



# Purification of xylose in simulated hemicellulosic hydrolysates using a two-step emulsion liquid membrane process



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## HIGHLIGHTS

- Xylose was purified from simulated hydrolysates through a two-step ELM process.
- Acetic acid or sulfuric acid was selectively removed and enriched in each ELM step.
- Sugar purification through the two-step ELM process seemed economically feasible.

## ARTICLE INFO

### Article history:

Received 18 May 2014

Received in revised form 5 July 2014

Accepted 17 July 2014

Available online 24 July 2014

### Keywords:

Xylose

Acetic acid

Simulated hemicellulosic hydrolysate

Emulsion liquid membrane

Two-step ELM process

## ABSTRACT

Purification of xylose in simulated hemicellulosic hydrolysates was attempted using a two-step emulsion liquid membrane (ELM) process. The effects of various experimental variables on extraction of each component in the hydrolysates were investigated in the ELM steps. In the first ELM step, acetic acid could be selectively removed from the hydrolysates and highly enriched in the stripping phase, and loss of xylose was insignificant. In the second ELM step, sulfuric acid could be selectively removed from simulated acetic acid-free hemicellulosic hydrolysates and somewhat enriched in the stripping phase. There was just small loss of xylose, and the final pH of the feed phase approached a pH level suitable for ethanol fermentation. Also, concentration of xylose in the feed phase was attained as an incidental outcome during each ELM run. Conclusively, the two-step ELM process was found to be a promising futuristic technology for purification of sugars in real hemicellulosic hydrolysates.

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## 1. Introduction

Bioconversion of sugars into ethanol has lately attracted the notice of those who try to get the alternation for fossil fuels because of their coming shortages. The sugars can be obtained through hydrolysis of lignocelluloses which consist of carbohydrate polymers (hemicellulose and cellulose) and an aromatic polymer (lignin). The most easily acid-hydrolyzed constituent part among them is hemicellulose because of its open-branched structure (Parajó et al., 1998). Dilute sulfuric acid hydrolysis has been most widely used to obtain a hemicellulosic hydrolysate from the lignocellulosic biomass (Grzenia et al., 2008). The hemicellulosic hydrolysate contains not just xylose-rich sugars but also inhibitors such as carboxylic acids, furans and phenolic compounds, which limit the yield of ethanol by suppressing fermentative organisms (Arruda et al., 2009; Nam et al., 2011). Among them, acetic acid is the most toxic compound for the organisms and

exists in the largest amount (Nam et al., 2011; Parajó et al., 1998; Zhou et al., 2013a,b). Also, even though the hydrolysates contain a small quantity of sulfuric acid, pH of the hydrolysates is too low to ferment the sugars effectively. Thus it is required to remove acetic acid as well as sulfuric acid from the hydrolysates before the fermentation. This work was a preliminary study on purification of sugars in real hemicellulosic hydrolysates so a mixture of xylose, acetic acid and sulfuric acid was chosen as simulated hemicellulosic hydrolysates here.

Many researchers have recently tried to remove acetic acid from simulated or real hemicellulosic hydrolysates using various separation technologies such as nanofiltration and ultrafiltration membranes (Weng et al., 2009; Zhou et al., 2013a,b), adsorption and chromatography (Nam et al., 2011; Sainio et al., 2011), liquid extraction (Grzenia et al., 2008) and biological treatment (Schneider, 1996). Because of low separation factor and/or high equipment and operating costs, they were unlikely to be economically efficient. Lee (2013) first applied a new cost-effective separation technology, an ELM process, to removal of acetic acid in simulated hemicellulosic hydrolysates. Acetic acid was selectively

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separated from the hydrolysates (feed phase) and concentrated into the stripping phase. Simultaneously, losses of xylose and sulfuric acid in the feed phase were very small. Conclusively, the ELM process was proven to be economically promising.

In this work, a two-step ELM process was considered to purify xylose in simulated hemicellulosic hydrolysates. Acetic acid was removed from the hydrolysates through the first ELM step, and sulfuric acid was subsequently removed from simulated acetic acid-free hemicellulosic hydrolysates through the second ELM step. A part of the current work, i.e. separation of acetic acid by the first ELM, is an extension of the previous ELM work (Lee, 2013) whose need is stated in the beginning of Section 3.2.

When sulfuric acid is used as a catalyst for hydrolysis of lignocellulosic biomass, it must be recovered and recycled right after separation of acetic acid from the hydrolysates because it is not cheap compared with the value of sugars in the hydrolysates (Baltz et al., 1982). According to recent studies (Lin et al., 2012; Telli-Okur and Eken-Saracoglu, 2008), nevertheless, alkali has been directly added to the acidic hydrolysates for neutralization and sulfuric acid has become irrecoverable. Since major expenses of lignocellulosic biomass hydrolysis are acid and neutralization costs, separation of the acid and its recycle to the process must be very important to enhance process economics (Neuman et al., 1987). Unfortunately, research on separation of sulfuric acid and sugars in hydrolysates is quite rare, except for its removal by addition of lime to acid hydrolysates. For this purpose, separation of sulfuric acid and xylose by the second ELM was first attempted in this work.

## 2. Methods

In the first ELM experiments, an aqueous feed solution (simulated hemicellulosic hydrolysate) was composed of acetic acid, D-xylose and sulfuric acid whose concentrations were determined on the basis of those in real hemicellulosic hydrolysates (Carvalho et al., 2005; Carvalho et al., 2006; Mancilha and Karim, 2003; Villarreal et al., 2006). An organic membrane solution consisted of C9232 (Infineum UK Ltd.), Span 85 (sorbitan trioleate) or their mixture as an emulsifier and kerosene as an organic solvent, and an aqueous stripping solution was NaOH solution. In the second ELM experiments, a mixture of xylose and sulfuric acid was used as an aqueous feed solution (simulated acetic acid-free hemicellulosic hydrolysate), where their concentration ranges investigated were almost the same as those in the first ELM experiments. An organic membrane solution was a mixture of C9232 and Span 85 dissolved in kerosene. Amberlite LA-2 (LA-2, a secondary amine, Merck), tri-n-octylamine (TOA, tertiary amine, Aldrich) or Aliquat 336 (quaternary amine, Aldrich) was used as an extractant of sulfuric acid. Na<sub>2</sub>CO<sub>3</sub> or NaOH solution was used as an aqueous stripping solution.

The first and the second ELM experiments were performed with the same batch-type glass reactor that Lee (2011, 2013) used. Water-in-oil (w/o) type emulsion was prepared by slowly pouring the stripping solution into a beaker containing the membrane solution with a homogenizer (T25, IKA Lab.) stirred at 12,000 rpm for 10 min. The volume of the stripping solution was equal to that of the membrane phase. At the start of each ELM run, the emulsion was poured in the glass reactor containing 420 cm<sup>3</sup> of the feed solution and the two immiscible phases were mixed at 360 rpm. The volume ratio of emulsion phase to feed phase was 1/6. The reactor was maintained at 25 °C during the ELM run. Samples taken from the reactor were separated into the feed and the emulsion phases using a filter paper and then the emulsion was broken by a freezing and thawing method in order to obtain the stripping phase (Lee, 2013).

The pH of the feed phase and the concentration of each component in the feed and the stripping phases were measured using a pH meter (F-55, Horiba) and high-performance liquid chromatography (HPLC, Waters), respectively. The HPLC analysis was conducted with a Supelcogel 610-H column (7.8 × 300 mm, Supelco). The column was maintained at 35 °C and 0.1% phosphoric acid solution was used as eluent at the flow rate of 0.5 ml/min. Peaks of xylose and sulfuric acid were detected by a refractive index (RI) detector (Waters 410) and that of acetic acid by a photodiode array detector (Waters 996) at 210 nm, respectively. Meanwhile, pure NaOH or Na<sub>2</sub>CO<sub>3</sub> solution was found to give RI chromatogram peaks at the same retention times as xylose and sulfuric acid. Even though the two peak areas for the alkaline solutions were not too large, the concentrations of xylose and sulfuric acid in the stripping solution containing NaOH or Na<sub>2</sub>CO<sub>3</sub> could be overestimated to some extent during the HPLC analysis, compared to their real concentrations. Accordingly, it should be noted that the apparent values for xylose and sulfuric acid concentrations in Tables 2 and 3 can be a little greater than their real values.

## 3. Results and discussion

Two types of ELM systems were considered in this work. The two terminologies, degree of extraction ( $DE_A$ ) and enrichment ratio ( $ER_A$ ) of solute A, were used to describe its extraction efficiency in the ELM systems. The solute A can be acetic acid, xylose, or sulfuric acid. They are defined as follows:

$$DE_A = \frac{C_{A0,feed} - C_{A,feed}}{C_{A0,feed}} \times 100 \quad (1)$$

$$ER_A = \frac{C_{A,strip}}{C_{A0,feed}} \quad (2)$$

where  $C_{A0,feed}$  is the initial concentration of solute A in the feed phase, and  $C_{A,feed}$  and  $C_{A,strip}$  are its concentrations in the feed and the stripping phases at any sampling time, respectively.

### 3.1. Transport mechanism for selective extraction of each acid in a two-step ELM process

Xylose in a simulated hemicellulosic hydrolysate, composed of three components, could be purified through a two-step ELM process. In other words, only acetic acid was preferentially removed from the simulated hydrolysate by the first ELM and then sulfuric acid was selectively removed from the acetic acid-free hydrolysate by the second ELM. Fig. 1 shows transport mechanism for selective extraction of each acid during purification of xylose by the two-step ELM process.

The only reactive component of C9232 is polyisobutylene succinimide (bis-succinimide) which contains amine functional groups and thus reacts with acids to form complexes (Lee and Hyun, 2013; Zhang and Lockwood, 2008). Contrary to expectations, very strong complexation of sulfuric acid with bis-succinimide of C9232 makes it difficult to release sulfuric acid into the stripping phase even under its extremely alkaline environment in an ELM system, thereby resulting in very low degree of extraction of sulfuric acid (Lee, 2013). In the first ELM system, therefore, C9232 functioned only as a carrier of acetic acid, while transport of xylose and sulfuric acid was insignificant. As shown in Fig. 1a, undissociated acetic acid (HA) and bis-succinimide (B) react together at the external interface between the feed and the membrane phases to produce acetic acid-bis-succinimide complexes [(HA)<sub>1.15</sub>B<sub>0.91</sub>] (Lee and Hyun, 2013). The complexes then diffuse through the membrane phase to the internal interface between the membrane and the stripping phases, where their decomplexation occurs and then

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