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Two-stage nanofiltration process for high-value chemical production from hydrolysates of lignocellulosic biomass through hydrothermal liquefaction

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ABSTRACT

Two-stage nanofiltration (TSNF) process was proposed for recovering high-value chemicals, including monophenols, cyclopentenones, glucose and acetic acid, from hydrolysates of lignocellulosic biomass (rice straw) through hydrothermal liquefaction (HTL). The separation performances of three single nanofiltration (NF) processes and three TSNF processes were studied. Results showed that at the first stage of (DL + DK) TSNF process, DL membrane had high glucose rejection of 97.12%, and lower acetic acid rejection as well as lower aromatics rejections than DK membrane. At the second stage, DK membrane had rather low acetic acid rejection of 5.04% to ensure acid separation from aromatics. Unlike glucose or acetic acid, aromatics were unable to be recovered into one fraction due to scattered rejections of different aromatic compounds on NF membrane. The (DL + DK) TSNF process was proved to be a feasible way to fractionate hydrolysates into three parts: glucose concentrate, monophenols and cyclopentenones concentrate, and acetic acid permeate.

1. Introduction

Annual lignocellulosic biomass production has been estimated to be 10 billion tons worldwide, of which agricultural residues have been about 70% [27]. The reutilization of large quantities of rice straw, a type of lignocellulosic agricultural residue, has a significant influence in promoting new energy exploitation, resource recycling [34], and environmental protection [7].

Hydrothermal liquefaction is a promising chemical transformation method for biomass utilization, due to its high product yield and low energy consumption [26,31]. However, complex compositions of lignocellulose and an array of chemical reactions (including dehydration and decarboxylation reactions) in the hydrothermal liquefaction of lignocellulose results in liquid products (known as hydrolysates) with complex compositions [24]. Hydrolysates from the hydrothermal liquefaction of lignocellulose contain sugars, acids, monophenols and cyclopentenones, the compositions of which are based on different process conditions [12,14,35].

The composition complexities make it difficult to obtain high-purity value-added chemicals from the hydrolysates, hence hindering application and industrialization of this technology. To make use of hydrolysates, separation methods such as solvent extraction have been studied. Solvent extraction was used to separate value-added chemicals, such as phenolic compounds, from the crude product of hydrothermal liquefaction [36]; however, the extracts were generally mixtures of many aromatic compounds that needed subsequent purification [5,18]. Compared to other separation methods, membrane separation has been shown to be an excellent pretreatment process for the removal of macromolecules, and is regarded to have great potential for future biorefineries, due to its low energy consumption, high separation efficiency and high quality of the final product [8,10].

With membrane separation, various tasks in biorefinery processes have been accomplished. Liu et al. separated sugars, acetic acid, furan, furfural and aromatic compounds in aqueous biomass hydrolysates by a NF membrane with molecular weight cut-off of 100 Da [19]. Polysaccharides and aromatics were preferentially retained in the concentrate stream so that sugars could be cleaned and concentrated. Persson et al. used a hybrid filtration and membrane filtration process to fractionate the process water from a thermomechanical pulp mill. Suspended matter, extractives, hemicelluloses and lignin were isolated in the retentate of the drum filter, microfiltration, UF and NF, respectively [23]. Shen et al. proposed the concept for a combined process with the sequential steps of activated carbon adsorption, ion exchange resin treatment and membrane concentration, which effectively recovered and

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concentrated hemicellulosic sugars from lignocellulose hydrolysates [28]. Ahsan et al. combined NF and a reverse osmosis process, and effectively recovered sugars and acetic acid from prehydrolysis liquor of kraft-based hardwood dissolving pulp process [1]. According to above mentioned studies, NF showed good selectivity and separation potential in separating and fractioning mixture solutions with complex compositions. However, most recent NF separation studies have mainly focused on hydrolysates from dilute acid pretreatment (DAP) for biological fermented conversion [6,13,25,33,37], with few membrane separation studies focusing on hydrolysates from direct HTL of lignocellulose biomass. Variation in liquefaction conditions led to different composition of hydrolysates from HTL and DAP. With lignin liquefied into hydrolysates in HTL, the resulting phenolic content can influence NF performance which can be quite different as compared to that of DAP hydrolysates. Besides, little work has been done with the recovery of monophenols and cyclopentenones from hydrolysates by membrane separation. Monophenols and cyclopentenones are important intermediates in the fine chemical industry and pharmaceutical industry. Separation and recovery of biobased chemicals from lignocellulose is good substitution for traditional chemical synthesis and gives relief for petroleum shortage.

To make full use of hydrolysates, to recover multiple chemicals and to cut down congestion of subsequent column chromatography for aromatics, in the present study, we have focused on separating high-value aromatic compounds from sugars and acids with TSNF process. First, ultrafiltration (UF) membrane separation was used as a pretreatment process of the feed in all NF processes. Second, three NF membranes were tested for their separation performance processing hydrolysates from permeate of the UF process. Finally, three TSNF processes were performed to determine if monophenols and cyclopentenones could be separated from sugars and acids, and be recovered into one fraction for further purification.

2. Materials and methods

2.1. Preparation of HTL hydrolysates

The rice straw used as raw material in this study was obtained from Shanghai Songjiang District. The rice straw was liquefied in a pilot scale reactor (80 L) at the Shanghai Fuhuan Bioenergy Co. Ltd. Each time, 45.0 kg of water and 3.0 kg of rice straw were fed into and mixed in the reactor. The HTL was carried out at 300 °C and 12.0 MPa. After a retention time of 30 min, the crude product of HTL was cooled to room temperature and was filtered by a 300-mesh screen. The mesh screen permeate was collected as the raw hydrolysates.

2.2. Membrane separation procedure

Four spiral-wound membrane modules—MW GE, DL and DK (General Electric Co., USA)—were used in this study. MW membrane was a UF membrane with molecule weight cut-offs (MWCO) of 20,000 Da. The MWCO of GE membrane according to the manufacturer was 1000 Da, and this was exactly the critical value of division of UF and NF membrane. Although it was announced as a tight UF membrane by the manufacturer, we treated GE membrane as a representative of NF membrane with larger MWCO in this study. The MWCO of the DL and DK membranes were between 150 Da and 300 Da according to manufacturer. Similar in surface chemistry, DK and DL membranes were semi-aromatic piperazine-based hydrophobic membranes which were coated to impart chemical resistance, at a cost of surface hydrophilicity [29]. However, DL was characterized as a high flux membrane by the manufacturer whereas DK was a high rejection membrane. Pure water permeability of DL and DK membrane was 5.53 L m^{-2} h^{-1} bar^{-1} and 6.26 L m^{-2} h^{-1} bar^{-1}, respectively, while NaCl rejection of DL and DK membrane was 66.4% and 50.4%, respectively [30]. The outer diameter of the membrane element was 4.6 cm, and the length was 30 cm. The membrane filtration area was 0.32 m^2, and the module had a 0.86 mm spacer.

The membrane filtration system was operated in a batch filtration mode, in which the retentate was recirculated to the feed tank and the permeate was continuously withdrawn. The cross-flow rate was 0.30 m^3 h^{-1}. The pressure was 5 bar for the MW and GE membranes, and 10 bar for the DL and DK membranes. The temperature was kept stable at 35 °C with a thermostatic water bath and circulating water cooling system.

Initially, MW membrane was used to filtrate the raw hydrolysates as a pretreatment process. Then, single NF experiments were conducted. The permeate of the MW membrane was used as the feed for three single NF processes. 10 L hydrolysates were fed with volume reduction factor (VRF) of 10 in both UF and single NF processes. 2 mL sample was taken from the tank and the permeate after filtration was completed, and the composition was analyzed with high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC–MS).

After single NF experiments, TSNF process experiments were performed. Three TSNF membrane combinations—GE + DL, GE + DK, DL + DK—were tested for feasibility whether monophenols and cyclopentenones were separated from both sugars and acids. The MW membrane also was used as a pre-filter process before TSNF experiments. MW pretreatment before both single process and TSNF had a VRF of 10, with a feed volume of 10 L. Permeate of MW membrane was collected and mixed in the bucket until the volume was enough for NF filtration. In the first NF stage, the feed volume was 10 L with a VRF of 10. And 9 L permeate was used as the feed for the second nanofiltration stage. In the second NF stage, a total of 7.2 L permeate was collected with a VRF of 5.

The membranes were cleaned with a NaOH solution (pH = 11) for 1 h at 40 °C. The system was thoroughly rinsed with deionized water after cleaning. The pure water flux at 5 bar and 30 °C was tested before the filtration (F_b) and after the cleansing (F_a). The flux decline was calculated as $\% \frac{F_b - F_a}{F_a}$.

2.3. Analytical methods

The chemical compositions of the hydrolysates and separated fractions were analyzed with HPLC and GC–MS.

The concentrates of glucose and acids were analyzed on a 7.8 × 300 Aminex HPX-87-H column (Bio-Rad, USA) at 55 °C with a refractive index detector at 50 °C. The mobile phase was 5 mmol of H_2SO_4 at a flow rate of 0.4 ml min^{-1}.

Monophenols and cyclopentenones were analyzed with an Agilent 6890/5973 GC–MS (Agilent, USA) equipped with an HP-5 MS capillary column (5% phenyl and 95% dimethylpolysiloxane, 30 mm × 0.25 mm × 0.25 mm). High-purity helium was used as the carrier gas with a flow rate of 1 cm^3 min^{-1}. 1 μL of the hydrolysate solutions (1:3 extraction by ethyl acetate) was injected into the column.

The GC oven temperature was held at 50 °C for 2 min and then programmed to reach 260 °C at a heating rate of 5 °C min^{-1}. The temperature of the injector and detector was set at 280 °C. Data were collected and analyzed using Agilent MSD ChemStation E.02 with the Wiley mass spectra library. Semi-quantitative analyses for aromatic compounds were performed according to the peak area of each compound.

Silicon content in the hydrolysate was determined using Inductively coupled plasma-atomic emission spectrometry