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 threat 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 CO₂ fractionation, molecular distillation and aqueous sodium hydroxide extraction have been studied for their usefulness in the aspects of phenol extraction. A conventional 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.
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, 99.9%) 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.

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:
The phenolic compounds extraction rate = the quantities of phenolic compounds collected in the dissolving solution × the content of phenolic compounds measured by GC/MS.

2.3. Sampling and analysis

The water content of the bio-oil was determined by Karl-Fischer titration (Mettler Toledo Co., Sweden). The model number of the Karl Fischer titrator was KF-1. The calorific value of the bio-oil was determined using an Auto Adiabatic Bomb Calorimeter (Nasren Co., Shanghai, China). The viscosity of the bio-oil was determined by a viscometer (Nasren Co., Shanghai, China). The pH of the solutions was measured using pH meter (Ohaus Co., US). The chemical compositions of the bio-oil were analyzed using GC/MS-QP2010 SE (Shimadzu, Japan), and the compounds were detected using a Mass Selectivity (MS) detector equipped with a Rtx-5MS (30 m × 0.25 mm × 0.25 μm) capillary column. The amount injected was 1 μL, and the split ratio was 25:1. Helium gas was employed as a carrier gas at a constant flow rate of 1.2 mL/min. The heating of the column started at 50 °C, where it was held for 5 min; then, the temperature was increased to 250 °C at a rate of 4 °C/min, at which point it was held for 5 min. The temperature of EI was 280 °C. The mass spectra obtained by GC–MS were interpreted based on an automatic library search (Wiley & NIST). The quantitative analysis of guaiacol in the model bio-oil was also carried out in the GC/MS through using external standard method. The solution of guaiacol in ethanol with different concentration (0.01%, 0.05%, 0.1%, 0.2% in sequence) was prepared and analyzed by the GC/MS. A linear function on the guaiacol was obtained and used as a baseline for the quantitative analysis of the phenols obtained in experiments.

Fourier transform infrared (FT-IR) analysis was performed on a Nicolet 330 FT-IR Spectrometer (Thermo Electron Corporation, US) to determine the functional groups in the guaiacol and the complex obtained. The solid complex was mixed and ground with KBr at a weight ratio of 1:100. Then, 60 mg of the mixture was pressed to a tablet. The tablet was placed in the sample holder and scanned from 4000 to 450 cm⁻¹ at a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Characteristics of complexes between Ca²⁺ and guaiacol

The complex was prepared in fairly good extraction rate at conditions of 4 mol/L of ammonia solution, 20 °C of reaction temperature and 20 min of reaction time. Fig. 2 shows the FT-IR spectra for guaiacol and the complex produced. As expected, the liquid guaiacol and the solid complex have similar FT-IR spectra. However, the transmittance of hydroxyl group in the complex is significantly lower than that of guaiacol. Meanwhile, the fingerprint peaks between guaiacol and the complex are different, which showed that the complex has the different chemical structures with guaiacol. If the guaiacol reacted with Ca²⁺ to produce the salt of calcium guaiacol, hydroxyl group in the complex should not be detected. However, hydroxyl group is definitely presented in the complex as Fig. 2 showed at peaks between 3400 and 3500 cm⁻¹, which indicates that the complexes formed instead of the salt of calcium guaiacol in the extraction process.

The complex of 1 g was solved into hydrochloric acid of 10 mL with 1 mol/L. The organic formed in the solved solution was extracted by acetic ether and further analyzed by GC/MS. As shown in Fig. 3, the pure guaiacol was detected in the GC/MS, which showed that the complex could be converted to guaiacol completely through dissolution by hydrochloric acid.

3.2. Effect of the concentration of ammonia solution

According to the preliminary experiments, the pH value is an important factor for the complex generation in the bio-oil. As a pH regulator, the usage amount of ammonia solution not only affects guaiacol extraction rate, but relates to the heating value of the residual bio-oil. Therefore, the effect of the concentration of ammonia solution in the range from 1 mol/L to 6 mol/L on guaiacol extraction rate was tested firstly in this study, while the reaction temperature and the reaction time were fixed at 20 °C and 20 min, respectively. Fig. 4 shows guaiacol extraction rate and pH value as a function of the concentration of ammonia solution. As expected, the concentration of ammonia solution played an important role for guaiacol extraction. Guaiacol extraction rate increased sharply from 8.3% to 45.2% with the concentration of ammonia solution increased from 1 mol/L to 4 mol/L. At the concentration of ammonia solution higher than 4 mol/L, the improvement of guaiacol extraction rate was slight. In the process of the experiments, we...
found that the viscosity of the model bio-oil increased significantly with the concentration of ammonia solution increasing over 4 mol/L. This phenomenon was due to that too much precipitation consisting of the complex and calcium hydroxide produced when ammonia solution with high concentration was added to the model bio-oil. It not only increased the difficulty of the next separation step, but led to the loss of some of the residual bio-oil adhering to the precipitation. The poor fluidity of the model bio-oil also could be a reason for reducing the generation of complex.

It is observed that the pH of the residual model bio-oil increased from 7.16 to 7.58 with increasing the concentration of ammonia solution from Fig. 4, which indicated that guaiacol extraction rate was affected by the pH value of the model bio-oil. Higher pH value increased the concentration of [OH⁻] ion, which favored the complex generation; however, too high pH value (>8) consumed more ammonia solution and reduced the fluidity of bio-oil. Therefore, 4 mol/L ammonia solutions will be chosen as an optimum condition for the further experiments in the crude bio-oil.

3.3. Effect of reaction temperatures

In order to investigate the effect of reaction temperatures on guaiacol extraction rate, the experiments were carried out at the conditions of 20 min of the reaction time and 4 mol/L of ammonia solution. As shown in Fig. 5, the effect of reaction temperatures on guaiacol extraction rate was obvious, and a lower temperature favors the complex. When the reaction temperature increased from 20 °C to 40 °C, guaiacol extraction rate decreased slightly from 36.6% to 35.9%. At temperature higher than 40 °C, guaiacol extraction rate decreased significantly to 31.2%. A simple experiment on the relationship between the solubility of the complex and temperature gives a reasonable explanation. Per 0.5 g of the complex was added into 30 g of the deionized water with temperature from 20 °C to 70 °C at steps of 10 °C. After 30 min, the solution with the complex was filtered, dried and weighted. The collected complex decreased from 0.47 g to 0.39 g when the temperature of the deionized water increasing from 20 °C to 70 °C, which verified that the solubility of the complex increased with temperature increasing. Therefore, the solubility of the complex in the model bio-oil remained high at higher reaction temperatures (>40 °C). It explained that guaiacol extraction rate decreased when the reaction temperature increasing.

The pH value of the residual model bio-oil increased from 7.53 to 7.82, with reaction temperature increasing from 20 °C to 70 °C. It indicated that [OH⁻] ion in the residual bio-oil decreased with the complex generation. Although guaiacol extraction rate reached to high at 20 °C, the inferior fluidity of the crude bio-oil in the lower temperature caused severely operational problem. The ideal guaiacol extraction rate also can be reached at 40 °C. For this reason, 40 °C was considered as an appropriate reaction temperature for the phenolic compounds extraction from crude bio-oil in this study.

3.4. Effect of reaction time

The effect of reaction time was studied when the concentration of ammonia solution and the reaction temperature were fixed at 4 mol/L and 20 °C. As shown in Fig. 6, guaiacol extraction rate remained high when reaction time was greater than 20 min, and decreased slightly, and decreased slightly below that point. This result indicates that the complex reaction between Ca²⁺ and guaiacol need sufficient time (>20 min). The pH value decreased from 7.8 to 7.53 with reaction time increasing from 5 min to 20 min. It again verified that [OH⁻] ion in the residual bio-oil decreased with the continuously production of the complex. When the reaction time increased over 20 min, guaiacol extraction rate and pH value kept stability, which indicated that the complex reaction reached to the balance in 20 min. Therefore, 20 min was chosen as the
optimum reaction time to test the phenolic compounds extraction method from crude bio-oil.

3.5. The phenolic compounds extraction from the crude bio-oil

The trends of guaiacol extraction rate from the model bio-oil with the reaction conditions of the concentration of ammonia solution, reaction time, and reaction temperature, have been investigated in detail. Compared with the model bio-oil, the composition of the crude bio-oil is much more complicated and unstable. Therefore, the extraction method should be further tested for the crude bio-oil. The crude bio-oil used in this study was produced from a bench-scale bubbling fluidized-bed fast pyrolysis reactor. 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. The yield of the total bio-oil is 61.9%, and the quantities of the collected bio-oil 2 and 3 occupy about 50% of the whole bio-oil. The water content, heating value, pH and viscosity from different bio-oil outlets were characterized, as shown in Table 1. The high viscosity of bio-oil 1 is not suitable for the experiment of the extraction method due to only 13.6% of water content, which can be used as fuel considering 22.6 MJ mol⁻¹ of heating value. The identified compounds of the crude bio-oil were analyzed by GC/MS, and were classified into 11 groups; phenols, acids, alcohols, ketones, aldehydes, ethers, furans, sugars, esters, heterocyclic compounds and others. The peak area % for acids and phenols in bio-oil 2 and 3 were 13.1%, 14.9%, 26.7% and 33.1%, respectively. Although the chromatographic peak area does not represent the actual content of the bio-oil, it is considered linear with its quantity [33]. The bio-oil 2 and 3 with high water content was suitable for the experiments of the new phenol extraction method in this study.

In the experiments, 40 g of the crude bio-oil was processed by the extraction method as Fig. 1 showed, and 2.9 g of phenolic compounds were collected. Fig. 7 shows the chromatograms of the chemical materials in the crude bio-oil and the phenol compounds extracted from the bio-oil. The identification of the peaks is shown in Table 2. It can be observed that phenolic compounds occupied about 93.07% of the total chromatographic peak areas, which strongly indicated that the new extraction method was effective for phenol extraction from the bio-oil. It deserved to notice that the extracted phenols still contains some impurities, such as furfural, 2-methyl-2-cyclopenten-1-one, and 1-(2-furanyl)-ethanone. This could be explained that these impurities can attach with the complex, and it is difficult to be washed clean by alcohol, which make them mixing into the phenolic compounds. In the process of the new extraction, only a small amount of ammonia solution was added into the bio-oils. The heating value of the residual bio-oil was reach to 11.3 MJ mol⁻¹, which showed that the residual bio-oil still can be used as fuel.

The acetic acid in the bio-oil was converted to calcium acetate in the process of extraction. Some researchers [34,35] reported that the pyrolysis bio-oil would quickly form two phases (40–80 wt.% of the upper phase, 20–60 wt.% of the bottom phase) through adding a little the aqueous salt solution. The calcium acetate in this bio-oil plays a similar effect with CaCl₂ or FeCl₃ reported in the literatures, which is helpful for the separation of aqueous and oil phase in the bio-oil. In this study, we further added suitable amount non-water-soluble organics (n-butyl alcohol with 25 wt.% of the bio-oil) into the residual bio-oil. The phenomenon of separating the aqueous and oil phase of the residual bio-oil was expected to achieve. Calcium acetate can be obtained through further drying and concentrating for the aqueous layer of the residual bio-oil. The further investigation is being carried out in our group. Calcium acetate is utilized extensively in industrial as the environment-friendly deicer which was called CMA. Some of researchers [36,37] are trying to make the CMA through utilizing the acetic acid in the bio-oil.

### Table 1
The properties of the fast pyrolysis oil.

<table>
<thead>
<tr>
<th></th>
<th>Bio-oil 1</th>
<th>Bio-oil 2</th>
<th>Bio-oil 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>The physical properties of bio-oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield of bio-oils (%)</td>
<td>31.2</td>
<td>16.6</td>
<td>14.1</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>13.6</td>
<td>22.3</td>
<td>27.3</td>
</tr>
<tr>
<td>Heating value (MJ mol⁻¹)</td>
<td>22.6</td>
<td>18.5</td>
<td>17.9</td>
</tr>
<tr>
<td>pH value</td>
<td>2.2</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Viscosity (cP, at 40 °C)</td>
<td>40.78</td>
<td>10.73</td>
<td>6.84</td>
</tr>
<tr>
<td>The component of bio-oils (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td>26.1</td>
<td>26.7</td>
<td>33.1</td>
</tr>
<tr>
<td>Acids</td>
<td>11.9</td>
<td>13.1</td>
<td>14.9</td>
</tr>
<tr>
<td>Alcohols</td>
<td>1.9</td>
<td>0.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Ketones</td>
<td>16.3</td>
<td>11.8</td>
<td>13.1</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>8.5</td>
<td>11.8</td>
<td>10.2</td>
</tr>
<tr>
<td>Ethers</td>
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<td>2.1</td>
<td>0.8</td>
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<td>Furans</td>
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<td>3.5</td>
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<td>7.7</td>
<td>7.3</td>
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<tr>
<td>Esters</td>
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<td>11.8</td>
<td>4.6</td>
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<tr>
<td>Heterocyclic compounds</td>
<td>10.2</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Others</td>
<td>13.9</td>
<td>10.5</td>
<td>10.3</td>
</tr>
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Fig. 7. Total ion chromatograms from crude bio-oil (top) and phenolic compounds (bottom) extracted from bio-oil (4 mol/L of ammonia solution; 40 °C of reaction temperature; 20 min of reaction time).
The oil layer of the residual bio-oil can be further used for the liquid fuel. Therefore, this pioneering research provides a possibility to extract phenolic compounds from the bio-oil, meanwhile, to produce environment-friendly deicer (CMA).

### 4. Conclusions

This pioneering research investigated the new method on phenolic compounds extraction from bio-oil, based on a characteristic that a complex will generate between most of phenolic compounds and Ca\(^{2+}\) under the condition of alkaline. FT-IR and GC/MS analysis revealed the complexes formed instead of the salt of calcium guaiacol in the extraction process. On the basis of the guaiacol extraction from the model bio-oil, 4 mol/L of ammonia solution, 40 °C of reaction temperature, and 20 min of reaction time were deemed appropriate. Testing of these conditions for 40 g of the crude bio-oil showed that the complex method obtained 2.9 g of phenol compounds with 93.07% of the purity. The whole extraction process does not discharge pollutants into the environment and the calcium hydroxide can be recycled. The residual bio-oil has the potential to produce the deicer of CMA.

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References


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