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Extraction of acetic acid, glycolaldehyde and acetol from aqueous solutions mimicking pyrolysis oil cuts using ionic liquids

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ABSTRACT

Value-added oxygenates, such as acetic acid (HAc), glycolaldehyde and acetol, are present in pyrolysis oil and its cuts in substantial amounts. This work describes the separation of these value-added oxygenates from artificial aqueous fractions of pyrolysis oil via liquid-liquid extraction. Three phosphonium ionic liquids (ILs), two imidazolium ILs and one benchmark organic mixture (40 wt% tri-*n*-octylamine in 1-octanol: TOA/1-octanol) were applied as solvents. Although suited as solvent for HAc and glycolaldehyde, the benchmark TOA/1-octanol showed a low acetol distribution coefficient (0.05), which makes it less suitable for use in an integrated oxygenates extraction process. Phosphonium ILs showed the highest affinities for HAc and glycolaldehyde, and reasonable affinity for acetol. However, none of these solvents could be applied to remove all oxygenates from the aqueous solution in a single extraction step, because of the difficulty of oxygenates evaporation from phosphonium ILs and the reactivity of glycolaldehyde with $P_{666,14}[N(CN)_2]$ in the presence of HAc, as was confirmed by NMR. Based on the good affinity of the imidazolium ILs for acetol, a two-step extraction process was proposed where Hmim[B(CN)₄] may be used to extract acetol and HAc in the first step and be regenerated by evaporation of the solutes, and $P_{666,14}[Phos]$ may be applied to extract glycolaldehyde in the second step and be regenerated by back-extraction with water.

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1. Introduction

Due to the rising concerns on climate change, biomass as renewable resource has gained growing interest for production of bio-based fuels and chemicals. Pyrolysis oil (also known as bio-oil), the liquid product of fast pyrolysis (heating biomass in absence of oxygen to temperatures above 400 °C), has been applied as a renewable fuel for generation of heat and power [1]. Next to direct use of the oil as fuel, also separation and valorization of attractive chemicals present in the pyrolysis oil such as aromatics and sugars have been widely studied [2–5]. Within the pyrolysis oil some other value-added oxygenates are also present in substantial amounts, such as acetic acid (HAc, 12%), glycolaldehyde (13%) and acetol (7.4%) [6].

These oxygenates offer interesting commercial opportunities. Glycolaldehyde can be used as an effective meat-browning agent [7] or as fermentation feedstock for production of ethylene glycol [8]. HAc as an important chemical reagent is primarily employed in the production of cellulose acetate and polyvinyl acetate [9]. Additionally, acetol can promote various reactions (e.g. dehydra-

tion, hydrogenation, oxidation) and produce numerous products including propylene glycol, acrolein, acetone and furan derivatives [10].

Prior to further upgrading, these chemicals need to be isolated from the pyrolysis oil mixtures. Direct distillation of these oxygenates is not feasible due to the poor thermal stability of the pyrolysis oil [11], and direct extraction with an organic solvent is not attractive as a certain amount of the solvent ends up in the pyrolysis oil phase [12]. A potential initial step is to apply a water wash, and collect the polar oxygenates in the aqueous fraction. Upon water addition to the pyrolysis oil, 80–90% of the oxygenates can be extracted to the aqueous phase, based on their polarity [13]. An elegant alternative for water wash can be a thermal fractionation by employing a series of condensers operated at different temperatures to condense fractions of the pyrolysis vapors based on the boiling points of the species in the fractions. By careful control of the condenser temperatures, aqueous fractions containing up to 10% HAc and 8% acetol can be obtained directly from one of the condensers [14]. Because both methods are not highly selective, many other compounds with either similar polarity or boiling points are present in the mixtures as well.

Several methods have been investigated to separate specific oxygenates from the aqueous fractions of pyrolysis oil. Nanofiltration

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has been employed by Ford and coworkers to recover HAC, but the membrane was irreversibly damaged by the phenolics that were also present in the solutions [15]. Liquid-liquid reactive extractions using tertiary amines have been widely studied for HAC recovery from aqueous solutions [16–18]. In one single stage, about 84 wt % HAC was recovered with 40 wt% tri-*n*-octylamine in 2-ethyl-hexanol at room temperature from the aqueous fraction of pyrolysis oil with 3.33 wt% HAC in the mixture at a 1:1 solvent to feed ratio [17]. However, solvent regeneration via vacuum distillation results in the loss of 2-ethyl-hexanol which may co-evaporate with the solute [19].

Stradal and Underwood have invented a process to isolate glycolaldehyde from pyrolysis oil [20]. The process shown in Scheme 1 comprises several steps: (i) water extraction to produce a water soluble fraction of pyrolysis oil; (ii) water evaporation to reduce water content; (iii) multiple evaporation and fractionation steps to remove the low and high boiling components and further concentrate glycolaldehyde; (iv) precipitation of glycolaldehyde from methylene chloride. The separation steps of evaporation and distillations should be operated carefully to prevent reactions of glycolaldehyde, e.g. low temperature, vacuum pressure, short residence time at high temperature. Multiple evaporation and condensation steps are not economic and it appears better to selectively extract glycolaldehyde and recover it from the solvent.

De Haan and co-workers have studied extensively on isolation of glycolaldehyde from aqueous fractions of pyrolysis oil by liquid-liquid extraction [8,18,19,21]. High extraction efficiency of glycolaldehyde can be achieved via reactive extraction with primary amines, but the regeneration is challenging due to the high stability of the formed Schiff-base [21]. Physical extraction of glycolaldehyde with 1-octanol was also investigated, but low overall glycolaldehyde yield (17.2%, the percentage of its initial mass in the feed) was obtained from the proposed process, due to the low distribution coefficient of glycolaldehyde (0.25) [8]. Acetol was also co-extracted with 1-octanol, but the distribution coefficient of acetol was low as well (0.17). The other alternative is co-extraction of glycolaldehyde during reactive extraction of HAC with TOA in 2-ethyl-hexanol [18]. High HAC recovery yield (80%) was obtained but less than 10 wt% of glycolaldehyde (the percentage of its initial amount in the feed) was extracted due to the low distribution coefficient of glycolaldehyde (<0.20). Thus, exploring of new solvents with higher distribution coefficients of these oxygenates may bring new process options with a smaller impact on the environment.

Ionic liquids (ILs), known as environmentally friendly solvents, have been proposed to be used for liquid-liquid extractions, e.g.

separation of aromatics from aliphatics [22–24] or from sugar solutions [3,5], recovery of precious metals for recycling [25]. Their negligible vapor pressure and high thermal stability allow ILs to be recovered from the extract by solutes evaporation, which uses potentially less energy than recovery of low boiling organic solvents where large amount of solvents are typically evaporated [3]. Moreover, the extractability of the solutes can be enhanced by tuning the combination of cations and anions. ILs have shown potential for extraction of acids (e.g. HAC, lactic acid, amino acid) from aqueous solutions [26–32]. However, there is no report on utilization of ILs to extract oxygenates from aqueous solutions of pyrolysis oil.

In this work, the feasibility and reusability of ILs to extract the oxygenates acetol, HAC and glycolaldehyde from the model aqueous solutions of pyrolysis oil is investigated. Three phosphonium ILs have been studied in this work due to their hydrophobicity and high affinity for acids [30,33]. Two other commercially available hydrophobic imidazolium ILs with tetracyanoborate anion are also investigated, as they have shown potential in extraction of polar compounds [34], and the solvent recovery may be straightforward through solute evaporation. The names and abbreviations of the studied ILs are shown in Table 1 and the structures of ILs and the oxygenates are drawn in Scheme 2. The organic solvent 40 wt% TOA in 1-octanol is also studied as comparison, because of its high distribution of HAC [30]. 1-octanol is used as diluent in this work, since it is available in the lab and has similar distribution coefficient for HAC as 2-ethyl-1-hexanol [17].

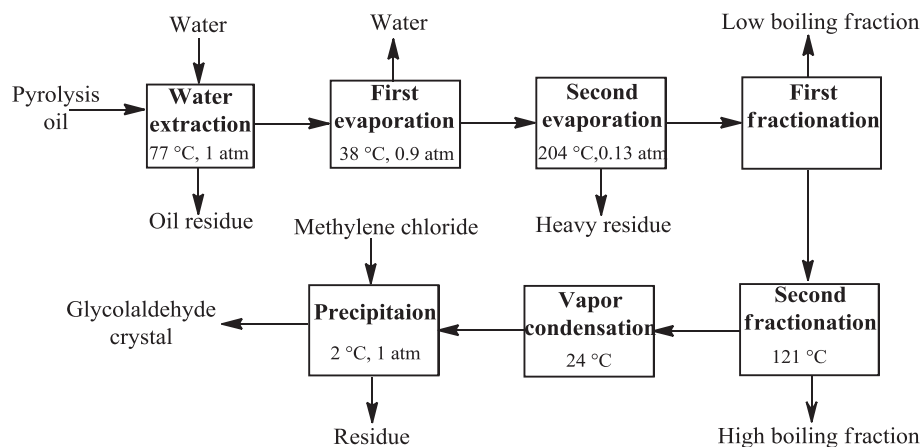
2. Experimental

2.1. Materials

Acetic acid (>99.7%), acetol (hydroxyacetone, 90%), glycolaldehyde dimer, tri-*n*-octylamine (98%), 1-octanol (>99%), toluene (>99.8%) and dimethyl sulfoxide-*d*₆ (>99.96%, DMSO) were purchased from Sigma Aldrich. The phosphonium ILs P_{666,14}Cl, P_{666,14}[N(CN)₂] and P_{666,14}[Phos] were obtained from Iolitec with a purity >95%. The imidazolium ILs Hmim[B(CN)₄] and Omim[B(CN)₄] were purchased from Merck with a purity >98%.

2.2. Liquid-liquid extraction

Three single solute solutions (10 wt% acetol, 10 wt% HAC and 5 wt% glycolaldehyde solution, respectively) and one mixed solutes solution (with 10 wt% acetol, 10 wt% HAC and 5 wt% glycolaldehyde together in milli-Q water) were prepared as feed solutions.



Scheme 1. Glycolaldehyde isolation process designed by Stradal and Underwood. The missing temperatures and pressures in the scheme are not given in Ref. [20].

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