



Kinetic behavior of biomass under oxidative atmosphere using a micro-fluidized bed reactor



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ABSTRACT

Isothermal and kinetic experiments have been performed using a micro-fluidized bed reactor to obtain kinetic parameters for the oxidative thermal decomposition of biomass materials (herb residue) with different oxygen concentrations (5, 10 and 20 vol.%) in the inlet gas stream. The kinetic parameters were calculated by Friedman–Reich–Levi (FRL) method and universal integral method. The releasing characteristics of CO, CO₂ and H₂ were significant affected by the oxygen concentration. The time for complete releasing the gas components was shorted with increasing temperature and oxygen concentration. An increase in activation energy for forming CO and CO₂ was observed at higher oxygen concentration, while the activation energy values of H₂ decreased. All the activation energies obtained under oxidative atmosphere were higher compared with that under inert environment.

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1. Introduction

It is well recognized that biomass energy is a very promising alternative to fossil fuels and may play an essential role in the future energy supply. In China, industrial biomass, such as herb residue from medicine industry, is considered as a kind of available and concentrated biomass resource [1]. Thermochemical conversion technologies, especially for pyrolysis and gasification, have received great attention for producing gas, liquid and solid fuels. The fluidized bed was the mainly reactor used for biomass thermochemical conversion and has become a research hotspot for years [2–4]. Particularly, herb residue has been tested by the authors to produce fuel gas by gasification using a fluidized bed gasifier [5,6], realizing its utilization for saving coal in Chinese medicine production.

Biomass thermochemical process consists of a series of complex reactions, and a detailed study is a key component in the efficient design of these conversion processes. Biomass pyrolysis under certain oxygen concentration is a fundamental thermochemical conversion process and is seen as an important step in gasification and combustion process. Thus, oxidative pyrolysis has been proved itself to be an important technique in biomass utilization and has

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attracted significant attention. Since the reactions occurred under oxidative condition are distinctly different from that under inert condition, several pathways have been proposed to explain the conversion mechanism of oxidative pyrolysis of solid fuels. Senneca et al. [7] found that burn off cannot be simply described as sequential reaction paths corresponding to purely thermal degradation and heterogeneous oxidation, and two extreme pathways were proposed based on their experiments. One pathway was described as the sequential steps of purely thermal decomposition of the fuel followed by combustion of char and volatiles matter. The other pathway described as that fixed carbon oxidation takes place in parallel to thermal decomposition and the releasing of volatile matter was enhanced by heterogeneous oxidation. Amutio et al. [8] studied the effect of oxygen on the lignocellulosic biomass pyrolysis process with different oxygen concentrations (5, 10 and 20 vol.%) in the inlet gas stream. They thought that pinewood oxidative pyrolysis is the sum of biomass pyrolysis and heterogeneous oxidation plus the combustion of the remaining char. Chouchene et al. [9] also found that olive solid waste pyrolysis under oxidative conditions took place according to three stages: drying, volatiles emission and char oxidation whereas only the two first stages occur in the case of pyrolysis under inert conditions. Up to now, many works still need be done to reveal the kinetic of biomass oxidative pyrolysis, especially the parameters for gas releasing to provide fundamental support for biomass gasification and combustion.

It is believed that the kinetics of biomass pyrolysis under inert and oxidative atmospheres is influenced by different equipment, experimental conditions and the physical and chemical properties of materials [10]. A wide range of reactors have been used to investigate biomass fast pyrolysis process [11] and fluidized bed reactors are the most common method [12]. However, the thermal gravimetric analyzer (TGA) is the mostly used in studying the kinetic parameters based on monitoring the mass variation of a spot sample in different atmospheres during a specified heating program [13–15]. Recently, the micro fluidized bed is also used to study the gas–solid reactions by Yu et al. [16], and this method has been verified having advantages in realizing the isothermal conditions and minimizing the interfacial diffusion limitations for gas–solid reaction analysis. The pyrolysis characteristics of herb residue under inert environment have been investigated in our previous work [17], while the kinetics under oxidative conditions still need to be studied for better understanding the gas forming law during biomass gasification and combustion.

For these reasons, in order to better insight the role of oxygen in biomass pyrolysis, a new micro-fluidized bed reactor system was designed to study the product gas generating characteristics under isothermal reaction conditions. The parameters for forming three major gas components (CO, CO₂ and H₂) under oxidative conditions were calculated. The effect of oxygen on pyrolysis degradation and gases generation is investigated and analyzed. We believe that the obtained pyrolysis kinetics can give a better understanding of the biomass oxidative pyrolysis process for generating gas components.

2. Experimental

2.1. Raw material properties

The herb residue originated from Henan Wanxi Pharmaceutical Co., Ltd, China, is used as a biomass material in the present study. The physical of the samples was analyzed before the experiment and summarized in Table 1, including the proximate and ultimate analysis. The particle size was in 80–120 μm by pulverizing and sieving so as to neglect the influence of the intra-particle diffusion, as suggested by Yu et al. [16]. The raw material was dried in a drier before each tests until no moisture was left in the sample.

2.2. Apparatus and procedure

The current experiments were performed using a micro fluidized bed reactor system, as presented in Fig. 1. The reactor designed in this article is 150 mm in height and consists of two porous plates which separate the reactor into three zones. The

middle zone of 20 mm in height between the two porous plates is the primary zone where pyrolysis reactions occur. Two branches were designed at the middle of the reactor, one for fuel particles injection by compressed gas (argon), the other one for temperature and pressure sensors installing. Argon gas was used as carrier gas and quartz sand with mean diameter of 0.25 mm was used as the fluidization medium. Before each test, Three grams of quartz sand was put into the lower layer and one gram was put into the upper layer. Oxygen–argon mixtures at 5, 10 and 20% (v/v) were used as purge gas with a gas flow of 1 L/min. The temperature of the furnace, carrier gas flow rate and actions of pulse sample injection are all controlled by a computer.

At the beginning of each test. The reactor was heated by the furnace in fluidization state to the desired temperature (600–850 °C), and then about 10 mg fuel sample was injected into the reactor for oxidative pyrolysis. The pyrolysis gas (CO, CO₂ and H₂) was measured by the mass spectrometer (AMETEK, American) continuously. To assure the reliability of the test results, each test is repeated for three times.

2.3. Kinetic methods

It is well known that model fitting method is mainly used for deducing kinetic parameters by analyzing the date obtained from thermal gravimetric analyzer (TGA). However, the reaction model assumption is usually hard to find to reflect the reaction mechanism correctly. In this article, the isothermal kinetic method was used by the micro fluidized bed reactor system to describe the gas components generation. The iso-conversional method was used to calculate the kinetics parameters directly by separating the reaction model function.

Firstly, the variation of the concentrations of the gas components with time can be measured by the mass spectrometer during each test, and then the activation energy can be gained using the model expressed as a function of the gases accumulated production.

$$m_t = \frac{12 \times \int_0^t \varphi_i \times q_v dt}{22.4} \quad (1)$$

$$m_{t_0} = \frac{12 \times \int_0^{t_0} \varphi_i \times q_v dt}{22.4} \quad (2)$$

$$x = \frac{m_t}{m_{t_0}} = \frac{\int_{t_0}^t \varphi_i \times q_v dt}{\int_{t_0}^{t_e} \varphi_i \times q_v dt} \times 100\% \quad (3)$$

where, m_t and m_{t_0} are the conversions of i (CO, CO₂ and H₂) at time t and the reaction end (t_0); φ_i represents the concentration of gas species i , and q_v denotes the flow rate of the product gas from the reactor. In the presence of oxygen, the kinetic law was expressed by the conversion factor as follows:

$$\frac{dx}{dt} = k(T)C_{O_2}^m f(x) \quad (4)$$

where $k(T)$ is the reaction rate constant defined by the Arrhenius equation and it is a constant in isothermal process, which means it can be separated from $f(x)$. C_{O_2} is the dimensionless v/v concentration of the oxygen, expressing the effect of the oxygen concentration on the reaction rate, and m is a reaction order parameter. The dimensionless C_{O_2} is necessary to provide a constant dimension for $k(T)$ with values of 0.05, 0.1 and 0.2 in the present work. Therefore, $k(T)C_{O_2}^m$ was a constant as well for a given experiment.

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

Table 1
Proximate and ultimate analysis of herb residue.

Fuel	Herb residue
<i>Proximate analysis (wt.%, db)</i>	
Volatile	74.30
Fixed Carbon	14.95
Ash	10.76
<i>Ultimate analysis (wt.%, daf)</i>	
Carbon	42.40
Hydrogen	6.20
Oxygen	47.39
Nitrogen	1.86
Sulfur	0.15
Others	2.00

db: dry basis; daf: dry ash free basis.

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