Bioresource Technology 209 (2016) 273–281

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Study on product distributions and char morphology during rapid co-pyrolysis of platanus wood and lignite in a drop tube fixed-bed reactor

Haiyu Meng, Shuzhong Wang *, Lin Chen, Zhiqiang Wu, Jun Zhao

Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China

HIGHLIGHTS

- Rapid co-pyrolysis behavior of platanus wood and lignite was studied.
- Obvious synergistic effects were found in product yields and gas components.
- The char surface morphology was studied using SEM technique and fractal theory.
- The biomass blending ratio significantly affected char surface morphology.

ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 1 March 2016
Accepted 2 March 2016
Available online 9 March 2016

Keywords:
Platanus wood
Lignite
Rapid co-pyrolysis
Synergistic effects
Char morphology

ABSTRACT

The rapid co-pyrolytic behavior of platanus wood and Pingzhuang lignite was explored in a drop tube fixed-bed reactor under nitrogen atmosphere. Synergistic effects were evaluated using the deviations between experimental and predicted values of product yields and gas components. Surface morphology of residual chars were also investigated applying the scanning electron microscopy technique (SEM). This study found that the experimental values of gas volume yields were greater than the predicted, and the maximum gas volume yield exhibited with 50% biomass blending ratio at 1000 °C. Positive or negative synergistic effects happened in gas components at different blending ratios and temperatures. The SEM results indicated that the differences of char surface morphology were evident. The fractal dimensions of residual chars increased with increasing biomass blending ratio, which may improve their gasification or combustion reactivity. The change in product yields and gas components was attributed to the secondary reactions and tar cracking.

1. Introduction

Biomass is an abundant, renewable and alternative energy resource with CO_2-free property (Guo and Bi, 2015; Li et al., 2014). Thermochemical conversion technologies are currently some of the most attractive methods to effectively utilize biomass energy due to their superior flexibility of the raw materials and various products (Meng et al., 2015b; Yuan et al., 2012). However, the shortages of biomass, such as wide distributions and low energy density, remarkably limit their widespread utilization for producing secondhand energy (Guo and Bi, 2015; Li et al., 2014). Co-thermochemical conversion technology of biomass and coal is an effective solution to these problems so as to increase the penetration of biomass energy, and has became the research hotspot in recent years (Guo and Bi, 2015; Wang et al., 2015). The addition of biomass can reduce fossil fuel usage and mitigate the environmental impacts (Wang et al., 2014). Co-pyrolysis is the initial stage of co-thermochemical conversion process, and may has some important impacts on the subsequent reaction, but also an independent process to produce high valuable products (Aboyade et al., 2013; Mao et al., 2015). Therefore, it is meaningful to conduct investigation on co-pyrolytic characteristics of biomass and coal in order to deeply comprehend co-thermochemical utilization process.

Recently, many studies have been focused on the characteristics of gaseous products, as well as the possible synergistic effects, in co-pyrolytic process of various biomasses blends with coals. However, the findings were controversial. Some investigators observed synergistic effects in gas yield and components (Aboyade et al., 2013; Krerkkaiwan et al., 2013; Li et al., 2014; Park et al., 2010). Nevertheless, other researchers were against the occurrence of such synergistic effects (Collot et al., 1999; Meesri and

---

* Corresponding author. Tel.: +86 29 82665157; fax: +86 29 82668708.
E-mail address: szwang@aliyun.com (S. Wang).

http://dx.doi.org/10.1016/j.biortech.2016.03.024

Moghtaderi, 2002; Weiland et al., 2012). Furthermore, the observed synergistic effects in gaseous products can also be classified into two types according to their different influences: affecting gas yield but not components (Aboyade et al., 2013; Wang et al., 2014); affecting both gas yield and components (Krerkkaiwan et al., 2013; Quan et al., 2014; Yang et al., 2014; Yuan et al., 2012). The differences of pyrolysis conditions, reactor types and feedstocks applied in above investigations may decide whether the synergistic effects existed, as well as the impacts. But so far, no research about characteristics of gaseous products has been conducted in co-pyrolytic process of coal and platanus wood (PW), an abundant city landscaping woody biomass with remarkable heat value in China. The PW is produced from *platanus acerifolia* that is widely used in the city landscaping, known as the king of roadside trees in the world. These trees are planted in a number of Chinese cities due to their great trunks, strong resistance to pollution and superior environmental flexibility (Dou et al., 2007). Because of the rapid growth rate, they are periodically pruned every year, and a large number of waste PW is produced in the pruning process. The authors previously explored the thermal characteristics and kinetics during slow co-pyrolytic process of PW and coals via a thermogravimetric analyzer, and found that there existed obvious synergistic effects on the volatile yields (Meng et al., 2015b). To triumphantly exploit system for the efficient co-thermochemical conversion of PW and coal, there is still an unsatisfied demand to explore interactions in rapid co-pyrolytic process, and their influences on product distributions.

In order to deeply understand pyrolysis process, many investigations on the characteristics of residual chars have been performed using different techniques, such as BET, Raman spectroscopy, Fourier transform infrared (FTIR), and TGA (Meng et al., 2015b; Wei et al., 2015). Some investigators reported that the physical characteristics of residual chars, such as pore size and specific surface area, were improved by adding biomass during pyrolysis process (Yuan et al., 2012). However, study on the evolution of surface morphology of residual chars, an important physical property affecting the reactivity of residual chars in further conversion process, is rarely conducted. Compared with the chars from isolated biomass or coal, the surface morphology of residual chars from co-pyrolysis may be more sophisticated due to the interactions between volatiles and chars. Scanning electron microscopy (SEM) technique has been extensively used to qualitatively explore surface morphology of residual chars (Krerkkaiwan et al., 2013; Li et al., 2014). Nevertheless, quantitative knowledge on the surface morphology of residual chars could be seldomly found from previous researches. This knowledge can be acquired through the fractal analysis of SEM micrographs. The fractal method for characterisation of surface morphology is insensitive to the structural specifics and the surface morphology can be quantitatively described by the fractal dimension (Risovic et al., 2008; Wang and Diamond, 2001). Consequently, it is meaningful to obtain quantitative knowledge about surface morphology of residual chars from PW/coal mixtures so as to forecast their reactivity.

In the present work, rapid co-pyrolytic characteristics of PW and lignite were explored applying a laboratory-scale drop tube fixed-bed reactor in order to obtain comprehensive information about the co-thermochemical conversion process. The product distributions of PW, lignite and their blends during rapid pyrolysis from 600 °C to 1000 °C were investigated, and much attention was paid to study the interactions between feedstocks. Surface morphology of the residual chars from rapid pyrolysis were also investigated by applying SEM technique and quantificationally analyzed based on the fractal theory. The objective of this study is to gather useful data and obtain valuable knowledge that can be used to design and operate co-thermochemical conversion system for the blends of biomass and coal.

2. Materials and Methods

2.1. Materials

The PW was gathered from the street of Xi'an, Shaanxi Province, China. Lignite (PZ) from Pingzhuang coal mine, Inner Mongolia, China, was selected for this investigation. The detailed description about the sample preparation can be found in previous research (Meng et al., 2015b). The PW was blended with PZ in three different blending ratios, and the blends were named "PWPZ3-7", "PWPZ1-1" and "PWPZ7-3" meaning that the mass proportions of PW in the blends were respectively 30%, 50%, and 70%. The homogeneous degree of the blends was guaranteed by continuously vibrating at a constant speed of 300 rpm for more than 12 h. The proximate, ultimate and chemical ingredients analysis results of the PW and coal are presented in Table 1. Identification of the major structure of PW, i.e., holocellulose (the sum of cellulose and hemicellulose), and lignin components was performed according to GB/T 2677.10-1995 and GB/T 2677.8-1994 criterion respectively.

2.2. Experimental system and procedure

Fig. 1 illustrates the schematic diagram of rapid co-pyrolytic experimental facilities. In this paper, a laboratory-scale drop tube fixed-bed reactor (inside diameter of 35 mm, length of 800 mm) was employed to conduct rapid pyrolysis experiments of PW, PZ and their blends, which was heated through an electrical resistance furnace. A porous quartz plate was designed in the middle of the quartz reactor tube, and a layer of quartz wool was placed on the plate to carry tested samples during pyrolysis experiments. The high purity nitrogen (99.999%) was introduced as inert gas with flow rate of 100 mL $\min^{-1}$ controlled by a mass flow meter.

Before the experiment, the valve *B* was closed, then the tested sample was firstly put into the hopper by opening the valve *A*. Closing the valve *A*, and the inert gas was introduced into quartz reactor. When the desired temperature was achieved, and kept constant for 10 min, the valve *B* was turned on, then the tested sample was instantly dropped onto the hot quartz wool and the rapid pyrolysis experiment started. The temperature investigated in this study was from 600 °C to 1000 °C. The gaseous products were swept out of the reactor by the inert gas, went through a glass wool filter, a gas washer and a silica gel drier, finally were gathered by a gas bag. The temperature of the furnace was kept at the preset value for 15 min since the tested sample was feeded to ensure that

Table 1
Proximate, ultimate and chemical ingredients analysis results of the PW and coal.

Material	PW	PZ
Proximate analysis (wt.%, ad)		
Moisture	9.88 ± 0.10	12.02 ± 0.12
Ash	0.8 ± 0.04	24.25 ± 0.16
Volatile matter	75.78 ± 0.28	38.32 ± 0.19
Fixed carbon	13.54 ± 0.14	25.41 ± 0.15
Ultimate analysis (wt.%, ad)		
Carbon	41.58 ± 0.48	44.49 ± 0.45
Hydrogen	5.14 ± 0.12	3.01 ± 0.10
Nitrogen	0.24 ± 0.05	0.79 ± 0.08
Sulfur	0.14 ± 0.02	0.89 ± 0.06
Oxygen^c	42.22 ± 0.43	14.55 ± 0.21
H/C atomic ratio	1.48	0.81
O/C atomic ratio	0.76	0.25
$Q_{net,ad}$ (MJ kg^{-1})	16.95 ± 0.22	18.79 ± 0.26
Lignocellulosic composition (wt.%, def)		
Holocellulose	81.29 ± 0.89	
Lignin	18.71 ± 0.25	

ad: air dried basis; c: calculated by difference; def: dry and extractive-free basis.