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Kinetic study on thermal decomposition of toluene in a micro fluidized bed reactor

Chao Gai [a], Yuping Dong [b,*], Pengfei Fan [b], Zhaoling Zhang [c], Jingcui Liang [c], Pengju Xu [c]

[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, PR China
[b] School of Mechanical Engineering, Shandong University, Jinan 250061, PR China
[c] Shandong Baichuan Tongchuang Energy Company Ltd., Jinan 250101, PR China

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ABSTRACT

This study concerned the pyrolysis behavior of toluene as the tar model compound. Pyrolysis experiments were carried out in a micro fluidized bed reactor (MFBR) under an isothermal condition. Pyrolysis kinetics for the gas components, including hydrogen, methane, ethylene and propane were calculated based on the model-free and model-fitting methods. Results showed that methane and ethylene were the major gas components at lower temperatures (650–800 °C) while propane and ethylene were the main composition of pyrolysis gas mixture at higher temperatures (800–850 °C). For the range of conversion fraction (20–80%), the apparent activation energy of propane (16.34 kJ/mol) was lower than that of ethylene (17.59 kJ/mol), then accompanied with methane (23.27 kJ/mol) and hydrogen (69.55 kJ/mol). The most probable reaction mechanism for the generation of hydrogen was three-dimensional diffusion while the evolution profiles of methane could be described by the mechanism of nucleation and growth. Chemical reaction was the most probable reaction mechanism for ethylene and propane. Results from the present study indicated that MFBR can enable a quicker reaction within the reactor than other traditional approaches. The generation of propane is easier to proceed compared to other hydrocarbons with smaller carbon numbers during pyrolysis of toluene. A comparison of kinetic models and experimental results suggested that the developed models closely predicted the thermal cracking behavior of toluene.

1. Introduction

Biomass has gained increasing attention due to the depletion of fossil fuels and environmental issues. Gasification is a typical technique to convert biomass to syngas for combustion/power generation [1,2]. However, tar is an inevitable byproduct during the gasification process [3–6]. Tar in the raw gases will coagulate into viscous liquid when the temperature is lower than its dew point. It will render a blockage of pipeline, filters, turbines and engines, which seriously affect the steady operation of the reactor system [7]. Consequently, tar reduction has become one of the most urgent problems for biomass utilization. Thermal cracking can convert tar into lighter gases at high temperatures without waste of extra energy retained in the tar [8,9]. It is an effective method to improve the quality of gaseous products during the conversion process.

The approach of modeling is expected to help design and scale-up of gasifier, optimization of operating conditions and prediction of reaction behavior. Besides, modeling can save more money and time compared to experiments, especially at a large scale [10,11]. Despite there is a certain amount of errors in the simulation results due to the simplified assumption, mathematical models have been observed to be effective in predicting the thermal cracking process. Many researchers have developed various mathematical models for the biomass gasification process, such as equilibrium, kinetic, and CFD models. Equilibrium model can provide the designer with a prediction of maximum yield of a desired product during the gasification process. However, the equilibrium conditions are not the real conditions inside the reactor, and thus the results are less reliable. Kinetic model involves parameters like reaction rate can provide a more accurate simulation for the reaction behavior, and the kinetic data is necessary for CFD modeling. Thermogravimetric analysis (TGA) is an universal approach to carry out kinetic modeling [12–14]. A certain amount of the sample has degraded before the temperature within the reactor reaching the desired level. Besides, it can't be operated under high gas velocity, which will make reactions restrained by diffusion. Therefore, the overall kinetics based on TGA can hardly reflect the intrinsic characteristics of thermal cracking of tar. To address these disadvantages, micro fluidized bed reactor (MFBR) [15,16] has

* Corresponding author. Tel.: +86 531 88392199; fax: +86 531 88873588.
E-mail address: dongyp@sdu.edu.cn (Y. Dong).

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been developed to investigate the kinetics of thermo-chemical conversion of biomass/model compounds. Micro fluidized bed is designed as the main body of the MFBR system to intensify heat and mass transfer within the reactor. Additionally, the mass loss in the initial stage of reaction can be avoided due to instantaneous feeding of reactants at desired reaction temperatures. It has been verified that this experimental system is effective in cases of thermo-chemical conversion of biomass. Besides, the kinetic parameters determined based on MFBR are less sensitive to the experimental noise and meet the intrinsic kinetic parameters better [17,18].

Tar is a complex organic compound, which is viewed as aggregate of oxygenates, phenolic compounds and olefins, aromatic and poly aromatic hydrocarbons (PAH). To overcome the complexity of the tar, model compounds have been used as reference in experimental or kinetic works for the thermal cracking of different tar components [19,20]. Although the composition and content of tar vary with gasification conditions, types of reactor or feedstock, the most commonly tar model compounds in previous literature are light tar compounds like benzene, toluene, phenol and cresols as well as heavy tar compounds such as naphthalene and anthracene. According to Sun et al. [21], during biomass gasification, part of heavy tar was thermal cracked to light tar at relatively low temperatures (500–600 °C). However, at higher temperatures (700–800 °C), the tar with heavy molecular weight was very resistant to cracking although the thermal cracking was the principal reaction of tar reduction. Gil et al. [22] investigated the impact of temperature on tar composition from wood gasification. It was observed that toluene, phenol and cresols were predominant at 700 °C, while naphthalene was the major components at 900 °C. Brage et al. [23] also observed a 50% decrease in toluene content when the temperature was raised from 700 to 900 °C. Conversely, the content of naphthalene increased gradually. Coll et al. [24] studied the pyrolysis behavior of tar model compounds. It was concluded that the order of these tar's reactivity was: benzene > toluene > anthracene > pyrene > naphthalene. Anis et al. [25] also concluded that toluene was much easier to be degraded than naphthalene. It suggests that the approach of thermal cracking in a certain temperature is more feasible for reduction of light tar instead of heavy tar. Therefore, the present study was more concerned about light tar, and toluene was chosen as the tar model compound due to its high content in the tar.

To date, many studies have been concerned on pyrolysis behavior and kinetics of toluene based on different heating reactors. Taralas et al. [26] studied thermal destruction of toluene in a non-isothermal tubular flow reactor. It was concluded that a first-order reaction rate could express the effects of temperature and residences on the toluene conversion process. Mani et al. [27] investigated the catalytic decomposition of toluene in a continuous flow packed bed reactor, and the kinetics of toluene removal was also found to follow first order reaction. Anis and Zainal [28] evaluated kinetic parameters for toluene conversion under microwave thermocatalytic treatment. It was concluded that the overall reaction rate was six times higher compared to conventional heating. It suggests that different heating strategy has a great effect on the decomposition of toluene, kinetic analysis should also be carried out for interpreting the experimental observations in MFBR. The current paper focused on the thermal decomposition behavior of toluene in MFBR. Then the kinetic parameters and most probable reaction mechanisms for the major gaseous products during toluene decomposition reactions were determined. The kinetic model was validated by comparing the prediction results to experimental results. These data may contribute to a better understanding of thermal cracking of tar.

2. Experimental

2.1. Reactor system

The scheme of MFBR is illustrated in Fig. 1. It mainly consists of a stainless steel syringe pump, a micro fluidized bed and a process mass spectrometer (Dycor ProLine, Ametek, USA). The micro fluidized bed mainly consists of heating furnace, quartz reactor and flow/pressure sensors. The quartz reactor is capable of bearing high temperatures around 1200 °C. The dimension of the quartz reactor is described as follows: the diameter is 290 mm; the height is 373 mm; the reaction zone's inner diameter is 20 mm and the height is 42 mm. The inner diameter of injection pipe is 3 mm. The flow rates of fluidizing gas and pulse gas are adjusted by the mass flow meter to maintain a steady-state of fluidization within the reactor. The process mass spectrometer can measure the relative content of gaseous products during the thermal decomposition of tar model compound online. The temperatures of the furnace and reactor, the pressures of the reactor and the actions of the sample injection system are all controlled by the computer.

2.2. Test procedure

For each test, the fluidization medium was quartz sand with particle sizes ranging from 65 to 80 meshes. The whole system was purged with argon (99.99% purity) as carrier gas and fluidizing gas. At the beginning of the test, 3.0 g of quartz sand as the fluidizing medium was loaded into the micro fluidized bed. The reactor system was sealed and then the fluidizing gas was fed to the reactor to fluidize the quartz sand in the reactor. When the reactor was heated to the preset temperatures, 10 ml of the toluene was fed into the reactor by the syringe pump. The produced gas was monitored online by the process mass spectrometer. According to Jess [29], the main products of pyrolysis of polycyclic aromatic hydrocarbons are hydrocarbons with smaller carbon numbers, and the intermediates are formed only to a limited extent. Therefore, this study concerned about the evolution properties of light gases in terms of hydrogen (H_2), methane (CH_4), ethylene (C_2H_4) and propane (C_3H_8). The corresponding gas yield (in mass against fuel) was determined by sampling the produced gas in the entire reaction time and in turn analyzed via a Micro-GC 3000. The total gas yield was the sum of yields of four produced gases mentioned above.

According to the literature [29,30], the optimum temperatures for thermal cracking of aromatic hydrocarbons ranged from 500 °C to 1200 °C. Dufour et al. [31] investigated the evolution of aromatic tar composition as a function of reaction temperature during pyrolysis of woody biomass in a quartz tubular reactor. It was reported that toluene was almost completely converted into PAHs between 800 °C and 900 °C, which is also consistent with Evans and Milne [32]. Świerczyński et al. [33] concluded that the most favorable conditions for investigating the toluene conversion were above 650 °C. Consequently, the preset temperatures in this study for pyrolysis of toluene were selected between 650 °C and 850 °C with intervals of 50 °C. Previous study [19] measured the temperature in the main reaction zone of MFBR during the pyrolysis process. It was observed that the temperature remained steady for a certain temperature, enabling an isothermal condition in MFBR.

To ensure complete fluidization of quartz sand, several preliminary tests were carried out to determine the optimum gas flow rate. We studied the effect of gas flow rate (100–900 ml/min) on the total gas yield at different temperatures (650–850 °C). It was observed that at any temperatures (650–850 °C), the total gas yield