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Reactive extraction and recovery of levulinic acid, formic acid and furfural from aqueous solutions containing sulphuric acid

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ABSTRACT

Levulinic acid (LA) can be produced from lignocellulosic materials via hydroxylation followed by an acid-catalyzed conversion of hexoses. Inorganic homogeneous catalysts are mostly used, in particular sulphuric acid, yielding a mixture of LA with sulphuric acid, formic acid (FA) and furfural. Significant attention has been paid to optimization of the yield, but purification of the LA is a challenge too. This work focuses on the separation of LA from the complex aqueous mixtures by liquid-liquid extraction. Two aqueous product feeds were considered, reflecting two different processes. One aqueous product stream contains sulphuric acid and LA, while the second product stream also contains formic FA and furfural. Furfural could be removed selectively via liquid-liquid extraction with toluene. For selective extraction of LA and FA without co-extracting sulphuric acid, 30 wt.% of trioctylphosphine oxide (TOPO) in methylisobutylketone (MIBK) was found most suitable, showing a high selectivity over sulphuric acid, and a high equilibrium partitioning of LA. When instead of MIBK, 1-octanol was applied as diluent, the co-extraction of FA was enhanced, while hexanoic acid suppressed the acid extraction. To obtain the LA pure, eventually a distillation is required, and the potential of temperature swing back extraction (TSBE) at 90 °C to pre-concentrate the acid solutions was evaluated for 30 wt.% TOPO in MIBK. This pre-concentration step increased the concentrations of LA and FA by a factor of 2.45 and 2.45 respectively, reducing the distillation reboiler duty from roughly 31.5 to 11.3 GJ per ton LA, at a cost of roughly 4.5 GJ heating duty per ton produced LA.

1. Introduction

Levulinic acid (LA) is widely described as one of the high potential platform chemicals which can be derived from lignocellulosic materials [1]. The predominant conversion route in production of LA starts with hydrolysis of the polymeric lignocellulosic materials into the hexose- and pentose monomers under acidic conditions. LA is formed via an acid-catalyzed reaction of the hexoses via the intermediate 5-hydroxymethylfurfural (5-HMF). Formic acid (FA) is obtained as an unavoidable side product. In parallel, the pentoses are converted into a second side product, furfural. The total yield of useful products is reduced by the formation of black insoluble particles, called humins, via a polymerization reaction [2]. This unwanted by-product can be removed together with the unreacted lignocellulosic materials by in situ filtration of the reaction mixture [3]. Various acidic materials have been reported to facilitate the reaction to LA. Usually homogeneous acid catalysts, such as inorganic acids [4–7], enzymes [8], acidic functionalized ionic liquids [9], organic acids [5] and metal salts of such acids [8] are considered. Besides those, heterogeneous acid catalysts i.e. ion exchange resins, were mentioned too [8,10]. Despite purification complications, inorganic acids are most often used in the conversion to LA, because very long reaction times are required to obtain similar yield when using a heterogeneous catalyst [11].

The homogeneous mineral acids hydrochloric acid and sulphuric acid can be used both, with sulphuric acid as preferred acid [12], due to the potential risk of releasing chlorine in the biosphere when using hydrochloric acid [11].

Research papers and patents focus mainly on the description of the pre-fractionation [4,5,13–15] or conversion [6,7,16–22] of various types of feedstocks to LA. In acid-catalyzed reactions of lignocellulosic materials to LA, two approaches are commonly applied

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Abbreviations: 5-HMF, 5-hydroxymethylfurfural; HPLC, High Pressure Liquid Chromatography; KF, Karl Fischer; DIPE, diisopropylether; TOA, trioctylamine; TOPO, trioctylphosphine oxide; TB, 4-*tert*-butylbenzenediol; TSBE, temperature swing back extraction; GJ, gigajoule.

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using strong inorganic acids, i.e. using high acid concentrations at mild temperatures (55–60 wt.% hydrochloric acid or 31–70 wt.% sulphuric acid at 20–50 °C), or diluted acids (<10 wt.%) at high temperatures of 170–240 °C [3,12,16,20,23–32]. The high reaction temperature and diluted catalyst option is most often applied [6,7,12,16,20,22,29,32]. This prevents the use of expensive equipment which can withstand the high acid concentration, which is considered beneficial over the advantage of high acid concentrations that according to Mullen et al. [6] Reunanen et al. [12] and Cuzens et al. [24] result in less char formation, a higher LA yield and fewer by-products at lower temperatures. .

After the conversion step, producing the LA, a complex aqueous product mixture is obtained, which needs further fractionation. Although the LA concentration in the mixture is strongly dependent on the type of lignocellulosic material used and the reaction conditions applied, often 3–8 wt.% has been found, for both FA and furfural a concentration of 1–5 wt.% was found [7,20,22,24,31,32].

For dilute high boilers such as LA, due to the low concentration of products in the aqueous stream, direct distillation is economically less favorable, and liquid-liquid extraction has been mentioned as potential technique for fractionating the product mixture [7,32].

Traditionally high molecular weight aliphatic amines [21,33–36] and organophosphorus extractants [12,37] have been used to extract carboxylic acids from diluted aqueous streams. In addition a large variety of physical solvents have been suggested such as alkylphenols [6,17], ketones [6], alcohols [6], fatty acids [6,12], esters [12], ethers [6,20], and halogenated hydrocarbons [6]. Very recently, a study has been reported using octanol, MIBK and furfural as physical solvents, and the heat duty to recover the LA from these solvents was compared [38]. Recently new extractants have been designed to further improve the extraction of carboxylic acids, such as aromatic amines [39] and ionic liquids [40–43]. Reyhanitash et al. [44] recently showed that both aliphatic amines and ionic liquids cause significant co-extraction of sulphuric acid, making them less suited for selective extraction of LA due to the presence of sulphuric acid as catalyst. Since the raffinate of the acid extraction is recycled back to the reaction step, and the product should not contain sulphuric acid, any sulphuric acid co-extraction results in the necessity of an additional catalyst recovery step.

It is thus important to find a solvent that shows a high selectivity for LA over sulphuric acid, and here, we report a solvent screening study focusing on the acid fractionation, which is a key step in the process allowing product isolation without loss of catalyst. Possibly, the acid fractionation is preceded by a furfural extraction section (but this might also be done afterwards). In the complete fractionation scheme, as shown in Fig. 1, these are the second and third sections. After the physical solvent screening for furfural removal, the composite solvent screening study was performed in two stages, in the first stage only sulphuric acid and LA were present in the mixtures, while in the second stage the more complex mixtures were applied that also contain FA and furfural.

Next to selectivity and distribution in the extraction process, any economically feasible process should exhibit good recyclability of the solvent. Next to the solvent screening, also recyclability by back-extraction at elevated temperature was investigated.

2. Experimental

2.1. Chemicals

All chemicals were purchased by Sigma Aldrich and used as received without further treatment, i.e. levulinic acid (98%), 1-octanol (≥99%), formic acid (≥95%), heptane (99%), 4-*tert*-butylcatechol (≥98.0%), 4-methyl-2-pentanone (≥98.5%), dodecane (≥99%), sulphuric acid (95.0–98.0%), toluene (≥99.9%), diisopropyl ether (≥98.5%), furfural (99%), 1-pentanol (≥99%), 1-butanol (≥99.7%), 1-hexanol (≥99%), hexanoic acid (≥98.0%), trioctylamine (99.6%) and trioctylphosphine oxide (99%).

2.2. Liquid – liquid extraction experiments

Liquid-liquid extraction experiments were conducted in 10 mL glass vials. An analytical balance was used to weigh all compounds in both phases with an accuracy of 0.5 mg. The biphasic systems in the vials was shaken rigorously using a mechanical mixer and consecutively shaken in a shaking bath for at least 20 h at a constant temperature. All the experiments have been performed at 25 ± 0.02 °C, with the exception of experiments where the temperature is indicated otherwise. The mass of the aqueous phase was kept constant at 4 g with a solvent to feed ratio of 1 (mass based). The aqueous phase contained 8 wt.% LA and 10 wt.% sulphuric acid, and in case the more complicated feed was used, also 5 wt.% FA and 5 wt.% furfural was added to the aqueous phase. These concentrations reflect achievable concentrations for the acid catalyzed conversion in various processes with various lignocellulosic feedstocks.

2.3. Analytical procedures

2.3.1. High Pressure Liquid Chromatography (HPLC)

The aqueous phase concentrations of LA, FA, furfural and sulphuric acid were determined with HPLC using an Agilent 1200 series apparatus, equipped with a Hi-Plex-H column (300 × 7.7 mm) and a refractive index detector (RID). 5 mM aqueous sulphuric acid solution was applied as eluent at a flow rate of 0.6 mL/min. The injection volume was 10 μL and the column oven was isothermally operated at 65 °C.

2.3.2. Karl Fischer Titration (KFT)

The water content of all the organic phases was analyzed with Karl Fischer Titration using a *787 KF Titrino 730 TiStand of Metrohm*, each sample was analyzed in duplo. A methanol/dichloromethane (volumetric ratio of 3:1) solution and HYDRANAL® were used as titrant. A standard deviation over all measurements was determined to be 0.19 vol.%.

2.4. Definitions

The reported distribution coefficients are defined on molar basis:

$$K_{D,i} = \frac{[i]_o}{[i]_{aq}} \left(\frac{mole/L}{mole/L}\right) \qquad (1)$$

where i represents LA, FA, sulphuric acid or furfural. The organic phase concentrations were determined using the mass balance, and taking into account the mass of water leached to the organic phase and the mass of solvent leached to the aqueous phase.

3. Results and discussion

Eight physical solvents were evaluated, both as monomolecular solvent, and as diluent when in a composite solvent with an extractant. In addition the process side product, furfural, was evaluated as described by Nhien et al. [38]. Though in presence of sulphuric acid, furfural was found to be unstable and formed humins.