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Short Communication

Microwave-assisted co-pyrolysis of brown coal and corn stover for oil production

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ABSTRACT

The controversial synergistic effect between brown coal and biomass during co-pyrolysis deserves further investigation. This study detailed the oil production from microwave-assisted co-pyrolysis of brown coal (BC) and corn stover (CS) at different CS/BC ratios (0, 0.33, 0.50, 0.67, and 1) and pyrolysis temperatures (500, 550, and 600 °C). The results showed that a higher CS/BC ratio resulted in higher oil yield, and a higher pyrolysis temperature increased oil yield for brown coal and coal/corn mixtures. Corn stover and brown coal showed different pyrolysis characteristics, and positive synergistic effect on oil yield was observed only at CS/BC ratio of 0.33 and pyrolysis temperature of 600 °C. Oils from brown coal mainly included hydrocarbons and phenols whereas oils from corn stover and coal/corn mixtures were dominated by ketones, phenols, and aldehydes. Positive synergistic effects were observed for ketones, aldehydes, acids, and esters whereas negative synergistic effects for hydrocarbons, phenols and alcohols.

1. Introduction

Coal to oil (C-to-O) through pyrolysis is extensively studied and used because of the increasing need for fuel oil and the abundant reserve of coal (Mushtaq et al., 2014). However, brown coal is not a suitable feedstock for the C-to-O process because of the potential environment effects such as emissions of SO_x, NO_x, and CO_2. And also, brown coal generally has low qualities, e.g., high ash content, low heating value, etc. Co-pyrolysis of brown coal and biomass is considered a potential solution and has received increasing attention because (a) biomass is environmentally friendly (releases less emissions of SO_x and NO_x due to the low contents of S and N), (b) biomass is CO_2 neutral (the released CO_2 can be fixed by plant through photosynthesis), (c) biomass is abundant (with annual primary production of approximately 220 billion tons; Hall and Rao, 1999), (d) biomass is renewable (Zhang et al., 2013), and (e) there may be positive synergistic effect between brown coal and biomass when they are co-pyrolyzed for oil production (Sonobe et al., 2008).

The synergistic effect during a co-pyrolysis process is generally demonstrated by the deviation between experimental and theoretical oil yields. An experimental oil yield higher than theoretical value means positive synergistic effect and lower experimental oil yield indicates negative synergistic effect. Some research results showed that there were distinguished positive synergistic effects between brown coal and biomass when they were co-pyrolyzed for oil production (Zhang et al., 2007; Wei et al., 2011). However, some results showed that brown coal and biomass behaved independently during the co-pyrolysis process, and the oil yield was linearly proportional to the percentages of brown coal and biomass in the feedstock mixture, indicating absence of synergistic effect between brown coal and biomass (Yılgın et al., 2010; Guan et al., 2015). Also, some researchers even observed negative synergistic effects between brown coal and biomass during the co-pyrolysis, drawing from the results that the experimental oil yield was lower than the theoretical oil yield (Mu et al., 2016). Still, the synergistic effect between brown coal and biomass during a co-pyrolysis process is controversial, and it is believed that the synergistic effect depends on many factors, e. g. biomass types, biomass/brown coal ratios, pyrolysis temperatures, reactor types, etc. Therefore, more cases and studies are still needed to help a better understanding of co-pyrolysis of brown coal and biomass for oil production. On the other hand,

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microwave-assisted co-pyrolysis of brown coal (BC) and corn stover (CS) for oil production has not been well studied or understood.

In this study, microwave-assisted co-pyrolysis of brown coal (BC) and corn stover (CS) was investigated. The oil yields and chemical compositions under different CS/BC ratio and pyrolysis temperature conditions were evaluated, and the synergistic effects were analyzed.

2. Experimental

Based on the materials and set-up used in the previous studies (Liu et al., 2017; Zhang et al., 2018), co-pyrolysis of brown coal and corn stover was further studied. For each experiment, 30 g of designed feedstock (CS/BC ratios were 0, 0.33, 0.50, 0.67, and 1) and 700 g of silicon carbide (30 grit) were mixed uniformly and then put in the quartz reactor. Prior to microwave heating, a vacuum of 120 mm Hg was run for about 15 min. With the help of silicon carbide, the pyrolysis heating rate was significantly improved. The total heating process lasted for 20 min, and 9 °C of cold water was used for cooling. After the experiment, the oil and char were collected and weighed to calculate the yields of oil and char, and the yield of gas was calculated by difference. Each experiment was repeated for two times and the average value was presented.

The chemical composition of the oil was analyzed using a gas chromatography/mass spectrometer (Liu et al., 2017). The synergistic effect between brown coal and corn stover during microwave-assisted pyrolysis process can be indicated by:

$$SE = \frac{Y_{\mathrm{Exp}} - Y_{\mathrm{The}}}{Y_{\mathrm{The}}} \times 100\% \qquad (1)$$

where:

SE is synergistic effect between brown coal and corn stover (%)
Y_{Exp} is experimental yield (wt% or area %)
Y_{The} is theoretical yield (wt% or area %)

The theoretical yield can be calculated through:

$$Y_{\mathrm{The}} = Y_{\mathrm{BC}} P_{\mathrm{BC}} - Y_{\mathrm{CS}} P_{\mathrm{CS}} \qquad (2)$$

where:

Y_{BC} is the experimental yield obtained from pyrolysis of brown coal (wt%, area %)
Y_{CS} is the experimental yield obtained from pyrolysis of corn stover (wt%, area %)
P_{BC} is the percentage of brown coal in the feedstock mixture (%)
P_{CS} is the percentage of corn stover in the feedstock mixture (%)

3. Results and discussion

3.1. Product yields

Fig. 1 shows the yields of oil, gas and char obtained from microwave-assisted co-pyrolysis of brown coal and corn stover at different CS/BC ratios and pyrolysis temperatures. It was observed that when the CS/BC ratio increased from 0 to 1, the yield of oil increased in the ranges of 6.62–34.04 wt%, 7.59–36.53 wt% and 8.10–36.35 wt% whereas the yield of gas increased in the ranges of 6.76–28.13 wt%, 8.77–30.90 wt%, and 9.77–33.00 wt% for the pyrolysis temperatures of 500, 550, and 600 °C, respectively. The increases in the yields of both oil and gas with increasing CS/BC ratio were due to the fact that corn stover produced much more oil and gas than brown coal when they were separately pyrolyzed under the same conditions (Abnisa and Daud, 2014). Consequently, the yield of char dropped when the CS/BC ratio was increased.

When the pyrolysis temperature increased from 500 °C to 600 °C, the yield of oil from brown coal increased whereas the yield of oil from corn stover increased initially and then decreased finally. These were because they had different thermal degradation processes and pyrolysis characteristics (Guan et al., 2015). Specifically speaking, brown coal

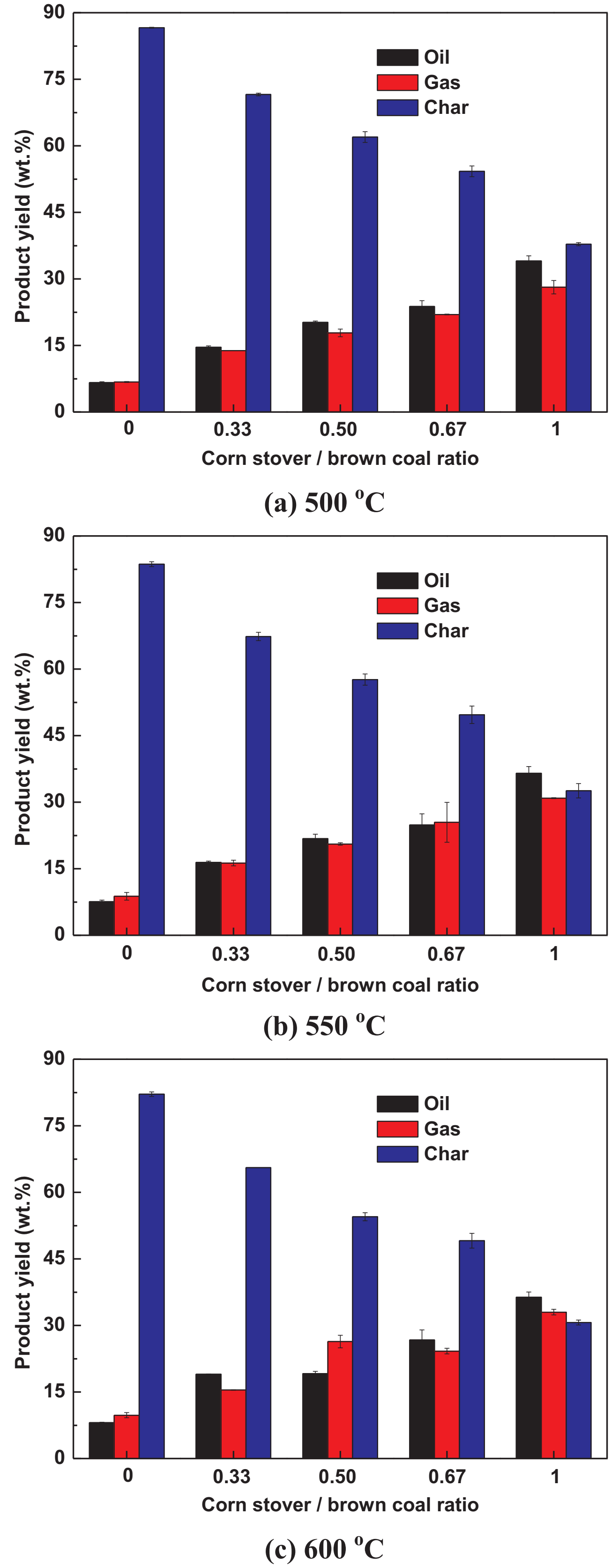

Fig. 1. Product yields at different CS/BC ratios and pyrolysis temperatures.