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Ion exchange separation for recovery of monosaccharides, organic acids and phenolic compounds from hydrolysates of lignocellulosic biomass

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ABSTRACT

This paper describes two effective ion exchange chromatography processes to separate and recover monosaccharides, organic acids and phenolic compounds from two kinds of hydrothermal liquefaction (HTL) hydrolysates derived under different temperatures. Anion exchange resin Amberlyst A21 (OH^-) and cation exchange resin Amberlite IR-120 (Na^+) were selected to separate synthetic solution and real hydrolystes by column chromatography. The results showed that glucose and acetic acid could be successfully separated by anion resin with purities of 87% and 98%, respectively. Acetic acid and phenol could be recovered by cation resin with purities up to 97% and 81%. In separation processes of real HTL hydrolysates, monosaccharides and organic acids in hydrolysate derived from low-temperature HTL were separated by anion exchange resin with recoveries of about 80% and 90%, respectively. Phenolic compounds in high-temperature HTL hydrolysate were recovered by cation exchange resin with recovery of about 70%.

1. Introduction

With serious energy depletion crisis of fossil fuel and environmental pollution problems, bio-based chemicals produced from renewable resources, such as lignocellulosic biomass, has drawn much attention as a sustainable production route. Hydrothermal liquefaction (HTL) is a kind of thermochemical process which could convert lignocellulosic biomass to liquid products known as hydrolysate, accompanied with some gas and solid products. Large amounts of high value-added chemical compounds dissolved in hydrolysate, including saccharides, organic acids, phenolic compounds, ketones and furfurals [1]. These compounds are widely used in food industry, chemical synthesis and pharmacy. Many of them are considered as some platform chemicals which can produce various high value-added derivatives.

However, the complex composition of hydrolysate hindered its application. In order to utilize the hydrolysate, different kinds of adsorbents [2–4] and membrane filtrations [5,6] were applied to separate target products in it. Considering the difficulty in regeneration of activated carbon, low selectivity of adsorption resin and high cost of membrane, ion exchange resin was a kind of popular and effective method to separate valuable compounds in hydrolysate.

Cation exchange resin was used for the separation of monosaccharides from sulfuric acid involved in the HTL reaction and some organic acids generated from HTL process [7,8]. In the process of xylitol production, several fermentation inhibitors including furfural and phenolic compounds were successfully removed by both cation and anion exchange resins to get purified saccharides for fermentation [9,10]. Some researchers tried to recover organic acids from hydrolysates with anion exchange resin [11,12]. Kun and Rojan separated fumaric acid and lactic acid respectively from different fermentation broths by using anion exchange resin [13,14]. As for phenol, the most commonly used method to produce it from hydrolysates was solvent extraction [15,16]. However, organic solvent was not environmental friendly, and the complicated procedures limited its application in industrial production. Production routes for phenolic compounds were limited in study, because they were usually considered as a kind of fermentation inhibitor. In fact, they could be separated from organic acids according to the theory of ion exclusive chromatography [17]. Aliphatic carboxylic acids and benzenecarboxylic acids could be separated by the cation exchange resin [18,19]. Zabkova recovered vanillin by passing the vanillate solution derived from Kraft lignin oxidation through a cation exchange resin column [20].

According to these researches, HTL hydrolysates had a profound potential to produce valuable compounds by ion exchange separation process. The objective of this paper was to recover major valuable components in HTL hydrolysates: monosaccharides, organic

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acids and phenolic compounds. First, cation exchange resin Amberlite IR-120 and anion exchange resin Amberlyst A21 in different ion forms were tested for their adsorption performance. Then, a synthetic solution was separated by selected resins to inspect their separation effects for glucose, acetic acid and phenol. Finally, suitable resin was applied to separate different kinds of HTL hydrolysates with different compositions. Monosaccharides and organic acids were successfully recovered by anion exchange resin while acids and phenolic compounds could be recovered by cation resins.

Compared with other researches using ion exchange resin to separate biomass hydrolysates, this study not only focused on the recovery of monosaccharides, which was commonly concerned as valuable components, but also successfully recovered organic acids and phenolic compounds from HTL hydrolysates which received far less attention than saccharides. For hydrolysates with different compositions, we selected different types of ion exchange resins to separate them, exploring the method to separate hydrolysates derived from different temperatures. It provided a comprehensive separation method for different kinds of valuable components in hydrolysates and had a more extensive range of application.

2. Experimental

2.1. Materials

The hydrolysates applied in the experiment came from rice straw and pine branches. Both of them were waste biomass and liquefied in a hydrothermal reactor with reaction time of 30 min and liquid-solid ratio of 15. For the rice straw, the liquefaction temperature was 300 °C. For pine branches, the temperature was 180 °C. After reaction, the biomass was degraded into a mixture of hydrolysates and solid residues, which was then filtered by a 300-mesh screen.

Reagents including glucose, xylose, arabinose, lactic acid, phenol, 2-methoxy phenol, 2,6-dimethoxy phenol, acetosyringone, hydrochloric acid, sodium hydroxide, sodium chloride and calcium chloride were analytical grade. Other reagents for high performance chromatography (HPLC) analysis including methanol, acetic acid and sulfuric acid were chromatographic grade. Purified water for HPLC analysis was produced from a MilliQ water system (Millipore, China).

2.2. Selection of ion exchange resins

Gel type strong acid cation exchange resin Amberlite IR-120 and macroporous weak base anion exchange resin Amberlyst A21 (Aladdin Industrial Co., China) were used as the adsorbent for separation. Both of them were converted into commonly used ion forms. The cation resins were in Na^+ and Ca^{2+} forms, and the anion resins were in OH^- and Cl^- forms. They were selected by adsorption equilibrium experiments conducted with three typical compounds in hydrolysate: glucose, acetic acid and phenol. About 0.02 g of resins was dispersed in single compound solutions with different concentrations. The concentrations of acetic acid and phenol were from 200 to 1000 mg/L, while the one of glucose was from 1 to 40 g/L. Then the mixtures were continuously shaken in a thermostatic oscillator with the rotational speed of 150 r/min at 298 K for 24 h. The adsorption isotherms were plotted and fitted with equations.

2.3. Separation process for synthetic hydrolysate

A synthetic solution was prepared to simulate HTL hydrolysates of biomass, with a concentration close to the real hydrolysate: 150 mg/L of glucose, 1000 mg/L of acetic acid and 100 mg/L of phenol. The pH of the model solution was detected by a pH meter.

Two kinds of ion resins in selected ion forms were packed into a glass column with a diameter of 10 mm. Resins were pretreated with hydrochloric acid and sodium hydroxide. The mass of resins were about 20 g and the length of the column was about 25 cm. The bed volume was about 20 mL.

The synthetic solution was passed through the resin column with an injection volume of 0.1 BV (bed volume). The eluent for the cation resin was deionized water and ethanol, and for the anion resin was 1 mol/L of sodium hydroxide solution. The effluent collected after separation by anion resin was neutralized by 1 mol/L of hydrochloric acid before analysis. Hydrochloric acid and ethanol was applied to regenerate the anion resin adsorbing phenol. When the cation resin was eluted by deionized water, the flow rate was 0.75 BV/h. In other elution processes, the flow rate was 3 BV/h.

2.4. Separation process for HTL hydrolysates from lignocellulosic biomass

The biomass hydrolysates were filtered by a 0.45 μm membrane before injected into the resin column and detected with a pH detector. The hydrolysate after HTL of rice straw at 300 °C was separated by the cation exchange resin while the hydrolysate liquefied by pine branches at 180 °C was separated by anion exchange resin. 0.1 BV of the hydrolysates was injected into the resin column. The eluents for cation and anion resins were the same as the ones used for the elution of synthetic solution. The flow rate in the elution process was 3 BV/h.

2.5. Analytical methods

The chemical compositions of hydrolysates and the concentrations of monosaccharides, organic acids and phenolic compounds were all analyzed by HPLC (Agilent 1100 Series with UV-detector and refractive index detector). The hydrolysates were filtered by a 0.22 μm membrane before injection.

The analysis of monosaccharides and organic acids relied on an Aminex HPX-87-H column. The mobile phase was 0.005 mol/L of sulfuric acid aqueous solution with a flow rate of 0.4 mL/min. The temperature of the column was 55 °C. The detector was a refractive index detector under 50 °C.

Phenolic compounds were analyzed by the Athena C18 chromatographic column with a mobile phase of 60% of acetic acid aqueous solution (wt.% = 1%) and 40% of methanol. The flow rate was 0.8 mL/min and the temperature of column was 20 °C. The wavelength of the UV detector was 276 nm.

3. Results and discussions

3.1. Selection of ion exchange resins

Before the fixed-bed column separation, the appropriate ion exchange resins with high selectivity and capacity were firstly selected through adsorption equilibrium experiment and isotherms. Figs. 1 and 2 describe the adsorption behaviors of glucose, acetic acid and phenol on cation and anion exchange resins in 298 K. These three kinds of substances were typical components in HTL hydrolysates of lignocellulosic biomass.

Cation exchange resins with Na^+ and Ca^{2+} ion forms were applied to adsorb glucose and phenol with different concentrations (Fig. 1). The isotherm of glucose (Fig. 1a) was linear fitting [21,22], because adsorption of monosaccharides on cation resin was driven by linear driving force approximation [23]. Although phenol is weak acidity, it could be slightly adsorbed on the cation exchange