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Experimental study on co-pyrolysis and gasification of biomass with deoiled asphalt

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ABSTRACT

The behavior of co-pyrolysis and gasification of biomass and deoiled asphalt (DOA) was investigated. The co-pyrolysis of three biomasses and DOA reflected no obvious synergetic effect on the char yield, but the char's graphite degree reduced greatly. For the DOA was melted and stuck to the biomass surface during pyrolysis, the co-pyrolysis char showed an obvious agglomeration. The gasification rate of the co-pyrolysis chars was greatly increased by the addition of biomass, and the gasification curve were much similar to that of a homogenous char, indicating the blends were quite uniform and the alkali and alkaline earth metals in biomass could catalyze DOA gasification greatly. Sunflower stalk which has the highest potassium content and mineral content promoted the gasification rate best. Kinetic analysis showed that the average *E* values of the co-pyrolysis chars increased compared with the pure biomass char. The co-gasification of DOA and biomass is a good choice for disposing DOA.

1. Introduction

Biomass is an organic fuel that is in abundance, clean and renewable, and the development and utilization of biomass energy are increasingly valued worldwide [1]. Gasification is an advanced conversion mode for which the solid fuel could be converted to into useful syngas and then be converted into many other valuable products using a host of well-known reactions, e.g., steam-methane reforming to produce methane, the Fischer-Tropsch reaction for liquid fuels [2]. Biomass is favorable for gasification as it always presents high gasification reactivity for the low graphitization degree of the amorphous carbon structure and high inherent alkali content originating from the nutritional requirements during growth process [3]. However, a series of problems such as the low calorific value and high CO_2 content of produced gas limited the development of gasification technology for biomass [4].

Deoiled asphalt (DOA) is a byproduct produced from solvent deasphalting process. The solvent deasphalting process has received a great deal of attention recently for it can remove asphaltenes and metal compounds effectively from heavy oil and provide a better quality of deasphalted oil for further upgrading. With the increasing upgrading of heavy oil and the development of the process, the amount of DOA would increase markedly [5]. Gasification seems to be an ideal route for DOA utilization [6,7]. Different from biomass, DOA has a high calorific value, while the gasification reactivity of the char is very low, thus the energy consumption and the cost of gasification are very high due to the high gasification temperature needed. Based on this, the co-gasification of biomass and DOA is proposed and it is thought to be a good way for solving the problems exist in individual gasification.

Recently, co-utilization of biomass and coal has been conducted, and the issues presented in dealing with biomass/coal alone can be significantly reduced [3,8–11]. What's more, synergetic effects that biomass performed in coal gasification have been reported, and the co-gasification has been proposed as an energy production bridge between fossil fuels and renewable fuels [7]. Other researchers also studied the co-gasification of biomass with tire, petroleum coke and so on, and they found that biomasses have a good catalytic effect and could be used as a good additive to these resources utilization [12–17]. However, few researches focused on the co-gasification of DOA with biomass. In our earlier study, the co-

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gasification of DOA char and biomass char was investigated and the results showed that corncob with rich potassium exhibited a good catalytic effect on DOA char's gasification [6]. While for the co-process of DOA and biomass in a large scale, it's easier to blend the raw DOA and biomass, and more types of biomass need to be studied to test the feasibility of this technology.

Thermogravimetric analyzer (TGA) is a useful tool for studying gasification behaviors for the high precision and well-controlled experimental conditions. Many researchers have studied isothermal gasification process of biomass char, coal char under CO_2 or steam conditions [3,7,13,15]. In isothermal mode, gasification is performed at a given temperature, reflecting the overall reaction characteristics of char in gasifier, and several temperatures must be chosen for a precise understanding of the kinetic characteristics. The non-isothermal gasification is usually conducted by a programmed reaction temperature variation, which reveals the gasification behavior of char under different temperatures and clarifies the relationship between heating rate and reaction characteristics [18]. Compared with the isothermal method, non-isothermal method is simple and easy because of avoiding the change of chemical and physical properties of the tested sample, and providing useful information via fewer experiments [19–23]. Miura and Silveston [23] confirmed the validity of the temperature programmed reaction (TPR) technique for analysis of non-catalytic gas-solid reaction. Other researchers also determined the kinetic parameters of the gasification of coal/biomass or blend chars in a series of non-isothermal experiments [20,21,24]. Thus in this paper, non-isothermal gasification experiments were employed.

The aim of this work is to use a simple set of analysis to give a novel appraisal to the co-gasification process of DOA with several kinds of biomasses. The co-pyrolysis characteristics of DOA and biomass were first studied by a fixed bed reactor. Then the gasification reactivity of the char was evaluated using non-isothermal thermogravimetric analysis and the kinetic parameters were compared.

2. Experimental

2.1. Samples

Deoiled asphalt (DOA, fine particles) was collected from the spraying granulation processes [5]. Corn stalk (CS), sunflower stalk (SS) and saw dust (SD) were chosen as the biomass samples. The CS and SS are major agro-wastes in North China, and the SD is a byproduct of the wood manufacturing industries. The proximate and ultimate analyses, along with high heating value (HHV) are given in Table 1. The biomasses contain more moisture and oxygen but less sulfur, and the heating value are much lower than that of DOA.

The biomass was blended with DOA to prepare different binary blends with varying proportions of biomass/DOA, the mass ratios have been selected as 10:90, 30:70, 50:50, 70:30, and 90:10, respectively. The blend from co-pyrolysis of CS/DOA with a ratio of 50:50 has been designated as 50CS50D, the blend of SS/DOA with a ratio of 50:50 has been designated as 50SS50D and the blend composed of SD/DOA with a ratio of 50:50 has been designated as 50SD50D.

2.2. Char preparation

Chars were prepared by a fixed-bed reactor as described earlier [25]. The crucible (35 mm i.d.×10 mm deep) loaded with the samples (~0.5 g) is placed in the upper part of the closed reactor with a N_2 flow rate of 450 mL/min to ensure the system air-free. Then the reactor is heated to 900 °C with a N_2 flow rate of 150 mL/min. The crucible is quickly pushed to the constant temperature zone of the reactor and stayed 30 min to ensure the completion of the devolatilization stage. After that, the crucible is lifted to the top of the reactor to make it rapidly cooled. Finally, the samples are taken out and measured, and then ground to less than 154 μm for use. All of the pyrolysis experiments were replicated three times for repeatability. The inorganic elements of the chars were determined by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, iCAP 6300, Thermo Fisher Scientific) and listed in Table 2. Though there is a big difference for the minerals contained in different type of biomass chars, the major inorganic elementals are K, Ca, Si, Mg, Al, Na, and Fe. The DOA ash content (0.75%) is very low, and the mineral composition is mainly the Ni, V and Fe, and no K is detected [6].

2.3. Gasification experiment

CO_2 gasification experiments were studied by a Setaram SETSYS TGA. About 5 mg of samples were put in an alumina crucible (8 mm i.d.×6 mm deep), and then: (a) purge the TGA system with CO_2 (99.8%) for 30 min; (b) ramp the furnace temperature to the final temperature with a heating rate of 10, 20, 40 °C/min under CO_2 (100 mL/min); (c) terminate the run when the mass of the sample does not change and decrease the furnace to room temperature. The data were obtained from step (b) subtract a blank run. All the gasification experiments were performed twice to verify the reproducibility, and the error of the experiments was within ±1%.

2.4. Data analysis

If there is no interaction between the two materials, then the char yield from the co-pyrolysis of the DOA and biomass could be calculated by Equation (1).

$$Y_{calc} = x_{biomass}\ Y_{biomass} + x_{DOA}\ Y_{DOA} \quad (1)$$

where $x_{biomass}$ and x_{DOA} represent the ratio of biomass and DOA in the blends, respectively. The $Y_{biomass}$ represents the biomass char yield and the Y_{DOA} represent the DOA char yield.

In order to find out whether the components of the blends interacted during gasification process, the calculated and

Table 1
Proximate and Ultimate analyses of samples.

Raw Sample	Proximate anal. (%, air dried basis)				Ultimate anal. (%, dry ash-free basis)					HHV (MJ/kg)
	M	A	V	FC[a]	C	H	O[a]	N	S_t	
CS	14.71	1.50	68.52	15.27	49.69	6.02	44.05	0.05	0.19	19.53
SS	11.09	10.40	58.82	19.69	47.60	5.94	44.29	0.28	1.89	17.05
SD	12.81	2.15	66.18	18.86	48.00	6.10	45.65	0.14	0.11	19.46
DOA	0.33	0.75	69.08	29.84	84.34	8.26	0.82	1.55	5.03	40.35

Note:
[a] By difference; S_t the total sulfur content.