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Mechanism of synergy effect during microwave co-pyrolysis of biomass and lignite

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ABSTRACT

This study reports the synergy effect during co-pyrolysis of Hailar lignite (HL) and palm kernel shell (PKS) biomass under microwave irradiation in the temperature range of 400–600 °C. The results showed that the synergy effect promoted the yields of tar and gas during co-pyrolysis experiments. Gas chromatography-mass spectrometry (GC–MS) analysis of tar showed that the formation of aliphatic hydrocarbons was promoted during co-pyrolysis of lignite and PKS biomass in expense of single-ring aromatic compounds, aliphatic carboxylic acids, alcohols, aldehydes, and ketones. The synergy effect also promoted the formation of H_2 and CO during co-pyrolysis. A two-stage pyrolysis reactor was used in order to investigate the mechanism of synergy during co-pyrolysis by isolating the secondary pyrolysis reactions. The two-stage pyrolysis results showed that secondary pyrolysis reactions were mainly responsible for synergy effect, resulting in higher gas and lower tar yields as a result of secondary tar cracking. HL and PKS chars promoted the formation of aliphatic hydrocarbons, CO, and CH_4 as a result of decarbonylation, decarboxylation, and demethylation reactions. Reforming of methane over HL and PKS chars led to an increase in concentrations of H_2 and CO during secondary pyrolysis reactions.

1. Introduction

Coal has been and will remain a major fuel for the world. With the excessive use and depletion of high-rank coals, the utilization of low-rank coals, such as lignite to supply energy demand is a promising and efficient option given their abundance and low cost [1–3]. However, lignite has some disadvantages such as low calorific value, high moisture content, and high CO_2 emissions, causing environmental issues during utilization [4]. Therefore, development of environmentally friendly conversion technologies for efficient utilization of low-rank coals is of great importance. Pyrolysis is considered as a promising method for converting low-rank coals into fuels and high value-added fine chemicals [5]. However, low H/C atomic ratio in lignite results in low yields of pyrolytic products. Biomass has a higher H/C atomic ratio and can act as hydrogen donor to improve lignite decomposition during co-pyrolysis. Biomass as a carbon-neutral fuel can decrease the carbon footprint of coal conversion technologies [6–10].

Published studies on co-pyrolysis of coal and biomass have mostly used conventional heating methods which suffer from non-uniform heating and low heating rates, leading to low pyrolysis efficiencies [11,12]. Alternatively, microwave pyrolysis can be used which has gained increasing interest in recent years. Microwave pyrolysis offers a number of advantages over conventional heating methods, such as higher heating rates, volumetric and selective heating, enhanced mass transport allowing faster volatiles release, and higher level of safety and automation [13–16]. Uniform heating during microwave pyrolysis allows better control of the process and the enhanced mass transport of volatiles leads to higher tar yields [16]. Coal and biomass are poor microwave absorbers [17]. Thus, these materials need to be mixed with effective microwave receptors to reach pyrolysis temperatures under microwave irradiation [16].

The synergy effect during co-pyrolysis of coal and biomass has been studied to some extent [2,4,11,18,19]. Synergy effect may alter the yield and composition of pyrolysis products [4,20,21]. During co-pyrolysis, hydrogen from biomass can stabilize the free radicals formed during coal decomposition. Li et al. [22] postulated that synergy effect may be caused by secondary pyrolysis reactions in gas phase. Jones et al. [21] observed that synergy effect decreased the aromatics and increased the yield of phenolic compounds in tar. However, the synergy effect during co-pyrolysis of coal and biomass is still controversial. Sadhukhan and co-workers [23] observed that the experimental and calculated values for the weight loss during co-pyrolysis of coal and

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Nomenclature

HL	Hailar lignite
PKS	Palm kernel shell
UHBP	HL on the upper bed and PKS on the bottom bed
UPBH	PKS on the upper bed and HL on the bottom bed
UHCBP	HL char on the upper bed and PKS on the bottom bed
UPCBH	PKS char on the upper bed and HL on the bottom bed

biomass blends were in good agreement. Vuthaluru [24] reported that no synergy effect was observed in activation energy during co-pyrolysis.

Although some studies have been carried out on co-pyrolysis of coal and biomass, the exact mechanism of interaction between lignite and biomass and the synergy effect is not clearly understood. This study reports the synergy effect during the co-pyrolysis of a Chinese lignite and palm kernel shell biomass under microwave irradiation in a temperature range of 400–600 °C. The effects of synergy on the yields and composition of pyrolysis products were investigated. The synergy effect was studied by comparing the pyrolysis products yields and distribution during pyrolysis of blends with those of individual fuels. Furthermore, the mechanism of interaction between coal and biomass during co-pyrolysis and the nature of synergy effect was studied. One of the mechanisms of synergy is the interaction of volatiles from one blend component with the other blend component during secondary reactions. However, this interaction has not been clearly understood in the literature. In order to investigate the effect of secondary reactions, a newly developed two-stage reactor was used to isolate the secondary pyrolysis reactions by comparing the experimental results obtained from the two-stage reactor with those from a single-stage reactor. The effects of co-pyrolysis temperature on the yields and composition of pyrolysis products were studied systematically. The tar and gas samples were analyzed by gas chromatography-mass spectrometry (GC–MS) and gas chromatography (GC), respectively. The findings of this study provide new insight on the mechanism of synergy effect during co-pyrolysis of coal and biomass.

2. Materials and methods

2.1. Sample preparation

Hailar lignite (HL) from Northeast China and palm kernel shell (PKS) biomass from Malaysia were used in this study. The proximate and ultimate analyses of HL and PKS samples are given in Table 1. The lignite and biomass samples were grinded and sieved to a particle size of less than 1.0 mm. To eliminate the effect of moisture, the raw materials and MW receptors were dried in a vacuum oven at 105 °C for 12 h prior to pyrolysis experiments. Silicon carbide (SiC) was used as the microwave receptor in pyrolysis experiments. SiC is an inert material and does not show any catalytic effects during pyrolysis.

Table 1
Proximate and ultimate analyses of Hailar lignite and palm kernel shell biomass.

Composition	Percentage	
	Raw HL	Raw PKS
Moisture content (wt.%, ad)	15.3	14.9
Volatile matter (wt.%, ad)	42.03	64.68
Ash (wt.%, ad)	10.03	1.64
Fixed carbon (wt.%, ad)	32.64	18.78
C (wt.%, daf)	62.03	49.90
H (wt.%, daf)	2.40	5.25
N (wt.%, daf)	0.74	0.36
S (wt.%, daf)	0.08	0.95
O (by difference) (wt.%, daf)	34.75	43.54
H/C	0.04	0.11
O/C	0.56	0.87
HHV (MJ/kg)	20.89	19.19

ad: air dried; daf: dry ash free.

2.2. Microwave-induced pyrolysis experiments

Pyrolysis experiments were carried out using two types of quartz reactors, i.e. single-stage and two-stage, which were placed in a microwave oven (Tangshan Microwave Thermal Instrument CO. Ltd., China) with maximum power output of 4000 W and a frequency of 2.45 GHz. The schematic diagram of experimental apparatus is shown in Fig. 1. When using single-stage reactor for co-pyrolysis experiments, a biomass-to-lignite blend ratio of 1:1 was chosen [16]. Lignite (ca. 5.0 g) and biomass (ca. 5.0 g) samples were evenly blended with microwave receptor at the mass ratio of 10:2. Microwave pyrolysis experiments were carried out at 400, 500, and 600 °C. Pyrolysis runs were carried out for 30 min at a microwave output power of 1000 W. The temperature of the sample was measured using a K-type thermocouple inserted into the sample from the top of the quartz reactor and recorded at 2 s intervals. The preliminary blank experiment without the addition of any samples showed that the temperature of thermocouple increased from 30 °C to around 50 °C during 30 min of microwave irradiation with a very slow heating rate. These results indicated that the microwave absorption by the thermocouple was negligible and the increase in sample bed temperature was due to microwave adsorption by the sample blend. Once reaching the desired pyrolysis temperature, the microwave oven equipped with automatic temperature control system used a minimum output power to maintain the temperature. High purity nitrogen (99.999%) with a flow rate of 200 ml/min was used as the carrier gas in pyrolysis experiments. Before each pyrolysis run, the quartz reactor was purged with high purity nitrogen gas for 30 min to ensure an inert atmosphere is achieved.

The two stage reactor was designed in order to investigate the effects of one blend component on secondary reactions of volatiles evolved from the other component. When using the two-stage reactor, two sample placement configurations were considered: (1) co-pyrolysis of lignite and biomass in separate beds (upper or bottom bed); (2) individual pyrolysis of lignite or biomass (bottom bed) in presence of the char from the other sample (upper bed). Configuration (1) allowed evaluation of the effect of biomass or coal on the volatiles from the other blend component during secondary reactions. Approximately 10.0 g of lignite and 10.0 g of biomass were placed on different beds. In this configuration UHBP refers to the case when HL was placed on the upper bed and PKS on the bottom bed, while UPBH refers to the case when PKS was placed on upper bed and HL on bottom bed. During co-pyrolysis and as the pyrolysis of blend components proceeds, chars are formed which may also alter the composition of volatiles during secondary reactions. Therefore in configuration (2), the catalytic effects of HL or PKS chars on secondary pyrolysis reactions during co-pyrolysis were studied. About 10.0 g of HL or PKS char was loaded onto the upper bed, and 10.0 g of the other raw material was blended with SiC at mixing ratio of 10:2 and loaded to the bottom bed. In this configuration, UHCBP referred to the case where HL char and PKS were placed on the upper and bottom beds, respectively. UPCBH referred to the case where PKS char and HL sample were placed on the upper and bottom beds, respectively. All the experiments using the two-stage reactor were carried out at 500 °C. Accordingly, the HL and PKS chars were prepared at 500 °C to represent the chars formed during co-pyrolysis under similar pyrolysis conditions. The high purity nitrogen gas was used as the carrier gas with a flow rate of 400 ml/min. During two stage pyrolysis runs, the bed temperatures were measured by placing two thermocouples into the upper and bottom sample beds (Fig. 1).

The volatiles formed during pyrolysis were passed through three consecutive condensers containing dichloromethane (Sinopharm

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