



Kinetic study and syngas production from pyrolysis of forestry waste



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ARTICLE INFO

Article history:

Received 2 November 2016

Received in revised form 13 December 2016

Accepted 28 December 2016

Keywords:

Forestry waste
Pyrolysis
Kinetic
Syngas

ABSTRACT

Kinetic study and syngas production from pyrolysis of forestry waste (pine sawdust (PS)) were investigated using a thermogravimetric analyzer (TGA) and a fixed-bed reactor, respectively. In TGA, it was found that the pyrolysis of PS could be divided into three stages and stage II was the major mass reduction stage with mass loss of 73–74%. The discrete distributed activation energy model (DAEM) with discrete 200 first-order reactions was introduced to study the pyrolysis kinetic. The results indicated that the DAEM with 200 first-order reactions could approximate the pyrolysis process with an excellent fit between experimental and calculated data. The apparent activation energies of PS ranged from 147.86 kJ·mol⁻¹ to 395.76 kJ·mol⁻¹, with corresponding pre-exponential factors of $8.30 \times 10^{13} \text{ s}^{-1}$ to $3.11 \times 10^{25} \text{ s}^{-1}$. In the fixed-bed reactor, char supported iron catalyst was prepared for tar cracking. Compared with no catalyst which the gas yield and tar yield were 0.58 N m³/kg biomass and 201.23 g/kg biomass, the gas yield was markedly increased to 1.02 N m³/kg biomass and the tar yield was decreased to only 26.37 g/kg biomass in the presence of char supported iron catalyst. These results indicated that char supported iron catalyst could potentially be used to catalytically decompose tar molecules in syngas generated via biomass pyrolysis.

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1. Introduction

Forestry wastes, in general, and all biomass residues, can be used as raw materials for the generation of liquid biofuels, syngas, chemicals, or charcoal via pyrolysis and liquefaction processes [1–3]. Thermochemical conversion methods, i.e. pyrolysis, gasification and combustion, are the most commonly employed and the most appropriate for these purposes. Most of the biomass have a heterogeneous property attributes to the fact that the biomass itself composes of numerous components, such as hemicellulose, cellulose, lignin, and minor amounts of extractives. Such of these components, in fact, contribute to the actual reaction mechanism of biomass pyrolysis possibly is extremely complex [4]. The proportion and composition of pyrolysis products are crosswise affected by many factors such as biomass type, feedstock pretreatment, and pyrolysis conditions. During the biomass pyrolysis, a large number of reactions take place in parallel and series, including dehydration, depolymerisation, isomerization, aromatisation, decarboxylation, and charring [4,5]. Kinetic modeling of pyrolysis can help to describe practical conversion processes and optimize the design of efficient reactors [6].

Thermogravimetric analysis (TGA) is a useful technique for studying the decomposition reactions of a solid and it has been widely used to study the apparent kinetics of biomass pyrolysis [7]. By using the TGA data, the kinetic parameters as well as pyrolysis mechanism can be determined according to different mathematical approaches. The single-step global model couples with different iso-conversional method, is the most used kinetic approach. However, as mentioned above, the biomass pyrolysis process is extremely complex due to the difference in decomposition of the biomass components. The iso-conversional method is considered to be conflicting rather than complementary when treating the kinetics of complex reaction system. According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee recommendations, multi-step reaction model is more suitable to simulate solid fuels (such as coal and biomass) pyrolysis kinetic [8]. Among many multi-step reaction models, distributed activation energy model (DAEM) is one of the commonly used in biomass pyrolysis kinetics studies [3,9]. Many methods such as model-fitting method, iso-conversional method and discretization method can be used to treat the DAEM and between them the discrete DAEM is even better for DAEM calculation.

During biomass pyrolysis, there are many obstacles need to be resolved before it further become a viable commercial renewable energy. The generation of tar in product gas is one of the major

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issues, which is known as energy waste, block pipeline, and even threat to human health. Methods of physical treatment, thermal cracking, plasma-assisted cracking, and catalytic reforming, etc. are considerable to eliminate the tar. Among these methods, catalytic reforming is considered the most promising approach for the tar removes as well as convert to combustible gas [10]. Various types of catalysts such as minerals (iron ores, clay minerals, olivine, calcined rocks) and synthetic catalysts (transition metals-based, activated alumina, alkali metal carbonates, FCC catalysts, and char/char-supported) have been studied on tar removal in biomass pyrolysis/gasification [11–16]. Among these catalysts, the char/char-supported catalysts have shown low costs and adequate catalytic activities for tar reforming during the pyrolysis/gasification of biomass.

In this study, behaviors and kinetics of a representative forestry waste (pine sawdust) pyrolysis were investigated using a discrete DAEM method via thermogravimetric analysis. Meanwhile, char supported iron catalyst used for syngas production was also investigated.

2. Experiment and methods

2.1. Materials

Forestry waste (Pine Sawdust (PS), belong the species of macrophanerophytes) was obtained from a furniture factory Wuhan City, Hubei Province, China. The sawdust was naturally dried for a period of 7 days and then grinded and screened into a size of <0.107 mm (pass a Tyler standard screen scale of 100 mesh). Table 1 gives the results of proximate and ultimate analysis of pine sawdust feedstock. Ultimate analysis of the PS samples was measured by a CHNS/O analyzer (Vario Micro cube, Elementar). Such an analysis gave the weight percent of carbon, hydrogen, nitrogen and sulfur in the samples simultaneously. The weight percent of oxygen was determined by differences. The proximate analysis of the PS was conducted following ASTM standard test methods. The low calorific value (LHV) of PS was calculated Mendeleev formula: $LHV \text{ (MJ/kg)} = 339.1C + 1256H - 108.8(O-S) - 25.1 (9H + M)$, (where M is the moisture content).

The chemical functional groups in PS were investigated by using FT-IR technique (Vertex 70, Germany). PS samples were ground to fine particles and mixed with KBr powder. The mass ratio of samples to KBr powder was 1:100. The spectral resolution was set at 4 cm^{-1} .

2.2. Thermogravimetric analysis (TGA)

TG/DTA Synchronous analyzer (Diamond TG/DTA, PerkinElmer Instruments) was used to perform the pyrolysis of the samples with sweeping gas of high purity nitrogen (flow rate 100 mL/min). The test temperature was raised from room temperature to 800 °C with various heating rates of 20, 30 and 50 °C/min for samples.

2.3. Catalyst

Biochar was obtained from a pilot-scale allothermal biomass gasification system which studied in our previous research [17].

The rice straw as a feedstock for gasification was from the farm in Wuhan City, Hubei province, China. Firstly, biochar was gently crushed and sieved into 0.5–1 mm size fraction. Secondly, the biochar sample was washed with deionized water for several times and oven dried (80 °C) as catalyst support. Fe/biochar catalyst, prepared by dissolving 21.6 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9(\text{H}_2\text{O})$ in 200 mL of deionized water, was mixed with 47.0 g biochar for 12 h under continuous strong agitation using a magnetic stirrer, and then dried at 105 °C for 24 h. The resulting product is the Fe/biochar catalyst.

2.4. Apparatus and procedure

The used facility in this experiment includes two stages which are pyrolysis zone and catalysis zone, shown in Fig. 1. The effective length of the pyrolysis furnace is 700 mm with an outer diameter (OD) of 80 mm (ID. 75 mm), and the fixed catalytic reactor is 800 mm in height and 65 mm in outer diameter (ID. 60 mm). Pyrolysis and catalytic bed are both made of quartz glass and externally heated by electrical ring furnaces. Before the experiments, 5.0 g catalyst was put into the catalytic furnace. Then, nitrogen (with a constant flow rate of 0.1 L/min) was injected into the reactor for 20 min to maintain an inert atmosphere. Subsequently, the pyrolysis and catalytic reactors were heated in a heating rate of 30 °C/min to achieve the set-point temperature (800 °C), respectively. 5.0 g PS was put into the stainless steel boat and placed into the middle of quartz tubular reactor. The set-point temperatures were considered as the pyrolytic and catalytic temperature which would be held for 15 min. During the experiment process, the volatile flowed out of the reactor and was condensed by ice bath. The condensable volatiles (i.e. bio-oil) were captured in the collector and the non-condensable gas whose volume was measured by a gas flow meter. The main composition of non-condensable gas was analyzed by GC 9800T which functioned based on a thermal conductivity detector (TCD) with TDX-01 columns. The temperatures of the injector, oven and detector were at 200 °C, 85 °C and 90 °C, respectively. The carrier gas in all analyses was argon. Standard gas mixtures were examined by the quantitative calibration. At the end of the pyrolysis, the furnace was cooled down to room temperature and the mass of the solid char as well as bio-oil yields could be calculated.

2.5. Distributed activation energy model (DAEM) kinetics

Conversion (α) form of apparent reaction rate of solid-state material thermal decomposition in TGA process can be described as:

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where t is the reaction time (s); T denotes absolute temperature (K); $k(T)$, also is known as the reaction constant, is the temperature dependent function in apparent kinetic; and $f(\alpha)$, which is known as the reaction mechanism model, is depends on its independent variable conversion (α):

$$\alpha = (m_0 - m_t)/(m_0 - m_f) \quad (2)$$

Table 1
Ultimate and proximate analysis of PS sample.^b

Ultimate Analysis (Wt.%)					Proximate Analysis (Wt.%)				LHV (MJ/kg)
C	H	O ^a	N	S	M	V	F	A	
46.36	5.75	43.62	2.26	0.32	4.54	82.18	16.13	1.69	16.81

M, Moisture Content; V, Volatile Matter; F, Fixed Carbon; A, Ash; LHV, Low Heating Value.

^a By difference.

^b Air dry basis.

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