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Research paper

Highly effective decarboxylation of the carboxylic acids in fast pyrolysis oil of rice husk towards ketones using $CaCO_3$ as a recyclable agent

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The carboxylic acids in fast pyrolysis oil (bio-oil) are one of the detrimental properties that impede its straightforward application in internal combustion engines. In this paper, a novel approach is proposed to convert the carboxylic acids in bio-oil to ketones efficiently. That is, the acids in a bio-oil derived from pyrolysis of rice husk were firstly transformed to their calcium salts by neutralization with $CaCO_3$ and then subjected to decarboxylation at high temperature to form ketones and regenerate $CaCO_3$ simultaneously. Due to various carboxylic acids contained in the bio-oil, both symmetric and asymmetric ketones were formed. Although phenols, aldehydes and saccharides had almost unnoticeable effect on the decarboxylation of carboxylic acids, they, particularly saccharides, tended to undertake carbonization reaction, leading to the char formation associated with $CaCO_3$ regenerated. After decarboxylation, the acidity of the upgraded bio-oil decreased dramatically from 167.62 to 1.98 mg of KOH/g, whereas its HHV increased from 18.38 to 27.59 MJ/kg. Although the upgraded bio-oil yield was only 46.10%, the energy efficiency could be reached to 69.20%. Decarboxylation of the water-soluble fraction, which was obtained by water extraction of the bio-oil, was also investigated. With the aid of water extraction, most of the acids and saccharides could be enriched in the water-soluble fraction, while the phenols were concentrated into the oil-soluble fraction. After decarboxylation of the water-soluble fraction, the HHV and acidity of the upgraded bio-oil were improved to be 30.05 MJ/kg and 1.03 mg of KOH/g, respectively. The energy efficiency could be enhanced to 77.59%.

1. Introduction

Fast pyrolysis oil, also called bio-oil, is a liquid product obtained by fast pyrolysis of biomass. Due to the simplicity in pyrolysis equipment and operation conditions as well as flexibility and adaptability with respect to biomass resources, fast pyrolysis of biomass to bio-oil is thought to be a very promising route for exploitation of biomass resource [1]. Up to now, this technology, however, has still been confronted with many obstacles because of the detrimental properties of bio-oil, such as its high water content and oxygen content which leads to low heat value, high acidity, variable viscosity, and thermal and chemical instability. The high acidity is mainly due to the high content of carboxylic acids in bio-oil and would cause serious corrosion issues during storage and application [2]. Normally, the carboxylic acids account for 20–30 wt% of the total mass of bio-oil, depending on the pyrolysis process and biomass resources, with pH value of about 2–3 [3,4]. Therefore, how to efficiently convert the carboxylic acids in bio-oil is of important significance either for the purpose of its straightforward application as transportation fuels in internal combustion engines or obtaining value-added chemicals.

The researchers and scientists around the world have attempted many methodologies decrease the carboxylic acids and ameliorate the bio-oil quality in the past several decades. Hydrogenation [5] is mainly expected to reduce the unsaturated compounds and oxygen

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content in bio-oil and thus enhance the stability and heat value. In most cases, unfortunately, this needs noble metal catalysts and high hydrogen pressure atmosphere. Furthermore, esterification [6–9] is more preferential than others (e.g. catalytic reforming, hydrogenation, etc.) because it is not only capable of converting the acids into esters with alcohols but also manipulating at mild temperature so that the side reactions can be suppressed to the most extent. However, the high water content in bio-oil usually makes the esterification reaction hard to react completely because it is a reversible reaction. Moreover, bio-oil is such an unstable mixture that many side reactions are likely to happen simultaneously, especially at high temperatures, resulting in undesirable products, tar, char and coke. Therefore, by simple esterification it is difficult to achieve high quality fuels. The acidity in the upgraded oil via esterification can only be reduced to tens of mg of KOH/g. To enhance the acid conversion, coupling techniques that combined esterification with extraction [10] or hydrogenation [7,8] simultaneously were also attempted.

It is well known that carboxylic acids can be decarboxylated into ketones under suitable conditions [11]. Early in 1858, Friedel [12] pioneered decarboxylation of calcium acetate to acetone associated with the formation of calcium carbonate under high temperature (Scheme 2), and this approach had been employed in the commercial manufacture of acetone until World War I. Noyce [13] compared the decarboxylation of calcium acetate, sodium acetate and their mixture aiming at higher yield of acetone. In an improved distillation procedure of calcium acetate, which involved removing the acetone vapor immediately from the high temperature zone by nitrogen or carbon dioxide at a temperature of 450–490 °C, more than 99% yield of acetone was obtained [14]. Subsequently, the decarboxylation of other metal salts of acetate, such as strontium, barium [15], silver and copper [16] as well as other carboxylates such as calcium formate and strontium oxalate [15] were studied. A number of transition metal oxides were also attempted to catalyze the decarboxylation of carboxylic acids, including Cr_2O_3 [17,18], ZrO_2 [19–21], MnO_2 [21], etc.

Decarboxylation of carboxylic acids to ketones in the presence of $CaCO_3$ is an environmentally friendly process because there is neither byproduct formed nor additional reaction media necessary. Although $CaCO_3$ takes part in the reaction, it can be viewed as a recyclable agent since it can be regenerated after completing the whole process. Recently, Shanks et al. [22] demonstrated that the organic acids in biomass pyrolysis vapors can be removed by chemical adsorption over $CaCO_3$. The spent $CaCO_3$ could be regenerated by heat treatment of the postreaction adsorbent and the adsorbed acids were simultaneously converted into ketones. To our best knowledge, this was the only research paper for upgrading a real bio-oil via decarboxylation up to now. Therefore, one of our objectives in this study is to assess whether the carboxylic acids in bio-oil can be converted effectively into ketones via decarboxylation for the simple reason that ketones are not only high quality fuels but also versatile chemicals. The other objective is to investigate the effect of the reactive compounds in bio-oil on the decarboxylation reaction and their changes during the ketonization of the carboxylic acids. In addition, the quality of the upgraded bio-oils was also evaluated.

2. Experimental section

2.1. Material and reagents

The bio-oil used in the experiments was produced by fast pyrolysis of rice husk in a fluidized bed reactor at 500 °C with a heating rate of 1000 °C/s and the residence time of less than 2 s. Its density and viscosity were 1.158 g/cm^3 and 20.37 mPa s respectively. Its ultimate analysis was C (46.21 wt%), H (6.2 wt%), O (47.02 wt%), and N (0.57 wt%), corresponding to in a formula of $CH_{1.584}O_{0.763}N_{0.011}$. All other chemicals were of analytical purity and used without further purification.

2.2. Experimental setup and procedure for decarboxylation

All of the decarboxylation experiments were performed on a home-made setup as illustrated in Fig. 1, which was mainly composed of a N_2 cylinder, a quartz tube reactor (50 cm of length, 2.5 cm of inside diameter) where the decarboxylation takes place, and a bubbling receiver. The tube reactor was heated by a tubular furnace equipped with a programmable temperature controller with an accuracy of ±1 °C (OTF-1200X-S, Kejing Materials Technology Co., Hefei, China). The bubbling receiver that contained absorbent was immersed in a low temperature bathing so as to trap the reaction effluents. The non-condensable gas was evacuated directly to the air. When performing the experiment, the calcium salt sample loaded in a quartz boat was placed inside the middle of the quartz tube reactor in advance. After sealing the system and purging the air inside with high purity N_2, the reactor temperature was elevated from room temperature to 120 °C at a ramp rate of 3 °C/min and maintained for another 30 min so as to evaporate the water and volatile compounds. Afterwards, the tube reactor was further heated to 550 °C at a ramp rate of 3 °C/min and held another 100 min, ensuring that the decarboxylation could take place completely. In the whole course, high purity nitrogen with a flow rate of 50 ml/min was used as the purge gas to flush out in time the product vapor into the receiver. The bubbling receiver was glassware so elaborately designed that it enabled the effluent gas to penetrate the absorbent in the form of fine bubbles and trapped the products effectively. In this way, the reaction product was collected and the secondary reactions could be suppressed to the utmost extent [14]. *n*-butanol was used as the absorbent. With low temperature bathing (−10 ± 1 °C), the absorption efficiency was expected to be further enhanced. To check the absorption efficiency of the apparatus, a control experiment was conducted using acetone as the reaction substrate in place of the calcium salt sample. The experimental result showed that as high as 99.60% of acetone was recovered (Table 1, entry 1), demonstrating the system had very high absorption efficiency and airtightness.

2.3. Experimental procedures

This work focused on decarboxylation of the original bio-oil (OBO) and its water-soluble fraction after water extraction. Fig. 2 shows a schematic of the research strategy for upgrading the bio-oil.

To convert the carboxylic acids in OBO to their calcium salts, 10.0 g of bio-oil was neutralized with 20 wt% excess of $CaCO_3$ (based on the total acid number of bio-oil determined by acid-base titration method) under room temperature and vigorously stirring condition. The neutralization reaction can be described as Scheme 1.

After neutralization with $CaCO_3$, the resulting calcium salt sample of OBO (Ca-OBO) was subjected to decarboxylation reaction at high temperature, generating three types of products: (1) solid residue (SR1) left in the tube reactor, which was mainly composed of $CaCO_3$ and char; (2) liquid product trapped in the bubbling receiver; and (3) non-condensable gas. The liquid product was a mixture of the organic condensable compounds, water and *n*-butanol. Due to the high water content in the liquid product, phase-splitting usually took place spontaneously to form an organic phase and an aqueous phase. The aqueous phase, which might contain