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Separation of phenols from lignin pyrolysis oil using ionic liquid

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ABSTRACT

The aim of this work was to propose an efficient process to extract phenolic compounds from bio-oils produced by lignin pyrolysis. The extraction of phenolic compounds from the crude bio-oils was performed in two steps. First, a 5-stages liquid-liquid extraction (LLE) was performed with a basic aqueous solution. The second step consisted of a 4-stages LLE carried out with either ethyl acetate or [Choline][NTf_2] ionic liquid as a green alternative solvent. It was found that the extraction of the phenolic compounds with the basic aqueous solution in the first LLE needs improvement. The extraction rates show that [Choline][NTf_2] is an excellent solvent for the recovery of phenolic compounds from aqueous solution as compared to the classical ethyl acetate organic solvent.

1. Introduction

Lignocellulosic biomass (*i.e.* wood, straw, etc.) is a natural widespread resource. It presents a huge potential of valorisation for various industrial sectors, especially foods, cosmetic and pharmaceutics without being in competition with agro-business. Many high added-value compounds can be extracted from lignocellulosic biomass and its derivatives, such as acids, alcohols, aldehydes, ketones esters, heterocyclic derivatives and phenolic compounds [1]. The acetyl groups of hemicelluloses provides acetic acid [2] while the lignin produces phenolic compounds of different size [3,4]. Most of these phenolic compounds present valuable properties such as antiallergenic, antimicrobial or antiviral effect [5], antioxidant properties [6–9], but also cardio-protective activities [10] or protective effects on hormone-dependent breast tumors [11]. Thus, phenolic compounds are valorized as raw materials or intermediates in the synthesis of pharmaceuticals [12–14], food flavours [15,16], food additives [16,17], flagrances [13,14,16], herbicides [18], and for the production of resins [19–21] or adhesives [20,22,23] as well.

Pyrolysis is a thermochemical conversion process, well investigated to date [24]. Biomass pyrolysis produces solid (char), liquid (the so-called bio-oil) and gas (*i.e.* CO_2, CO, CH_4, H_2, etc). Two main pyrolysis processes can be defined. Flash pyrolysis is carried out at moderate temperature (450–600 °C), high heating rates (> 1000 °C) and low residence time of the biomass inside the pyrolysis furnace (< 2 s). Inversely, the slow pyrolysis is carried out at low temperature and high residence time. According to the operating conditions, the production of one or several phases can be optimized. While the slow pyrolysis favours the production of char [25], the flash pyrolysis provides high added-value compounds [26].

These last decades, the extraction of phenolic compounds from various natural resources rises more interest. Among various techniques described in the literature, phenolics are extracted using membrane [27], preparative chromatography [28–33]) or distillation [34–42]. The liquid-liquid extraction (LLE) using various solvent [20,32,33,43–49] is still the most commonly used. Indeed, many issues were reported with distillation, such as the reactivity of bio-oil [41,49] or the poor selectivity and efficiency [32,38,40,47] caused by their complex composition and the non-stability of the bio-oil. To date, liquid-liquid extraction seems the easiest way of phenolic compounds extraction using small device and occurring under mild conditions (*i.e.* atmospheric pressure and room temperature). In LLE, the phenolic compounds extraction is based on the partial miscibility of aqueous and organic solvents.

For liquid-liquid extraction of phenolic compounds, several solvents are at disposal with some advantages and drawbacks. Alkaline solutions are often investigated for the extraction of compounds from the crude bio-oil [20,43–45,47,50,51]. Some authors succeeded to effectively extract families of compounds such as phenols [50,51]. Yet, for Amen-Chen et al. [47] and Greminger et al. [52], an efficient extraction using aqueous solution requires pH higher than 11 and a multiple stages LLE. Nevertheless, according to Meier and coworkers, Maggi and Delmon, and Galceran and Eek [43–45], this method of extraction was not effective enough, causing the redistribution of the compounds in the phase and (sometimes) precipitation. Hence, another LLE is often performed consecutively.

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Many organic solvents were investigated for the recovery of phenolic compounds from the previous aqueous phase resulting from this first alkaline extraction, among them ethyl acetate [47], methylisobutylketone MIBK [47,52], dichloromethane [53,54], toluene [55], ether [20,56], or diisopropyl ether [52]. Then, the recovery of the compounds from the organic phase is generally performs *via* distillation. Since many organic solvents are very or partially miscible with water, a distillation step following LLE is carried out for a partial recovery of the solvent [57] and require lots of energy. Yet, the huge volumes of solvent, constitutes the main LLE drawback related to organic solvent use, especially for health applications, which strongly restrict them. Hence, the improvement of process needs solvent with higher extraction capacity and lower toxicity than those reported for commonly used organic solvents.

These last few years, ionic liquids have been investigated for the extraction of phenolic compounds as a potential alternative of organic solvent. Indeed, ionic liquids are a new kind of solvent with specific properties such as a low vapor pressure and a high thermal and chemical stability. To date, only few studies investigated the possibility to use ionic liquids as a way to extract phenolic compounds. Garron et al. [58] showed that some hydrophobic imidazolium ionic liquids containing bis(trifluoromethylsulfonylimide) [NTf_2] anion are effective for the extraction of guaiacol from aqueous solutions. In our previous work [59], we also evidenced that [Choline][NTf_2] was a good solvent for the extraction of phenol, guaiacol and syringol from aqueous solution.

In this work, we propose to study the efficiency of extraction process of phenolic compounds from different bio-oils obtained by lignin pyrolysis. The efficiency of the NaOH aqueous liquid liquid extraction is determined. The second liquid-liquid extraction IS performed with ionic liquid or ethyl acetate for comparison. Efficiencies and selectivities towards phenolic compounds are also discussed.

2. Materials and method

2.1. Chemical reagents and solvents

Standards of phenol (CAS 108-95-2), guaiacol (CAS 90-05-1), syringol (CAS 91-10-1), pyrocatechol (CAS 120-80-9), o-cresol (CAS 95-48-7), vanillin (CAS 121-33-5), toluene (CAS 108-88-3) and o-xylene (CAS 95-47-6) were purchased from Sigma-Aldrich. Ethyl acetate (CAS 141-78-6) was supplied from Sigma-Aldrich and ethanol (CAS 64-17-5) from Carlo Erba. 1-octene (CAS 111-66-0) was purchased from Sigma-Aldrich. Sodium hydroxide (CAS 1310-73-2) in pellets was purchased from Sigma-Aldrich. Protobind lignin 1000 was purchased from Green Value. Choline bis(trifluoromethylsulfonyl)imide [Choline][Ntf_2] ionic liquid was purchased from Io-li-tec with a purity of 99% (w/w). Deionized water was used for all the experiments.

2.2. Bio-oil production

The device used for lignin pyrolysis is described elsewhere [60]. Pyrolysis of organosolv lignin (475 mg, anhydrous basis) was conducted in a tubular reactor set at 500 °C and continuously swept with 300 mL/min of N_2 (analytical purity). The vapours were injected in a fixed bed of catalysts and mixed with a flow of 300 mL/min of H_2. The detailed experimental procedure has been presented elsewhere as well as the method of catalyst preparation [60]. It has been shown that iron is selective and cheap catalyst for hydrodeoxygenation reactions [61,62]. Furthermore, bio-oils produced by hydrodeoxygenation of lignin are much more stable than bio-oils produced by (non-catalytic) pyrolysis of lignocellulosic biomass. The vapours were collected into methanol-containing impingers. Methanol was used as a solvent to improve pyrolysis vapour sampling in impingers. The fractions were collected into a flask and sample was added with 0.2 µL of 1-octene as internal standard for quantification. Then, the methanol of the diluted bio-oil was removed using rotary evaporation to obtain the crude bio-oil (vacuum, 40 °C). It has been checked that after evaporation of methanol, no modification of composition was observed in the bio-oils. Six bio-oils notated from 1 to 6 were produced according to different operating conditions. Bio-oil 1 has been produced with 10 wt% iron in activated carbon (10% Fe/AC), 0.2 g of catalyst at 500 °C in the fixed bed. Bio-oil 2 was produced without catalyst (empty reactor at 500 °C), bio-oil 3 with 10% Fe/AC (2 g at 500 °C), bio-oil 4 with 2 g of 10% Fe/AC at 450 °C, bio-oil 5 with 2 g of catalyst at 400 °C, bio-oil 6 with 0.2 g at 400 °C.

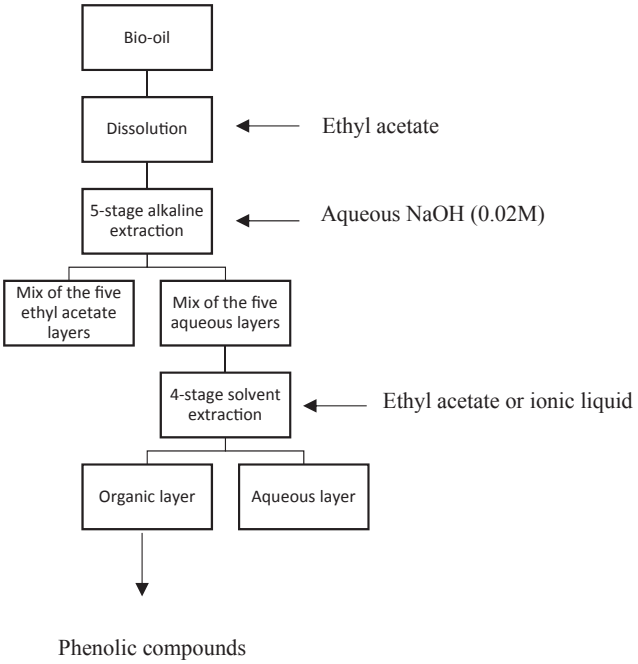

Fig. 1. Steps of the extraction of phenolic compounds from bio-oil.

2.3. Liquid-liquid extraction

The liquid-liquid extraction procedure used in this work is a modified version of the one described in Amen-Chen et al. [47]. The procedure was divided into four steps (Fig. 1): (1) dilution of the bio-oil in ethyl acetate, (2) liquid-liquid extraction with basic aqueous solutions, (3) acidification of the aqueous layer with chloride acid (2M) and (4) liquid-liquid extraction with a solvent.

Briefly, the crude bio-oil diluted in ethyl acetate (1:1 weight ratio) was washed with an aqueous hydroxide solution NaOH at 0.02M (1:1 weight ratio, pH value of 12.1). The phases were splitted in a separatory funnel, and the aqueous phase was collected in a flask. The bio-oil was washed five times with fresh aqueous sodium hydroxide solution. Then, the resulting bio-oil was diluted in ethanol and a volume of 0.5 µL of 1-octene was introduced for quantification of the remaining compounds.

The five aqueous layers were combined and acidified with acid chloride (2M) until reaching a pH 6 value. The studied solvent (ethyl acetate or [choline][NTf_2]) was then added to the mixture (0.5:1 solvent/aqueous phase, w/w) for the recovery of the phenol. The phases were separated with a separatory funnel and the organic layer containing phenolic compounds was collected. The aqueous phase was washed four times with fresh solvent (ethyl acetate or ionic liquid). A volume of 0.5 µL of 1-octene was introduced to each organic sample for quantification. Before analysis, the ionic liquid samples were diluted into ethanol to reduce their viscosity.

2.4. Sample analysis

The analysis of the oil fractions was performed with an Agilent