



Co-pyrolysis of Chinese lignite and biomass in a vacuum reactor



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HIGHLIGHTS

- Vacuum reactor, high temperature and low heating rate were employed for co-pyrolysis.
- Product yields, char structure, gas and tar compositions were studied.
- Remarkable synergetic effects were observed.
- Potential explanations for synergetic effects were discussed.

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ABSTRACT

A vacuum fixed bed reactor was applied to pyrolyze lignite, biomass (rice husk) and their blend with high temperature (900 °C) and low heating rate (10 °C/min). Pyrolytic products were kept in the vacuum reactor during the whole pyrolysis process, guaranteeing a long contact time (more than 2 h) for their interactions. Remarkable synergetic effects were observed. Addition of biomass obviously influenced the tar and char yields, gas volume yield, gas composition, char structure and tar composition during co-pyrolysis. It was highly possible that char gasification, gaseous phase interactions, and secondary tar cracking were facilitated when lignite and biomass were co-pyrolyzed.

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1. Introduction

Recently, co-utilization of low rank coal (lignite) and renewable fuels has received increasing attention for economic and environmental advantages. Particularly, in China, that is an urgent demand. China has abundant lignite, while, unfortunately, it's not suitable to use lignite directly because of its low energy quality (high moisture content and low heating value) and negative contributions to environment (pollutants and CO₂ emission). Co-processing lignite with biomass which is renewable and environmentally friendly can solve this problem to a large extent.

Co-pyrolysis is one of the promising methods. Many studies have carried out pyrolysis of lignite/biomass blends to examine the existence of synergetic effects. Generally, biomass, as the hydrogen-donor during co-pyrolysis, can rapidly release much more volatiles (such as CO, CO₂, H₂O and H₂) which may promote "gas–lignite" interactions, char gasification, secondary tar cracking and gaseous phase interactions, leading to variations in reaction

kinetics, product distributions, tar and gas compositions (Li et al., 2013; Weiland et al., 2012; Sonobe et al., 2008; Zhang et al., 2007; Vuthaluru, 2004). Besides, the present of alkali and alkaline earth metals (AAEM) in biomass can invite a catalytic effect, facilitating those interactions in further (Vassilev et al., 2010; Keown et al., 2008; Veraa and Bell, 1978).

However, the findings, not as expected, were controversial. Some researchers observed synergies in products' yields and compositions of tar and gas (Li et al., 2014; Kreckkaiwan et al., 2013; Haykiri-Acma and Yaman, 2010; Park et al., 2010), while others reported the lack of synergistic effects during co-pyrolysis (Aboyade et al., 2013; Idris et al., 2010; Sadhukhan et al., 2008; Meesri and Moghtaderi, 2002). The differences of pyrolysis conditions (temperature, heating rate, pressure, contact time, etc.), reactor types and fuel types employed in those studies might determine whether synergy effects were observed.

In this work, a vacuum fixed bed reactor was applied to pyrolyze lignite, biomass (rice husk) and their blend with high temperature (900 °C) and low heating rate (10 °C/min). Pyrolytic products were kept in the vacuum reactor during the whole pyrolysis process, guaranteeing a long contact time that reported

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as the key factor for observing synergies in tar and gas compositions (Jones et al., 2005). Vacuum pyrolysis char, which has more “open” pore structure and is more reactive than atmospheric pyrolysis char (Ismadji et al., 2005), was expected to promote char gasification in this study. Low heating rate was employed during pyrolysis to facilitate “gas–lignite” interactions based on the different volatile release rates of lignite and biomass (Sonobe et al., 2008). And the high temperature was anticipated to benefit char gasification and secondary tar cracking (Krerkkaiwan et al., 2013; Zhong et al., 2012). Char, tar and gas were characterized with Brunauer–Emmitt–Teller (BET), gas chromatography–mass spectrometry (GC–MS) and gas chromatography (GC) techniques.

2. Methods

2.1. Experimental samples

Rice husk from rural area of Tianjin city and lignite from Neimeng Province, China were used in this study. The samples were ground to 0.13–0.18 mm and dried at 105 °C for 24 h. Rice husk and lignite were blended complying with the ratio of 1:1 in weight. The proximate and ultimate analyses were taken place in a tube furnace and Vario MACRO CHN/CHNS element analyzer respectively according to GB483-87 in China. Proximate and ultimate analyses of samples are listed in Table 1.

2.2. Experimental apparatus and procedure

All pyrolysis experiments were carried out on a fixed bed pyrolysis system. The inner size of the fixed bed reactor is 0.3 m × 0.3 m × 0.4 m (height). N₂ was used to purge air in the fixed bed reactor after samples were loaded, and then removed by a vacuum pump, providing a vacuum space for pyrolysis experiments. The initial total pressure in the reactor was around 5 kPa (−95 kPa). Final total pressures when pyrolysis processes ended were below 25 kPa (−75 kPa) according to actual experiments. The reactor was kept closed during the whole pyrolysis process. Approximately 10 g samples were used in each experiment. Each sample was heated from ambient temperature to desired temperature at a rate of 10 °C/min and kept at that temperature for 2 h. Experiment temperature in this study was 900 °C. Volatile products (tar and gas) were pumped out. The tar, condensed in traps and connecting pipelines, was recovered by washing with isopropanol as a solvent. A rotary evaporator was used to remove the solvent and water from tar which, afterwards, was weighed and collected. Non-condensable gas was measured by a cumulative volume flow meter and collected by gas bags. The char was collected and weighed when the temperature in the reactor was lower than 100 °C. Each experiment in this study was repeated three times.

Table 1
Proximate and ultimate analysis of samples.

Description	Lignite	Rice husk
<i>Ultimate analysis (dry basis)</i>		
Carbon (wt.%)	53.65	37.62
Hydrogen (wt.%)	4.12	4.91
Nitrogen (wt.%)	0.41	0.53
Sulfur (wt.%)	0.46	0.12
Oxygen (wt.%)	35.93	40.92
<i>Proximate analysis (dry basis)</i>		
Volatiles (wt.%)	56.98	66.82
Fixed carbon (wt.%)	37.59	17.28
Ash (wt.%)	5.43	15.90

2.3. Characterization

The nitrogen adsorption and desorption at 77.35 K using char samples were applied for BET analysis. Samples were degassed at 300 °C for 6 h before adsorption. The pyrolysis gas was analyzed by Agilent 7890A GC/TCD with a Molsieve 5A packed column (6 ft × 1/8" × 2 mm). Chemical compounds of tar were analyzed by a GC–MS instrument (Agilent 6890 GC-5795C MS) with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was programmed to hold at 50 °C for 3 min, ramp to 280 °C at 15 °C/min and hold at 280 °C for 5 min. The injector split ratio was set to 10:1, and the injector temperature was 300 °C. The flow rate of the He carrier gas was 1 mL/min.

2.4. Calculations

Average relative deviation between experimental value and calculated value was applied to analyze whether synergetic effect exists in the co-pyrolysis process. In this study, the blend ratio is a fixed value (1:1). The calculated values can be calculated by Eqs. (1)–(3):

$$\text{Cal}_{\text{yield},i} = \frac{Y_{\text{lignite},i} + Y_{\text{biomass},i}}{2} \quad (1)$$

$$\text{Cal}_{\text{mfra},m} = \frac{F_{\text{Lgas},m} \times Y_{\text{lignite,gas}} + F_{\text{biogas},m} \times Y_{\text{biomass,gas}}}{Y_{\text{lignite,gas}} + Y_{\text{biomass,gas}}} \quad (2)$$

$$\text{Cal}_{\text{char},n} = \frac{E_{\text{Lchar},n} \times Y_{\text{lignite,char}} + E_{\text{biochar},n} \times Y_{\text{biomass,char}}}{Y_{\text{lignite,char}} + Y_{\text{biomass,char}}} \quad (3)$$

where $\text{Cal}_{\text{yield},i}$ is the calculated yield (or volume yield) of i , including char, tar and gas. $Y_{\text{lignite},i}$ and $Y_{\text{biomass},i}$ are lignite and biomass experimental yields of i . $\text{Cal}_{\text{mfra},m}$ is the calculated molar fraction of gas component m . $F_{\text{Lgas},m}$ and $F_{\text{biogas},m}$ are molar fractions of gas component m in lignite gas and biomass gas, respectively. $Y_{\text{lignite,gas}}$ and $Y_{\text{biomass,gas}}$ are experimental volume yields of lignite gas and biomass gas. $\text{Cal}_{\text{char},n}$ is the calculated value of char's characteristic n , including volatiles content, fixed carbon content, ash content, BET surface area, pore volume and average pore size. $Y_{\text{lignite,char}}$ and $Y_{\text{biomass,char}}$ are experimental yields of lignite char and biomass char. $E_{\text{Lchar},n}$ and $E_{\text{biochar},n}$ are experimental values of lignite char's and biomass char's characteristic n . The average relative deviations can be calculated by Eq. (4):

$$\text{Average relative deviation} = \frac{|\text{Blend experimental value} - \text{Calculated value}|}{\text{Calculated value}} \times 100\% \quad (4)$$

3. Results and discussion

3.1. Product yields

The experimental and calculated product yields from the pyrolysis of lignite, rice husk and their blend are shown in Fig. 1a and b, respectively. Tar and char yields of the blend were lower than those of parent fuels and calculated values. The average relative deviations were 24.8% and 17.2%, respectively. The gas volume yield of the blend was obviously higher than that of both lignite and rice husk. The average relative deviation between the blend gas volume yield and calculated value was 24.5%. These results indicated remarkable synergetic effects during co-pyrolysis of lignite and rice husk. It was likely that the addition of biomass (rice husk) facilitated char gasification and secondary cracking of condensable compounds in tar, which, in further, led to the increase of gas yield and the decrease of tar and char yields.

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