysate (Table 1). These compounds and concentrations were chosen based on summary of compositions of hydrolysates of various origins [24,29]. pH of this solution was about 3.

Samples collected during the experiments were analyzed by High Performance Liquid Chromatography (HPLC) on a Betamax Neutral Column (150 mm × 4.6 mm i.d., 5 μm particle size; Thermo-Electron Corporation, Courtaboeuf, France) for inhibitors and a Nucleodur 100-5 NH2-RP column for sugars, as already described in Nguyen et al. [24].

2.2. Nanofiltration membranes

DK-2540 and NF270-2540 membranes that give best performance in removing inhibitors and retaining sugars were previously selected on a DSS-Labstack M20 device (Alfa Laval, France) [24]. Their characteristics are presented in Table 2. Both membranes are of semi-aromatic piperazine amide type. As far as we can call “holes” or “pores” the voids in their structure, they have a radius of about 0.4 nm, close to that of some reverse osmosis membranes in the range 0.3–0.45 nm [30–32]. Therefore these membranes can be considered as very dense ones.

2.3. Filtration experiments

Experiments were run at 20 °C on a production bench-scale unit from Polymem (France) equipped with a 2540 spiral-wound membrane (effective membrane area $S=2.6\ m^2$) (Fig. 1). Main parts of the system are made of stainless-steel in order to avoid artifact solute adsorption in the pilot. Pressure probes allow the measurement of inlet and outlet pressures on the feed side, when atmospheric pressure is considered on the permeate side. This pilot plant can be operated in “batch recycling mode” (both permeate and retentate returned to the feed tank) so as to maintain a constant feed concentration, or in “concentration mode” (retentate recycled back to the feed tank while permeate is removed) in order to increase the Volume Reduction Ratio (*VRR*).

Before treatment on the spiral-wound membrane, each solution was previously micro-filtrated on 10 μm and 3 μm cartridges. For each new condition tested, a 30 min stabilization time was respected before any sampling and measurement. Then permeate flux (J_p) or water flux (J_W) was calculated by permeate flow-rate measurement:

$$J_p,\ J_W = \frac{v(t)}{S}\ \left(ms^{-1}, \text{usually expressed in } Lh^{-1}m^{-2}\right) \quad (1)$$

where $v(t)$ is the permeate flow-rate ($m^3\ s^{-1}$ or $L\ h^{-1}$) and S the effective membrane area (m^2).

Table 1
Model hydrolysate composition and solutes characteristics.

Solute	MW (g mol^{-1})	log K_{ow}[a]	Concentration (g L^{-1})
Acetic acid	60	−0.17	5
Furfural	96	0.41	0.5
HMF	126	−0.09	1
Vanillin	152	1.21	0.05
Xylose	150	−1.98	15
Arabinose	150	−2.91	5
Glucose	180	−3.24	10

[a] K_{ow}=Partition coefficient of the solute between octanol and water.