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Study of a new complex method for extraction of phenolic compounds from bio-oils

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ABSTRACT

This paper reports a new extraction method on phenolic compounds separation from bio-oil. Through adding appropriate amount of calcium hydroxide into the bio-oil, using ammonia solution to adjust pH > 7 of the bio-oil, the complex was gradually generated in the bio-oil. Then the complex is filtered, and further dissolved by hydrochloric acid. High purity phenolic compounds collected from the dissolving solution are considered as crude products. In order to investigate the mechanism of the phenolic compounds extraction, a model bio-oil was prepared. In the process of phenol extraction from the model bio-oil, the complex formed was characterized by FT-IR and the phenols collected were detected by GC/MS. The results demonstrated that a complex formed instead of a salt of calcium guaiacol in the extraction process. Parameters investigated were the concentration of ammonia solution (1–6 mol/L), reaction temperature (20–70 °C) and reaction time (5–35 min). On the basis of the model bio-oil test, 4 mol/L of ammonia solution, 40 °C of the reaction temperature, and 20 min of the reaction time were chosen as optimum reaction conditions. Testing of these conditions for 40 g of the crude bio-oil showed that the complex method extracted 2.9 g of phenolic compounds with the purity of 93.07%. Meanwhile, the whole extraction process does not discharge pollutants into the surrounding environment.

1. Introduction

Biomass fast pyrolysis is a complicated thermochemical process in which biomass materials undergo decomposition at a moderate temperature of about 500 °C and experience short reaction times in the absence of oxygen to produce liquid products called bio-oil, along with solid chars and incondensable gases [1–4]. Bio-oil is a complicated mixture with hundreds of organic compounds, including alcohol, organic acids, phenol, aldehyde, ketone, etc. [5]. Some of these chemicals, such as phenols, are important raw materials and additives in industry [6–8]. Total amount of phenolic compounds in the pyrolysis oil vary from 21.0% to 29.8% depending on feedstock used and operating conditions [9]. Compared with phenols derived from petroleum fuel, these phenolic compounds are renewable and easily obtained. It can be not only used as a phenol replacement in phenol–formaldehyde resins [10] or novolac resins [11] but also as raw materials of antioxidants [12]. However, the composition of bio-oil is so complicated that the cost of phenol extraction process is still too high. Unpurified phenol severely reduces the quality of the downstream products. Pollutants discharge in the process of phenol extraction also bring a potential threaten for the surrounding environment [2]. Such reasons limit the extensively utilization of these phenolic compounds. Therefore, to develop a high efficiency, low cost and environmental friendly phenol extraction technology is essential for the widespread utilization of the renewable phenols from bio-oil.

Various developed extraction technologies such as organic solvent extraction, supercritical CO_2 fractionation, molecular distillation and aqueous sodium hydroxide extraction have been studied for their usefulness in the aspects of phenol extraction. A conversional organic solvent extraction method [13–16] can concentrate phenolic compounds into a certain phase through several steps. However, too much consumption of organic solvents and pollutants discharge in the extraction process has tended to prevent the industrial acceptance of this technology [11]. In recent years, with the rapid development of supercritical fluid extraction [17,18] and molecular distillation [19–21] in medicine and food industry, the reports on the application of these technologies to extract phenolic compounds from bio-oil has gradually increased [22–25]. These technologies achieve a satisfactory effect for isolating the chemicals from the bio-oil, but the conditions of using the technologies are rather harsh. A well-known extraction method by sodium hydroxide solution is so far the most mature technology of recovering phenolic compounds from coal-derived oils in industry

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[26]. Similarly, it is suitable for phenols extraction from bio-oil, as well as reaches to ideal phenols extraction efficiency [27,28]. However, lots of water is introduced into the bio-oil in the extraction process of this technology, which leads to the residual bio-oil abandoned.

A cyclic chelate complex will generate between most of phenolic compounds and Ca^{2+} under the condition of alkaline [29]. Based on that, adding appropriate amount of calcium hydroxide into the bio-oil, it will firstly react with the acetic acid which existed in the bio-oil. The generation of calcium acetate meant that Ca^{2+} is introduced in the bio-oil. Then using ammonia solution to adjust pH > 7 of bio-oil, phenolic compounds and calcium ion will generate complex. After the complex is filtered, and dissolved by hydrochloric acid; high purity phenolic compounds is collected from the dissolving solution by the extraction of acetic ether. The residual bio-oil can be further utilized because only a little ammonia solution is introduced into the bio-oil. This pioneering research investigated the new extraction technology to isolate phenolic compounds from bio-oil, for the purpose of lower cost, higher phenolic compounds extraction rate, no environmental pollutants discharging and the residual bio-oil available.

The objectives of this study were (1) to examine the feasibility of Ca^{2+} as a complex agent for the extraction of phenolic compounds and (2) to determine the effect of operating parameters (i.e., the consumption of ammonia solution, reaction time, and reaction temperature) on the extraction of phenolic compounds from bio-oils. A model bio-oil was prepared to investigate the mechanism of complex derived from Ca^{2+} and phenolic compounds. The new extraction method also will be further verified to the crude bio-oil.

2. Experimental

2.1. Materials

The model bio-oil consists of 10 wt.% of acetic acid, 20 wt.% of guaiacol, 35 wt.% of glycol and 35 wt.% deionized water. Acetic acid (Aladdin, 99.9%) is chosen as a representation of all the acidic chemicals in the bio-oil; guaiacol (Aladdin, 99.9%) represents all the phenolic compounds. Another chemical compound presented in the model bio-oil needs to satisfy two conditions: it should make acetic acid, guaiacol, itself and deionized water mutually soluble; and it should not react with other chemical materials in the extraction process. Based on the two reasons, the inert glycol (Aladdin, 99.5%) was chosen as a substitution of other chemical materials in the bio-oil except acetic acid, phenolic compounds and water. Calcium hydroxide, hydrochloric acid and ethanol used in the study were also purchased from Aladdin.

The crude bio-oil used in this study was produced from a bench-scale bubbling fluidized-bed fast pyrolysis reactor with 1 kg/h production capacity, which was designed by the Energy College at Xiamen University in China. The pyrolysis reactor was generally operated at a temperature of 450–500 °C and a residence time of below 1.5 s. There are three bio-oil outlets in the pyrolysis reactor in terms of different cooling effects consisting of quenching, water cooling and icy cold, which are called bio-oil 1, bio-oil 2 and bio-oil 3 in sequence. Details of the pyrolysis system are shown in Ref. [30]. In this study, the crude bio-oil is derived from the fast pyrolysis of pine sawdust, and the physicochemical characteristics of pine wood used can be found in Ref. [31].

2.2. Extraction of phenolic compounds

The extraction route of phenolic compounds from the model bio-oil/crude bio-oil was performed as shown in Fig. 1. At room temperature, 2.48 g of the powder of calcium hydroxide was added to 40 g of the bio-oil with the magnetic stirring for 2 h. Acetic acid presented in the bio-oil reacted with calcium hydroxide to produce calcium acetate, which meant that the complex agent, Ca^{2+}, was introduced into the bio-oil. As a pH regulator, 6 mL of the ammonia solution (Aladdin, 99.9%) with different concentrations was added dropwise to the bio-oil, accompanied by continuously stirring. The complex (light pink color in the model bio-oil) gradually appeared in the bio-oil. The mixture was filtered with a Büchner funnel using medium-speed filter papers under a vacuum pump (Jinteng Co., China). The complex on top of the filter paper was then collected and washed for three times by ethanol, and further dried in a vacuum drying oven at 105 °C for 4 h to remove traces, and weighed. The dried complex was dissolved in 6 mL of hydrochloric acid with 4 mol/L of concentration for 20 min. 8 mL of acetic ether was used for extracting the phenolic compounds in the dissolved solution. The phenolic compounds dissolved with acetic ether were separated using a rotary evaporator at 70 °C with reduced pressure of 25 in. of mercury. Acetic ether was recycled and the high purity phenolic compounds as a crude product are concentrated at the bottom of round flask. Other researchers have used similar forms of this method [9,32]. The powder of calcium hydroxide can be recycled through adding sodium hydroxide solution to the water layer of the dissolved solution.

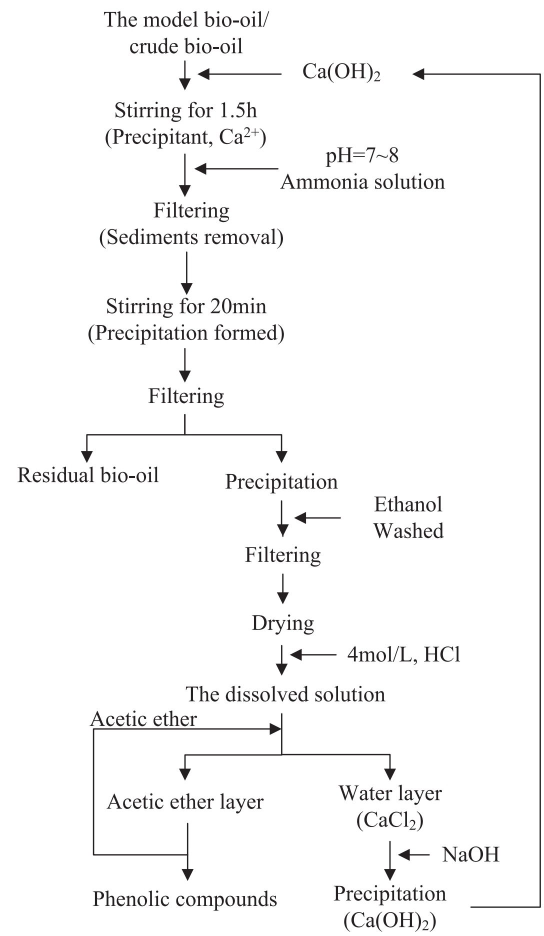

Fig. 1. Complex procedure for the extraction of phenolic compounds from the model bio-oil/the crude bio-oil.

Parameters investigated were ammonia solution with different concentration from 1 mol/L to 6 mol/L at steps of 1 mol/L; the reaction temperatures in the range of 20–70 °C at steps of 10 °C; the reaction time ranged from 5 min to 35 min at steps of 5 min. The phenolic compounds extraction rate is expressed as follows: