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Effects of the component interaction on the formation of aromatic structures during the pyrolysis of bio-oil at various temperatures and heating rates

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ABSTRACT

This study focuses on the effects of interactions among bio-oil components on the formation of aromatic structures of bio-oil during its thermal treatment processes at various temperatures and heating rates. A bio-oil sample and its extracted fractions were pyrolyzed in a fixed-bed reactor at 300–800 °C at different temperatures and heating rates. The results show that the pyrolytic products (including the yields and aromatic structures) from raw bio-oil and its extracted fractions are significantly different, which proves the existence of the interactions between the aromatic components and light components of the bio-oil. Additionally, those interactions are determined by the pyrolysis temperature and heating rate to different extents, which further leads to the evolution of aromatic structures during the pyrolysis of bio-oil. For example, owing to the presence of the aromatic-poor fraction, the aromatic compounds (especially ≥ 2 rings) from the pyrolysis of bio-oil are less than that of the aromatic-rich fraction at relatively low temperatures (≤ 500 °C), especially at slow heating rates. This is because the polymerization, as the main interactions, promotes the transformation of more aromatic compounds (over wide range of ring sizes) into coke at these conditions. At fast heating rates, among the complex interactions, the self-gasification of bio-oil is intensified at high temperatures (≥ 700 °C), resulting in lower secondary coke yields and tar yields as well as the concentration of aromatic compounds (especially ≥ 2 rings).

1. Introduction

Bio-oil is a promising renewable energy source produced from the fast pyrolysis of biomass [1–3]. Its parent biomass mainly comprises lignin, cellulose and hemicellulose [4], hence the generated bio-oil can be regarded as the lignin-/cellulose-/hemicellulose-derived species, which is made up of intrinsically complex compositions containing hundreds or thousands of compounds [5,6]. Among all the components, the lignin-derived species are the major aromatic source of bio-oil, and the evolution of these aromatic compounds is of great importance for the utilization of bio-oil [7,8]. Aromatic compounds are the promising feedstock for the production of fine chemicals [9], which also can be the unfavorable factor to induce the coke formation on the reactor and catalyst during the thermal treatment processes [10,11].

Heating the bio-oil under pyrolytic conditions constitutes the very first stage of all the thermal utilization processes of bio-oil [12,13]. It is of particular interest to understand the pyrolytic behaviors of bio-oil as well as the evolution of the aromatic structures at the pyrolytic conditions. As critical operational parameters, temperature and heating rate can affect the thermal conversion process of bio-oil obviously [13,14]. It changes the composition and yield of the pyrolytic products by changing the involved reactions of the processes [13,15]. During heating, the compounds of bio-oil become quite reactive [16–18] toward reactions like polymerization and decomposition. For example, the small aromatic ring structures can be polymerized to form large aromatic ring structures, which is not desirable as they are difficult to be upgraded and the big aromatic structures may act as active coke precursors to generate coke [19–21].

Additionally, due to the complicated and active nature, the compounds in bio-oil could react with each other during pyrolysis, thus the

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reactions responsible for the formation of aromatic structures are complex, involving the interactions among bio-oil compounds. The interactions, which has been experimentally proved to exist during the pyrolysis of bio-oil [7,21], play an important role in influencing the pyrolytic behaviors of bio-oil. The interactions can drastically modify the evolutionary processes of bio-oil as well as the composition of the final products. For example, when the temperature is low (e.g. < 400 °C), the light compounds (such as acids, alcohols, furans, cyclic ketones and monosaccharides which are mainly considered as the hemicellulose/cellulose pyrolytic compounds [7]) can promote the transformation of the aromatic compounds of bio-oil into coke. Therefore, the knowledge about the interactions among bio-oil components is critical in investigating the evolution of aromatic structures of bio-oil during its thermal treatment processes.

As mentioned above, heating rate can affect the involved reactions during the thermal utilization of bio-oil. Clearly, the interactions, which belongs to the involved reactions, are also affected by the heating rate. However, to our best knowledge, the interactions between light components and aromatic components of bio-oil at various heating rates have not been studied. Therefore, in this study, the bio-oil was deliberately separated into aromatic-rich fraction (ARF) and aromatic-poor fraction (APF) via the n-hexane extraction to investigate the interactions between light components and aromatic components of bio-oil during its pyrolysis. The bio-oil and its extracted fractions were pyrolyzed at 300–800 °C at three different heating rates, i.e. fast (ca. 200 °C/s), medium (ca. 20 °C/s), and slow (ca. 0.33 °C/s), to gain further insight into the interactions involved. In addition to the quantification of coke and tar yields, the tars were characterized with an ultraviolet (UV) fluorescence spectrometer and a gas chromatography/mass (GC/MS) spectrometer to trace the overall formation of aromatic structures during pyrolysis.

2. Materials and methods

2.1. Preparation of bio-oil and its fractions

Bio-oil used in this study was obtained from the fast pyrolysis of rice husk [13] and then stored in a freezer (−16 °C) until required. Solvent extraction can separate bio-oil into two chemical groups efficiently before upgrading or using as chemical feedstock and the solvent can be recycled [22]. Therefore, the n-hexane was used to separate the bio-oil into two fractions. Fig. S1 shows the experimental flow diagram for the bio-oil separation and the pyrolysis experiments. Almost all the aromatic compounds were enriched in the n-hexane soluble fraction via the extraction, which will be discussed below. Therefore, the bio-oil was separated into aromatic-rich fraction (ARF) (~48.6 wt% of bio-oil) and aromatic-poor fraction (APF) (~51.4 wt% of bio-oil) via the n-hexane extraction. Rotary evaporator and vacuum pump were used to evaporate all n-hexane at 35 °C after the extraction experiments, little compounds in ARF were lost during the evaporation. The samples were stored in a freezer (−16 °C) until required.

2.2. Experimental systems and procedures

The pyrolysis experiments were carried out in a fixed-bed reactor as shown in Fig. S2, and the details are given in the Supplementary information. Briefly, for the experiments at slow, medium and fast heating rates, 1.00 ± 0.05 g of samples were pyrolyzed at 300–800 °C at three different heating rates: fast (ca. 200 °C/s), medium (ca. 20 °C/s) and slow (ca. 0.33 °C/s). For each experiment, the sample was held for 5 min at the target temperature before the reactor was cooled down rapidly in N_2 atmosphere outside of the furnace.

Tar exiting the reactor was captured in tar traps containing HPLC grade CH_2Cl_2/CH_3OH mixture (80:20 by volume). Two types of tar were determined by the method in previous work [7]. "Trapped tar" refers to the tar trapped in the CH_2Cl_2/CH_3OH mixture in the traps. "Washed tar" refers to the collected residuals from the washing of the quartz basket and reactor using the solvent mixture. The total tar was the sum of the trapped tar and the washed tar.

The solid residuals produced from the pyrolysis experiments, which cannot be dissolved into the CH_2Cl_2/CH_3OH mixture, were experimentally defined as "coke" [21]. As known that the pyrolysis of bio-oil involves two steps: the reactions before the volatilization (defined as primary reactions) in the liquid phase which takes place inside the basket and the reactions after the volatilization (defined as secondary reactions) in the volatile phase which takes place outside the basket. Therefore, the coke in the basket was defined as "primary coke", while the coke in the reactor was defined as "secondary coke" [13]. The total coke was the sum of the primary coke and the secondary coke.

2.3. Characterization of aromatic structures in tar

2.3.1. GC–MS analysis

The tar samples were analyzed using an Agilent GC–MS (7890A GC plus 5975C MS detector) with a capillary column (DB-Wax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 mm). 1 μL of sample was injected into the injection port, set at 250 °C in a splitless configuration. The column was operated in a constant flow mode using helium as the carrier gas (1 μL/min, purity > 99.99%) and initially maintained at 40 °C for 3 min before it was increased to 250 °C at a heating rate of 5 °C min^{-1}, and thereafter held for 10 min. It was not possible to obtain the calibration curves for all the compounds, therefore, in this study, the peak area of the compound was used to gauge the changes in their concentration as a function of reaction conditions [8,16,23]. The peak area was multiplied by a correction factor "mass of trapped solution/mass of feedstock" to express the area on the basis of "per gram of feedstock".

2.3.2. UV fluorescence spectroscopy

UV fluorescence spectra of tars were recorded using an Agilent Cary Eclipse fluorescence spectrometer with a constant energy difference of −2800 cm^{-1}. The bio-oil/tar solution was diluted with methanol (purity (GC): ≥ 99.9%) to 4 ppm (wt.). The wavelength is a brief indication of the aromatic ring sizes (e.g. < 290 nm for monorings, 290–370 nm for aromatic ring systems containing two-three fused benzene rings, etc.) [7,24]. At the same concentration, the fluorescence intensity was multiplied by the bio-oil/tar yield to express the fluorescence intensity on the basis of "per gram of feedstock" [25], so the fluorescence intensity became a semi-quantitative reflection of the "yields" of the aromatic ring systems during pyrolysis.

3. Results and discussion

3.1. Aromatic structures of the original bio-oil and its extracted fractions

Fig. 1 shows the synchronous spectra of bio-oil and its extracted fractions. It can be seen that most of the aromatic compounds of bio-oil are in ARF. Fig. 2 and Table 1 also show that similar types of aromatic structures (mainly with single-ring) exist in both the bio-oil and its ARF. However, the relative lighter compounds (such as acids, alcohols, furans, cyclic ketones and monosaccharides which mainly considered as hemicellulose/cellulose pyrolytic compounds [7]), with retention times shorter than 21 min (shown in Fig. 2), are found to be presented mostly in the bio-oil and APF. The water contents of bio-oil, ARF and APF, as determined by Karl Fischer titration (AKF-1B from HOGON) via the volumetric method, are respectively 26.00 wt%, 0.07 wt% and 50.00 wt %. Obviously, light compounds are enriched in the APF and the aromatic compounds are enriched in ARF through the n-hexane extraction of bio-oil.