INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 7956–7964

Available online at www.sciencedirect.com

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Pyrolysis behavior and kinetic study of phenol as tar model compound in micro fluidized bed reactor

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ARTICLE INFO

Article history:
Received 26 January 2015
Received in revised form
2 April 2015
Accepted 17 April 2015
Available online 12 May 2015

Keywords:
Tar
Phenol
Pyrolysis
Kinetics
Micro fluidized bed reactor

ABSTRACT

Thermal cracking characteristic of phenol as the model compound of biomass tar was investigated on a micro fluidized bed reactor. Pyrolysis kinetics for individual gaseous component, including hydrogen, methane, carbon monoxide and carbon dioxide were determined based on the iso-conversional and model-fitting approaches. Results indicated that carbon monoxide accounted for the biggest percentage of the total gas yield during pyrolysis of phenol. The evolution profiles of hydrogen energy and carbon monoxide were more affected by reaction temperature compared to methane and carbon dioxide. In the major conversion fraction from 20% to 80%, the apparent activation energies of methane (49.67 kJ/mol) and carbon dioxide (30.87 kJ/mol) were lower than that of hydrogen (145.2 kJ/mol) and carbon monoxide (53.35 kJ/mol). The most probable reaction mechanism for the formation of hydrogen and methane was three-dimension diffusion while chemical reaction and contracting sphere could describe the generation of carbon monoxide and carbon dioxide, respectively.

Introduction

Gasification is generally viewed as one of the most promising options for converting biomass to gaseous biofuels. However, the generation of tar is a bottleneck problem during this thermo-chemical conversion process [1–3]. As a typical byproduct, tar will be condensed when the temperature is lower than its dew point, rendering the blockage of downstream equipments such as engines, filters and turbines [4], which will severely affect the stable operation of equipments [5]. Besides, the generation of tar causes a partial loss of input energy [6,7]. Tar removal has been a key issue for utilizing biomass.

As one of the tar reduction methods, thermal cracking can convert tar into lighter gases with small molecules (e.g. hydrogen, methane and carbon monoxide) under high temperatures and certain residence time. This approach can reduce the content of tar without secondary pollution and waste of extra energy retained in the tar [8–10]. It is a potential method to improve the efficiency of thermo-chemical of

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http://dx.doi.org/10.1016/j.ijhydene.2015.04.098

biomass and get extensive studies. Additionally, with the presence of catalysts (e.g. acid catalysts, metal catalysts and activated carbon catalysts), the reaction temperature and residence time can be further decreased to reduce the energy consumption [11–13]. It should be noted that as high temperature is required to crack the tar, the concept of two-stage gasification facilities contributes to better results with respect to this issue. It usually separates the pyrolysis and gasification processes into two varied stages, and tar can be thermal decomposed into gases under higher temperatures by partial combustion of the volatiles between the two stages. This arrangement contributes to the production of gas products with a higher caloric value and lower tar content [14–16].

During this process, kinetic analysis is a promising way to elucidate the reaction mechanisms, which are usually investigated by thermogravimetric analysis (TGA) [17,18]. The thermogravimetric analyzer can monitor the evolution of sample mass in real time. However, the main disadvantage is that the sample needs to be feed into the reaction chamber at normal temperature and there is a small mass-lose before reaching the preset temperature. Besides, due to the limitation of structure and design principle, TGA could not be carried out under the condition of high gas velocity [19,20]. To address this deficiency brought by TGA, Institute of Process Engineering in Chinese Academy of Sciences, Shandong University and Shandong Baichuan Tongchuang Energy Company developed the micro fluidized bed reactor (MFBR). This instrument is mainly composed of a micro fluidized bed and a process mass spectrometer. It can send the samples into the reactor instantaneously when the temperature within the reactor is heated to the preset level. Therefore, the reaction time can be greatly shortened. The process mass spectrometer can analyze the relative concentration of gaseous products online. Then the kinetic parameters can be determined based on the evolution profiles of gaseous product under different temperatures. MFBR can minimize the inhibition of the diffusion and realize the isothermal reaction process in situ [21].

Tar is composed of numerous organic compounds with high boiling points. The main compositions of tar are polycyclic aromatic hydrocarbons (PAHs) in terms of phenol, toluene, benzene, naphthalene, anthracene and styrene [22–24]. Since the tar composition is extremely complex, most studies select one or two compounds of PAHs as the tar model compound, such as toluene [25,26], benzene [27,28] and naphthalene [29,30], but few studies are concerned with the compound of phenol, which is one of the major compositions of tar [31]. This work selected phenol as the tar model compound. The pyrolysis behavior of phenol was investigated in MFBR. Then the kinetic parameters as well as the most probable reaction mechanisms for the reaction processes were determined.

Methods

Experimental facility

Fig. 1 illustrates the schematic diagram of micro fluidized bed reactor system (MFBR). It is mainly composed of a sample feeding system, a micro fluidized bed and a process mass spectrometer (Dycor ProLine, Ametek, USA). The feeding system is driven by an electromagnetic valve that can release about 10 ml gas per single pulse to send the sample into the reactor within 0.1 s. The pulsed gas originated from a compressed gas stream with the pressure of 0.2 MPa. The fluidized bed reactor is the key part of the MFBR, which is made of quartz and it is capable of bearing high temperatures around 1200 °C for a long time. The overall height and diameter of the fluidized bed reactor are 373 mm and 290 mm, respectively. The internal height and diameter of the reaction zone are 42 mm and 20 mm, respectively. The mass spectrometer can measure the relative content of gaseous products during the pyrolysis of tar online. The temperatures of the reactor and furnace, the pressures of the reactor as well as the actions of the sample feeding system are all controlled by the computer.

Experimental procedure

In this study, quartz sand was selected as the fluidization medium due to the poor catalytic influence on tar cracking. The particle sizes were ranged from 0.2 mm to 0.25 mm. At the beginning of each test, 3.0 g of quartz sand as the fluidizing medium was loaded into the fluidized bed reactor. 10 ± 0.1 mg phenol (Analytical pure, Tianjin Damao Chemical Reagent Factory, China) was placed at the sample-feeding system. After the system was sealed, the fluidizing gas, argon with 99.99% purity, was fed to the reactor to fluidize the quartz sand in the reactor. After several preliminary tests, the gas flow rate was kept at 500 ml/min to ensure all quartz sands were fully fluidized, providing an optimum reaction condition. Afterwards, the reactor was heated to the preset temperatures. Then the pulse valve of the sample-feeding system was switched on to inject the sample into the reaction zone in MFBR, which initiated the pyrolysis reactions. The evolution of produced gas was monitored online by a mass spectrometer. According to Fuentes-Cano et al. [29] and Jess [32], the thermal cracking of polycyclic aromatic hydrocarbons lead to hydrocarbons with smaller carbon numbers and the intermediates are formed only to a limited extent. Consequently, the light gases including hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) are investigated in the present study. The four gaseous products were all sampled in the entire reaction time to be analyzed via Micro-GC 3000 for quantifying the corresponding yield. The total gas yield was the sum of yields of the four gaseous products investigated in the present study.

According to Fagbemi et al. [33], the thermal cracking of tar is effective above 500 °C. Jess [32] concluded that the temperatures within 1200 °C were necessary for the thermal decomposition of aromatic hydrocarbons as tar model compounds. Dufour et al. [31] carried out a pyrolysis experiment of woody biomass in a quartz tubular reactor and investigated the evolution of aromatic tar composition as a function of reaction temperature. It was reported that with the temperature increasing from 700 °C to 1000 °C, the mole fraction of phenol in the total amount of quantified aromatic tar was gradually decreased from around 25% to 1%. Vivanpatarakij et al. [34] carried out a thermodynamic analysis of biomass gasification, and it was concluded that at a lower operating