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Pyrolysis kinetics of biomass (herb residue) under isothermal condition in a micro fluidized bed

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ABSTRACT

Herb residue is one of the most important industrial biomass in China in terms of availability and potential for use as a bioenergy resource. The kinetics of the thermal decomposition of this fuel in an inert atmosphere was evaluated using a micro fluidized bed. The isothermal differential analysis was applied for determination of kinetic parameters for the major gas components formation including reaction order, activation energy and pre-exponential factor. The temperature inside the micro fluidized bed was steady and the pyrolysis reaction of herb residue finished in around 10 s at 600–800 °C. The reaction time for complete releasing of individual gas components was shorter at higher temperature. Experimental results showed that under the conditions studied, the values of activation energy for generating H_2, CO, CO_2 and CH_4 were 18.90, 12.05, 10.48 and 11.31 kJ/mol respectively, corresponding to the values of pre-exponential factor in the range of 0.88–1.38 s^{-1}. The results indicated that H_2 was the most difficult to form due to the highest activation energy, while generating CO was the easiest corresponding to the lowest activation energy. Compared with TGA and other analysis approaches, the kinetic parameters obtain by the micro fluidized bed were significantly lower benefiting from its quick reaction features.

1. Introduction

An increasing demand for energy with the fast economic growth has revived interest in the development of renewable energy sources. Alternative fuels derived from biomass are regarded as a promising energy resource which can be used as substitutes for petroleum or natural gas [1,2]. Moreover, biomass resources, such as wood, agricultural products, and industrial residue, are CO_2-neutral energy resources with low content in nitrogen and sulfur, and the corresponding fuels are therefore seen as clean energy compared with fossil fuels [3]. Herb residue studied in this text represents a kind of concentrated industrial biomass resource in China, and it was recently tested by the authors to produce fuel gas using a fluidized bed gasifier [4,5]. Pyrolysis which is seen as an important step in biomass gasification process is a fundamental thermochemical conversion process that can be used to convert biomass directly into fuels. Thus, pyrolysis has proved itself to be an important technique in biomass utilization and has attracted significant attention [6,7].

A thorough understanding of pyrolysis kinetics of biomass is a key component in the efficient design of biomass conversion processes. Thermogravimetric analysis (TGA) has been generally used to analyze biomass pyrolysis kinetics based on monitoring the mass variation of a spot sample under a specified heating program. The kinetics of thermal decomposition of a variety of biomass samples, such as wood [8], agricultural wastes [9,10], process residues [11–13] and organic wastes [14] were studied by non-isothermal thermogravimetry method under different atmosphere. Most of the values of activation energy ranged from 100 to 300 kJ/mol in different conversion range. Based on the thermogravimetric analysis method, many mathematical approaches have been developed to deduce the kinetic parameters [15], while these approaches are usually on the basis of preliminary assumption of a certain reaction order and reaction model [16,17]. In addition, TGA can be carried out in isothermal conditions as well, but there always a small mass loss before the pyrolysis reaching the given temperature, resulting in a certain error for the measuring method [18,19]. According to Yu et al. [20], there are still many drawbacks when testing biomass pyrolysis by TGA, such as inevitable gas diffusion and temperature deviation caused by the highly endothermic or exothermic reactions. Thus, the overall kinetics deduced

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from thermogravimetric analysis method can hardly reflect the process intrinsic characteristics of biomass pyrolysis.

Fluidized bed reactor has been verified having advantages in fast on-line feed, minimized diffusion inhibition, quick heating for isothermal conditions and testing at arbitrary temperatures and in various gaseous atmospheres [20,21]. Kinetic parameters can be achieved using the fluidized bed reactor as well based on measuring the releasing of major gas components (CO, H_2, CO_2 and CH_4) in the thermal degradation of the tested sample. Also, it can be pointed out that the values of reaction order, activation energy and pre-exponential factor for generating the gas components should be close to intrinsic characteristics of biomass pyrolysis as the interfacial diffusion limitations for biomass particles reactions is minimized.

The aim of the present work was to investigate the characteristics and kinetics under isothermal condition in a micro fluidized bed reactor to describe the thermal decomposition process of herb residue. This study undertook analyses of product gas generating characteristics by a mass spectrometer, and the direct Arrhenius plot method was employed to derive kinetic parameters for forming four major gas components (H_2, CO, CO_2 and CH_4), including the reaction order, activation energy and pre-exponential factor. Parallel tests using the same samples in TGA were conducted and the kinetic parameters were compared to further estimate performance of the micro fluidized bed. It is hoped that the obtained pyrolysis kinetics can give a better understanding of the biomass pyrolysis process for generating gas components.

2. Experimental

2.1. Raw material properties

The biomass material used in this study was herb residue originated from Henan Wanxi Pharmaceutical Co., Ltd, located in the southwest of Henan province of China. The herb residue samples were air-dried, crushed and then sieved before the pyrolysis tests. The chemical analysis of the fuel simples is summarized in Table 1, showing that the volatile and carbon contents are around 74% and 15% respectively. The proximate analysis and ultimate analysis were carried out through the methods described in our previous report [22]. As suggested by Yu et al. [23], the influence of the intra-particle diffusion would be negligible for the fuels with sizes below 120 μm. Therefore, the fuel particles in 80–120 μm was used in this article by pulverizing and sieving.

2.2. Apparatus and procedure

The pyrolysis experiments in this article were performed using a micro fluidized bed reactor system to obtain the pyrolysis gas data as a function of time under isothermal conditions. The schematic diagram of the experimental apparatus is presented in Fig. 1 and its main components are: a fluidized bed reactor of 20 mm in diameter, an on-line pulse sample feeding system, a temperature and pressure sensor and a mass spectrometer (AMETEK, American) for on-line gas analyzing.

The reactor designed in this article is 150 mm in height and consists of two porous plates to separate it into three zones. The lower zone is designed to realize uniform distribution of the fluidized gas, like the wind chamber of the fluidized bed. The middle zone of 40 mm in height is the zone between the two porous plates where pyrolysis reactions occur. The upper zone of 60 mm in height is the zone above the upper porous plate where fine particles escaping from the lower stage are caught to realize complete reaction. Two branches were designed at the middle of the reactor, one for fuel particles injection by compressed gas, the other one for temperature and pressure sensors installing. Quartz sand with mean diameter of 0.25 mm was used as the fluidization medium in the reactor and argon gas was used as carrier gas during the experiments. The temperature of the furnace, carrier gas flow rate and actions of pulse sample injection are all controlled by a computer. Meantime, the temperatures inside the reactor, pressures at the reactor inlet and outlet and the date of the product gas from the mass spectrometer are logged into the computer.

Before each test, three grams of quartz sand was put into the lower layer and one gram was put into the upper layer. The minimum fluidization velocity (U_{mf}) under ambient condition was first detected by measuring the pressures at the gas inlet and bottom of the upper porous plate. The value of U_{mf} detected was 0.019 m/s, corresponding to the gas flow rate of 355 mL/min. In order to ensure the good fluidization of sand, the flow rate of the fluidizing gas was 500 mL/min, and thus the superficial velocity of the fluidizing gas was around 0.027 m/s under ambient condition. The reactor was heated by the furnace in fluidization state to the desired temperature (600–850 °C) for the herb residue pyrolysis. After that, about 10 mg fuel sample was injected into the reactor and the pyrolysis gas (CO, H_2, CO_2 and CH_4) was measured by the mass spectrometer continuously. To assure the reliability of the test results, each test is repeated for three times.

2.3. Kinetic methods

2.3.1. Isothermal kinetic method

A diverse set of possible mechanisms of biomass decomposition have been elucidated in previous literature reviews. In this work, the kinetic study was to describe the gas components generation under isothermal condition, and the mechanisms should belong to the multi-component mechanism which was considered originally proposed in [24,25]. This mechanism was available for predicting the formation rates and the yields of reaction products or solid- and gas-phase intermediates. The mechanism was verified in [26,27] to study the biomass pyrolysis kinetics based on series reactions taking into account the presence of several zones in the isothermal weight loss curves. Based on this, integral data concerning generation of the product gas under isothermal condition was measured by a mass spectrometer in this study. The corresponding final kinetic parameter values are estimated so as to get the best fit with the combustible gas yield by herb residue pyrolysis.

In this study, quick heating for isothermal reaction conditions can be realized by the micro fluidized bed reactor. Referring to Yu et al. [20] and Manyà et al. [28], the kinetic parameters of biomass pyrolysis in isothermal process were calculated generally using the shrinking core model. During the experiments, the variation of the concentrations of the product gases with time under different reaction temperatures can be measured by the mass spectrometer, and then the activation energy can be gained using the model expressed as a function of the gases accumulated production.

Table 1
Chemical composition of herb residue.

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

ar.: as received basis; db: dry basis; daf: dry ash free basis.