



Fast co-pyrolysis of biomass and lignite in a micro fluidized bed reactor analyzer



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HIGHLIGHTS

- Synergetic effect of fast co-pyrolysis of biomass and lignite was investigated.
- Iso-conversional method was used to analyze kinetics under isothermal condition.
- Activation energies for each individual gas products were calculated.
- Reaction mechanisms for co-pyrolysis were evaluated.

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ABSTRACT

The co-pyrolysis characteristic of biomass and lignite were investigated in a Micro Fluidized Bed Reaction Analyzer under isothermal condition. The synergetic effect was evaluated by comparing the experimental gas yields and distributions with the calculated values, and iso-conversional method was used to calculate the kinetic parameters of formation of each gas component. The results showed that synergetic effect was manifested in co-pyrolysis. For the range of conversion investigated, the activation energies for H₂, CH₄, CO and CO₂ were 72.90 kJ/mol, 43.90 kJ/mol, 18.51 kJ/mol and 13.44 kJ/mol, respectively; the reactions for CH₄ and CO₂ conformed to 2 order chemical reaction model, and for H₂ and CO conformed to 1.5 order chemical reaction model; the pre-exponential factors for CH₄, CO₂, H₂ and CO were 249.0 S⁻¹, 5.290 S⁻¹, 237.4 S⁻¹ and 2.693 S⁻¹, respectively. The discrepancy of the kinetic parameters implied that there were different pathways for forming the different gas.

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1. Introduction

JiaDuoBao residue (JR) is the residual waste of Chinese herbal tea. As a typical kind of industrial biomass, JR has a large and concentrated output. It is especially suitable for industrial-scale utilization compared to agricultural biomass and forestry biomass, as there is no need to worry about the seasonal nature of JR availability.

Biomass pyrolysis is extremely important to the utilization of biomass. It is not only an effective way to produce high performance fuel but also the first step of all the other thermochemical technologies. Researchers have paid attention to it for a long term, but only in recent years has the technology of co-pyrolysis of biomass and coal become the research hotspot (Chen et al., 2012; Kar,

2011). Studies show that synergetic effect tends to happen in the co-pyrolysis of biomass and coal. According to these studies, abundant hydrogen released from biomass pyrolysis can be utilized by the pyrolysis process of coal to promote the carbon conversion of coal (Ding et al., 2014; Kerkkaiwan et al., 2013; Song et al., 2014a). Further, the incorporation of coal may solve the problems of difficult biomass fluidization and low caloric value of the gas products.

Reaction kinetic analysis is commonly used to analyze the reaction process since it is capable of revealing the reaction process and product characteristics. Additionally, as discussed in a previous paper, it is vital to supply guidance on the feasibility, design, and scaling of industrial gasification reactors, as well as pave the way for optimizing the operating conditions (Gai et al., 2013a). However, there are few work studying kinetics of co-pyrolysis. Moreover, previous researches mainly focused on non-isothermal pyrolysis experiment based on temperature programming method

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(Pan et al., 1996; Wu et al., 2014). Actually, in recent decades non-isothermal method has become a dominant technique due to the low sensitivity to experimental noise compared to traditional isothermal methods. However, synergetic effect was rarely observed in temperature programming way as a result of the different pyrolysis temperature ranges of biomass and coal. Furthermore, since the reaction temperature is determined by the reaction time and heating rate, it is impossible to separate the reaction temperature and reaction time when studying the co-pyrolysis kinetics via non-isothermal kinetic method, leading to complexity in kinetic calculation and great uncertainty in quantification (Yu et al., 2013a). Therefore, the results thus obtained are unsuitable to describe the reaction mechanism.

The calculation with the isothermal method tends to be much simpler by separating reaction temperature and reaction time, despite high sensitivity to experimental noise. Furthermore, the isothermal method based on fast heating can solve the asynchronism of pyrolysis of biomass and coal because the samples are heated at the same time and therefore volatile released from biomass and coal overlaps each other. The Micro Fluidized Bed Reaction Analyzer (MFBRA), developed by the Institute of Process Engineering, Chinese Academy of Science, may be used to realize fast pyrolysis under isothermal reaction condition (Liu et al., in press; Song et al., 2014b). The MFBRA is characterized by high heating rate, on-line feed and minimized diffusion inhibition. It can minimize the limitation of heat and mass transfer by using micro fluidized bed reactor. Moreover, secondary reactions are effectively suppressed since volatile products released are rapidly carried away by the carrier gas during pyrolysis. In a MFBRA, the mass-loss in the initial time of reaction is avoided owing to online feed. Due to the above features of MFBRA, as well as the employing of relative conversion in the corresponding calculation, the kinetic parameters calculated are less sensitive to the experimental noise than that derived from non-isothermal method. Thereby the isothermal method based on experiment in a MFBRA has significant advantage over non-isothermal method.

The experiment carried out by Soncini et al. (2013) showed that co-pyrolysis synergies were more significant as coal rank decreases. In this study, an isothermal fast co-pyrolysis experiment of JR and Xiaolongtan lignite (XL) was conducted in a MFBRA to investigate the synergetic effect and calculate the kinetic parameters for each individual gas components of the co-pyrolysis with iso-conversional method. It is expected that the kinetic parameters obtained can provide an in-depth understanding of the co-pyrolysis process. In addition, the parameters are expected to be valuable for building the kinetic model for designing and scaling of industrial pyrolysis reactors, and for guiding the component control craft and providing references for effective utilization of industrial residue.

2. Methods

2.1. Raw material properties

JR and XL were selected as the biomass and coal. XL, which has been commonly used as fuel in power plants, is a kind of low rank

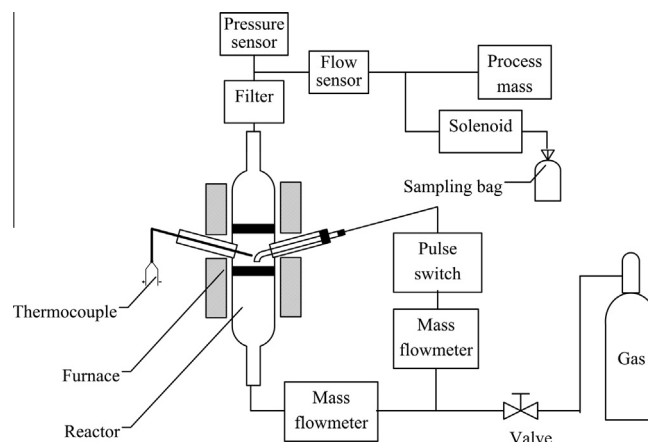


Fig. 1. Schematic diagram of MFBRA.

coal from Xiaolongtan, YunNan province, China. In this study, the feeds were first dried, and then reground and sieved into 0.150–0.180 mm in order to reduce the intra-diffusion limitation. Biomass fraction P (mass fraction of JR accounted for the mixed material) used were 0%, 10%, 20%, 40%, 50% and 100%, respectively. Quartz sand soaked in hydrochloric acid and processed by high-temperature roasting with particle size of 0.180–0.212 mm was chosen as the fluidization medium particles. The proximate analysis and ultimate analysis of the raw materials are presented in Table 1.

2.2. Experimental setup and procedure

The schematic diagram of the experimental system is shown in Fig. 1. It consists of a fluidized bed reactor, a sampling device, a detection device and certain necessary control devices. The fluidized bed reactor has two stages and a total height of 150 mm; its major reaction zone is 20 mm in diameter and 60 mm in height.

The experiment was conducted according to the following procedure. Three grams of quartz sand were put into the lower stage of the reactor. After all parts were fixed, 0.020 g of sample were loaded into the sample inlet. In this experiment, argon at flow rates of 300 mL/min under atmospheric pressure was used to fluidize the particles in the reactor to minimize diffusion inhibition. The gas of the outlet was monitored online by a rapid process mass spectrometer (Ametek, LC-D). Till the temperature of major reaction zone rose to the set value and the curve that the mass spectrometer displayed became smooth, the samples were blown into the major reaction zone instantaneously to initiate the pyrolysis by pulse gas (argon). The pulse jetting not only fed the sample into the reactor but also accelerated the mixing and heating of the sample. During the pyrolysis, the fine particles escaping from the lower stage were caught by the upper stage. In another branch, the pulse switch opened synchronously to collect the generated gas, the constituent of which was analyzed in a gas chromatography (Agilent 3000) after the experiment. The reaction temperatures were determined as 873 K, 923 K, 973 K, 1023 K, 1073 K and 1123 K, respectively.

Table 1
Proximate analysis and ultimate analysis of the raw materials.

Raw materials	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				
	Moisture	Volatile	Fixed carbon	Ash	C	H	O	N	S
JR	11.36	66.61	16.34	5.690	44.18	6.020	41.42	2.580	0.130
XL	19.55	33.64	33.26	13.55	56.51	3.610	16.80	1.610	0.560

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