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Monophenols separation from monosaccharides and acids by two-stage nanofiltration and reverse osmosis in hydrothermal liquefaction hydrolysates

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ABSTRACT

Through hydrothermal liquefaction (HTL), lignocellulosic biomass is directly hydrolyzed into small organics like monosaccharides, monophenols and acids, which can be used as valuable chemicals by further purification. This study aims at investigating the feasibility of simultaneous separation of monophenols from sugar and acids in model lignocellulosic hydrolysate solution through two-stage nanofiltration (NF) and reverse osmosis (RO) process. The effects of pressure, temperature and pH on the solute retentions and permeate flux were examined with an eight-solute sugar-monophenols-acids model solution. NF-RO (DK-SE) two-stage membrane process was performed to confirm the multistage separation performance of model hydrolysates under an optimal operation condition. Results showed that membranes with higher water permeability had better performance in separation of sugar from monophenols. The decrease in temperature promoted separation of both acetic acid and monophenols from sugar, while higher pressure and lower temperature favored separation of acetic acid from phenols. The pH should be kept at low values to maintain good monophenols simultaneous separation of from sugar and acids. The maximum separation factors of acetic acid over 2,6-dimethoxyphenol and 2,6-dimethoxyphenol over glucose were 99.59 by RO membrane SE and 29.99 by NF membrane DK, respectively. Two-stage membrane process (DK NF+SE RO) was proven to be a feasible way to fractionate model HTL hydrolysates into three parts: incomplete hydrolyzed biomass fragments, monophenols riched concentrate, and acetic acid permeate.

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1. Introduction

With the background of energy shortage and environment crisis, there are increasing interests in transforming biomass to bio-fuels and bio-chemicals. Lignocellulose is one of the most abundant biomass in the world with annual production of 10 billion tons worldwide [1]. Lignocellulosic biomass is mainly composed of three components: cellulose, hemicellulose and lignin. HTL of lignocelluloses is the thermochemical conversion of lignocelluloses biomass into bio-based chemicals and liquid fuels by processing in a subcritical water environment with or without the presence of a catalyst for sufficient time to break down the solid biopolymeric structure to mainly liquid components [2,3]. Due to its high product yield and low energy consumption, HTL was regarded as a promising method for biomass conversion [4,5].

The basic reaction mechanism of HTL can be divided into three steps: (1) depolymerization of the biomass; (2) decomposition of biomass monomers by cleavage, dehydration, decarboxylation and deamination; (3) recombination of reactive fragments. The main intermediates are monosaccharides and oligomers, fatty acids, amino acids, furfural and 5-hydroxymethylfurfural [6]. Intermediates are dehydrated and decarboxylated into smaller molecules, or recombined to form reactive fragments. Final products of HTL of lignocellulose could be divided into liquid products and solid residues (denoted to hydrochar which mainly contains incompletely hydrolyzed biomass residues and recombined reactive fragments). Solid residues was a new source of adsorbents. Liu et al. transformed rice straw-derived hydrochar to a highly efficient magnetic adsorbent for triclosan removal in waste water treatment field [7]. However, liquid products have a complex composition which mainly contains the following chemical species or several of them: oligosaccharides, lignin fragments, monosaccharides, phenol derivatives, acids, cyclopentenes, long chain alkanes, esters, ketones and aldehydes [8,9]. The composition is influenced by temperature, pressure, concentration, and presence of homogeneous or heterogeneous catalysts [6]. Extraction is

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generally used to obtain bio-oils from water products. However, the bio-oil is unsuitable for vehicle combustion because of its high viscosity, high water content, corrosivity and low heating value [10]. Therefore, the other way of utilizing HTL hydrolysates – refining value-added chemicals like phenols and acids from liquid products through separation and purification methods – is beneficial for development of HTL technology.

Many separation methods such as distillation, extraction, adsorption resin and membrane separation have been used for separation of HTL hydrolysates. Distillation is generally used in chemical engineering, but it is not preferred due to the high energy demand. Yang et al. used selective extraction to separate bio-oil into light oil, mid-weight oil and heavy oil, which were rich in phenols, aromatic oligomers and alkanes, respectively [11]. However, the remaining water products including high concentration of acids were undisposed and hard to be exploited after extraction, since water product was contaminated by organic solvent. Moreover, the organic solvent was unfriendly to the environment and disobedient to the green chemistry concept. Adsorption resin was proved to remove phenols from aqueous solutions [12]. In a previous study, the total amount of phenolic compounds separated from the hydrolysate of HTL were increased from 18% to 78% with modified adsorption resin [13]. But the recovery of resin was difficult and the cost of total process was very expensive. Compared with other separation methods, membrane separation is a promising method for the separation of high valued chemicals from HTL hydrolysates.

Membrane separation has attracted attention in recent years in fields of waste water treatment, milk industry, pharmaceutical industry and petroleum industry due to its chemical state maintenance, low energy consumption, high separation efficiency and high quality of the final products [14,15]. In the hydrolysates, the value-added aromatic compounds like monophenols had molecular weights around 90–200 g/mol, and the high concentrated acetic acid had molecular weight of 60 g/mol. However, the incomplete hydrolyzed biomass fragments or oligomers recombined in the hydrolysate process by intermediates had molecular weights larger than 500 g/mol [16]. With molecular weight cut-off of between 200 and 1000 g/mol, NF could effectively separate monophenols and acetic acid from the hydrolysates. At the same time, the concentrate of NF which contains uncompleted hydrolyzed biomass fragments or resynthesized low polymers could be used as biomass source to be hydrolyzed again. Zhou et al. achieved complete acetic acid separation from glucose (180 g/mol) with NF membrane and demonstrated a better performance for acetic acid recovery with an RO membrane [17,18]. Monosaccharides are much larger than acetic acid in molecular weight so that the separation of acetic acid from xylose and glucose can be achieved by NF or RO. Similarly, comparing the difference in molecular weight of acetic acid and monophenols, acetic acid may be separated from monophenols by NF or RO. However, molecular weight differences of monophenols from both monosaccharides and acids were less prominent, so the feasibility of separation monophenols from sugar and acetic acid should be further investigated by filtration experiment. Lyu et al. tried two-stage NF process on HTL hydrolysate and obtained three usable fractions, but separation factor of acetic acid over monophenols was too low to recover acetic acid of high quality [19]. Yet so far, NF and RO separation performances for monosaccharides, monophenols and acetic acid haven't been compared. The two-stage NF and RO process is worth investigating for its performance on separating and concentrating monophenols and acetic acid recovery.

This work investigated the effects of operational conditions (pressure, temperature and pH values) on rejections of monosaccharides, monophenols and acids in a model hydrolysate. Separation performance of NF and RO were compared at the same time with ten membranes including four RO membranes and six NF membranes. Then, under optimized conditions, the two-stage membrane process was used to separate hydrolysates into three fractions, and the separation performance in concentration and separation was analyzed.

2. Experimental

2.1. Solutes and membranes properties

D-(+)-Glucose was purchased from Sinopharm Chemical Reagent Co., Ltd, China. D-(+)-Xylose, Levulinic acid ($P_{99.0\%}$, AR), acetic acid ($P_{99.9\%}$, HPLC) and pH buffer standard solution were purchased from Aladdin Industrial Co., China. Phenol, 2-methoxyphenol and 2,6-dimethoxyphenol were purchased from Shanghai Yiji Industry Co., China. L-(+)-Lactic acid was purchased from Shanghai Urchem Co., Ltd, China. Model solution was prepared with chemicals and deionized water. Composition, concentration and solute properties of model solution were shown in Table 1. The concentrations were based on the composition in typical hydrolysates derived from HTL of rice straw in pilot scale under 280 °C and 12 MPa for 30 min. Acetic acid was rich in hydrolysates and several high-valued phenolic compound species existed in hydrolysates. The pH values of model solution were adjusted with NaOH or HCl solutions. Purified water in this study was produced from a MilliQ water system (Millipore, China).

2.2. Membrane and filtration experiment

Ten flat-sheet commercial thin-film polyamide membranes, including six NF membranes (DK and DL provided by GE Osmonics©, NF90 and NF270 from Dow FilmTec©, and XN45 and TS40 provided by Trisep) and four RO membranes (SE and SG provided by GE Osmonics©, BW30 and BW30FR provided by DOW FilmTec©), were employed in this study.

Table 1
Properties of focused compounds.

Compounds	Molecular formula	Molecular weight ($g\ mol^{-1}$)	Dissociation constant (pK_a)	Concentration ($mg\ L^{-1}$)
Glucose	$C_6H_{12}O_6$	180.16	12.28[a]	500
Xylose	$C_5H_{10}O_5$	150.13	12.15[a]	500
Acetic acid	CH_3COOH	60.05	4.756[a]	2000
Lactic acid	$C_3H_6O_3$	90.08	3.858	1000
Levulinic acid	$C_5H_8O_3$	116.12	4	1000
Phenol	C_6H_6O	94.11	9.99	100
2-Methoxyphenol	$C_7H_8O_2$	124.14	9.93	100
2,6-Dimethoxyphenol	$C_8H_{10}O_3$	154.16	10	100

[a] From [20].

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