



The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating

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HIGHLIGHTS

- ▶ Microwave pyrolysis of torrefied biomass favored phenols and sugars production.
- ▶ Organic acids were greatly reduced in bio-oils from pyrolysis of torrefied biomass.
- ▶ Bio-oil from pyrolysis of torrefied biomass contained up to 7.5 area% hydrocarbons.
- ▶ Syngas from pyrolysis of torrefied biomass was rich in H₂, CH₄, and CO.

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ABSTRACT

Microwave pyrolysis of torrefied Douglas fir sawdust pellet was investigated to determine the effects of torrefaction on the biofuel production. Compared to the pyrolysis of raw biomass, the increased concentrations of phenols and sugars and reduced concentrations of guaiacols and furans were obtained from pyrolysis of torrefied biomass, indicating that torrefaction as a pretreatment favored the phenols and sugars production. Additionally, about 3.21–7.50 area% hydrocarbons and the reduced concentration of organic acids were obtained from pyrolysis of torrefied biomass. Torrefaction also altered the compositions of syngas by reducing CO₂ and increasing H₂ and CH₄. The syngas was rich in H₂, CH₄, and CO implying that the syngas quality was significantly improved by torrefaction process.

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1. Introduction

Fossil oils are the primary energy resource in the past and today's transportation fuel supply. However, the fossil oils are not renewable and the application of fossil oils brings environmental problems, for example, that carbon dioxide emission in the combustion of fossil oils contributes to the global warming. These problems motivate scientists and researchers to look for the renewable energy resources. Biomass is one of important and large amount renewable fuel sources. Unlike the fossil oils, biomass is planted and collected annually that can provide a continuous energy supply. Biomass is considered carbon neutral as its carbon is recycled from the atmosphere (Ragauskas et al., 2006). Biomass are playing important role in energy supplies. In US, the potential capacity of biomass is up to 1.3 billion dry tons annually which can replace a large portion of current petroleum consumption (Perlack et al., 2005).

Pyrolysis is a thermal chemical technology conducted at temperatures ranged from 400 to 600 °C in the absence of oxygen (Scott and Piskorz, 1984). During pyrolysis biomass is heated and decomposed to produce bio-oil, biochar, and syngas. In recently years, biomass pyrolysis has received interests to produce high yield liquids as they are promising hydrocarbon biofuels which can be easily transported, burnt directly in thermal power stations, or upgraded to obtain a hydrocarbon fuel. Traditional biomass pyrolysis processes such as fixed and fluidized bed reactors, use heating provided by heated surface, sands, and hot gas (Meier and Faix, 1999; Czernik and Bridgwater, 2004; Mohan et al., 2006). The particle size of biomass feed material is an important parameter in determining the efficacy of pyrolysis. Very fine feedstock is required by conventional pyrolysis in order to obtain high heating rates (Sensoz et al., 2000; Yi et al., 2008; Moghtaderi et al., 2004). Pyrolysis oil and char yields were found to be largely dependent on particle sizes (Sensoz et al., 2000). Microwave pyrolysis is one of the thermo-chemical technologies by heating biomass with microwave irradiation. The major advantage of the microwave heating process over conventional heating methods is the nature of internal fast and uniform heating by microwave irradiation

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(McKendry, 2002; Miura et al., 2000). Previous reports showed that biomass microwave pyrolysis can be induced in large-size particles and produce high bio-oil yields which are similar to the fluidized bed pyrolysis (Lei et al., 2009; Ren et al., 2012). Microwave pyrolysis has been successfully applied to processing plant residues (Lei et al., 2009; Yu et al., 2007; Huang et al., 2010), wood (Miura et al., 2000, 2004; Ren et al., 2012), and sewage sludge to produce bio-oil, gas, and biochar (Dominguez et al., 2006; Tian et al., 2010).

Bio-oils are carbon based liquid which has some similar properties to the petroleum fuel such as low solid content and low viscosity (Czernik and Bridgwater, 2004; Mohan et al., 2006). Bio-oils have high carbon content and can be combusted directly in boilers, gas turbines, and slow and medium-speed diesel engines for heat and power applications. Bio-oils also have low nitrogen and sulfuric content. Therefore, bio-oils are considered to be very promising hydrocarbon fuels. However, the crude bio-oils contain high moisture content which is up to 15–30 wt.%. The elemental analysis showed that the bio-oils contain about 35–40 wt.% of oxygen which is much higher than that of petroleum fuels. The pH value of crude bio-oils is around 2.5 due to the existence of organic acids. The heating value of bio-oil is ~17 MJ/kg which is lower than half of energy from petroleum fuels. These properties make the bio-oil immiscible with gasoline and difficult to integrate into the current petroleum refinery system.

Torrefaction is a mild thermal chemical technology at relatively low reaction temperature of 200–300 °C to improve the biomass quality (Bergman and Kiel, 2005). The mechanisms analysis for biomass torrefaction indicates that the hemicelluloses are deeply decomposed and cellulose and lignin are partially decomposed. Below the temperature of 250 °C the limited decomposition and carbonization of hemicelluloses were mainly involved accompanied with the minor lignin and cellulose decomposition. But at the temperatures over 270 °C, further carbonization of hemicelluloses and limited decomposition and carbonization of lignin and cellulose occurred. The strong torrefaction with a serious weight loss occurred in the temperature regime above 275 °C (Bridgeman et al., 2008; Chen and Kuo, 2011; Prins et al., 2006a). Thus, during torrefaction the moisture of biomass will be removed by evaporation and some organic acids such as acetic acid will be driven off from biomass by the hemicelluloses decomposition. The O/C ratio of torrefied biomass will be significantly decreased as the decomposition of hemicelluloses and dehydration of cellulose and lignin occurred during torrefaction (Prins et al., 2006b). Therefore, torrefied biomass contains less moisture and high carbon content. These characteristics benefit the further process such as combustion and gasification. It has been proved that torrefied biomass can generate electricity with a similar efficiency to coal and improve the syngas quality by gasification (Lipinsky et al., 2002; Bergman et al., 2005a,b).

The objective of this study was to investigate microwave pyrolysis of torrefied Douglas fir sawdust pellets. The effects of torrefaction conditions on yields of bio-oil, syngas, and biochar were determined. The characteristics of bio-oil and syngas from torrefied biomass microwave pyrolysis were determined by GC/MS and GC respectively.

2. Methods

2.1. Materials

Douglas fir sawdust pellets purchased from Bear Mountain Forest Products Inc. (USA) were used as raw materials for torrefaction. The pellets were made from 100% natural Douglas fir wood sawdust. The raw pellets had an average diameter of 6 mm and an average length of 10 mm. Proximate and elemental analysis of

Table 1
Proximate and elemental analyses of Douglas fir pellet.

Characteristics	Douglas fir pellet
<i>Proximate analysis (wt.%)</i>	
Moisture	4.82
Volatile matter	76.08
Fixed carbon	18.89
Ash	0.21
<i>Elemental analysis (wt.%)</i>	
Carbon	47.9
Hydrogen	6.55
Nitrogen	0.08
Oxygen	45.57
HHV (MJ/kg)	19.4

raw Douglas fir pellet were showed in Table 1. The higher heating value (HHV) of raw Douglas fir pellet was 19.4 MJ/kg.

2.2. Torrefied biomass preparation

The torrefaction of Douglas fir pellets was conducted in a batch microwave oven which was described in our previous report (Lei et al., 2009; Ren et al., 2012). Two-hundred grams of Douglas fir pellets was placed in a half liter quartz flask inside of the microwave oven. The power input for the microwave oven was 600 W at 2450 MHz. The reaction temperature was measured by an infrared temperature sensor attached to the microwave reactor manufactured by Sineo Microwave Chemistry Technology Company (Shanghai, China). After reaching desired reaction temperatures, the microwave reactor equipped with automatic temperature/power control used a minimum power (e.g. 0–100 W) to maintain the desired reaction temperatures. Two variable conditions, reaction temperature and time were used in the torrefaction process. A central composite experimental design (CCD) was employed for evaluating the effects of torrefaction conditions on the biofuel production of torrefied biomass pyrolysis. The reaction temperatures were ranged from 240 to 310 °C with the central point of 275 °C and the step changes of 25 °C. The reaction time was ranged from 8 to 22 min with the central point of 15 min and the step changes of 5 min based on CCD. Total 11 experiments with four axial points ($\alpha = 1.41$) and three replications at the center points were employed for the torrefied biomass preparation (Table 2).

2.3. Torrefied biomass pyrolysis

Torrefied biomass pyrolysis was performed in the batch microwave oven which was the same apparatus used for the biomass torrefaction process. The power input for microwave pyrolysis was used at the 700 W. About 100 g of torrefied biomass was placed in a half liter quartz flask inside of the microwave oven. Microwave pyrolysis of torrefied biomass was conducted at the reaction temperature of 480 °C and reaction time of 15 min as in this reaction condition the highest bio-oil yield of biomass microwave pyrolysis can be obtained according to the previous experiment (Ren et al., 2012). During pyrolysis the heavier volatiles were condensed into liquids as bio-oils and the lighter volatiles escaped as syngases at the end of the condensers where they were either burned or collected for analysis. Char was left in the quartz flask. The weight of syngas product was calculated by difference using following equation:

$$\text{Weight of syngas} = \text{initial torrefied wood pellet mass} - \text{bio-oil mass} - \text{biochar mass} \quad (1)$$

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