



Full Length Article

Acid-treatment of bio-oil in methanol: The distinct catalytic behaviours of a mineral acid catalyst and a solid acid catalyst



Liping Wu, Xun Hu, Shuai Wang, M.D. Mahmudul Hasan, Shengjuan Jiang, Tingting Li, Chun-Zhu Li*

Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

The different catalytic behaviour of solid acid catalyst and mineral acid catalyst towards the acid-treatment of bio-oil was investigated. The hydrogen ions in the mineral acid catalyst such as sulfuric acid homogeneously dispersed in the reaction medium made the conversion of main components of bio-oil including carboxylic acids, sugars and phenolics more efficient. In comparison, there was a steric hindrance for these components of bio-oil to access the hydrogen located in the local surface of the solid acid catalyst such as Amberlyst 70. This negatively affected their conversions during the acid-treatment. However, the inhomogeneous distribution of hydrogen ions from Amberlyst 70 in the reaction medium created high concentration of hydrogen ions in the local vicinity of the solid catalyst surface of the catalyst, which is found to be crucial for the occurrence of the etherification reactions. Understanding how the dispersion of hydrogen ions of catalyst affect the esterification of bio-oil can provide useful information for the development of the effective catalysts for upgrading of bio-oil.

1. Introduction

Bio-oil, the liquid product from the pyrolysis of biomass, is a complex mixture of various organics [1–4]. The complexity of bio-oil leads to the instability of bio-oil, creating many difficulties for its applications [5–9]. Improving the stability of bio-oil via upgrading of bio-oil can make it more suitable for the further hydrotreatment [10–12]. Esterification is a simple method to transform the carboxylic acids in bio-oil into neutral esters [13–15]. In our previous study, we found that esterification could not only transform the acids in bio-oil, but also other components such as sugars, aldehydes and many other reactive components into stable products [16–18]. Esterification is thus an important way of upgrading of bio-oil. Although a considerable amount of acids intrinsically exists in bio-oil, they are not able to efficiently catalyse the esterification of bio-oil, due to their relatively weak acidity [19]. External catalyst is thus required and is also one of the key factors affecting the efficiency of the esterification of bio-oil.

Mineral acids and solid acid catalysts are two main kinds of acid catalysts used in the esterification of bio-oil [20–29]. The difference between the two types of catalysts can be remarkable. Mineral acids such as sulfuric acid and hydrochloric acid have strong acidity and the hydrogen ions can disperse homogeneously in bio-oil. The steric barrier for the bio-oil molecules to access the hydrogen ions is small. Moreover, it is difficult to deactivate the mineral acid catalyst via polymerisation

reactions as the hydrogen ions are dispersed in the liquid medium, but not confined on the surface of a support. In comparison, solid acid catalysts like solid acidic resin (e.g. Amberlyst 70) show quite different physicochemical properties. The hydrogen ions are confined in the local vicinity of the catalyst, but not dispersed homogeneously in the reaction medium. Filling of the pores of the catalyst via polymerisation could easily deactivate the catalyst [23].

Compared with mineral acids, the local concentration of the hydrogen ions on or near the external and internal surface of a solid acid catalyst is much higher than that in the bulk reaction medium [20]. A solid acid catalyst is thus less corrosive than a mineral acid to the reactor. In addition, solid acid catalysts can be easily separated and recycled, while separation of mineral acids from the liquid products is very difficult and energy-intensive. Solid acid catalysts thus have better potential for the esterification of bio-oil, due to the recyclability and low corrosiveness. However, the hydrogen ions mainly disperse in the pore of the solid acid catalyst, which creates an issue for accessing the hydrogen ions on/in catalyst, especially for the heavy components in bio-oil. It is thus important to understand how the dispersion of hydrogen ions and steric effects affect the esterification of bio-oil, which provides essential information for the development of an effective solid acid catalyst for the esterification of bio-oil.

In this study, we focused on the effects of the dispersion of hydrogen ions on the conversion of the main components of bio-oil during

* Corresponding author.

E-mail address: Chun-Zhu.Li@curtin.edu.au (C.-Z. Li).

esterification. Sulfuric acid and Amberlyst 70, which are two typical acid catalysts with distinct dispersion of hydrogen ions in bio-oil, were evaluated in the esterification of bio-oil and their reaction behaviours will be compared.

2. Experimental

2.1. Preparation of bio-oil

The bio-oil used in this study was produced from the pyrolysis of mallee wood biomass in a grinding pyrolysis reactor at 450 °C with 54 rpm rotating rate. The detailed pyrolysis procedure can be found elsewhere [30].

2.2. Acid-catalysed experiments

An autoclave (Autoclave Engineers) equipped with a magnetic stirring device was used to conduct the acid-catalysed conversion of bio-oil. In a typical experiment, bio-oil and methanol at a mass ratio of 1:1 with a chosen catalyst (Amberlyst 70 or sulfuric acid) was loaded to the autoclave at room temperature. The acid-catalysed reactions were performed in nitrogen. The stirring rate was 500 rpm. The reactor was heated up to the required temperature (70, 120 or 170 °C). Once reaching the required temperature, one sample was taken for analysis (the “0 min” sample) and others were taken subsequently at a time interval of 30 min. The residence time for each experiment was 120 min. Once an experiment was complete, the furnace was taken off from the reactor and the valve of the cooling coil in the reactor was opened to use running water to cool down the reactor. All the products

including used catalyst and liquid were collected and filtered. The residue on the filtration paper was washed with a mixture of methanol and chloroform at a volume ratio of 1–4 until the filtrate was colourless. The solid residue was then dried in oven at 105 °C for 4 h to constant weight.

In order to compare the catalytic effects of Amberlyst 70 and sulphuric acid on the same basis, the amount of hydrogen ions in sulphuric acid ($\text{H}_2\text{SO}_4 = 2\text{H}^+ + \text{SO}_4^{2-}$) catalyst loaded was equal to that in the Amberlyst 70 loaded.

2.3. Analytical methods

In this study, bio-oil and the products were analysed by GC–MS (HP6890 GC and HP5973 MS), which was equipped with an HP-INNOWAX capillary column having a length of 30 m, a diameter of 0.25 mm and a film thickness of 0.25 μm [13,15]. The carrier gas was helium at a flow rate of 3.0 ml/min. For the analysis of a typical sample, a total of 1 μl of sample was injected into the injection port set at 250 °C at a split ratio of 50:1. The temperature of the column was kept at 40 °C for 1.6 min with helium as the carrier gas. The temperature of the column increased from 40 to 260 °C at a heating rate of 10 °C/min and was held for 7 min at 260 °C. The conversion of typical compound was as defined as follows (mol basis):

$$\text{Conversion (\%)} = \left(1 - \frac{M_i}{M_o}\right) \times 100\% \quad (1)$$

M_i : amount of target compound in product; M_o : amount of target compound loaded in reactor.

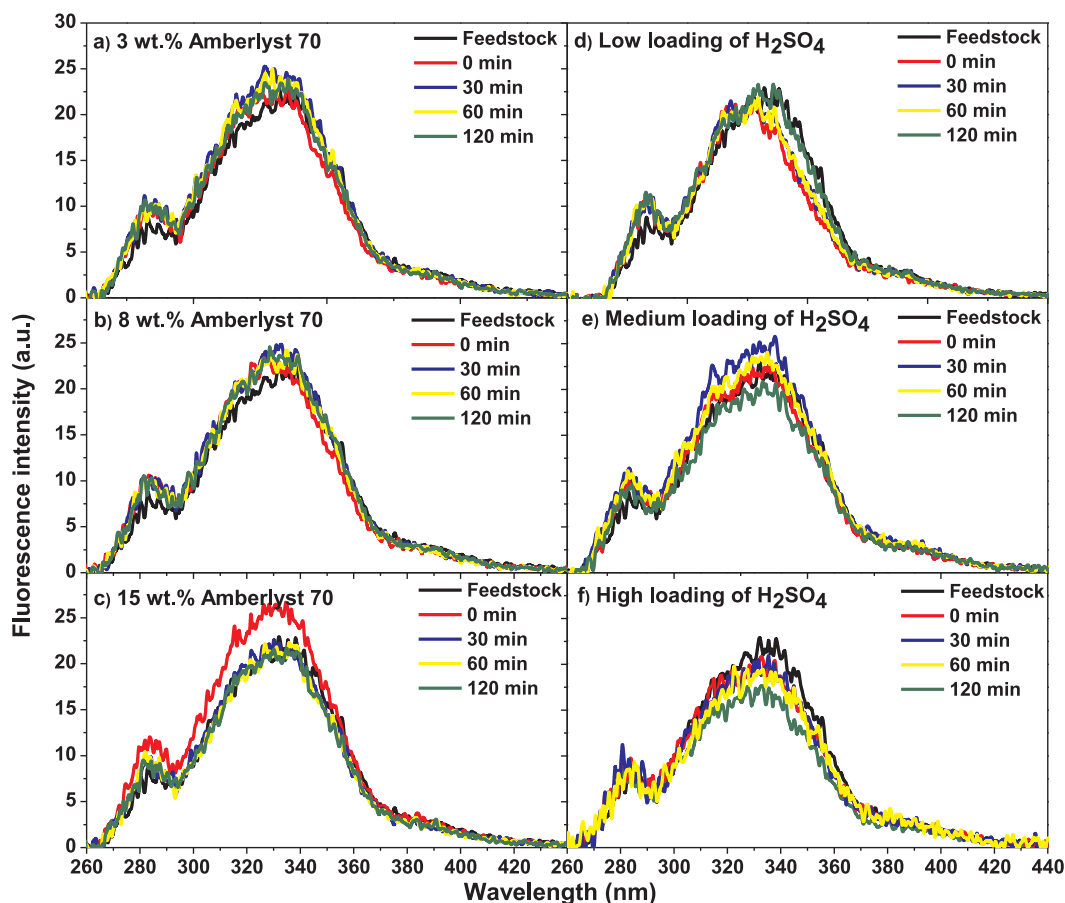


Fig. 1. The fluorescence spectra of bio-oil feedstock and the products from acid treatment of bio-oil in methanol at 70 °C with a stirring rate of 500 rpm as a function of reaction time with Amberlyst 70 (a, b, c) or sulfuric acid (d, e, f) as the catalysts. The fluorescence intensity is on bio-oil basis. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amounts of hydrogen ions in the cases of 3, 8 and 15 wt% Amberlyst 70, respectively.

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