



Effects of heating rate on the evolution of bio-oil during its pyrolysis

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ABSTRACT

Bio-oil from the fast pyrolysis of biomass can be converted to solid carbon materials, chemicals and syngas by various thermochemical conversion methods. As a first step in all of these processes, bio-oil undergoes drastic components changes due to its exposure to the elevated temperature. Understanding the effects of heating rate on bio-oil transformation during its pyrolysis is therefore crucial for effective utilization of bio-oil. In this study, a bio-oil sample produced from the fast pyrolysis of rice husk at 500 °C was pyrolyzed in a fixed-bed reactor at temperatures between 300 and 800 °C at three different heating rates: fast (≈ 200 °C/s), medium (≈ 20 °C/s), and slow (≈ 0.33 °C/s). In addition to the quantification of coke and tar yields, the tar was characterized with an ultraviolet (UV) fluorescence spectroscopy, a gas chromatography/mass spectrometer (GC/MS) and a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). Our results indicate that slow heating rates promote polymerization of bio-oil components, particularly at low temperatures (< 500 °C), resulting in higher primary coke yields than that of the fast heating rates. Decomposition reaction was found to be pronounced at fast heating rates, causing decreases in the tar yields and abundance of light compounds. The increases in the yields of the secondary coke, the formations of more condensed aromatic structures and macromolecules ($m/z > 500$) were also promoted at fast heating rates via the more intense secondary reactions.

1. Introduction

Biomass, unlike fossil hydrocarbon sources, is clean, renewable, widely distributed and carbon neutral. Transformation of biomass into solid (char), liquid (bio-oil) and gaseous products can be easily achieved via pyrolysis technology. Bio-oil, which is the targeted product of the fast pyrolysis of biomass, has potentials as a feedstock for chemical [1–3] and liquid fuel productions [4–6]. During the pyrolysis of biomass, due to its moderate operating temperature, most inorganic elements (e.g. K and Si) are retained in the residual char [7,8]. This makes the obtained bio-oil “cleaner” than the biomass feedstock. In addition, the energy density of bio-oil is 5–10 times higher than its parent raw material, giving it considerable advantages of being a storable and a transportable fuel [9,10].

Bio-oil can be further processed or converted via many ways [11–13], such as gasification, catalytic cracking, hydroconversion and esterification. In all of these thermal conversion processes, the very first step involves the heating of bio-oil to elevated temperatures under

pyrolytic conditions. As a critical operating parameter during the pyrolysis stage, heating rate influences the nature and the composition of the final products. For example, the light compounds, aromatic structures and heavy components in the bio-oil could be various in different pyrolytic conditions. The evolution of these components during the pyrolysis is determined by the pyrolytic conditions such as heating rate, mostly. In addition, it is well known that pyrolysis reactions involve primary and secondary reactions. The secondary reaction mainly refers to the further reaction of the products from the primary reaction [14,15], which always involve the radical recombination reactions [16]. Since the radical fragments can be generated from volatiles during the pyrolysis, and they are highly reactive which can react with each other to produce additional secondary products, such as coke and soot [17,18]. Heating rate can influence both primary and secondary reactions by changing mass and heat transfer [19]. At low heating rates the chance for secondary reaction to take place is minimal, while at fast heating rates secondary reaction becomes dominant. For example, during the pyrolysis of coal or biomass, slow heating rates, which

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impose long residence time at low temperatures, enhance dehydration and cross polymerization reactions leading to higher char yields [20]. While at fast heating rates, primary volatiles may undergo secondary reactions through competitive pathways, either via polymerization to form char or via cracking to form lighter volatiles [20,21], especially at high temperatures.

Additionally, compared to other fuels, bio-oil has a very complicated composition, with hundreds or thousands of compounds containing a wide range of reactive functional groups, such as carboxylic acids, aldehydes and sugars, which are exceedingly reactive even at room temperature [22]. Upon heating, these compounds become even more reactive towards polymerization, which drastically modify the composition of bio-oil [23]. Meanwhile, the degree of the reactions involved during the pyrolysis of bio-oil varies with heating rate and temperature, which further influence the evolution of the bio-oil due to the varying reactions. The final products could be totally changed with the different heating rates. Therefore, it is believed that heating rate may have intricate influences on reaction behaviors of the bio-oil, contributing significantly to the differences in the final products. However, present knowledge regarding the effects of heating rate on the evolution of bio-oil is insufficient to allow a full understanding of the pyrolytic behaviors of bio-oil, such as the evolution of bio-oil as well as the yields and compositions of its products.

This study aims to investigate the effects of heating rate (0.33–200 °C/s) on the pyrolysis of bio-oil in the temperature range of 300–800 °C. In addition to the quantification of coke and tar yields, the tar was characterized with an ultraviolet (UV) fluorescence spectroscopy, a gas chromatography/mass spectrometer (GC/MS) and a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) in order to trace the overall development of aromatic ring systems, as well as the evolution of light and heavy components during pyrolysis.

2. Experimental details

2.1. Materials

The bio-oil used in this study was produced from the pyrolysis of rice husk in a fluidized-bed reactor at 500 °C. The bio-oil yield was about 50.0 wt%. The rice husk was crushed and sieved and the fraction of particle sizes between 0.106 and 0.150 mm was chosen for subsequent proximate and ultimate analysis. Before the analysis, the chosen sample was placed in the air circulation oven at 80 °C for 24 h. The proximate, ultimate analysis of the rice husk are shown in Table 1. The bio-oil was stored in a freezer (−16 °C) before the experiments. The bio-oil was mixed with polyethylene glycol (polyethylene glycol: bio-oil ≈ 1.2: 1) to make a solid mixture, the ultimate analysis of bio-oil was calculated based on the result of ultimate analysis of the solid mixture and pure polyethylene glycol (via the mass of bio-oil and polyethylene glycol used). Each ultimate analysis of the mixture was repeated for 4 times to avoid accidental error. The ultimate and heating value analysis of the bio-oil sample are shown in Table 2. The viscosity of bio-oil was 50 mm²/s at 25 °C measured by a Kinematic Viscosimeter. The density of bio-oil was 1.15 g/ml measured by a high precision balance and a measuring cylinder. The high heating value (HHV) of the samples were calculated via a correlation based on ultimate analysis

Table 1
Proximate and ultimate analyses of the biomass sample (wt.%).

	Proximate analysis (air dry basis)				Ultimate analysis (air dry basis)				HHV (kJ/g)
	Volatile	Ash	Moisture	Fixed carbon ^a	C	H	N	O ^a	
	66.06	14.96	5.45	13.53	41.69	5.40	0.28	52.63	17.17
σ^b	0.508	0.108	0.032	0.432	0.040	0.014	0.032	0.085	0.030

^a By difference.

^b Standard deviation.

Table 2
Ultimate analysis of the bio-oil sample (wt.%).

	Ultimate analysis (ash free basis)				HHV (kJ/g)
	C	H	N	O ^a	
	51.24	8.76	0.01	39.99	22.12
σ^b	0.523	0.273	0.001	0.750	0.725

^a By difference.

^b Standard deviation.

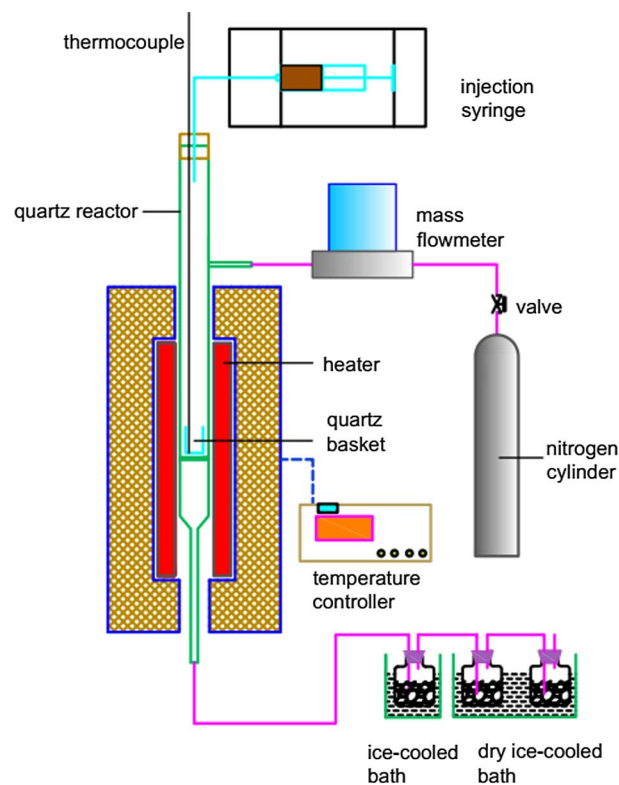


Fig. 1. Schematic diagram of the quartz fixed-bed reactor used in this study.

[24]. The water content of bio-oil, as determined by Karl Fischer titration (AKF-1B from HOGON) via the volumetric method, was about 26.0 wt%.

2.2. Experimental systems and procedures

The pyrolysis of bio-oil was carried out in a fixed-bed quartz reactor with an inner diameter of 29 mm and the length of heated zone of 280 mm (Fig. 1). The reactor was externally heated with an electrical furnace equipped with a programmed temperature controller. The nitrogen (purity of > 99.999%) with the flow rate of 150 ml/min was used as a carrier gas. Before the feeding of the bio-oil sample, the reactor was firstly purged with nitrogen for 30 min to remove any impurity gases. A thermocouple was placed inside a quartz basket to show the actual reaction temperature. Experiments were conducted at three

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