PYROLYTIC KINETICS OF STEAM EXPLODED LIGNIN BY TG/DTG ANALYSIS

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ABSTRACT

Steam exploded lignin (SEL) thermal decomposition was investigated by thermogravimetric technique (TG/DTG) within the temperature range from room temperature to 920°C under different heating rates (10, 20, 30, 40, and 50°C·min^{-1}). Little differences in the mass losses with heating rates were observed from TG analysis. It was established that SEL pyrolysis consisted of three main stages: water evaporation (< 200°C); devolatilization of organic volatiles (200-600°C); and char formation (> 600°C). The kinetic processing of non-isothermal TG/DTG data was performed by model-free methods proposed by Flynn-Wall-Ozawa (FWO) and Kissing-Akahira-Sunose (KAS). The average activation energies calculated from FWO and KAS methods are 74.2 kJ·mol^{-1} and 173.2 kJ·mol^{-1}, respectively. Experimental results showed that values of kinetic parameters from both methods were analogous and could be successfully applied to understand the complex degradation mechanism of SEL. It is also helpful to achieve a better understanding of the devolatilization process of different type of biomass.

KEYWORDS: Steam explosion, lignin, pyrolysis, kinetics, TG/DTG.

INTRODUCTION

A comprehensive understanding of the thermal decomposition of biomass such as lignin is of great importance in evaluating the influence on thermal behavior activity of evolved gas, volatile liquid, and residual solid under pyrolysis conditions. Upon heating in inert atmosphere, the three dimensional structure of lignin would undergo to adversely changes due to release of gases and volatiles (Furutani et al. 2018, Jiang et al. 2018).

Thermal analysis techniques, such as thermogravimetric analysis (TG/DTG), are often employed for studying the weight loss information of pyrolysis process and acquiring kinetic parameters during thermal decomposition reactions, which is essential in lignin conversion system designing and operating (Liu et al. 2008, Luo et al. 2012, Wang et al. 2014, Li et al. 2014).

On the other hand, steam explosion process is a well-recognized method to deconstruct biomass, e.g., lignin, in order to improve their digestibility (Singh et al. 2015), which is a thermophysico-chemical process providing mechanical destructuration of biomass by vapor cracking and explosive decompression (Jacquet et al. 2015, Maniet et al. 2017). However, due to the complexity of structure and the heterogeneity of components, the determination of the pyrolysis process of steam exploded lignin (SEL) is very difficult, which consists of lots of physical changes and chemical reactions. Until now, there is rare literatures of the pyrolysis of SE pretreated lignin. Few detailed pyrolysis kinetics information about SEL pyrolysis was found in the available literature. The lack of data leads to difficulties in understanding thermal behavior of SEL.

The purpose of this paper is to gain further insight into pyrolysis behavior of SEL for the improvement of thermal decomposition efficiency. The pyrolysis process was studied by TG/DTG under Helium atmosphere in the temperature ranging from room temperature to 920°C under non-isothermal conditions (10, 20, 30, 40, and 50°C·min^{-1} heating rates). The kinetic parameters of SEL pyrolysis process by isoconversional method were also determined. To our knowledge, this is the most detailed thermal and kinetic characterization of SEL pyrolysis to date.

MATERIAL AND METHODS

Materials

The lignin sample was generated from residues of bio-ethanol production coupled with steam explosion process, supplied by Biological Engineering Laboratory, Nanjing Forestry University (Chu et al. 2013, Lai et al. 2014). The steam explosion pretreatment process was described in our previous report (Wu et al. 2019), e.g., steam explosion treatment with temperature 180°C and treatment pressure 1 MPa for 10 min, then the pressure was reduced to 0.5 MPa, and the sample with steam was suddenly discharged into the explosion tank at atmosphere pressure. After treatment, the lignin sample was thoroughly washed with water and centrifuged at 3000 rpm to separate solid, e.g., steam exploded lignin (SEL). Purification of SEL was operated by alkali-solution (sodium hydroxide aqueous solution) and acid-isolation (dilute sulfuric acid solution) methods (Guo et al. 2013). In detail, SEL was dissolved in 1 mol·l^{-1} sodium hydroxide aqueous solution under stirring for 2 h, then mixture was filtered and filtrate was acidified to pH of 2-3 to precipitate lignin. After filtration and being washed repeatedly with distilled water, the SEL sample was dried in an oven at 105°C for 3 h, the original materials were crushed and pulverized to a size of < 0.2 mm before they were analyzed (Gu et al. 2017).

Analysis procedure

TG/DTG analysis operational conditions were similar with our former report (Gu et al. 2012). The pyrolysis process of SEL was studied by a STA8000 TGA thermogravimetric simultaneous thermal analyzer under helium atmosphere (flow rate 50 mL·min^{-1}; temperature range from room temperature to 920°C, heating rate 10, 20, 30, 40, and 50°C·min^{-1}). The thermal analyzer's microbalance sensitivity is less than ±0.1 μg and temperature precision is ±0.5°C. The initial weight of samples loaded into the crucible was 10 mg ± 0.5 mg to avoid the heating transfer limitation. Duplicate experiments were carried to eliminate test errors and guarantee the repeatability.

Kinetic theory

The kinetics of reaction in solid-state are described by the following Eq. 1:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{1}$$

Conversion α is normalized form of weight loss data of decomposed sample and is defined as follows:

$$\alpha = 1 - \frac{m_{(t)} - m_f}{m_0 - m_f} \quad (\%) \tag{2}$$

where: $m_{(t)}$ - the experimental mass at each monitoring time,
m_f - the final mass,
m_0 - the initial dry mass.

According to Arrhenius equation, the temperature dependence of the rate constant k is given by:

$$k = A \cdot \exp(-\frac{E}{RT}) \quad (\text{min}^{-1}) \tag{3}$$

where: Ea - the activation energy (kJ·mol^{-1}),
T - the absolute temperature (K),
R - the gas constant (8.314 J K^{-1}·mol^{-1}),
A - the pre-exponential factor (min^{-1}).

Combination of the two Eqs. e.g. 1 and 3, gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of TGA results.

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp(-\frac{E}{RT}) \tag{4}$$

The expression of the function $f(a)$ and its derivative $f'(a) = -1$ are used for describing solid-state first order reaction, and the mathematical function $f(a)$ could be restricted to the following expression:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where: n - the reaction order.

According to the classical theory for the kinetics of chain reaction (Laidler 1965). Substituting expression (5) into Eq. 4 gives the expression of reaction rate in the form:

$$\frac{d\alpha}{dt} = A \exp(-\frac{E}{RT}) (1 - \alpha)^n \tag{6}$$

For non-isothermal TGA experiments at linear heating rate $\beta = dT/dt$, Eq. 6 can be written as:

$$\frac{d\alpha}{dT} = (\frac{A}{\beta}) \exp(-\frac{E}{RT})(1 - \alpha)^n \tag{7}$$

This equation expresses the fraction of material consumed in the time. Biomass thermal decomposition usually has an order of reaction of 1.0 ($n = 1$).

In this work, the activation energy was obtained from non-isothermal TGA. The methods used to calculate kinetic parameters are called model-free non-isothermal methods and require a set of experimental results at different heating rates, i.e., Flynn-Wall-Ozawa (FWO) method and Kissing-Akahira-Sunose (KAS) method.

The FWO method (Ozawa 1965, Flynn et al. 1966) was an integral technique which expressed straight lines at different heating rates according to relationship between the logarithm of the heating rate and reciprocal temperature at constant mass loss, in which the apparent activation energy of degradation was calculated from the slope of linear relationships. This method could obtain apparent activation energy (Ea_α) from a plot of natural logarithm of heating rates, $\ln\beta$, versus $1000/T_{\alpha i}$, which represents the linear relation with a given value of conversion (α) at different heating rates (β). And $T_{\alpha i}$ is the corresponding temperature of the DTG curve at a given conversion (shown in Fig. 1).

$$\ln(\beta_i) = \ln\frac{A_\alpha E_\alpha}{Rg(\alpha)} - 5.331 - 1.052\frac{E_\alpha}{RT_{\alpha i}} \tag{8}$$

where: $g(\alpha)$ - constant at a given value of conversion, e.g., $g(\alpha) = -ln(1-\alpha)$ when n=1.0. The subscripts i and α denotes given value of heating rate and given value of conversion, respectively. The activation energy E_α is calculated form the slope -1.052 E_α /R.

Similarly, the KAS method (Kissinger 1956) could also obtain the value of activation energy from a plot of $ln(\beta/T_{\alpha i}^2)$ against $1000/T\alpha i$ for a series of experiments at different heating rates (β), where $T_{\alpha i}$ is the corresponding temperature of the DTG curve at a given conversion (α). The subscripts i and α denotes given value of heating rate and given value of conversion, respectively. The equation is based on the following expression:

$$\ln(\frac{\beta}{T_{\alpha i}^2}) = -\frac{E_\alpha}{RT_{\alpha i}} + \ln(\frac{A_\alpha R}{E_\alpha g(\alpha)}) \tag{9}$$

The apparent activation energy can be obtained from a plot of $\ln(\beta_i/T_{\alpha i}^2)$ versus $1000/T_{\alpha i}$ for a given value of conversion, α, where the slope is equal - E_α /R.

RESULTS AND DISCUSSION

TG/DTG analysis

The TG/DTG curves obtained by heating SEL at different heating rates (10, 20, 30, 40, and 50°C·min^{-1}) in the temperature range from room temperature to 920°C under Helium atmosphere are shown in Fig. 1. As shown in Fig. 1a, five mass loss curves almost coincide. The residual products (chars) at increasing of heating rates were 43.6 wt%, 42.9 wt%, 42.6 wt%, 40.3 wt%, and 39.7 wt%, respectively. This trend is in accordance with the fact that the acceleration of thermal decomposition reaction is unavoidable due to shorter reaction time corresponding to increasing heating rates. In general, the heating rate could be an important factor to affect the pyrolysis process including mass loss, gaseous or volatile products released, and so on (Caballero et al. 1996, Galano et al. 2017). Therefore, different heating rates were employed to investigate the effect of heating rate on pyrolysis.

All the thermo-analytical curves presented the same profiles, which were slightly shifting toward higher temperatures at increasing heating rates. Three principal regions of mass losses were recognized on TG curves (Fig. 1a), e.g., water evaporation (stage I), devolatilization

of organic volatiles (stage II) and char formation (stage III), whereas one main peak was identified on the corresponding derivative TG curves (see Fig. 1b). In detail, the initial decrease in weight is due to water release where temperature is below 200°C, which is related to the extraction of moisture and adsorbed water in the substrate (Abdullah et al. 2010) (see stage I). The second stage is the primary pyrolysis of SEL, as the temperature increases from 200 to 600°C. For example, the weight decreases sharply with the maximum weight loss rate of -5.7 wt%/min at the heating rate of 20°C·min⁻¹. The temperature corresponding to the maximum weight loss rate of sample is about 364°C. A large amount of gas species such as CO_2, CO, CH_4 and H_2O are released in this stage, which indicate that they mainly come from this primary pyrolysis stage (see stage II). As the temperature continues increasing (above 600°C), the weight variation is very small with less amount of gaseous or volatile species releasing and char is formed (see stage III).
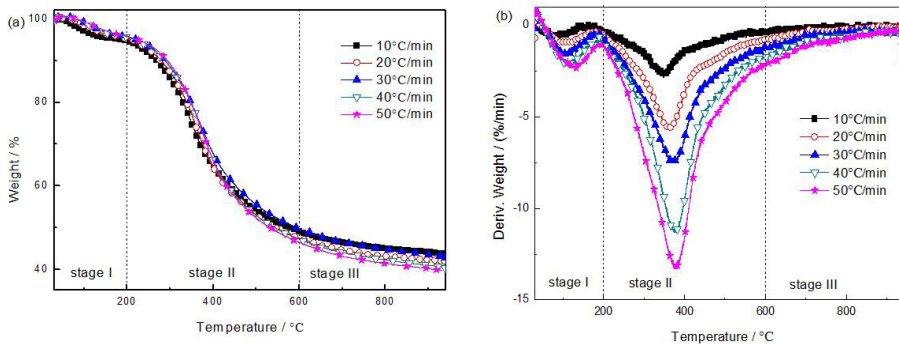

Fig. 1: Curve of TG (a) and DTG (b) for SEL at different heating rates.

Kinetic analysis

The results obtained from thermogravimetric analysis were elaborated according to model-free methods to calculate the kinetic parameters. The activation energy *(Ea)* and pre-exponential factor (A) were obtained by FWO and KAS methods.
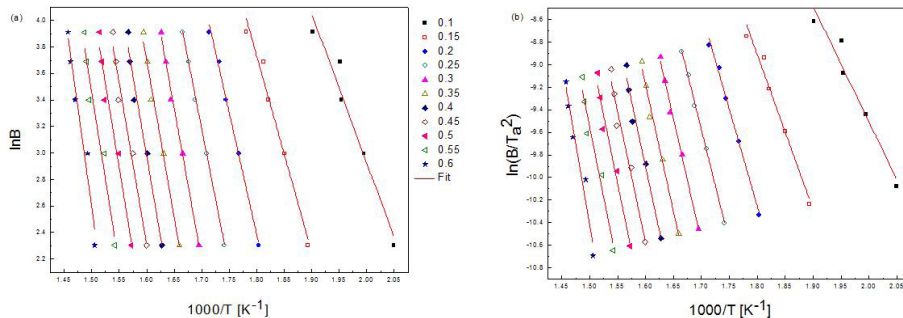

Fig. 2: Linearization curves of FWO (a) method and KAS (b) method for SEL.

Flynn–Wall–Ozawa method (FWO)

The kinetic parameters obtained by FWO method were calculated according to Eq. 8, for a given value of conversion, α. To determine the kinetic parameters, we chose the same value

of α from range 0.1 to 0.6 for all curves at different heating rates. The FWO plots of $\ln(\beta i)$ versus $1000/T\alpha i$ (K-1) for different values of conversion are shown in Fig. 2a. The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of regression line were given in Tab. 1. The calculated squares of the correlation coefficients, R2, corresponding to linear fittings in Fig. 2a, were in range from 0.94 to 0.99.

Kissing–Akahira–Sunose method (KAS)

The kinetic parameters for SEL pyrolysis were calculated using KAS method according to Eq. 9, for a given value of conversion, α. Similarly, we chose the same value of α from range 0.1 to 0.6 for all curves at different heating rate and we found the corresponding temperature. The KAS plots of $ln(\beta_i/T_{\alpha i}^2)$ versus $1000/T_{\alpha i}$ (K-1) for different values of conversion are shown in Fig. 2b. The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of regression line were given in Tab. 1. The calculated squares of the correlation coefficients, R^2, corresponding to linear fittings in Fig. 2b, were in range from 0.93 to 0.99.

Tab. 1: Activation energy and Arrhenius constants obtained by FWO and KAS methods during SEL pyrolysis.

Conversion α	FWO method			KAS method		
	E (kJ·mol-1)	LnA (min-1)	R2 (%)	E(kJ·mol-1)	LnA (min-1)	R2 (%)
0.10	89.02	19.26	94.22	85.24	17.98	93.04
0.15	117.15	24.38	97.22	114.20	23.09	96.75
0.20	145.00	29.47	99.25	143.09	28.23	99.14
0.25	166.71	33.22	99.80	165.62	31.94	99.77
0.30	181.52	35.54	99.35	180.95	34.17	99.28
0.35	187.77	36.18	98.34	187.31	34.64	98.16
0.40	191.97	36.45	97.01	191.54	34.75	96.68
0.45	192.77	36.10	96.35	192.20	34.21	95.95
0.5	201.30	37.23	95.87	200.99	35.26	95.43
0.55	206.56	37.64	94.22	206.32	35.54	93.61
0.6	236.74	42.50	94.67	237.82	40.50	94.18
Average value	174.23	33.45		173.21	31.85	

*R^2 corresponding to linear fittings.

In Tab. 1, we can observe that apparent activation energies for the pyrolysis of SEL are not similar for all conversions, which indicates that the existence of a complex multistep mechanism that occurs in the substrate. The average value of apparent activation energy is 173.2-174.2 kJ·mol-1 according to FWO and KAS methods, respectively. It was shown that values of kinetic parameters from both methods were analogous and could be successfully applied to understand the complex degradation mechanism of SEL.

CONCLUSIONS

In this paper, a comprehensive pyrolysis kinetics study of steam exploded lignin (SEL) is presented. Thermogravimetric analysis was investigated under helium atmosphere at different heating rates of 10-50°C min-1. Thermal decomposition of SEL proceeds in three stages: water

evaporation, devolatilization of organic volatiles and char formation. It was found that the main pyrolysis process occurred at about 200°C - 600°C. Effect of heating rate on TG and DTG curves was also investigated. Activation energy and pre-exponential factor were calculated with FWO and KAS methods and dependent on conversion due to the complex mechanism of reaction during SEL pyrolysis process. The values of activation energy obtained from two methods are in good agreement, e.g., 174.2 kJ·mol^{-1} and 173.2 kJ·mol^{-1}, respectively. Experimental results showed that the model-free methods could describe the complexity of SEL thermal decomposition process.

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