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# Multi-step separation of monophenols and pyrolytic lignins from the water-insoluble phase of bio-oil

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ABSTRACT

To realize a high-value utilization of the water-insoluble phase of bio-oil, acid and alkaline solutions combined with organic solvents have been employed to separate the monophenols and pyrolytic lignins from this phase. The phenolic fraction B, obtained by reactive extraction of the water-insoluble phase, was found to be rich in phenolic compounds, with a high concentration of 94.35%, wherein the content of guaiacols reached 48.27%. Furthermore, Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and gel-permeation chromatography (GPC) analyses of the pyrolytic lignins showed the primary structural units to be of the guaiacol and syringol types. Polymers with molecular weight higher than 1000 dominated in the high-molecular-weight pyrolytic lignin, whereas the low-molecular-weight pyrolytic lignin contained more reactive phenolic hydroxyl groups.

## 1. Introduction

Bio-oil, a liquid product by biomass fast pyrolysis, is a complicated liquid mixture containing several hundreds of chemicals. As a result, it exhibits some inferior properties, such as high water content, high oxygen content, low heating value, and strong corrosiveness [1,2]. These drawbacks make it difficult to be directly used as a vehicle fuel. Therefore, several upgrading technologies have been developed to improve the quality of bio-oil, including catalytic hydrodeoxygenation [3,4], catalytic cracking [5,6], steam reforming [7,8], catalytic esterification [9,10], supercritical upgrading [11,12], and so on. However, a single upgrading technology cannot realize efficient conversion of all of the components due to the complexity of bio-oil. Studies of the effects of catalytic cracking and steam reforming on major chemical families in bio-oil showed that carboxylic acids and ketones behaved in high reactivity and catalyst stability, while phenols were difficult to convert [13–15]. The efficient conversion of phenols often required severe reaction conditions such as hydrodeoxygenation under high hydrogen pressure [16]. High-molecular-weight phenolic oligomers not only show low reactivity, but also have a high propensity to generate coke under heating conditions, which will lead to catalyst deactivation. Consequently, the separation of bio-oil could make the different upgrading technologies more efficient for different fractions, and also provides an initial stage for the subsequent isolation of valuable chemicals.

Distillation and solvent extraction are common isolation and fractionation technologies. Due to the thermal and chemical instability of bio-oil, as well as its high content of high-boiling-point compounds, traditional distillation has a low distillate yield and suffers from coking [17]. To solve this problem, Wang et al. introduced molecular distillation technology as a suitable means of separating thermally sensitive chemicals [18,19]. Their research on the separation characteristics of bio-oils showed that this method resulted in high distillate yields without obvious coking, and the obtained fractions were successfully upgraded to produce better fuels [20]. Another promising isolation method is solvent extraction, which is commonly applied in bio-oil characterization. Among many solvents, water is a cheap and efficient one. Bio-oil can be separated into water-soluble and water-insoluble phases after water extraction, and the separated phases can be treated individually [21]. The water-soluble phase predominately consists of low-molecular-weight acids and ketones with high reactivity. It has been proven that acetic acid and levoglucosan can be efficiently isolated from the water-soluble phase of bio-oil [22,23]. In the upgrading research, the bio-oil water-soluble phase is widely used for steam reforming and can generate a high hydrogen yield [24]. In addition, in moderate hydrodeoxygenation and catalytic cracking processes, the bio-oil water-soluble phase has also been chosen as a raw material to produce hydrocarbons, alcohols, and olefins [24,25]. Although the bio-oil water-soluble phase shows good upgrading performances, studies on the upgrading of the water-insoluble phase have been limited due to the complexity

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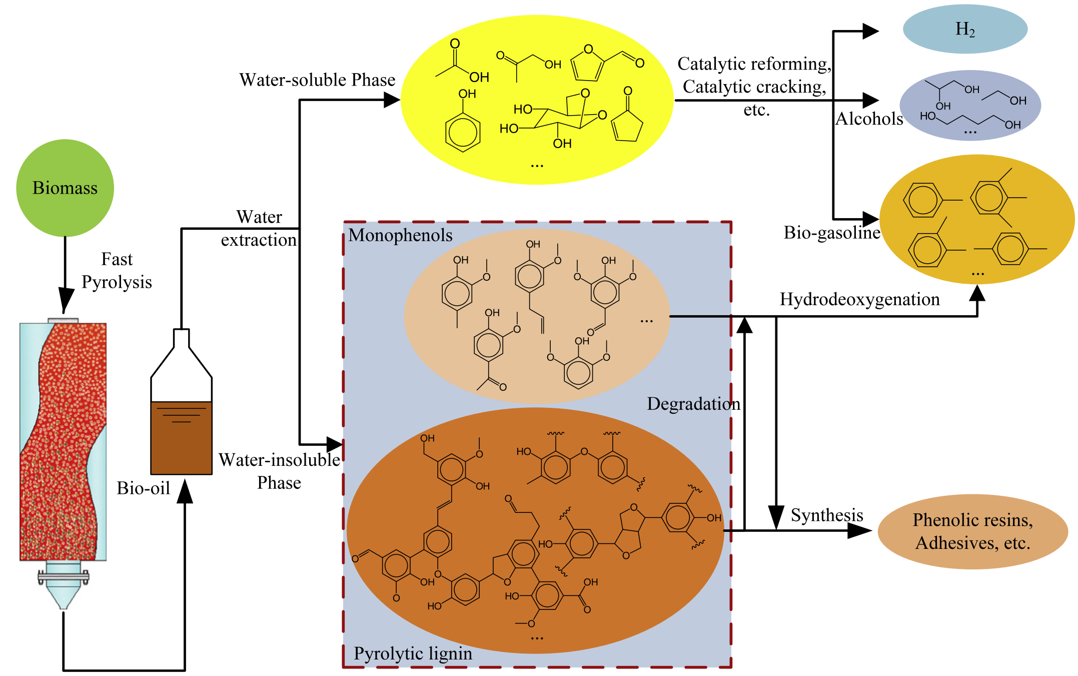

**Fig. 1.** Upgrading of bio-oil based on the high-efficiency separation.

of its composition. It is mainly composed of lignin-derived products, including monophenols such as phenol, guaiacol, and syringol, as well as phenolic oligomers (or pyrolytic lignin). The monophenols can be converted into hydrocarbons through hydrodeoxygenation, but the pyrolytic lignin is difficult to be upgraded due to its chemical inertness. Therefore, besides more efficient utilization of the water-soluble phase, it is also very necessary to further separate the water-insoluble phase into several fractions, and then to upgrade them individually with suitable technologies. The main design scheme is shown in Fig. 1. The water-soluble phase is upgraded by catalytic cracking, steam reforming, etc., and the water-insoluble phase can be used to further extract the monophenols and pyrolytic lignin. The monophenols can be converted into hydrocarbons by hydrodeoxygenation, while the pyrolytic lignin can be degraded into monophenols and be upgraded sequentially, or be used for the synthesis of phenolic resins, adhesives, specialty polymers [26], etc. This bio-oil integral utilization scheme can combine the extraction of valuable chemicals from bio-oil with the production of high-grade fuels. Acidification is initially used in the extraction of lignin from alkali black liquor by gradually reducing the pH, which is a common approach to extract the alkali lignin [27,28]. Pyrolytic lignin is the structural fragment of lignin, so this method is also suitable for the purification of pyrolytic lignin. Herein we carried out a detailed research on the multi-step separation of monophenols and pyrolytic lignins from the bio-oil water-insoluble phase by using acid solution, alkaline solution, and organic solvents. The physico-chemical properties of the separated fractions have also been investigated with different detection technologies.

## 2. Experimental

### 2.1. Multi-step separation of bio-oil

The bio-oil was obtained by the pyrolysis of lauan sawdust in a fluidized bed pyrolysis reactor with a feeding rate of 5 kg/h. The reaction temperature was 550 °C. Detailed information on the pyrolysis reactor can be found elsewhere [29]. Before the experiment, the raw bio-oil was filtered to remove solid particles.

In this study, a multi-step separation procedure was adopted for solvent fractionation of the bio-oil, as shown in Fig. 2. At room temperature, 30 g of bio-oil was added dropwise to 30 mL of deionized water, with stirring under ultrasonication. An upper water-soluble phase and a bottom water-insoluble phase were obtained after about 30 min. Then, the subsequent steps were focused on the separation of the water-insoluble phase. 2.5 mol/L NaOH solution was used to dissolve the organic phase with the assistance of ultrasonication. At $pH \approx 14$, most of the water-insoluble phase was dissolved in the NaOH solution, and could then be extracted with 100 mL of $CH_2Cl_2$ to obtain neutral macromolecule fraction A (FA). The $CH_2Cl_2$-insoluble alkaline solution was then acidified with 1 mol/L HCl to pH 6.4. The precipitate, collected by filtration and dried at 40 °C, was named as high-molecular-weight pyrolytic lignin (HMWPL). And then 100 mL of $CH_2Cl_2$ was used to extract the chemicals from the acidic solution. Afterwards, the $CH_2Cl_2$-insoluble acidic solution was further acidified with 1 mol/L HCl to pH 1.5. And the precipitate formed was low-molecular-weight pyrolytic lignin (LMWPL). Subsequently, 100 mL of $CH_2Cl_2$ was also used to extract the chemicals from the acidic solution. The above two $CH_2Cl_2$ extracts were then concentrated in vacuo at 25 °C to obtain phenolic fraction B (FB) and fraction C (FC), respectively. All the chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Analysis of bio-oil and pyrolytic lignins

The identification of phenolic compounds in the bio-oil and in the extracted fractions was carried out with a Trace DSQ II gas chromatography coupled with a mass spectrometer (GC–MS). A DB-WAX polar capillary column produced by Agilent Co. was used. The initial column temperature was 40 °C for 1 min, and was then increased to 240 °C at a ramping of 8 °C/min and kept at this level for 10 min. The relative content of each phenolic compound was determined by peak area normalization.

Fourier-transform infrared spectroscopy (FTIR) of the pyrolytic lignin was performed on a Nicolet 5700 FTIR spectrophotometer (Thermo Fisher Co.). 1–2 mg of pyrolytic lignin was carefully ground with 100 mg of KBr, and the mixture was pressed into a