



The kinetics model and pyrolysis behavior of the aqueous fraction of bio-oil

Shaomin Liu^a, Mingqiang Chen^{b,*}, Qingsong Hu^b, Jun Wang^b, Lihong Kong^b

^aSchool of Earth Science and Environmental Engineering, Anhui University of Science and Technology, Huainan 232001, PR China

^bSchool of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, PR China

HIGHLIGHTS

- ▶ The pyrolysis characteristics of the aqueous fraction of bio-oil are studied.
- ▶ The pyrolysis of aqueous fraction of bio-oil can be divided into three stages.
- ▶ The most probable mechanism functions and kinetics model were finally obtained.
- ▶ Comparison of the calculated value and the experimental results was performed.

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ABSTRACT

The pyrolysis behavior and kinetics of the aqueous fraction of bio-oil were studied through thermogravimetric (TG) analysis. Based on the experimental data, activation energies and kinetic parameters were calculated by the Achar differential method and the Coats–Redfern integral method, then the most probable mechanism functions and kinetics model were obtained at last. The results show that the pyrolysis of bio-oil aqueous fraction can be divided into three stages, that is, the volatilization of volatile fractions, the decomposition stage of heavy fractions and char combustion. The experimental results show that the activation energy of volatilization is higher than that of the decomposition stage. The first stage was expressed as the first order reaction and the second stage the second order reaction. The correlation coefficient between the two stages illustrates that the reactions are in well conformity with each other and the calculated value of conversion is consistent with the experimental results.

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1. Introduction

Bio-oils refer to the complex mixtures of oxygenated organic compounds including water, carbonaceous materials and structured compounds (Bridgwater, 1999; Mullen and Boateng, 2008; Medrano et al., 2011). They can be separated into oil phase and aqueous phase by adding water. The aqueous phase consists of carbohydrate-derived compounds and light oxygenated compounds (Azad et al., 2012). Due to the lack of fossil fuel resources and the growing greenhouse effect, the utilization of bio-oil as a potential fuel substitute can satisfy the human society's need for energy with wide application prospect (Chen et al., 2011; Garcia et al., 2000; Rioch et al., 2005; Huber and Dumesic, 2006; He et al., 2012). Bio-oil can be used as low level fuels to provide heat or generate power (Czernik and Bridgwater, 2004; Chiaramonti et al., 2007), or used in internal engine after upgrade (Xu et al., 2008; Du et al., 2009).

The pyrolysis of bio-oil is the initial stage of its combustion and gasification, so it is related to the thermal chemical use of bio-oil and the in-depth investigation of pyrolysis kinetics of bio-oil is of vital importance. Many systematic studies have been done on the pyrolysis characteristics and kinetics of bio-oil as well as its compounds (Yahya and Ihsan, 2002). However, the pyrolysis characteristics of crude bio-oil components have represented some issues such as coke formation and low heating value. So far, although many studies (Strenziok and Kinstner, 2001; Kok, 2012; Branca et al., 2005a,b, 2006; Shahla et al., 2012) have been reported, the fundamentals relative to the pyrolysis of bio-oil have not been fully understood. Additionally, great interest has been addressed to the utilization of bio-oil aqueous fraction and the kinetics pyrolysis model of bio-oil aqueous fraction has rarely been studied.

So the chief objectives of this study are concerned with the pyrolysis characteristics and kinetics aiming at providing some meaningful data for the design as well as the optimization of the related gasification and combustion reactor.

Thermal analysis of water soluble components in bio-oil, which is made from stalks waste and conducted under air atmosphere, as well as the effects of heating rate on pyrolysis and combustion

* Corresponding author. Tel./fax: +86 554 6668742.

E-mail addresses: shmliu@aust.edu.cn (S. Liu), mqchen@aust.edu.cn (M. Chen).

characteristics were investigated. Achar and Coats–Redfern methods are used to determine the best reaction mechanism function and to calculate the kinetic parameters, respectively.

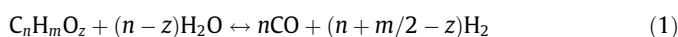
2. Methods

2.1. Experimental material

The bio-oil used for thermal analysis was obtained by pyrolysis of wheat stalk in a small scale fixed bed in our laboratory. The sample was prepared by mixing the bio-oil and distilled water while the water phase of this mixture was used for thermal analysis. The elemental composition and properties of the bio-oil are shown in Table 1.

2.2. Thermal analysis methods

Thermal analysis of the samples was conducted on TA SDT 2960 under air atmosphere with a flow rate of 60 mL/min and the amount for analysis was about 10 mg. The heating rate was controlled to be 10, 30 and 80 °C/min, respectively, and the samples were heated from room temperature to 800 °C. The basic chemical formula of the water-soluble fractions in bio-oil can be represented by $C_nH_mO_z$ (Vagia and Lemonidou, 2008). The steam of bio-oil aqueous fractions reforms according to Eqs. (1)–(3).



The hydrogen efficiency can be calculated according to Eq. (1). The mole ratio of H_2 obtained in stoichiometric potential is defined as hydrogen yield as Eq. (4):

$$Y(H_2) = \frac{\text{moles of } H_2 \text{ obtained}}{\text{moles of } H_2 \text{ in stoichiometric potential}} \times 100\% \quad (4)$$

The mole ratio of CO (CH_4 , CO_2) obtained to carbon in the feed is defined as CO (CH_4 , CO_2) yield as Eq. (5):

$$Y(CO, CH_4, CO_2) = \frac{\text{moles of } (CO, CO_2, CH_4) \text{ obtained}}{\text{moles of carbon in the feed}} \times 100\%. \quad (5)$$

3. Results and discussion

3.1. The effect of heating rate on the pyrolysis characteristics of bio-oil

Fig. 1(a) and (b) shows the TG and DTG curves of the bio-oil under air atmosphere with heating rates of 10, 30 and 80 °C/min. It can be seen that the weight loss process can be divided into three stages similar to those reported (Wang et al., 2009, 2008; Zhang et al., 2002). In the first stage, a DTG peak is observed between 30 and 135 °C, which are the volatilization of low boiling point compounds and water as well as the decomposition of thermally unstable compounds. At heating rates of 10, 30 and 80 °C/min, the DTG peak appears to be around 69, 85 and 87 °C, respectively. Fast weight loss begins at 30 °C and more than 55% of the total weight of the sample is lost. Bio-oil aqueous fraction consists of 80% water and 20%

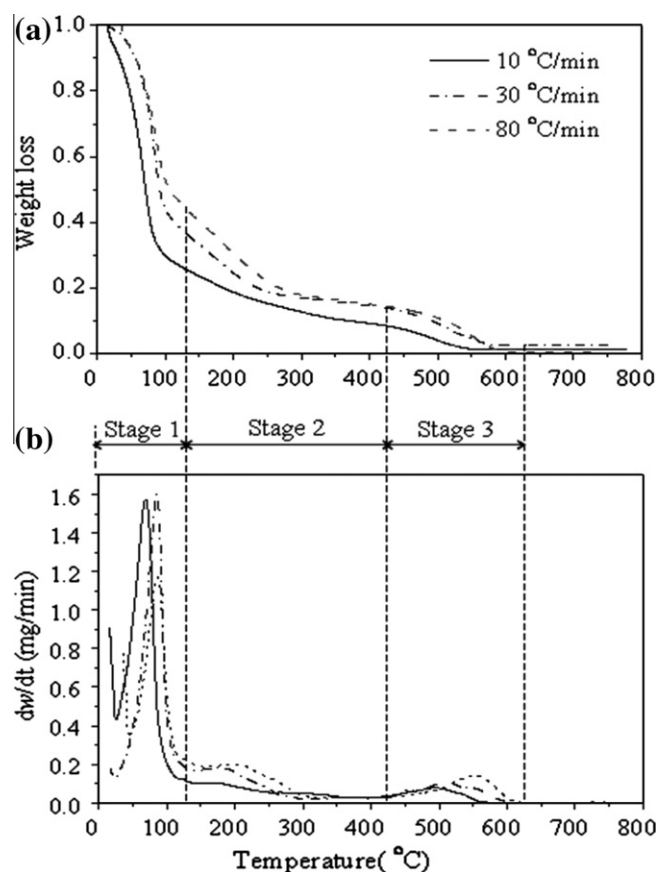


Fig. 1. Thermal pyrolysis characteristics of bio-oil aqueous fraction at different heating rates: (a) TG curves and (b) DTG curves.

organics. While these organics contain a large sum of volatile compounds (Vagia and Lemonidou, 2007), such as formic acid, acetic acid, acetaldehyde, acetone, methanol, and ethanol, which are easier to decompose at lower temperature. The second stage of the degradation lies between 111 and 420 °C. In this stage, the degradation reactions of large molecules like phenols and saccharides occurred and reaction between different components also occurred to form semi-coke, tar and light gases. The total weight loss in this stage is around 35%. The weight loss rate at this stage is nearly constant and a small hump is observed on DTG curves corresponding to this stage. In the first and second stage, the decomposition, and the oxidation of the major portion of bio-oil aqueous fraction also led to the formation of residual tarry products. The third stage is the combustion of residual products formed in the first and second stage. Based on the TG and DTG curves, the degradation occurs between 389 and 622 °C and the total weight loss of this stage is around 10%. The combustion of the residual tarry products occurs when the combustion temperature is reached, the starting temperature of weight loss and the temperature corresponding to the maximum velocity of weight loss all increase with the increasing heating rate. The combustion ends at the temperature of 584, 612 and 622 °C at heating rates of 10, 30 and 80 °C/min, respectively. The results suggest that high-molecular-weight compounds have enough time

Table 1
Elemental composition and basic properties of bio-oil.

Sample	C W (%)	H W (%)	O W (%)	N W (%)	S W (%)	Water W (%)	Kinematic viscosity CST (313 K)	pH	HHV (MJ/kg)
Bio-oil	29.86	9.95	59.728	0.405	0.067	44.21	2.84	3.01	19.3

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