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Green liquor extraction of hemicellulosic fractions and subsequent organic acid recovery from the extracts using liquid–liquid extraction

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ABSTRACT

Extractions of hard- and softwood chips were carried out using green liquor with varying alkali charges (1%, 3%, and 5% on dry wood weight). The pulp yield of a mill was sustained while producing a by-product stream of extracted hemicellulose. The extractions were performed at 180 °C for 18 min and the pre-pulping extracts contained mostly xmg (= xylose + mannose + galactose), acetic acid, and formic acid. We investigated the use of a liquid extractive agent in removing fermentation inhibitors. The extraction potential of each solvent was examined at an organic to aqueous phase ratio of 1:1. The liquid–liquid extractions were performed at different temperatures (25–65 °C) and pH values (0.5–3.5) for 36 min. The extraction potentials of trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TAPO) were compared to determine their application in industrial-scale extraction. It was determined that the acetic acid extraction efficiency of TAPO was higher than that of TOPO. The maximum acetic acid extraction yields for the extracts derived from hard- and softwood were 83.1% and 82.1%, respectively, using TAPO as an extractant at 25 °C and pH 0.5.

1. Introduction

In pulp mill-based biorefineries, the production of wood pulp can be supplemented by the coproduction of high-value chemical products and liquid fuels (Um et al., 2011). Through biorefineries, the forest product industry has been able to obtain the necessary infrastructure and resource base to enable short-term deployment of lignocellulose-based bioproduct technologies. The pre-pulping extraction of hemicellulose may provide a new feedstock for biofuel production, thus, increasing the total revenue stream for the pulp and paper industry (Ragauskas et al., 2006; van Heiningen, 2006).

Several pre-pulping extraction technologies have been proposed for removing hemicellulose from biomass such as steam explosion, dissolution with organic solvents or alkali solutions, treatment with dilute acid or enzymes, and water extraction (via autohydrolysis). It has been shown that when pre-pulping extraction is carried out using dilute green liquor (GL) as the solvent, the pulp yield from the mill can be sustained throughout the by-production stream of extracted hemicelluloses (van Heiningen, 2006). GL, the partially recovered form of kraft liquor, is obtained after the combustion of black liquor in the recovery boiler by dissolving the boiler smelt in water. It contains several compounds including sodium carbonate, sodium sulfide, and sodium hydroxide (Um et al., 2011).

In pre-pulping extraction, some decomposed compounds (mainly acetic acid) hinder the subsequent bioconversion of the solubilized sugars into desired products by reducing fermentation rates and conversion yields (Um et al., 2011). Acetic acid is one of the major inhibitory compounds released during pre-pulping extraction that can also be sold as a chemical feedstock if separated and purified. The block flow diagram in Fig. 1 represents the biorefinery concept of pre-pulping extraction and acetic acid recovery. Acetic acid is ubiquitous in hemicellulose hydrolyzates when hemicellulose and, to some extent, lignin are acetylated (Fengel and Wegener, 1989; Klinke et al., 2004). The inhibitory effect of acetic acid ($pK_a = 4.75$ at 25 °C) is strongly influenced by pH. When the pH of a hydrolyzate is lower than 4.75, the protonated form of acetic acid is dominant in solution. As this form of the acid is lipophilic, it can diffuse through the cytoplasmic membrane and detrimentally affect cell metabolism (Lohmeier-Vogel et al., 1998). Although the effect of acetic acid can be reduced by conducting the bioconversion at high pH (above or around 6.0), fermentation at this neutral pH is suboptimal. It would be ideal to recover acetic acid prior to fermentation because it may also fetch value in the chemical market.

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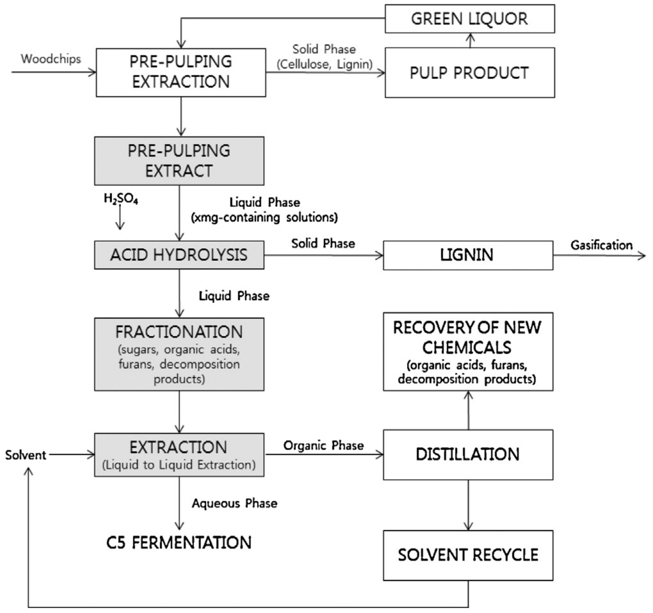

Fig. 1. Block flow diagram representing the process of pre-pulping extraction in a biorefinery plant producing wood pulp, fermentation-derived alcohol, and acetic acid. Note: acetic acid recovery is the focus of this study.

Current methods for extraction of acetic acid from ethanol fermentation broths are time consuming and costly. Various technologies have been reported for the separation of organic acids from complex mixtures. Examples are: (catalytic) distillation (Xu et al., 1999), adsorption using ion-exchange resins (Anasthas and Gaikar, 2001), and microemulsion liquid membrane separation (Wiencek and Qutubuddin, 1992). The separation of acetic acid from aqueous solutions by simple rectification is very difficult, requiring multiple column purification stages and a high reflux ratio, thus incurring high running costs (Anasthas and Gaikar, 2001; Wasewar et al., 2004). Liquid–liquid extraction (LLE) is a process used to separate two miscible compounds using a solvent that preferentially dissolves one of them (Dramur and Tatli, 1993; McCabe and Smith Harriott, 1993; Briones et al., 1994; Arce et al., 1995). Previous studies have shown that LLE can successfully separate acetic acid from aqueous solutions (Um et al., 2011). The use of organophosphorus compounds and alkylamines with high molecular weights dissolved in various diluents has been explored for the LLE of acetic acid from aqueous solutions. Partition coefficients (P_c) for these systems vary between 3 and 5 (Ricker et al., 1979; Senol, 1999; King, 1992; Sabolova et al., 2001; Um et al., 2011). Senol (1999) reduced the molar loading for carboxylic acid removal from water to greater than one using alamine 336 in halogenated hydrocarbon diluents. Several solvents have been applied to the removal of acetic acid from pre-pulping extracts. The use of trioctylphosphine oxide (TOPO) as an extractant for the removal of fatty acids from aqueous solutions has been demonstrated (Heisel, 1977; Niitsu and Sekine, 1978; Wardell and King, 1978; Ricker et al., 1979; Hano et al., 1990; Reisinger and King, 1995; Juang and Wu, 1999; Al-Mudhaf et al., 2002; Wisniewski and Pierzchalska, 2005). TOPO complexes strongly with carboxylic acids in organic phases because of its high hydrogen-bond acceptor basicity, thereby enhancing the transfer of carboxylic acids into the organic phase. In addition, TOPO is characterized by excellent stability, high boiling point, and low solubility in water. Al-Mudhaf et al. (2002) reported the separation of acetic acid from aqueous NaCl solutions into cyclohexane containing varying concentrations of TOPO as the extractant at 30 °C. They found that TOPO was required to optimize organic acid recovery.

Table 1
Chemical composition of hard- and soft woodchips on dry basis.

Components	Type	
	Hardwood (%)	Softwood (%)
Glucan	34.15	37.59
XMG (xylan + mannan + galactan)	23.08	20.41
Arabinan	2.45	2.93
Total sugar	59.68	60.93
Acetate	5.54	2.23
Klason lignin	18.51	24.93
Extractives	2.85	6.20
Total non-carbohydrates	26.90	33.36
Total (total sugars + total non-carbohydrates)	86.58	94.29

Tri-*n*-alkylphosphine oxide (TAPO) is a liquid phosphine oxide, which also has potential applications in the solvent extraction of both organic and inorganic solutes from aqueous solutions. It has been shown to remove carboxylic acids from effluent streams and arsenic impurities from copper electrolytes. A liquid TAPO was developed by Watson et al., which consisted of a mixture containing four trialkylphoshine oxides with *n*-hexyl-and *n*-octyl substituents (Watson et al., 1998). The main benefit of extractants with a high organic solubility is that highly concentrated solvents can be prepared. These organic phases recover solutes (like acetic acid) that are normally weakly attracted to this kind of solvent. Processes in petrochemical plants, wood pulping mills, and other chemical facilities also often generate aqueous effluent streams containing carboxylic acids (in particular acetic acid) (Madane, 2013).

The objective of this study is to investigate the recovery efficiency of acetic acid from pre-pulping extracts using different types of solvents (TOPO and TAPO) in a single batch LLE. The optimal extraction conditions were determined through the following steps: Step (1), the optimal pre-pulping extraction conditions were selected; Step (2), the effect of temperature and pH on the LLE of selected pre-pulping extracts was investigated; Step (3), a comparison was made between the extraction efficiency of TOPO and TAPO; Step (4), the extraction yields of the extractants with two different extracts were compared; and Step (5), the sugar retention after LLE was assessed.

2. Methods and materials

2.1. Raw materials

Mixed hardwood and softwood chips were used throughout this study. The most prevalent hardwood species in the woodchip samples were oak (*Quercus* sp.), while the softwood species mostly contained pine (*Pinus rigida Mill*). Both hard- and softwood chips were supplied by Deadong Industrial Co., Ltd. (Gyeongsang-do, Korea). Woodchip samples with average sizes of 35.2 × 20.8 × 4.4 mm and 32.1 × 18.5 × 5.4 mm were selected using a mechanically vibrated horizontal screen. The screened woodchips were used directly in the GL chemical extraction studies. Some of the screened chips were ground to an average size of 30–40 mesh (0.595–0.420 mm) using a laboratory knife (POLYMIX® PX-MFX 90D, KINEMATICA AG, Luzern, Switzerland). The milled woodchips were used to determine the total solid/moisture ratio and carbohydrate content in the biomass. The chemical composition of woodchips on a dry basis is listed in Table 1. The raw woodchips were analyzed quantitatively for their composition according to the National Renewable Energy Laboratory (NREL) analytical procedures: NREL/TP-510–42618 (structural carbohydrates) and 42623 (sugars, byproducts, and degradation products in liquid fractions) (Sluiter et al., 2011; Sluiter et al., 2006). The lignin and extractives in the raw woodchips and extraction liquor were analyzed quantitatively for their composition according to the NREL analyti-