Co-pyrolysis of pine sawdust and lignite in a thermogravimetric analyzer and a fixed-bed reactor

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HIGHLIGHTS

- Co-pyrolysis of lignite and biomass was studies in a TGA and a fixed-bed reactor.
- Synergetic effects promoted the evolution of volatiles at all temperatures.
- Hydrogen yield increased with increasing the pyrolysis temperature.
- Co-pyrolysis promoted the yields of phenols and guaiacols in tar.

ARTICLE INFO

ABSTRACT

Co-pyrolysis characteristics of lignite and pine sawdust were studied in a TGA and a fixed-bed reactor. The effects of pyrolysis temperature and blending ratio on the yield and composition of pyrolysis products (gas, tar, and char) were investigated. TGA experiments showed that pine sawdust decomposition took place at lower temperatures compared to lignite. With increasing the pine sawdust content in the blend, the DTG peaks shifted towards lower temperatures due to synergetic effect. In fixed-bed experiments, the synergetic effect increased the yield of volatile matter compared to the calculated values. The major gases released at low temperatures were CO_2 and CO. However, hydrogen was the primary gaseous product at higher temperatures. During co-pyrolysis, concentrations of benzene, naphthalene, and hydrocarbons in the tar decreased, accompanied by an increase in phenols and guaiacol concentrations. With increasing pyrolysis temperature, the OH, aliphatic CH, C=O, and C—O functional groups in char decomposed substantially.

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1. Introduction

Low-rank coals including lignite and sub-bituminous coals account for nearly half of the world coal reserves (Yu et al., 2013). Generally, low-rank coals have low heating value and high moisture and oxygen contents. The high moisture content in low-rank coals (25–60%) results in low calorific value, low efficiency, high transportation cost, and high CO_2 emissions. Concerns in the past few decades regarding the increasing energy demand on one hand and environmental impact of utilization of these fossil fuels have resulted in calls for more renewable and alternative energy sources (Tahmasebi et al., 2013). In order to address the global climate change problems and mitigate the environmental

issues, fossil fuel consumption needs to be reduced and replaced by renewable energy resources. Biomass is one of the most abundant and promising renewable energy sources and is considered as CO_2 neutral with low contents of sulfur. However, biomass utilization is limited due to seasonal harvesting, high transportation costs and lower fuel density (Li et al., 2014).

Pyrolysis is the initial step in thermal conversion of fuels such as combustion and gasification. However, pyrolysis can also be considered as a single and independent process to produce liquid fuels and chemicals (Park et al., 2010). Production of fuels and fine chemicals from coal is limited due to the low H/C ratio. Supplying the hydrogen by addition of biomass can increase the thermal conversion and product yields (Park et al., 2010). During the co-pyrolysis of coal and biomass a synergy effect can be expected to produce more volatiles. Synergetic effect in co-processing of coal and biomass has been reported in the literature (Park et al., 2010; Sonobe et al., 2008; Zhang et al., 2007; Zhu et al., 2008).

Sample	HL	PS
Moisture content (wt.%, ad)	14.88	9.47
Volatile matter (wt.%, ad)	33.98	72.51
Ash (wt.%, ad)	10.3	1.69
Fixed carbon (wt.%, ad)	39.02	16.33
C (wt.%, db)	61.99	46.49
H (wt.%, db)	5.05	6.22
N (wt.%, db)	0.8	0.13
S (wt.%, db)	0.26	<0.01
O (by difference) (wt.%, db)	21.6	45.46
H/C	0.08	0.13
O/C	0.35	0.98

ad: air dried; db: dry basis.

The composition of products may also change as a result of synergy effect (Haykiri-Acma and Yaman, 2007). One possible reason for the synergy during co-processing of coal and biomass is that the H/C molar ratio of biomass is higher compared with coal which can facilitate coal decomposition (Kumabe et al., 2007; Park et al., 2010; Sonobe et al., 2008; Zhang et al., 2007). Because of the different experimental conditions such as heating rate, temperature, type of reactor, and type of coal/biomass in different studies, the extent of synergy effect during coal and biomass co-pyrolysis may vary (Haykiri-Acma and Yaman, 2010; Li et al., 2013; Park et al., 2010; Zhang et al., 2007). It has been reported that synergy effect occurred in gaseous phase, which was mainly caused by the secondary reactions (Li et al., 2013). The synergy effect has also been reported in some thermogravimetric analysis (TGA) studies (Haykiri-Acma and Yaman, 2010; Sonobe et al., 2008; Vuthaluru, 2004). However, the influence of synergy effect is still controversial and not fully understood. Aboyade et al. (2013) reported that no synergetic effect was observed in solid, liquid, and gas yields. It has also been shown that the weight loss of the biomass and coal blends were in good agreement with the values of individual fuels (Sadhukhan et al., 2008).

Although the co-pyrolysis of coal and biomass is reported in literature, however previous investigations were concerned on the pyrolysis conditions required to obtain a maximum oil yield as well as pyrolysis kinetics. The information on the difference between the behavior of biomass and lignite during fast pyrolysis and the effects of their co-pyrolysis on product composition is scarce. A better understanding of biomass and lignite behavior during co-pyrolysis is necessary in order to achieve a more efficient lignite utilization process and mitigate the environmental issues. As stated above,

the influence of synergy effect during co-pyrolysis is still controversial and not fully understood. Therefore, in this study a systematic and comparative investigation of pyrolysis characteristics of Chinese Hulunbeir lignite (HL) and pine sawdust (PS) was carried out in a TGA and a fixed-bed reactor. This study is focused on the confirmation of synergy effect and the effect of co-pyrolysis on the composition of pyrolysis products for possible production of fine chemicals and hydrogen-rich syngas. The effects of the blending ratio and pyrolysis temperature on product yields and distribution were also studied. The synergistic effect in co-pyrolysis experiments was investigated by comparing the product yields and distribution of gas, tar and char during pyrolysis of blends with those obtained during pyrolysis of individual fuels. The char, oil and gas were analyzed by Fourier transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC–MS), and gas chromatography (GC), respectively. These results of this study can be used in order to better understand the behavior of biomass and coal blends upon heating.

2. Methods

2.1. Sample preparation

Hulunbeir lignite (HL) from Inner Mongolia region in north China and pine sawdust (PS) from the north-east China were used as the raw materials in this study. Proximate and ultimate analyses of lignite and biomass samples are given in Table 1. The lignite and pine sawdust samples were ground and sieved into particles size of 0.15–0.5 mm and <0.125 mm, respectively, and were then dried at 105 °C for 2 h. The two fuels were mixed at biomass to coal ratios of 0:100, 20:80, 50:50, 80:20, and 100:0 (wt.%) prior to each pyrolysis experiments.

2.2. Experimental apparatus and methods

The TGA experiments were carried out in a NETZSCH STA 449 F3. In order to avoid the diffusion limitations, small amount of samples (about 10 mg) were loaded in the Pt crucible and were heated from room temperature to 1000 °C at a heating rate of 10 °C/min under nitrogen at a flow rate of 80 ml/min. Each experimental run was repeated at least twice to ensure the reproducibility of the results.

The fixed-bed pyrolysis experiments were carried out in a vertical fixed-bed tubular quartz reactor with an internal diameter of 2.0 cm heated by an electric furnace. The schematic diagram of the fluidized-bed experimental setup used in this study is shown in
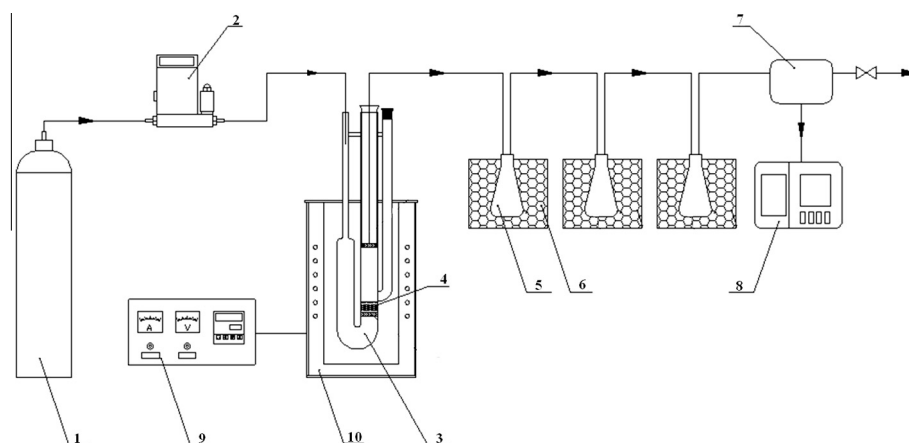

Fig. 1. Schematic diagram of experimental setup: (1) nitrogen gas cylinder; (2) mass flow meter; (3) quartz reactor; (4) sample; (5) dichloromethane; (6) Ice-bath; (7) gas bags; (8) GC; (9) temperature controller; (10) electric furnace.