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Oxidative pyrolysis of mallee wood biomass, cellulose and lignin

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ABSTRACT

The oxidative pyrolysis of mallee wood, cellulose and lignin was performed and the bio-oil products were analysed to understand how the externally added oxygen react with the pyrolysis products. Both wood cylinders of diameter 8 mm and fine particles (90–300 µm) were pyrolysed in this study to understand the combined effects of biomass particle size and the presence of oxygen. The results revealed that, at a low oxygen concentration, the gas-phase oxidation of volatiles would improve the yields of levoglucosan and syringaldehyde, as well as unsaturated hydroxyl ketones/aldehydes for small wood particles through the oxygen-induced radical reactions. Although oxygen could facilitate the production of some compounds in bio-oil through the gas-phase reactions, it did lead to decreases in the heavy bio-oil yield due to the over-oxidation of some pyrolysis products (e. g. aromatics, lactones, unconjugated alkyl aldehydes/esters and carboxylic acids). The effects of oxygen on the pyrolysis of wood cylinders were more complicated than mallee wood particles due to the secondary reactions of volatiles and the reactions involving the pyrolysing particle surface. The interactions between the polysaccharide-derived and lignin-derived products in gas phase might affect the oxidation of volatiles, changing the formation of pyrolytic products (e.g. levoglucosan and syringaldehyde).

1. Introduction

Biomass is an important alternative for the depleting fossil fuels due to its renewable and nearly carbon-neutral nature. Fast pyrolysis is a processing technology to convert biomass into liquid fuels and chemicals. Heat supply is one of the main challenging issues to be considered in the scaling up of a pyrolysis technology. Oxidative pyrolysis is one potential solution for the problem, which has attracted significant interests during the past decades [1–5]. During the oxidative pyrolysis, a portion of pyrolytic products can be oxidised, which generates partial or all the energy required for the pyrolysis process. This auto-thermal pyrolysis system is preferable for the commercialisation of pyrolysis technologies in term of lowering the capital costs. Although a few laboratory researches based on the oxidative pyrolysis of biomass have been reported previously, there is still a gap to the scaling up of this technology. Providing the better fundamental knowledge about the influence of oxygen on pyrolysis products is essential for the advancement of oxidative pyrolysis technology. In terms of the oxidative pyrolysis process of lignocellulosic material, the process is really complicated [6]. As been previously reported [6,7], the oxidative pyrolysis process would involve the thermal degradation of biomass, the oxidation of biomass/biochar and the gas-phase oxidation of primary volatiles. Also, the thermal degradation of biomass can be possibly accelerated by the oxidation reactions. All these reactions would influence each other and finally modify the yields and composition of pyrolytic products. Thus, the presence of oxygen is expected to have strong impacts on the pyrolysis behaviour of biomass. If we could understand and control the reaction pathways for the oxidation of bio-oil components, we can optimise the operation parameters and predict the compositions of product from oxidative pyrolysis.

Some other efforts have been made to understand the influence of oxygen on the bio-oil from fast pyrolysis [3–9]. For instance, Amutio et al. [3] carried out the oxidative pyrolysis of biomass in a conical spouted-bed reactor and observed that the addition of oxygen increased the bio-oil yield due to the increased water production and slightly changed the organic composition of bio-oil. Kim et al. [4,5] studied the effects of oxygen on the pyrolysis of raw and acid-infused red oak in a fluidised-bed reactor. It was found that oxygen ranging from 0.525 to 8.4 vol% could not affect the bio-oil yield, but decrease the acid and pyrolytic lignin in bio-oil. Also, a small amount of oxygen would enhance the yields of sugars and phenols [4,5]. In a word, the inclusion of certain amounts of oxygen could improve the acidity and quality of bio-oil. However, in all these studies, oxygen pre-mixed in pre-set concentration was fed into the whole reactor. The oxidation of biomass/

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biochar or oxidation of pyrolysis volatiles might take place during this process. It is not well known what is the relationship between oxidation reactions and specific bio-oil composition. Although Kim et al. [4] suggested some possible reaction mechanism about influence of oxygen on levoglucosan formation, these suggestions have not been experimentally verified. This study aims to experimentally investigate how the exact reaction changes the yield and compositions of bio-oil, and which species have been formed or consumed during the oxidative pyrolysis.

In addition, the oxidative pyrolysis can be widely applied to tar reduction in the co-pyrolysis/gasification technology. During the process, the heavy primary volatiles from pyrolysis reactor are partially oxidised to low molecular weight compounds. Many of the researches studied the partial oxidation at gasification temperatures (700–1050 °C) of pyrolysis volatiles with a particular focus on the total amount of tar and the evolution of polycyclic aromatics [10–13]. But the dependence of bio-oil composition and the in-situ gas-phase oxidation of volatiles taking place in the same pyrolysis reactor at lower temperatures (e.g. 500 °C) have not been cleared yet now. For this reason, in this work, oxygen is fed into the same pyrolysis reactor from different inlets to evaluate the influence of in-situ gas-phase oxidation of volatiles on bio-oil species.

Published literature [14] have elucidated that pyrolysis products of biomass were dependent on biomass components (hemicellulose, cellulose, lignin and inorganic matter) and their interactions. Significant cellulose-lignin interactions during pyrolysis were also observed by Hosoya and Wu research groups [15,16]. Although the effects of interactions between hemicellulose, cellulose and lignin on the product distributions during the inert pyrolysis have been widely investigated [15–17], their influences on the in-situ gas-phase oxidation of volatiles are rarely discussed. It is expected that their interactions would also affect the pyrolysis products under air atmosphere.

Moreover, these observations have mostly been made using fine biomass particles as the feedstock. Pulverisation of biomass into fine particles is a big challenge in the industrial application of pyrolysis. The overall yield and compositions of bio-oil are significantly affected by the particle size of biomass, which is mainly due to the heat and mass transfer limitations in a big biomass particle [18–21]. The temperature gradient and transfer phenomena inside a particle would impact the oxidative pyrolysis of biomass. It is imperative to investigate the oxidative pyrolysis of large biomass particles (i.e. > 10 mm), since the pyrolysis of large biomass particles is less energy intensive and has a lower operating cost. Therefore, this study investigated the oxidative pyrolysis of the biomass with varied particle sizes. From the view of the application of oxidative pyrolysis technology, understanding how oxygen affect on the pyrolysis products would be help to selectively modify the compositions of bio-oil from pyrolysis via adjusting the oxygen inlet and concentration. Oxygen was either added into gas-phase for the direct oxidation of volatiles, or added to react with the solid and volatiles. These results help to understand how the intra-particle mass transfer limitations and gas-phase oxidation reactions affect the yields and composition of bio-oil. Cellulose and lignin were also used to investigate how the interactions between polysaccharide-derived and lignin-derived products influence the in-situ oxidation of pyrolysis volatiles. These results would provide supports for reactor design and process optimization, which facilitated the feasibility of oxidative pyrolysis process in industrial scale.

2. Materials and methods

2.1. Feedstock

Mallee wood cylinder and particle samples were used in the present study. Mallee wood cylinders had a length of about 10 mm and a diameter of about 8 mm. Wood particles were sieved to a size range of 90–300 μm. Wood samples contained 42.4, 23.8 and 24.7 wt% of cellulose, hemicellulose and lignin [22]. The ultimate analyses (wt%, daf) of wood sample were as follows: C (48.4 wt%), H (6.3 wt%), N (0.1 wt%) and O (45.2 wt%, by difference) [23]. Wood samples were kept in a freezer (about −10 °C) before use. Cellulose and alkaline lignin were purchased from Simga–Aldrich. All the samples were dried at 105 °C for 10 h before use.

2.2. Experimental procedure

The pyrolysis of mallee wood biomass was carried out at 500 °C using fluidised-bed reactors with about 60 g of clean silica sand as the fluidised bed. Two types of reactors were used in this study. These reactors were mainly comprised of the reaction zones, feeding tube, fluidising gas inlet and product gas outlet. The pyrolysis of mallee wood cylinders was performed in a two-frit reactor. The configuration details and schematic diagram of reactor could be seen in previous work [24]. The two frits divided the reactor as the pyrolysis zone at the bottom and the feeding section at the top. The total length of reactor was 420 mm and the diameter of pyrolysis section was 60 mm. The feeding tube with a diameter of 14 mm was inserted into the reactor before experiment. The bottom of feeding tube was placed about 2 mm above the sand bed. Samples were fed into the inner tube of reactor via the electric vibrator and wrapped with fluidising sand during the experiment. The pyrolysis of mallee wood particles was performed in a three-frit reactor [25]. The quartz reactor was divided into two stages by three frits. The length and diameter of main reactor body was 160 mm and 40 mm, respectively. The height of top stage was 30 mm and that of bottom stage was 130 mm. The bottom stage of reactor was the pyrolysis section. Samples were fed into the sand bed via the water-cooled probe. The whole reactor was placed inside the furnace during the experiment and the water-cooled probe was wrapped with kaowool.

For the pyrolysis in an inert atmosphere, ultrahigh purity argon (99.999%) was used as the fluidising gas and the feeding gas. Their flow rates were 1.5 L·min^{-1} and 1.0 L·min^{-1}, respectively. For the oxidative pyrolysis, oxygen was added in the form of air. Air was fed into the reactor in two different ways. In one way, air was mixed with the fluidising gas and fed into the bottom of reactor. In this case, oxygen would take part both in the thermal degradation of biomass and in the subsequent oxidation reactions. This process was termed as the 'solid- and gas-phase' mode (S/GM) oxidative pyrolysis. In the second way, air was injected into the top stage of reactor where solid biomass or char was absent. Only the oxidation of volatiles took place. This process was termed as the 'gas-phase' mode (GM) oxidative pyrolysis. The flow rate of air varied from 0.03 to 1.04 L·min^{-1} and the flow rate of the fluidising gas correspondingly ranged from 1.47 to 0.46 L·min^{-1} to maintain the total flow rate of air and fluidising gas at 1.5 L·min^{-1}. The concentration of air was in the range of 0.0–41.6 vol%, which corresponded to 0.0–8.7 vol% of oxygen. When the target temperature (500 °C) was achieved, small particle feedstocks were continuously fed into the three-frit reactor within 30 min. For the large particle feedstock, wood cylinders were fed into the two-frit reactor and maintained at 500 °C for 30 min. Pyrolysis process was quenched once the reactor was lifted out of the furnace. The fluidising gas was still supplied until the reactor was cooled down to room temperature.

2.3. Quantification and characterisation of bio-oil

Bio-oil was collected in chloroform/methanol mixture (4: 1 by volume) in a cold trap system. The trap system contained three cold traps in series. The first one was placed in the ice water bath (0 °C) to condense the steam and light fractions, and the last two traps were cooled in the dry ice bath (−78 °C) to condense the rest of volatiles [26,27]. The bio-oil collected in three cold traps was mixed. In this study, the heavy bio-oil yield is defined as the residue of collected bio-oil solution that would not evaporate at 35 °C after 4 h. The detailed collection and measurement procedure could be found elsewhere [25–27]. Thus, the