



Full Length Article

Reaction behaviour of light and heavy components of bio-oil in methanol and in water



Liping Wu, Xun Hu, Shuai Wang, MD Mahmudul Hasan, Shengjuan Jiang, Lei Zhang, 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 main components in bio-oil behave differently during the thermal treatment in water or in methanol. Water cannot stabilize the aromatics in bio-oil. Consumption of the aromatics with mono-ring and two fused benzene rings and the formation of the aromatics with three or more fused benzene ring aromatics were observed during the thermal treatment in water. In methanol, the fluorescence intensities of the mono-ring, the aromatics with the two fused ring structures and three-ring aromatics increased. Methanol could stabilize the aromatics and retain them in the reaction medium. The conversion of mono-ring phenolics in thermal treatment of bio-oil in water and their formation in methanol was further confirmed with GC-MS measurement. In addition, it was found that the effects of acetic acid and formic acid on the conversion of the aromatics in bio-oil were negligible. This was probably due to the relative weak acidities of acetic acid and formic acid or the presence of the internal heavy carboxylic acids in bio-oil. However, the conversion of the aromatics in bio-oil was significantly promoted by the strong acids such as Amberlyst 70.

1. Introduction

Bio-oil is a liquid product produced from the pyrolysis of biomass, which is a renewable source of biofuels and chemicals [1–5]. However, bio-oil contains many oxygen-containing compounds, leading to the thermal instability and high acidity of bio-oil, and restricting the direct use of bio-oil as a transportation fuel [6–8]. Esterification and hydro-treatment are important routes for the upgrading of bio-oil to biofuels [9–12]. Both technology routes involve the thermal treatment of bio-oil [13–16]. During the thermal treatment of bio-oil, many oxygen-containing components become very reactive, leading to the polymerisation of bio-oil [17–23]. Understanding how the thermal treatment affects the polymerisation of the main components in bio-oil is essential to optimise the reaction conditions for the upgrading of bio-oil via esterification or hydrotreatment.

This study focuses on the reaction behaviour of aromatics in bio-oil during its thermal treatment in methanol and in water. The selection of methanol as a solvent was mainly because the esterification of bio-oil was generally performed in alcohols. Our previous results [24] indicated that carboxylic acids could be esterified with methanol. Reactive carbonyl functional groups in aldehydes could also be converted via acetalisation with methanol. Sugars and sugar oligomers, which were derived from the degradation of lignocellulosic biomass and

played an important role in the instability of bio-oil, can also be stabilised via the acid treatment in methanol [24,25]. However, the reaction behaviour of aromatics in bio-oil under the condition of esterification is largely unknown.

In addition to the externally added alcohol, the most intrinsically abundant component in bio-oil is water. Water in bio-oil was mainly produced from the pyrolysis of dry biomass, amounting to 20–40 wt% of bio-oil [26–28]. In our previous studies [29,30], we found that water imposed remarkable effects on the conversion of levoglucosan, the major anhydrate sugar in bio-oil.

Therefore, understanding how some reactive components like aromatics behave during the thermal treatment of bio-oil can provide very important information for developing advanced upgrading processes for the (selective) conversion of the aromatics in bio-oil.

During the esterification of bio-oil, it was found [17] that the solvent used during the heating up of bio-oil can drastically affect the behaviour of bio-oil. Figuring out the effects of different solvents on the reactive components of bio-oil can also provide vital information for optimising the reaction conditions for the upgrading of bio-oil. Therefore, this study aims to investigate the reaction behaviour of different components in bio-oil in alcohol-rich or water-rich media under various experimental conditions.

* Corresponding author.

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

Table 1
Product distribution under different reaction conditions.

Reaction medium	Mass ratio ^a	Bio-oil type	Bio-oil (g)	Holding temperature (°C)	Product distribution	Aqueous phase (%)	Solid phase (%)
Methanol	1:1	Bio-oil	40	130	One phase	–	–
Methanol	1:1	Bio-oil	40	180	One phase	–	–
Methanol	1:1	Bio-oil	40	230	One phase	–	–
Methanol	1:1	L-bio-oil ^b	40	230	One phase	–	–
Methanol	1:1	H-bio-oil ^c	40	230	One phase	–	–
Water	1:1	Bio-oil	40	130	Two phase	84	16
Water	1:1	Bio-oil	40	180	Two phase	81	19
Water	1:1	Bio-oil	40	230	Two phase	78	22
Water	1:1	L-bio-oil	40	230	One phase	–	–
Water	1:1	H-bio-oil	40	230	Two phase	58	42
Water	1:1	H-bio-oil	40	230	Two phase	59	41
–	–	Bio-oil	80	130	One phase	–	–
–	–	Bio-oil	80	180	Two phase	51	49
–	–	Bio-oil	80	230	Two phase	47	53
–	–	L-bio-oil	80	230	One phase	–	–
–	–	H-bio-oil	80	230	One phase	–	–
–	–	H-bio-oil-AA ^d	80	230	One phase	–	–
–	–	H-bio-oil-FA ^e	80	230	One phase	–	–

The holding time of all the experiments is 120 min.

^a Mass ration is between bio-oil and reaction medium.

^b L-bio-oil refers to the light fraction of bio-oil obtained by the vacuum distillation at 70 °C.

^c H-bio-oil refers to the heavy fraction of bio-oil obtained by the vacuum distillation at 70 °C.

^d H-bio-oil-AA means 4 wt% acetic acid was added into heavy bio-oil.

^e H-bio-oil-FA means 3 wt% formic acid was added into heavy bio-oil.

2. Experimental

2.1. Preparation of bio-oil

The bio-oil sample was prepared with a grinding pyrolysis reactor with mallee woody biomass at 450 °C with 54 rpm rotating rate. For grinding pyrolysis, steel balls inside the reactor were used to crush biomass and also heat the biomass. Two tandem cyclones were used to separate the solid char and vapours. After separation, the vapours were condensed in condensers cooled by water and dry ice in sequence. The final brown liquid named bio-oil was stored in a freezer. A detailed description of the reactor system and experimental procedure can be found elsewhere [26]. The basic properties of the raw bio-oil are available in our previous publication [31].

The light bio-oil and heavy bio-oil were obtained by vacuum distillation at 70 °C. The mass ratio of the light part to the heavy part was 1:2.02. The bio-oil feedstock in this study was one phase, although the water content was 30.0 wt%. This amount of water was miscible with oligomeric lignin-derived compounds in bio-oil due to the solubilising effects of other polar hydrophilic compounds.

2.2. Thermal treatment of bio-oil

The thermal treatment of bio-oil was performed under nitrogen in an autoclave reactor. Typically, bio-oil or bio-oil with methanol or water at a mass ratio of 1:1 were loaded into the reactor. After the reactor was assembled, nitrogen was used to purge the air inside the reactor for three times. The reactor was then heated to pre-set temperature and the residence time for each experiment was 120 min. Once the experiment was finished, the reactor was cooled down by a cooling coil with running water.

2.3. Analytical methods

A Perkin-Elmer LS50B spectrometer was used to analyse liquid samples to get the UV-fluorescence spectra of bio-oil feedstock and products [24]. Briefly, a sample were loaded into a specific cell made of quartz, and then was placed into the chamber for analysis. The synchronous spectrum was recorded using a constant energy difference of

2800 cm⁻¹ with a slit width of 2.5 nm and a scan speed of 200 nm/min. UV-fluorescence spectroscopy can be used to characterise aromatic structure in the feedstock and products. The wavelength reflects the aromatic ring size in the sample. In general, compounds with big conjugated- π structures appear at long wavelength.

Bio-oil feedstock and thermal treatment products were analysed with GC-MS equipped with a HP-INNOWAX capillary column [17,18]. 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 μ l of sample was injected into the injection port set at 250 °C at a split ratio of 50:1.

The negative conversion is used to express the formation of a given species. The conversion of typical compound was defined as follows (mol basis):

$$\text{Conversion}(\%) = \left(1 - \frac{M_1}{M_0}\right) \times 100\%$$

M1: amount of target compound in product

M0: amount of target compound loaded in reactor

The potential coke yield refers to the residue after thermal treatment in the thermogravimetric analyser (PerkinElmer Pyris 1 TGA) under nitrogen atmosphere at 500 °C. Generally, a sample of 10–20 mg was added into a crucible and weighed accurately in the instrument chamber. The temperature was then increased to 500 °C at a heating rate of 10 °C/min under nitrogen (100 ml/min). The temperature was held for 10 min at 500 °C. The residue was defined as potential coke.

A ThermoScientific Flash 2000 CHNS/O analyser was used to determine elemental composition of bio-oil feedstock and products. The C, H and N elements in the samples (wet basis) were determined directly while the oxygen (wet basis) content can be calculated by difference.

3. Results and discussion

Table 1 summarises the reaction conditions and distribution of products from the thermal treatment of bio-oil. The reaction behaviour of bio-oil in methanol and water was quite different. With bio-oil or heavy bio-oil and externally added water as reactants, the products obtained were a watery phase and a paste. In addition, with increasing

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