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Separation of galactose, 5-hydroxymethylfurfural and levulinic acid in acid hydrolysate of agarose by nanofiltration and electrodialysis

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HIGHLIGHTS

- A two-stage membrane process with nanofiltration and electrodialysis is proposed.
- Removal of 5-HMF & levulinic acid (LA) from agarose hydrolysate by nanofiltration.
- For simultaneous hydrolysate detoxification and 5-HMF & LA recovery.
- Effective separation of 5-HMF and LA from each other by electrodialysis.

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ABSTRACT

A two-stage membrane process for the separation of galactose, 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) has been proposed. The first step of nanofiltration (NF) is to remove 5-HMF and LA from galactose solution obtained by the hydrolysis of agarose, the main component of red algal galactan for the reduction of its microbial toxicity. 5-HMF and LA are inhibitory to fermentation but at the same time useful compounds themselves with many applications. The second step of electrodialysis (ED) is to separate 5-HMF and LA in the permeate from NF. More than 91% of 5-HMF and up to 62% of LA could be removed from agarose hydrolysate, while galactose was almost completely retained by NF. Further removal of LA was expected to be possible with no loss of galactose by operating the NF process in a diafiltration mode. 5-HMF and LA could be effectively separated from each other by ED.

1. Introduction

Red algal galactan such as agar and carrageenan can be readily decomposed to monosaccharides (i.e. galactose) by using acid catalyst (Jeong and Park, 2010; Kim et al., 2010a). However, simultaneously, byproducts are formed during acid hydrolysis, which are toxic to fermentative microorganism and inhibit their metabolism. For example, as agarose, the main component of agar, is hydrolyzed by hydrochloric or sulfuric acid, 5-hydroxymethylfurfural (5-HMF) is formed from the degradation of 3,6-anhydrogalactose due to its acid-labile. Its inhibitory effect is similar to that of furfural, causing a significant inhibition of glycolysis and a long lag-phase (Banerjiee et al., 1981). 5-HMF is rehydrated to levulinic acid (LA) under the acidic condition. It inhibits cell growth through ATP depletion, toxic anion accumulation, and inhibition of aromatic amino acid uptake (Palmqvist and Hahn-Hagerdal, 2000b; Zaldivar and Ingram, 1999). Meinita et al. (2012) reported that 5-HMF and LA formed from acidy hydrolysis of red algal galactan (*Kappaphycus alvarezii*, *cottonii*) inhibited cell growth and ethanol production of *Saccharomyces cerevisiae*. In order to use such acid hydrolysates containing 5-HMF and/or LA as fermentation media for the production of useful bioproducts, it would be necessary either to avoid the formation of inhibitory compounds or to remove them from the hydrolysate.

Recently, a number of physical, chemical and biological separation methods to remove, although partially, toxic compounds from various types of hydrolysates have been proposed for the enhancement of fermentation efficiency (Mussatto and Roberto, 2004). Above-mentioned separation processes include evaporation, solvent-extraction, precipitation, over-liming and adsorption with activated carbon and ion exchange resin (Cho and Kim, 2009; Huang et al., 2008; Palmqvist and Hahn-Hagerdal, 2000a). These methods are economically and environmentally unattractive due to high processing cost, waste generation (i.e. gypsum) and/or considerable loss of fermentable sugars (Meinita et al., 2012). Nanofiltration (NF) is a promising membrane separation technology, having its low energy consumption and no secondary waste

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Nomenclature

C	solute concentration [M]	ΔP	transmembrane pressure difference [bar]
C_s	solute concentration in system [M]	P_s	solute permeability [L/m^2 h]
C_m	solute concentration at membrane surface [M]	R_{obs}	observed rejection [–]
C_p	solute concentration in permeate [M]	R_{real}	real rejection [–]
ΔC	concentration difference [M]		
J_s	solute flux [mol L/m^2 h]	*Greeks*	
J_v	solution flux [L/m^2 h]	$\Delta\pi$	osmotic pressure difference [bar]
L_p	pure water permeability [L/m^2 h bar]	σ	reflection coefficient [–]

generation. The applications of NF for the separation of toxic compounds from lignocellulosic biomass hydrolysate were reported by several groups (Qi et al., 2011; Weng et al., 2009, 2010). However, the separation of toxic compounds, by NF from the acid hydrolysate of red algal galactan or agarose is not reported yet.

5-HMF and LA themselves are versatile platform compounds to be converted into useful biofuels and chemicals. For instance, 5-HMF can be hydrogenated into dimethylfuran (DMF), which is a promising biofuel with a higher energy density and boiling point than ethanol (Roman-Leshkov et al., 2007). 5-HMF and its derivatives could potentially replace voluminously consumed petroleum-based building blocks, which are currently used to make plastics and fine chemicals (Ohara et al., 2010). LA is a very versatile building block for the synthesis of (bulk)-chemicals for applications like fuel additives, polymer and resin precursors (Werpy et al., 2004).

This study was aimed to demonstrate the feasibility of 5-HMF and LA removal from agarose hydrolysate and then recovering each of them in a pure form. The proposed process had two steps: the first one to remove 5-HMF and LA by NF from agarose hydrolysate to lower its toxicity and the other one to separate them by ED. ED was employed because it could effectively separate charged molecules like LA from uncharged ones like 5-HMF.

2. Methods

2.1. Materials

D-(+)-Galactose (>99.7%) was purchased from LPS solution, Co., Korea. And 5-hydroxymethylfurfural (5-HMF) and LA were purchased from Sigma–Aldrich, Inc., USA. All other chemicals were of analytical grade. In a series of hydrolysis experiments prior to this study, as agarose was hydrolyzed by acid catalysts such as HCl or H_2SO_4, galactose, 5-HMF and LA were produced as main compounds with little amount of unidentified brownish compounds. Only these three components have been reported to be the major components of red algal galactan hydrolysate (Jeong and Park, 2010). Model solutions, simulating acid hydrolysate of red algal galactan, were prepared by dissolving galactose, 5-HMF, and LA into distilled water to obtain a mixture solution containing 2 g/L glucose, 2 g/L 5-HMF, and 2 g/L LA. The pH of model solutions was adjusted by adding NaOH to model solutions.

2.2. Nanofiltration experiments and theoretical background

Nanofiltration experiments with TFC-SR3 membrane (Koch Membrane Systems, Inc., USA) were performed using a laboratory-made flat-sheet cross flow module. TFC-SR3 membrane was employed in this study. Physical properties of this membrane are: pH resistance, 3.0–10.0; isoelectic point , 3.84; contact angle, 48.5°; molecular weight cut-off, 200 g/mol; membrane pore radius, 0.38 nm; average permeability, 5.7 L/m^2 h bar (Munari and Schäfer, 2010). Since the molecular weight cut-off of the membrane is 200 g/mol, it was expected that 5-HMF (M.W.: 126 g/mol) and LA (M.W.: 116 g/mol) could be removed into the permeate and glucose (M.W.: 180 g/mol) could be retained in the feed solution. The effective membrane area was 60 cm^2. For washing, the membrane was rinsed with ultrapure water until an initial water flux was recovered. All experiments were carried out in a batch mode with the retentate recycled to the feed vessel with no feed and bleed streams. Sampling was started 1 h after the application of a new operating condition to avoid the influence of the previous run. The permeate was collected, and the accumulated volume was measured for flux measurement. One milliliter of the permeate collected was taken for analysis. The remaining volume of permeate was recycled to the feed vessel. In all experiments, the collected sample volume was less than 10 mL. Such amount of sampling was quite small compared to the feed volume of 4 L and thus the artifact caused by sampling was considered to be negligible. After each experiment, the module was rinsed with ultrapure water. Unless otherwise specified, the feed solution was a model solution containing 2 g/L galactose, 2 g/L 5-HMF, and 2 g/L LA and the solution pH was 4.0. This composition was adopted considering preliminary experimental results that, as 5 g/L agarose was decomposed, about 2 g/L galactose, 0–2 g/L 5-HMF and 0–2 g/L LA were produced. Since the membrane used in this study, TFC-SR3 was known to be seriously damaged at pH's lower than 3.0, the pH of the hydrolysate feed solution was adjusted to 4.0 or higher as required by using NaOH. The pH of the original hydrolysate was below 3.0. The operating pressure was varied in the range from 3.5 to 27.6 bar (50–400 psig). Unless otherwise specified, the system temperature was controlled at 30 °C, and cross-flow rate was maintained at 1.56 m/s.

The transport of solute through NF membranes can be described by irreversible thermodynamics where the membrane is considered as a black box. The solution flux, J_v and the solute flux, J_s are described by Kedem and Katchalsky (1963):

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \tag{1}$$

$$J_s = P_s\Delta C + (1-\sigma)CJ_v \tag{2}$$

where, L_p, ΔP, C, ΔC, P_s, $\Delta\pi$ and σ denote pure water permeability, transmembrane pressure difference, solute concentration, concentration difference between the feed and permeate solutions, solute permeability, osmotic pressure difference and reflection coefficient, respectively.

Starting from Eqs. (1) and (2), Spiegler and Kedem proposed the following equation for the relationship between the real rejection R_{real} and solution flux, J_v (Kim et al., 2012). In this study, a high cross-flow velocity was adopted in all the experiments to eliminate the concentration polarization effect. Thus, the real rejection R_{real} is assumed to be equal to the observed rejection, R_{obs},

$$R_{real} \equiv R_{obs} = 1 - \frac{C_p}{C_s} = 1 - \frac{1-\sigma}{1-\sigma\exp\left[\left(\frac{\sigma-1}{P_s}\right)J_v\right]} \tag{3}$$

where, C_s and C_p are the concentration of each component in the system and permeate solutions, respectively.