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Evolution of aromatic structures during the reforming of bio-oil: Importance of the interactions among bio-oil components

Yi Wang [a], Xun Hu [a], Daniel Mourant [a], Yao Song [a,b], Lei Zhang [a], Caroline Lievens [a], Jun Xiang [b], Chun-Zhu Li [a,*]

[a] Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Western Australia 6845, Australia
[b] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 470074, China

HIGHLIGHTS

- Interactions among bio-oil components are important to the evolution of aromatics during bio-oil reforming.
- Steam alone negligibly affects the interactions among main components in bio-oil.
- Catalyst enhances interactions among bio-oil components during bio-oil reforming.
- Catalyst could enhance radical release from non-aromatics during bio-oil reforming.
- Effects of interactions on the evolution of aromatics became weaker at high temperatures.

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ABSTRACT

Steam reforming of bio-oils is a viable way to produce syngas, but certain challenges need to be overcome before its commercial application. One of the main issues is the formation of tar and coke. Investigation of the evolution/formation of aromatic structures in steam reforming is an effective way to understand the mechanism of tar/coke formation. In this study, the pyrolysis, steam reforming and catalytic steam reforming of mallee wood bio-oil and its lignin-derived oligomers were conducted in a quartz reactor at various temperatures (500–850 °C). The product tars were characterised by ultraviolet (UV) fluorescence spectroscopy. The results indicate that the interactions among the compounds degraded from lignin and cellulose/hemicellulose obviously affect the evolution of aromatic structures during the catalytic steam reforming of bio-oil. Furthermore, Raman spectroscopy of the catalyst provided information on the interactions of the volatile compounds and the deposit on the catalysts.

1. Introduction

Bio-oil, a complex mixture of chemical compounds produced from pyrolysis of biomass, is foreseen to play an increasing role in the global energy market. For example, it can be upgraded into liquid transport biofuels or reformed into syngas [1–4].

Among the numerous possible applications for bio-oil, the catalytic steam reforming of bio-oil could become an efficient process to produce syngas or hydrogen [5–9]. However, many obstacles still exist before this technology route can be commercialised. For example, the incomplete reforming of bio-oil would produce tarry materials that can contaminate the product gas, increasing its propensity to form coke and deactivate catalysts [10,11].

Bio-oil contains multiple compounds possessing various complex aromatic ring systems originating from the thermal decomposition of biomass components (e.g. lignin, cellulose and hemicellulose) and the interactions among the intermediates from these components during pyrolysis [12,13].

Our previous study has shown that drastic changes in aromatic ring systems occurred during the pyrolysis of bio-oil. Those changes strongly influenced the formation of tar and coke [14,15]. Insufficient knowledge exists about the evolution/formation of aromatic ring systems during the steam reforming of bio-oil. In particular, the evolution of aromatic structures is the result of a whole array of gas-phase reactions involving active species/intermediates such as radicals. A bio-oil contains reactive functional groups that vary with the feedstock composition (e.g. the relative proportion and structures of cellulose, hemi-cellulose and lignin) [16]. These reactive functional groups are largely responsible for the formation of radicals and thus contribute to the evolution of aromatic ring systems [14]. Our previous studies have shown that the origins of many species or families of compounds could be traced back to the key components of biomass

* Corresponding author. Tel.: +61 8 9266 1133; fax: +61 8 9266 1138.
E-mail address: chun-zhu.li@curtin.edu.au (C.-Z. Li).

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such as lignin, cellulose and hemi-cellulose [16–18]. It is also possible to separate lignin-derived oligomers from other bio-oil components [14,17,19,20]. Therefore, a study to trace the evolution of aromatic structures from lignin-derived species and from other bio-oil species could give some detailed insights into the reaction mechanism of aromatic structures during the reforming of bio-oil. Moreover, comparison of aromatic structures from different families of bio-oil would give great insight into the importance of the interactions among bio-oil components to the evolution of aromatic ring systems during the reforming of bio-oil.

As part of our ongoing efforts to understand the evolution/formation of aromatic ring systems during the reforming of bio-oil, this study aims to study the catalytic/non-catalytic steam reforming of bio-oil at different temperatures between 500 and 850 °C. Char-supported iron catalysts [21] were used in this study due to their great potential of commercial applications. To gain further insight into the reactions, the lignin-derived oligomers separated from bio-oil were also reformed under similar conditions but in isolation from other bio-oil components. Ultraviolet (UV) fluorescence spectroscopy was used to trace the development of aromatic ring systems during the reforming process. Fourier transformed Raman (FT-Raman) spectroscopy was used to characterise the changes in the char structures of the char-supported iron catalyst.

2. Methodology

2.1. Preparation of bio-oil and bio-oil fractions

The bio-oil was produced from the pyrolysis of mallee eucalypts (*Eucalyptus loxopheba* ssp. *lissophloia*) wood at fast heating rates in a fluidised-bed reactor (nominally 1 kg/h) at 500 °C. A detailed description of the feedstock, the pyrolysis reactor system, the experimental procedure to produce bio-oil and the properties of the bio-oil has been given in our previous publications [4,13–18,13,18,22]. The bio-oil was stored in a freezer (about −10 °C) until required in further experiments described herein.

The fraction of lignin-derived oligomers was separated from the bio-oil by cold water precipitation and followed by a CH_2Cl_2 extraction, as previously reported in details elsewhere [23,24]. Again, the sample was dried and stored in a freezer until required.

2.2. Catalyst preparation

The char-support iron was produced from pyrolysis of iron-loaded brown coal. Briefly, Loy Yang brown coal (Victoria, Australia) was pulverised and sieved into a size ranging from 106 to 150 μm. The properties of the coal are as follows: C, 70.4; H, 5.4; N, 0.62; S, 0.28; Cl, 0.1; O, 23.2 and VM, 52.2 wt% (daf basis) together with an ash yield of 1.1 wt% (db) [25]. The raw coal was then mixed in an aqueous solution of 0.2 M H_2SO_4 with a ratio of the solution to coal of 30:1 by mass and stirred in an argon atmosphere for 24 h. The slurry was then filtered and washed with deionized water until a constant pH (4.5–5.0) value of the filtrates was achieved. After drying, a negligible amount of inorganic species in the acid-washed coal because almost all carboxylates (–COOM) have been converted into acids (–COOH), and it is termed as the H-form coal. The H-from coal was then impregnated with 1 wt% Fe by ion-exchanging with an $FeCl_3$ solution to produce a so-called Fe-loaded coal.

A one-stage fluidised-bed/fixed-bed reactor [25,26], was used to produce the catalysts at 800 °C using a furnace. After Fe-loaded coal (about 25 g) were loaded, the quartz reactor was heated at about 10 °C/min to 800 °C with 0.5 L/min of argon flow. The reactor was then held for 15 min at the peak temperature with the additional supply of 30 vol.% steam. After that, the reactor was lifted out of the furnace to be cooled down to room temperature with the continuous argon flow. The fresh char-supported iron catalysts were then collected and stored in a freezer (about −10 °C) for the reforming experiments.

2.3. Pyrolysis/reforming experiments

The reforming of the bio-oil and its lignin-derived oligomers were conducted using a quartz reactor system which was used in a previous study [14]. Similar structures and operations were conducted, although differences in this study were made to the introduction of catalyst and steam.

Steam was injected at the bottom part of the reactor through the same line as the fluidising gas, which was controlled by a high performance liquid chromatography (HPLC) pump. In any catalytic reforming experiment, a proper amount (~1 g) of catalyst was preloaded into the top part of the reactor and both the top and bottom stages of the reactor were operated at the same temperature (in a temperature range of 500–850 °C). Tars were trapped by a series of three tar traps containing a mixture of chloroform and methanol (80:20 by volume, HPLC-grade) at the outlet of the reactor [27,28].

Also, blank experiments without feeding of feedstock were conducted to study the effects of steam on the catalyst char structure alone.

2.4. UV–fluorescence spectroscopy

A Perkin–Elmer LS50B spectrometer was used to record the UV–fluorescence spectra of tars. The details of configuration of the instrument and analysis method are able to be found elsewhere [14]. Notably, at the same concentration, the fluorescence intensity was multiplied by the tar yield to express the fluorescence intensity on the basis of "per gram of feedstock", in this case either gram of bio-oil or lignin-derived oligomers [13,14,28,29].

2.5. Spent catalyst washing

After reforming experiment, part of spent catalysts (about 0.2 g) were mixed in a mixture of HPLC-grade chloroform and methanol (80:20 by volume) and stirred for 24 h [32]. UV–fluorescence spectroscopy and gas chromatography–mass spectrometry were used to analyse the solution to determine species removed from the spent catalyst. However, the negligible fluorescence intensities of the catalyst-washed solutions indicate that the physical adsorption of large aromatic ring systems by the catalyst was very limited. There was no obvious peak observed in the chromatogram of catalyst-washed solutions. Therefore, the amount of species physically absorbed on the spent catalysts is negligible.

2.6. Char structures of catalysts

A Perkin–Elmer Spectrum GX FT-Raman spectrometer was used to characterise the structural features of fresh and used char-supported iron catalysts. A detailed description of the instrument and sample preparation can be found elsewhere [30,31]. In this study, IR grade KBr was used to dilute the sample to a concentration of 0.5 wt%. To minimise the effects of concentration and particle size of char on the Raman intensity, all samples were ground for 15 min. The laser wavelength for excitation was 1064 nm, the laser power was 150 mW and the spectral resolution was 4 cm^{-1} for every Raman spectra reported in this study. The diameter of the incidental laser spot was about 1 μm.

All Raman spectra (from 800 to 1800 cm^{-1}) were deconvoluted into 10 Gaussian bands using GRAMS/32 AI software, and a detailed discussion of the assignment of Raman bands can be found elsewhere [21,30–32]. Normally, the D band mainly represents