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Formation of coke during the pyrolysis of bio-oil

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HIGHLIGHTS

- ▶ Coke can be formed by heating bio-oil over a wide range of temperature.
- ▶ Coke can be formed from both cellulose/hemicellulose-derived and lignin-derived components in bio-oil.
- ▶ The interactions among different components in the bio-oil play an important role in the formation of coke.

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ABSTRACT

Bio-oil from the pyrolysis of biomass can be upgraded into high quality liquid biofuels or utilised as a feedstock to boilers and gasifiers. The coke formation is a particularly serious problem for the upgrading of bio-oil as well as the direct utilisation of bio-oil. The effects of bio-oil chemical composition on the coke formation are keys to the understanding of the mechanism of coke formation. A bio-oil sample produced from the fast pyrolysis of mallee wood at 500 °C and the lignin-derived oligomers separated from the bio-oil were pyrolysed in a two-stage fluidised-bed/fixed-bed reactor at temperatures between 250 and 800 °C. In addition to the quantification of coke yield, UV-fluorescence spectroscopy was used to trace the formation and evolution of aromatic ring systems during pyrolysis. Our results indicate that both water-soluble and water-insoluble bio-oil fractions can form coke even at very low temperatures. The interactions among the species derived from cellulose/hemicellulose and lignin, especially the interactions involving their oligomers, are important to the observed coke yield, especially at low temperatures.

1. Introduction

Pyrolysis is an important route of biomass utilisation. In particular, the pyrolysis of biomass produces bio-oil that can be used in many ways, including being upgraded into liquid transport biofuels or being used directly as fuels for conventional boilers or modern gasifiers [1–4].

Bio-oil will have to be heated up first when the bio-oil is to be chemically upgraded, to be combusted or to be gasified/reformed. As the bio-oil is heated up, it will undergo many types of reactions such as thermal decomposition reactions, which often result in the formation of solid carbonaceous materials (coke) as a result of radical recombination and/or polymerisation reactions [5,6]. The formation of coke is a particularly serious problem for the upgrading or processing of bio-oil. For example, the coke can foul/deactivate the catalyst for bio-oil upgrading [7,8]. The coke deposit may also plug the downstream equipment of a gasification system.

Bio-oil has a very complicated chemical composition, having hundreds or thousands of compounds with a wide range of functional groups [9,10]. These species in bio-oil have originated from the thermal decomposition of biomass components such as lignin, cellulose and hemicelluloses as well as the interactions among the intermediates from these biomass components. Many species in bio-oil, having reactive functional groups, such as carboxylic acids, aldehydes and sugars, are exceedingly reactive even at room temperature. As bio-oil is heated up, these species in bio-oil become even more reactive. Bio-oil species will therefore continue to decompose and interact with each other. The reactions responsible for coke formation are thus exceedingly complex, forming a reaction network, involving both decomposition and polymerisation reactions. The mechanism of coke formation during the thermal decomposition of bio-oil remains poorly understood. In particular, little is known about the importance of the interactions among various bio-oil species from different biomass components as bio-oil is heated up. While separating a bio-oil into its constituent species is impossible, a bio-oil can be separated into various fractions having distinctly different properties. Investigating the formation of coke from each fraction as well as that from the whole

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bio-oil will gain significant insight into the complicated mechanism of coke formation from the pyrolysis of bio-oil.

This study aims to investigate the coke formation during the thermal decomposition (pyrolysis) of bio-oil when the bio-oil is heated up to elevated temperatures (250–800 °C). To gain further insight into the reactions involved, the lignin-derived oligomers separated from bio-oil were also pyrolysed under similar conditions. In addition to the quantification of coke yield as a function of temperature, UV-fluorescence spectroscopy was used to trace the formation and evolution of aromatic ring systems in bio-oil during pyrolysis.

2. Methodology

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

The details of bio-oil pyrolysis have been given elsewhere [11]. Briefly, the bio-oil used in this study was produced from the pyrolysis of mallee eucalypt (*E.* loxopheba ssp. *lissophloia*) wood at fast heating rates in a fluidised-bed reactor (nominally 1 kg/h) at 500 °C [12–14]. The bio-oil contained 19 wt% of water. The bio-oil was separated into water-soluble and water-insoluble fractions through the cold water precipitation [9,15]. The water-insoluble fraction was further washed with CH_2Cl_2 to produce CH_2Cl_2-soluble (~18.0 wt% of bio-oil) and CH_2Cl_2-insoluble (~3.6 wt% of bio-oil) fractions. The water-insoluble–CH_2Cl_2-soluble fraction and water-insoluble–CH_2Cl_2-insoluble fraction together contain most of aromatic ring systems (especially the larger aromatic ring systems) in the bio-oil [11]. These two fractions contain mainly lignin-derived materials, especially lignin-derived oligomers [16–19]. Therefore, in this paper, these two fractions are termed as light lignin-derived oligomer fraction and heavy lignin-derived oligomer fraction, respectively.

The pyrolysis of bio-oil and lignin-derived oligomers was carried out in a two-stage fluidised-bed/fixed-bed quartz reactor [11,20,21]. The bio-oil was fed into the reactor via an air-cooled injection probe, using a syringe pump (KD Scientific 410CE) equipped with a 20 ml stainless steel syringe (feeding rate was 100 mg/min). The solid feedstock (water-insoluble–CH_2Cl_2-soluble fraction and water-insoluble–CH_2Cl_2-insoluble fraction) particles were entrained in a feeder with argon (1 L/min) and fed into the fluidised bed at 100 mg/min via an injection probe. The gas residence time inside the reactor was maintained roughly constant by adjusting the flow rate of fluidising gas.

Three tar traps containing HPLC grade $CHCl_3$:CH_3OH mixture (80:20 by volume) cooled respectively with ice–water (the first trap) and dry ice (the second and third traps) baths were used to trap the tar [20–22].

In this study, the solid residual produced from pyrolysis experiment that cannot be dissolved into $CHCl_3$:CH_3OH mixture is experimentally defined as “coke”. The reactor after an experiment was washed and then dried at 105 °C for 30 min with air supply to evaporate the solvent used for tar washing. The coke was then burned with air. The coke was measured as the weight difference of the reactor before and after the coke was burned.

The preparation of water-soluble and water-insoluble fractions from bio-oil based on the cold water precipitation method necessitated the use of a large amount of water. This presented a practical difficulty to concentrate the bio-oil organic species dissolved in the water (i.e. water-soluble fraction) into a form that can be easily fed into the pyrolysis reactor to determine the coke yield from the pyrolysis of this water-soluble bio-oil fraction. The evaporation of water would necessarily also evaporate a large proportion of the water-soluble bio-oil fraction having boiling points similar to that of water. Any impurities in the original water used for the precipitation of bio-oil would also have been concentrated into the final residual after evaporation, rendering the coke yields from the subsequent pyrolysis of solid residual unreliable. Based on the above consideration, no attempt was made to concentrate the water-soluble fraction for pyrolysis. Instead, the coke yield from the water-soluble bio-oil fraction was calculated as:

$$\text{Coke}_{\text{water-solube}} = \frac{(\text{Coke}_{\text{Bio-oil}} - \text{Coke}_{\text{L-LDO}} \times \text{wt\%}_{\text{L-LDO}} - \text{Coke}_{\text{H-LDO}} \times \text{wt\%}_{\text{H-LDO}}}{1 - \text{wt\%}_{\text{L-LDO}} - \text{wt\%}_{\text{H-LDO}}}$$

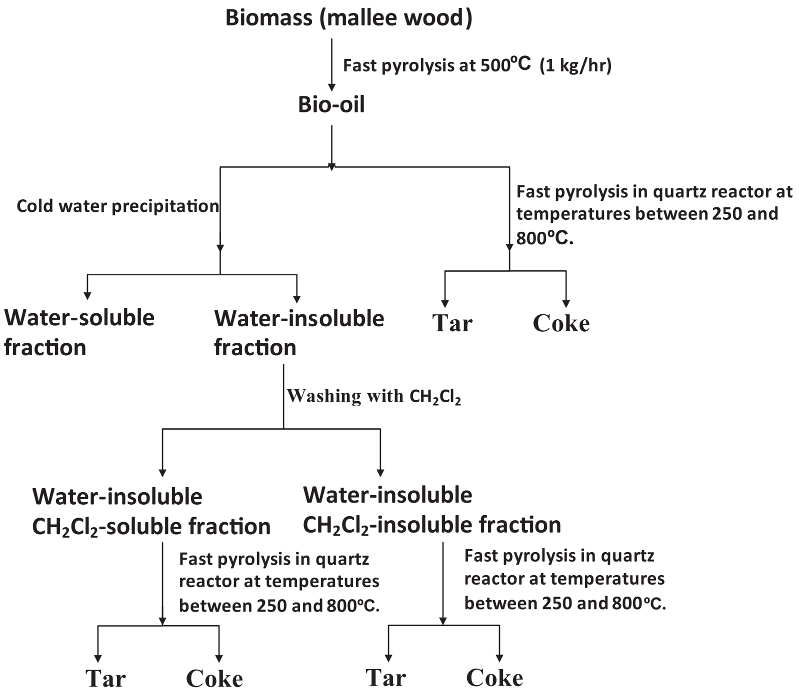

Fig. 1. A flow chart of the types of experiments including the preparation of bio-oil, the separation of bio-oil fractions and the pyrolysis of bio-oil and its fractions.