Chemical Engineering Journal 260 (2015) 605–615

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Retention and flux characteristics of nanofiltration membranes during hemicellulose prehydrolysate concentration

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HIGHLIGHTS

- Six organic membranes were screened for concentrating a Kraft hemicellulose prehydrolysate.
- The influence of the feed conditions on the retention properties and flux decline was evaluated.
- A response surface model was developed for optimizing the membrane filtration system.
- Nanofiltration membranes can be utilized in integrated biorefinery processes.

ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form 26 August 2014
Accepted 3 September 2014
Available online 16 September 2014

Keywords:
Membrane filtration
Prehydrolysate
Kraft process
Furfural biorefinery
Hemicelluloses concentration

ABSTRACT

The prehydrolysate generated in the Kraft pulping process prior to cooking of wood chips can be converted into value added products such as furfural, ethanol or xylitol. To make a furfural biorefinery economically feasible, it is proposed to reduce the energy use and process equipment size by concentrating the prehydrolysate stream prior to conversion. This work demonstrates the feasibility of simultaneously concentrating the hemicellulosic sugars and acetic acid in the prehydrolysate solution from a Kraft dissolving pulp mill by nanofiltration membrane. The performances of 6 commercial organic membranes made of polyamide, cellulose acetate and polypiperazine amide polymers and of different Molecular Weights Cut Off (MWCO) were evaluated. Special attention was directed to high retention of sugars, acetic acid and furfural. A membrane with a MWCO of about 200 Da and total sugars retention of 99% was selected. Cleaning of the membrane using NaOH returned the permeate flux up to 75% of the pure water flux level prior to use. A response surface model correlating the permeate flux to the temperature and pressure of the system has been developed.

1. Introduction

Forest biomass comprises of three main types of polymers; cellulose, hemicellulose and lignin. In a Kraft dissolving pulp process, the hemicelluloses are typically extracted in a prehydrolysis step prior to chemical delignification of the wood chips. The prehydrolysate stream obtained is made up mainly of the hemicellulosic sugars (C_5 and C_6 sugars) along with lesser quantities of organic acids, phenolic compounds and furfural. The cellulose fibers are processed into pulp after delignification. The extracted hemicelluloses fraction is merged with the lignin fraction that is removed during delignification and usually directed to the recovery cycle where it is combusted to produce energy. A better use of the hemicelluloses would be to divert the prehydrolysate stream and convert the sugars into biofuels or bioproducts such as ethanol, furfural or xylitol [1]. To minimize the cost of valorizing the sugars, concentration of the prehydrolysate is mandatory before the conversion of the sugars into any value added product. Concentration allows to reduce the energy consumption and the investment cost for the subsequent process steps of the biorefinery. The concentration objectives (component separation and final sugars concentration) depend on the targeted biorefinery final product. For a Kraft pulp mill that uses hardwood as a feedstock, it is proposed to produce furfural from the prehydrolysate through the dehydration of the C_5 sugars. The C_5 sugars in the prehydrolysate make up to 80% of the total sugars. Furfural is a platform chemical for bioproducts that can substitute industrial organic compounds, which are currently produced from fossil sources. Furfural can also be converted into liquid biofuels [1,2] or used as a solvent in

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http://dx.doi.org/10.1016/j.cej.2014.09.007
1385-8947/

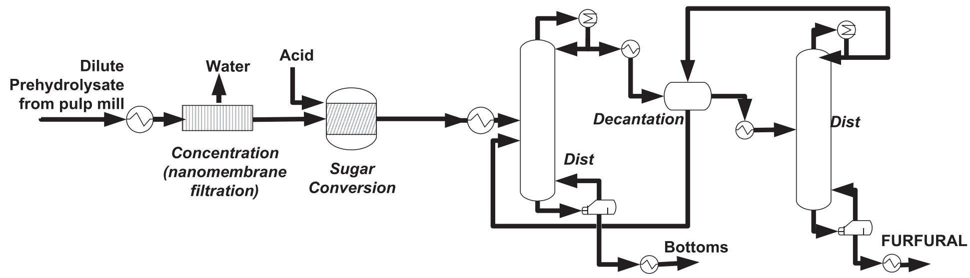

Fig. 1. Proposed biorefinery for producing furfural from hemicellulose prehydrolysate [5].

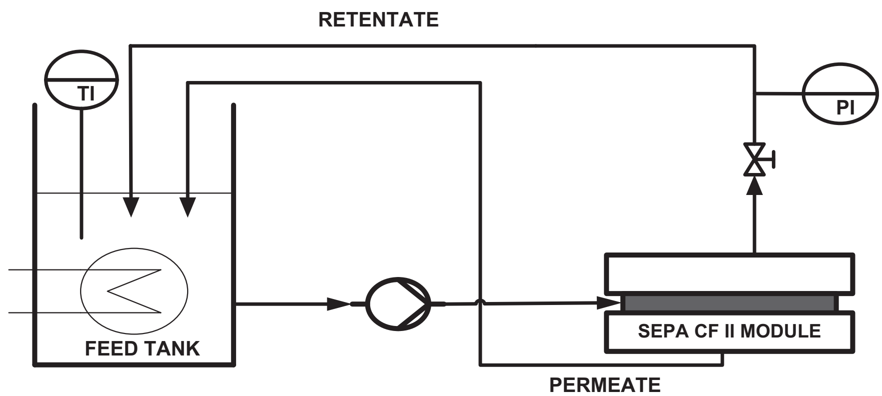

Fig. 2. Schematic membrane screening setup in closed loop mode.

petrochemical refineries [3] and as pesticides or nematocides [4]. A process for producing furfural from hemicelluloses prehydrolysate has been proposed by Ajao et al. [5] and it is illustrated in Fig. 1. After concentration of the prehydrolysate, the furfural is produced by two subsequent reactions; the oligomeric sugars in the prehydrolysate are hydrolyzed into sugar monomers which are then converted into furfural. A low pH is required to enhance the conversion process and this can be provided by introducing mineral acid into the reactor. Purification of furfural is done by distillation. Since furfural forms an azeotrope with water and has an azeotropic point of 35% wt, a decantation step is required between the two distillation columns to get above the azeotropic point.

In a biorefinery for furfural production, an important requirement for the concentration step is to retain the acetic acid along with the sugars; organic acids provide a low pH and act as catalysts, thereby reducing the mineral acid required for pentoses conversion to furfural [6]. Concentration with the typical use multi-effect evaporators is not feasible because the organic acids in the prehydrolysate are volatile and would be lost. Furthermore, evaporators have high energy consumption due to the latent heat for water that must be supplied. Membrane concentration on the other hand requires a lower amount of energy as it does not involve a phase change. The hemicellulose prehydrolysate treated in this work is a complex solution containing several organic compounds and the sugars present range from simple monomers to oligomers. The organic acids, phenolic compounds and furfural also influence the retention and flux that can be obtained during concentration [7]. The use of membrane filtration presents some challenges that must be addressed before economically feasible membrane concentration of prehydrolysate can be carried out. A suitable membrane that is capable of simultaneously retaining the sugars and organic acids with acceptable energy consumption must be used. Also, the occurrence of flux decline over the life of a membrane makes it important to determine if the operation would necessitate frequent cleaning or changing of the membrane. Lastly, there is a limit beyond which the permeate flux of the membrane would be too low and further concentration of the prehydrolysate will not be possible. To the best of our knowledge, the application of membrane filtration to real prehydrolysate solution for a furfural biorefinery has not been investigated. Also, the effect of varied operating conditions on the flux decline has not been investigated. Thus, the objectives of this work have been to screen commercially available membrane suitable for hemicelluloses concentration, determine the flux reduction of a selected membrane over extended periods of use and develop a model relating the operating conditions to the membrane flux and useful life.

Screening of six commercial organic membranes made of polyamide, cellulose acetate and polypiperazine amide polymers and having different Molecular Cut Off Weights (MWCO) between 100 and 500 Da was carried out. In the screening experiments, the separation of components in a prehydrolysate solution generated from a wood supply similar to that of a Canadian dissolving pulp mill was determined for all membranes. The selected membrane for the concentration studies had a MWCO of about 200 Da. The effect of feed condition on flux decline has already been documented [7], this is the first paper to clearly demonstrate how it relates to the concentration of hemicelluloses prehydrolysate from a Kraft dissolving pulp process. The generated data could be applied to the design of efficient membrane concentration systems and successfully used in forest biorefinery processes.

2. Materials and methods

2.1. Prehydrolysate generation

The prehydrolysate used in this study was generated in a 56 L digester using a 60% Aspen–40% Maple wood furnish. The typical compositions of the wood chips are shown in Table 1.

The wood chips had a moisture content of 37% and were purged with steam (138 kPa) to remove the air content and preheat the