Upgrading of Bio-oil by Removing Carboxylic Acids in Supercritical Ethanol

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Abstract

In this work, the effects of the ratio of ethanol to bio-oil, and reaction time on the removing of these carboxylic acids were studied as well as the addition of external acid such as H$_2$SO$_4$, H$_3$PO$_4$ or zeolite. The results showed that carboxylic acids in crude bio-oil could easily esterified with ethanol in the supercritical system, and the formation of esters was affected greatly by the reaction parameters. Ethyl acetate was generated obviously at higher volume ratio of ethanol to bio-oil and reached the selectivity of 100% at the volume ratio of ethanol to bio-oil of 5:1 after 2 h reaction, whereas more side reactions were carried out in lower or higher ratio of ethanol to bio-oil. The addition of external acid would decrease distinctly the formation of esters due to more side reactions, indicating that these carboxylic acids could be effectively removed under the acidic system arising from the internal ionization of ethanol.

Keywords: Bio-oil, Upgrading, Carboxylic acids, Ethanol, Esters

1. Introduction

Bio-oil, mainly generated from fast pyrolysis of biomass, has been considered as a potential renewable energy source to replace for diminishing fossil fuels because of its cleaning, low cost and abundant raw materials. Bio-oil is mostly composed of a variety of organic compounds including acids, aldehydes, ketones, and phenols [1-3]. The organic acids (e.g., formic acid, acetic acid, and propionic acid) and aldehydes are inclined to be reactive, and aldehydes can perform homo-polymerization and acetalization with alcohols at low temperature under acidic conditions [4,5], which can cause the instability of bio-oil during the normal storage. Meanwhile, these organic acids in bio-oil would lead to high acidity with the...
pH value less than 3.0 and corrosiveness to the gasoline or diesel engines when it was used as transportation fuels without upgrading. Thus, it is very important that bio-oil should be upgraded to lower the acidity and improve the stability of storage and the suitability for fuels.

A lot of upgrading techniques such as catalytic processing have been reported for the improvement in the quality of bio-oil [6,7]. Recently, esterification under supercritical fluids such as water, methanol or ethanol, has been attracted on the removing of organic acids in bio-oil with or without catalysts due to the unique properties of the supercritical fluid system with faster rates of mass and heat transfer, and dissolving power [8,9]. Notably, ethanol can not only react with these carboxylic acids in bio-oil to produce the corresponding esters, but also can act as a reaction medium in the supercritical system.

In this work, the bio-oil from the pyrolysis product of sawdust at 600 °C was selected as feedstock, which contains about 40% carboxylic acids, and the removing of these carboxylic acids was carried out in supercritical ethanol. The effects of reaction parameters such as temperature, the ratio of ethanol to bio-oil, and reaction time on the conversion of acids were studied in detail. In addition, H2SO4, H3PO4 or zeolite was also selected as external acid to investigate the esterification between these carboxylic acids and ethanol.

2. Experimental section

The experiments were carried out in a stainless steel autoclave with a capacity of 100 ml at 250 °C and 7.0 MPa. Typically, a total amount of 60 ml ethanol and bio-oil with different volume ratios was mixed and fed into the autoclave. The reactor was flushed in advance with N2 for five times so as to remove air contained in the reactor. A series of experiments were conducted with other volume ratio of ethanol to bio-oil (10:1, 5:1, 3:1, 1:1) at temperature of 250 °C. All the liquid products were collected from the reactor per run and filtered before analysis. The crude bio-oil used in this experiment was provided by Qingdao University of Science and Technology of China. The analysis of bio-oils and all liquid products after esterification were performed on an Agilent GC-7890A gas chromatograph (HP innowax capillary column 19091N-133N, 30m×250µm×0.25µm) equipped with a mass spectrometer (5975C) by using 99.995% of He as the carrier gas. The relative content of each constituent was determined by peak area normalization due to the complicated composition of samples.

3. Results and discussion

3.1. GC/MS analysis for the components of bio-oil

The component of crude bio-oil was analyzed by GC-MS. Acids were found to be the most in bio-oil with the content of 42.2% and these acids are basically composed of organic monoacid such as acetic acid, propanoic acid and 4-hydroxy-butanoic acid, however, acetic acid was dominated with the content of 35.93%. Aldehydes were observed to be in the form of hydroxy-acetaldehyde with the content of 8.41%, accompanying with 1.72% of furfural. Notably, the amount of these aldehydes was much lower than that of ketones which was about 23.2% in bio-oil, wherein the amount of 1-hydroxy-2-propanone reached 18.15%. In addition, the total amount of 1,2-ethanediol, phenols and phenol derivatives was around 15.6%, which showed a bit suppression on the further upgrading of bio-oil.

3.2. Effect of different volume ratio of ethanol and bio-oil on esterification

Figure 1 shows the effect of the ratio of ethanol to bio-oil on esterification. Acetic acid was completely conversed at the ratio of ethanol to bio-oil in the range of 1:1 to 10:1. However, the selectivity of ethyl acetate increased to 96.6% at the ratio of 3:1. The content of carbon dioxide and ethyl ether was 0.75% and 0.87%, respectively, which both were much lower than that at the ratio of 3:1(not shown here). This
indicates that acetic acid was mainly esterified with ethanol and the intermolecular dehydration of ethanol was also weakened. The selectivity of ethyl acetate reached a value of 100% at the ethanol to bio-oil ratio beyond 5:1. The sugar disappeared completely at the ethanol to bio-oil ratio of 5:1, and then increased with further addition of ethanol. Acids in raw bio-oil were all converted into esters with ethanol. No obvious distinction was found in the product distribution after esterification in the presence of excessive ethanol.

Figure 1 Effect of the ratio of ethanol to bio-oil on the esterification of bio-oil and ethanol for 2h reaction.

3.3. Effect of reaction time on the esterification performance in supercritical ethanol

Figure 2 shows the results of the esterification between ethanol and bio-oil as a function of reaction time. The conversion of acetic acid was found to be 100% in the initial 30 min, and then kept unchanged during 180 minutes. However, the amount of ethyl acetate was different as a function of reaction time. The selectivity of ethyl acetate was lower with the value of 52.4% after 30 min reaction, and then increased distinctly with increasing reaction time. The formation of ethyl acetate was the most with the selectivity of 99.5% after 120 min reaction. Meanwhile, acids in crude bio-oil were all converted into esters in supercritical ethanol. A small amount of furfural with the content of 0.53% was still detected during the first 30 min reaction, and then disappeared completely as a function of reaction time. In addition, ethanol was inevitably carried out the intermolecular ehydration into ethyl ether under the supercritical system, and the formation of ethyl ether was detected to be 3.88% after reaction for 180 min.

Figure 2 The esterification between ethanol and bio-oil as a function of reaction time.

3.4. Effect of external acid added on the esterification performance in supercritical ethanol

The results of effect of external acid on esterification are shown in Figure 3. It was found that acetic acid was completely converted in the supercritical ethanol system after 2h reaction in the presence of sulfuric acid, HZSM-5(38) and HZSM-5(100), whereas 2.31% of acetic acid was still remained with the conversion of 93.5% when phosphoric acid was added. However, all these external acids resulted in the distinct decrease in the formation of ethyl acetate. As sulfuric acid or phosphoric acid was added to the system, the selectivity of ethyl acetate was found to be 57.8% or 39.6%, respectively. A similar behavior occurred in the addition of HZSM-5(38) and HZSM-5(100), wherein the selectivity of ethyl acetate in the former was much less than that in the latter. Most importantly, the formation of ethyl acetate in the bare
supercritical ethanol system was much higher than those obtained with the addition of external acids. This implies that the weak proton acid arising from ionization of ethanol can favor esterification, and that these external acids added would restrain the ionization degree of ethanol in the supercritical system.

![Figure 3 Effect of external acids on the esterification between bio-oil and ethanol.](image)

4. Conclusions

All carboxylic acids in crude bio-oil were completely converted in the supercritical ethanol system. The selectivity of ethyl acetate was various under the different conditions. Higher ratio of ethanol to bio-oil would result in higher selectivity of ethyl acetate, which reached the value of 100% at the ratio of ethanol to bio-oil of 5:1. Moreover, ethyl acetate was significantly increased as a function of reaction time. The selectivity of ethyl acetate was detected with the value of 52.4% in the initial 30 min, and increased sharply up to 100% after 120 min reaction. In addition, the formation of ethyl acetate was restrained by adding external acids.

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