



Gasification kinetic analysis of the three pseudocomponents of biomass-cellulose, semicellulose and lignin



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HIGHLIGHTS

- Kinetic analysis of the pseudocomponents of biomass were investigated.
- Two reaction stages were investigated for semicellulose and lignin.
- The Multi-peaks method was used to fit the Gaussian distribution model.
- Friedman method and master plot method were used to determine the kinetic model.

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ABSTRACT

The gasification kinetic analysis of the three pseudocomponents (hemicellulose, cellulose and lignin) of biomass decomposition in the agent of CO₂ were investigated. The Multi-peaks method was used to fit the Gaussian distribution model of DTG curves. The Friedman method was used to estimate the effective E_a , and the master plot method was used for the determination of the kinetic model. The results showed that there were two reaction stages for semi-cellulose and lignin. The DTG curves of semicellulose and lignin cannot be fitted by Gaussian distribution model. The E_a were ranged from 80 to 220 kJ mol⁻¹ for the three pseudocomponents. The F_n model could describe the kinetic process of stage I of semi-cellulose decomposition. Both cellulose and stage II of semicellulose decomposition could be described by A_n model and the two reaction stages of the lignin were fitted the R_n model very well.

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1. Introduction

Energy crisis and global warming are considered as two severe problems worldwide (Appels et al., 2011; Jin and Enomoto, 2011; Lee et al., 2010). Scientists have been in search of renewable and sustainable energies, at least in part, substituting fossil energies for a long time (Zheng et al., 2010). Among all of the renewable resources, biomass is the only one which contains carbon source to be converted into solid, liquid and gaseous products (Zhang et al., 2013). It is a clean, cost-effective, being CO₂ neutral, having low sulfur content renewable material which can be used for heat and fuel production. It is one of the largest energy source reserve in the world (Chen et al., 2011). By 2050, with growing population and demand, bioenergy could contribute between 25% and up to 33% of global supply (Zhang et al., 2013).

The biomass gasification is one kind of thermochemical conversion technology. It has several potential benefits over traditional combustion (Arena, 2012). It is a promising biomass technology aiming at efficient and clean utilization: first converting carbona-

ceous material into combustible gas which contains CO, H₂ and CH₄, in the gasification sector by employing a thermal-chemical method and then using the gas to drive turbines or engines for power generation in the electricity sector (Arena, 2012; He et al., 2009; Yin et al., 2012; Zhou et al., 2012).

The thermogravimetric analysis (TGA) was the most commonly used thermoanalytical technique for thermal conversion studies (Lai et al., 2012; Liu et al., 2009; Sanchez et al., 2009). The literature showed that a gasifying agent such as CO₂, H₂O or O₂ was an important factor affecting on the gasification rate (Nonaka et al., 2013). Although the pyrolysis under inert (N₂) conditions has been studied in the literature to some extent, little information is available for the thermal decomposition characteristics and kinetics in CO₂ atmosphere (Lai et al., 2012).

Several researchers (Cai et al., 2013; Li et al., 2008; Zhou et al., 2013) have investigated the three parallel reaction model of biomass pyrolysis. The model assumes that lignocellulosic biomass contains three independently reacting pseudocomponents (hemicellulose, cellulose and lignin), and therefore, that the global thermal decomposition behavior reflects the individual behavior of these pseudocomponents, weighted by the composition, and they also assume the DTG curve of the three pseudocomponents fitted

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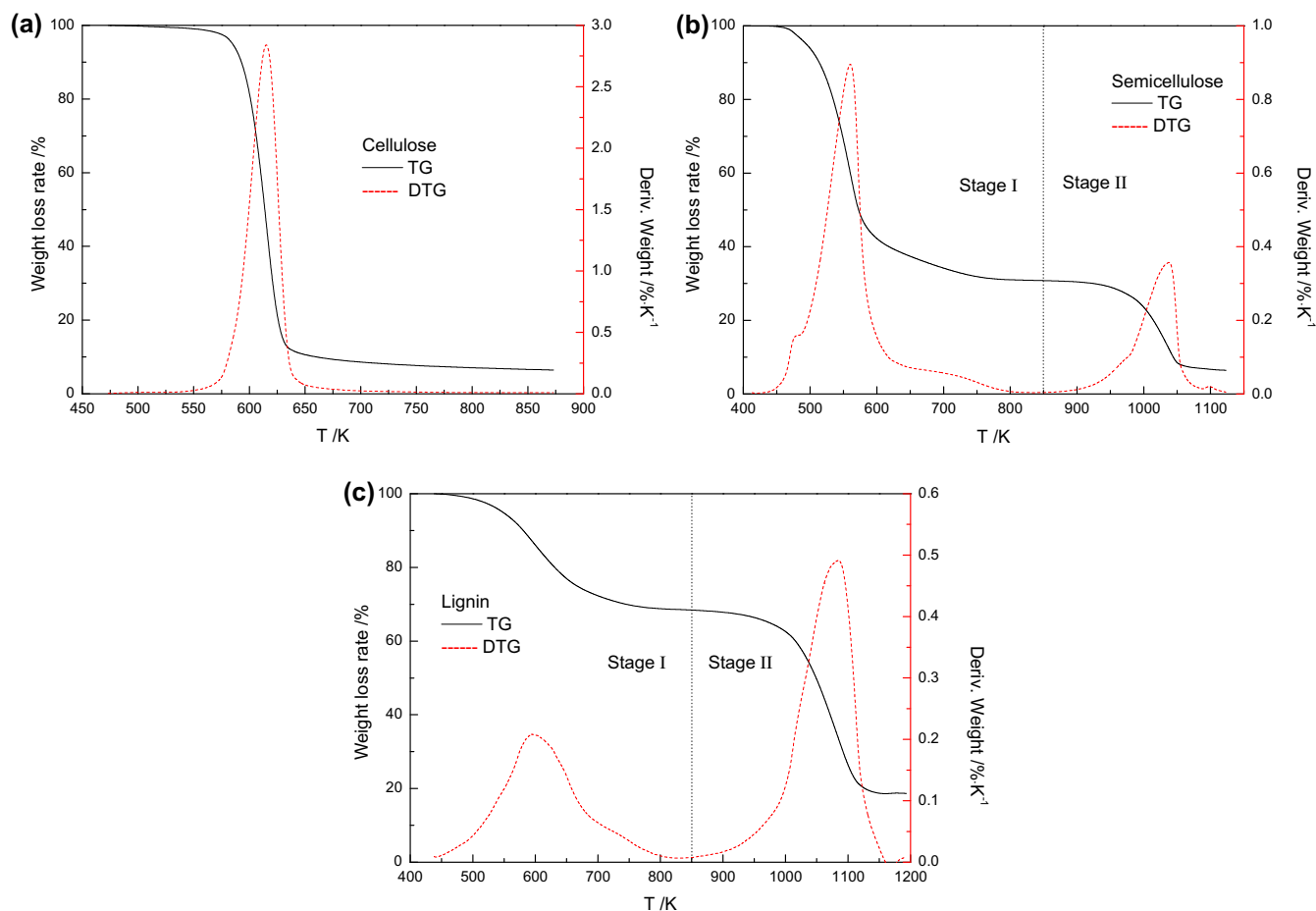


Fig. 1. The TG and DTG analysis of three pseudocomponents in CO_2 atmosphere at the heating rate of 10 K/min: (a) Cellulose; (b) Semicellulose; (c) Lignin.

the Gaussian distribution model. But in our previous work, both the DTG curves of semi-cellulose and lignin could not fit the Gaussian distribution model for the pyrolysis (N_2 agent) and the gasification (CO_2 agent) process.

In this work, the gasification kinetic analysis of the three pseudocomponents (hemicellulose, cellulose and lignin) of biomass decomposition in the agent of CO_2 were investigated. The Multi-peaks method was used to fit the Gaussian distribution model of DTG curves. The Friedman method was used to estimate the effective E_x , and the master plot method was used for the determination of the kinetic model.

2. Methods

2.1. Material

Cellulose (CAS No.: 9004-34-6), semicellulose (CAS No.: 9014-63-5) and lignin (CAS No.: 8068-05-1) were supplied from Sigma-Aldrich Co., Ltd. (USA). In this study, cellulose was a polysaccharide composed of long chains of $\beta(1,4)$ linked D -glucose units. The hemicellulose was refined from the beechwood. The low sulfonate content alkali lignin was chosen in this study. Prior to experiment, the feedstock materials were put into an oven to outgas the water at the temperature of 378 K for 12 h.

2.2. Thermogravimetric analysis

A thermogravimetric balance was used for all kinetic analysis tests. Non-isothermal TGA was performed using a TA Instruments Q5000IR analyzer. The temperature range was from 313.15 to

1273.15 K, with heating rate (HR) 10 K min^{-1} . CO_2 and N_2 were used as the purge gas. They were metered by mass flow controllers and set to 80 mL min^{-1} for CO_2 and 20 mL for N_2 .

2.3. Determination of the E_x

The most common application of the isoconversional analysis was developed by Friedman and is used in this work. The method involves computing the logarithms of the Arrhenius rate equation to get (Aboyade et al., 2011):

$$\ln \left[\beta \left(\frac{d\alpha}{dT} \right)_\alpha \right] = \ln [A_x f(\alpha)] - \frac{E_x}{RT_\alpha} \quad (1)$$

where β is the heating rate, α is the extent of conversion, A is the pre-exponential factor; E is the activation energy; R is the gas constant; and T is the absolute temperature and $f(\alpha)$ is the reaction model. For a given value of the degree of conversion, the plot of $\ln \left[\beta \left(\frac{d\alpha}{dT} \right)_\alpha \right]$ versus $1/T$ should be a straight line whose slope can be used to evaluate the activation energy. Through Friedman's method, we can get different values of the activation energies for a process depending on the conversion degree.

2.4. Master-plots method for determining kinetic model

If the temperature of the sample is changed by a controlled and constant heating rate, the kinetic expression by the Arrhenius expression can be described by

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (2)$$

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