Pyrolysis kinetics of filter mud from sugar mills

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Abstract. In order to facilitate the possible reuse of filter mud from sugar mills as boiler fuels or producing biochar that involves pyrolysis process, thermogravimetric analysis (TGA) was employed to analyze the pyrolysis kinetics of it. In TGA tests, filter mud were heated from 30 °C to 800°C at different heating rates (5, 10, 15, 20, 25 and 30 °C/min) in the atmosphere of nitrogen, and the relevant parameters of kinetics were performed by methods of Flynn–Wall–Ozawa (FWO) and the Kissinger–Akahira–Sunose (KAS). The results shown that the average activation energy analyzed by FWO and KAS were 322.28 and 321.93 kJ/mol, the average enthalpy were 289.04 and 288.24 kJ/mol, the average Gibbs free energy were 207.87 and 208.01 kJ/mol, respectively, the pre-exponential factors varied in the range of 10²²–10³⁹ s⁻¹.

1. Introduction
Filter mud, as one of the major by-products accounting for 3%−4% of the sugar production, makes large volume wastes to be handled, containing fiber, sucrose, coagulated colloidal organics, protein, calcium salts, etc. In the conventional treatment, most of the filter mud are returned to the fields as harmless disposal options. However, filter mud has been increasingly disagreeable among farmers in China because it is practically ineffective as an agricultural fertilizer, which generates intense heat and foul odor due to further fermentation and takes lengthy time to decompose naturally[1]. Furthermore, it is inconvenient to transport and store as a result of keeping approximately 70%−80% water content. In recent years, the filter mud has become increasingly unacceptable to farmers and thus a burden on the environment.

As a biomass, the filter mud could be of comprehensively recyclable, such as, reusing it as a boiler fuel after drying or producing biochar from it through pyrolysis are feasible recycles among others. In China, some sugar factories produce white sugar through a two-step process that raw sugar is made first and be refined later. These factories always experience shortages of fuel for boilers during the off-crop refinery, it could be a beneficial alternative to recycle the dried filter mud as the burning fuel. Biochar is a carbon-rich material obtained by pyrolysis of biomass materials under the absence of air/oxygen, which has various applications including soil amendment, waste stream management, etc [2]. Apparently the filter mud from sugar mills can be a good feedstock for biochar production. These possible reuses of the filter mud all involve pyrolysis process during application.
The pyrolysis kinetics and thermal properties are key parameters in understanding the characteristics of a biomaterial to be used as a fuel or to produce biochar. Previously, Wang [3] measured the combustion characteristics of filter mud from a raw sugar mill. In this paper, the pyrolysis behaviour of filter mud and its kinetic parameters are examined using TGA.

2. Materials and methods

2.1. Preparation and Characterization of Samples
The filter mud used in this study was supported by Liangqi Sugar Industry Co., Ltd, Guangxi Autonomous Region, China. Samples were collected, dried, crushed, and then passed through a 0.2 mm screen. The screened samples were sealed in a wide-mouthed bottle.

2.2. Thermogravimetric analysis
The TGA of the filter mud was carried out by a simultaneous thermal analysis system (STA 449 F5 Jupiter, NETZSCH GmbH, Germany). Small alumina crucibles with 6–8 mg of samples were placed in the system and heated from 30 °C to 800 °C at the rate of 5, 10, 15, 20, 25 and 30 °C/min, respectively. The inert gas was Nitrogen, and the flow rate was 20 mL/min. All of the tests were carried out at least three times, and an arithmetic average value was attained.

2.3. Kinetic analysis of pyrolysis
The pyrolysis could be expressed as following:

\[
\text{Biomass} \xrightarrow{k} \text{Volatile substances} + \text{Char}
\]

The volatiles are the total amount of gas and tar, \( k \) represents the rate constant.

The conversion from solid to volatile products can be described by equation (1):

\[
\frac{da}{dt} = kf(\alpha)
\]  

(1)

The conversion \( \alpha \), which is the weight loss of the sample during decomposition, could be defined as:

\[
\alpha = \frac{m_i - m_\alpha}{m_i - m_f}
\]  

(2)

in which \( m_i \) is the initial mass of the filter mud, \( m_f \) is the terminal mass, and \( m_\alpha \) is the mass at time \( t \).

\( k \), which meaning is as before, is the function of the sample’s temperature \( T \), and could be expressed by Arrhenius equation:

\[
k = Ae^{(-E_a/RT)}
\]  

(3)

where \( A \) is the pre-exponential factor, \( E_a \) is the activation energy of the pyrolysis reaction.

The heating rate \( \beta \) is defined as:

\[
\beta = \frac{dT}{dt} = \frac{dT}{da} \frac{da}{dt}
\]  

(4)

Given that \( \beta \) is fixed in TGA, incorporating Equation (1), (2) and (4), and integrating \( f(\alpha) \), the formula \( G(\alpha) \) as follows is obtained:

\[
G(\alpha) = \int_0^\alpha \frac{da}{f(\alpha)} = A \int_{T_0}^\infty \exp\left(-\frac{E_a}{RT}\right)dT
\]  

(5)

where, \( T_0 \) is the initial temperature of the material. Note that formula (5) has no explicit solution. For the situation like that, researches such as Doyle [4], Agrawal and Sivasubramania [5] stated several interpolation formulas, as well as Nikolaev et al [6] and Frank-Kameneshii [3] adopted the approximations.
2.4. Model-free method

By the model-free method, the kinetic parameters of the pyrolysis could be obtained through curves of the different heating rates at the same conversion rate, instead of assuming any reaction model of \( f(\alpha) \). The International Thermal Analysis and Thermal Assay Federation Dynamics Committee highly recommends these methods [7]. Among the same conversion method, methods of Kissinger, Friedman (FR), Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO) and Vyazovkin (V) are parts of the most popular representatives. In this study, the KAS and FWO methods were used.

2.4.1. FWO method. \( E_\alpha \), which represents the apparent activation energy, could be obtained by the method of FWO [8-9] with a plot of \( \ln \beta \) versus \( 1/T_\alpha \) that describes the linear relationship between the heating rate and the given conversion value. The final FWO equation derived using the Doyle approximation method is as followed:

\[
\ln(\beta_i) = \ln \left( \frac{A_\alpha E_\alpha}{R g(\alpha)} \right) - 5.331 - 1.052 \frac{E_\alpha}{RT_{ai}}
\]

(6)

The subscripts \( i \) and \( a \) represent the heating rate and the conversion rate, respectively, and \( E_\alpha \) comes from the slope of \(-1.052E_\alpha/R\).

2.4.2. KAS method. The KAS method [10] is widely accepted in biomass pyrolysis kinetics studies. The final equation derived using the Doyle approximation method is as followed:

\[
\ln \left( \frac{\beta}{T_{ai}^2} \right) = \ln \left( \frac{A_\alpha R}{E_\alpha g(\alpha)} \right) - \frac{E_\alpha}{RT_{ai}}
\]

(7)

The apparent activation energy could be carried out by plotting \( 1/T_{ai} \) for a given conversion value, and the slope is \(-E_\alpha/R\).

The pre-exponential factor \( A \) is analysed as below:

\[
A_\alpha = \beta E_\alpha \exp \left( \frac{E_\alpha}{RT_m} \right) / RT_m^2
\]

(8)

where \( T_m \) is the maximum value of temperature.

Parameters of the thermodynamics, including enthalpy (\( \Delta H \)), Gibbs free energy (\( \Delta G \)), and entropy changes (\( \Delta S \)), are performed as follows:

\[
\Delta H = E_\alpha - RT
\]

(9)

\[
\Delta G = E_\alpha + RT_m \ln \left( \frac{K_B T_m}{h A_\alpha} \right)
\]

(10)

\[
\Delta S = \frac{\Delta H - \Delta G}{T_m}
\]

(11)

Where \( K_B=1.381\times10^{-23} \) J/K, \( h=6.626\times10^{-34} \) J·s.

3. Results and discussion

3.1. Thermal degradation process

Figure 1 shows the weight loss of filter mud in the pyrolysis under the inert atmosphere. The materials were heated from 30°C to 800°C at heating rates of 5, 10, 15, 20, 25 and 30 °C/min. The filter mud was composed of different components with different decomposition temperature regions [11]. The decomposition of the filter mud was performed in three stages. The first one is the dehydration of the materials, in which the hydrolysis of weakly bound water molecules and some extracts were observed at a temperature of 110°C. The second one was primarily the decomposition of cellulose and hemicellulose and some volatile substances while the temperature increased from 150°C to 510°C. In
the third stage, the decomposition of lignin was occurred during passive pyrolysis in the range of 150–800°C. In the process of passive pyrolysis, fixed carbon is the main product.

Figure 2 shows the derived thermogravimetric curves of the filter mud at different heating rates. The raising heating rates increased the peak of temperature. The change of the heating rate-dependent peak was as results of the undesirable heat transfer and the changes in reaction mechanism. More specifically, relatively low heating rates were prefer to the reaction because biomass particles were continuously heated and the interior heat transfer of the biomass was improved. Increase in heating rates resulted to release more volatiles, leaving less residues after pyrolysis.
3.2. Dynamic analysis

Kinetics parameters that are significant for the design of thermodynamic processes efficiently in the process of biomass conversion, like the activation energy and pre-exponential factor, were performed using the model-free method. According to Figure 3, the conversion rate variations were as functions of temperature under the condition of different heating rates. The isocon versional apparent activation energies calculated using the FWO and KAS models and the results are shown as Figure 4 and Figure 5.

Figure 3. Relationship between the temperature and the conversion rate of the filter mud at different heating rates.

Figure 4. Lineal regression by the FWO method.

Figure 5. Lineal regression by the KAS method.
Table 1. Conversion Rate Activation Energy and Related Kinetic Parameters.

| Conversion Point (α) | Activation energy (kJ/mol) | Pre-exponential factora (s⁻¹) | R² | ΔH² (kJ/mol) | ΔG² (kJ/mol) | ΔS² (kJ/mol) |
|---------------------|----------------------------|-------------------------------|----|-------------|-------------|-------------|
| FWO method          |                            |                               |    |             |             |             |
| 0.2                 | 215.62                    | 1.08E+22                      | 0.93 | 182.38     | 204.19     | -36.53      |
| 0.3                 | 252.40                    | 9.43E+24                      | 0.96 | 219.16     | 207.98     | 18.73       |
| 0.4                 | 351.03                    | 1.51E+33                      | 0.93 | 317.79     | 209.61     | 181.21      |
| 0.5                 | 370.82                    | 1.20E+37                      | 0.97 | 337.58     | 209.47     | 214.59      |
| 0.6                 | 393.61                    | 8.70E+39                      | 0.90 | 360.37     | 208.19     | 254.91      |
| 0.7                 | 373.61                    | 1.90E+37                      | 0.90 | 340.37     | 207.21     | 223.05      |
| 0.8                 | 298.87                    | 5.68E+28                      | 0.91 | 265.63     | 208.45     | 95.78       |
| Average             | 322.28                    |                               |    | 289.04     | 207.87     |             |
| KAS method          |                            |                               |    |             |             |             |
| 0.2                 | 214.59                    | 2.31E+22                      | 0.93 | 181.47     | 204.32     | -38.27      |
| 0.3                 | 250.27                    | 8.14E+24                      | 0.96 | 218.21     | 207.87     | 17.32       |
| 0.4                 | 350.56                    | 1.67E+33                      | 0.93 | 318.36     | 209.67     | 182.06      |
| 0.5                 | 373.87                    | 1.32E+37                      | 0.97 | 335.88     | 209.62     | 211.49      |
| 0.6                 | 392.66                    | 7.78E+39                      | 0.93 | 357.53     | 208.34     | 249.89      |
| 0.7                 | 375.81                    | 1.78E+37                      | 0.93 | 342.56     | 207.54     | 226.16      |
| 0.8                 | 295.76                    | 4.68E+28                      | 0.94 | 263.67     | 208.72     | 92.04       |
| Average             | 321.93                    |                               |    | 288.24     | 208.01     |             |

*a calculated at a heating rate of 15 ℃/min

The kinetic parameters were calculated by equation (6), (7) and (8), the results were shown in Table 1. When the conversion rate was less than 0.3, the activation energy was higher than 200 kJ/mol. According to the previous research [12], the activation energy was used to obtain an understanding of the reactivity of fuels, which reflects the minimum energy required in a reaction. The increase of apparent activation energy occurred in the first stage of pyrolysis and decreased with the increase of the conversion. As shown in Figure 6, the activation energy increased when the conversion rates varied from 0.2 to 0.6, indicating that this stage was an endothermic reaction. The activation energy decreased for the conversion rates to vary from 0.7 to 0.8, indicating that this stage was an exothermic reaction. The variation in activation energy was owing to the complex reactions under inert gas conditions [13].

The change in activation energy may also be due to the contents of components in the biomass and the interactions between them. The average activation energies calculated over the entire conversion range using the FWO and KAS methods were 322.28 and 321.93 kJ/mol respectively. The difference in activation energy was resulted from the approximation of the temperature integral of the model-free method and the reasonable deviation in the calculation. The pre-exponential factors obtained by methods of FWO and KAS fell within the range of 10²⁵–10³⁹. Usually, a low pre-exponential factor (<10⁹) indicates that the reaction is a surface reaction, whereas a high pre-exponential factor indicates a high degree of complexity of the reaction. The change in factor with conversion was owing the complex constituent of the materials and the reactions occurred in the process of decomposition. Meanwhile, the pre-exponential factor increased with the increasing heating rates.
3.3. Thermodynamic parameters

The calculation results of the thermodynamic parameters by using Equations (9–11) are listed in Table 1. In pyrolysis, enthalpy is the sum of energy that consumed by the conversion of biomass into various products, such as oil, natural gas, and coke. Figure 7 shows the relationship between enthalpy change and conversion rate. The enthalpy changes calculated using the FWO and KAS methods were 289.04 and 288.24 kJ/mol respectively.

Gibbs free energy, which is also call free enthalpy, refers to the increase of the total energy due to the formation of the activated complex in the system [14–16]. The Gibbs free energies at different heating rates analysed by the FWO and KAS methods are shown in Figure 8 and 9, which were 203.33–211.46 kJ/mol and 202.06–211.68 kJ/mol, respectively.

Figure 10 and 11 show the entropy changes calculated by the FWO and KAS methods, respectively. The entropy changes of the filter mud had both negative value (−38.27 kJ/mol) and positive value (257.32 kJ/mol). A negative $\Delta S$ value indicates that the product produced by the dissociation of the bond was less complex than the initial reactant. A low $\Delta S$ value means that the material is close to its thermodynamic equilibrium through some physical and chemical changes. In this state, the material shows minimal reactivity and requires more time to form an activated complex. By contrast, a high $\Delta S$ means that the reactivity is remarkably high and less time is spent in forming the activated complex.
4. Conclusions
The pyrolysis behavior of filter mud and the kinetic parameters were examined by thermogravimetric analysis (TGA), details of research are as following:
1. Three variation phases were concluded in the pyrolysis of filter mud from sugar mills, and the major behavior that weight loss occurred in the second state (150–510°C). Relatively a low heating rate was propitious to the pyrolysis of the filter mud.
2. Both of the FWO and the KAS models could well describe the pyrolysis process of the filter mud. The average activation energy calculated by FWO and KAS methods were 322.28 and 321.93 kJ/mol, the average enthalpy were 289.04 and 288.24 kJ/mol, the average Gibbs free energy were 207.87 and 208.01 kJ/mol, respectively, and the pre-exponential factors were in the range of $10^{22}–10^{39}$ s$^{-1}$.

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