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The Kinetics Studies and Thermal Characterisation of Biomass

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Abstract

This work aims to investigate and develop a method to evaluate and predict the combustion behaviour and combustion efficiency of different biomass commonly used in power plants via simple characterisation methods. 11 types of agricultural and industrial wastes were characterised using thermogravimetric analyser to obtain the derivative thermogravimetric (DTG) data and kinetic parameters. For the samples tested, the initiation temperatures were found to be in the range between 224.39℃ and 260.33℃, whilst the local minimum temperatures between 2 peaks were within the range of 360.36 to 382.74℃. It was established that there is a clear, direct relationship between the pre-exponential factor and the temperature interval for the first step of combustion. This trend was apparent and recorded for the 2 heating rates tested.

Keywords: Biomass; kinetics; burnout; combustion behaviour

1. Introduction

Energy has always been the foundation of social and economic development. However, the rapid rising energy consumption coupled with the heavily fossil fuel-dominated energy structure have led to significant pressure on global energy reserves and growing emission of greenhouse gases. Researches on the development of non-fossil

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energy are of prime importance for the survival of human being and sustainable future. Biomass, the earliest energy used by man, is renewable, abundant and CO_2 neutral. This has attracted the interest of various governments worldwide in the efforts to protect and preserve the environment. The corresponding policies released by the Chinese government under the guidance of the "Renewable Energy Law" have profound positive effects on the development of biomass energy in China [1]. In 2013, biomass energy accounted for 0.9% of all energy consumption in China and the electricity generation capacity of biomass energy was 42 billion kWh, which accounted for 0.8% of the total generation [2]. The transition of fossil fuels to biomass energy is still on an increasing trend. According to the development goal of the latest "13th Five-Year Plan (2016-2020)" released by the state council of China, the large-scale developments and utilization technologies for renewable energy are and will be energetically promoted, especially in developing biomass power generation with high efficiency and low costs [3].

Most of the works reported on combustion are focused on ash behaviour during combustion [4, 5], however, little attention had been given to ignition and burnout which are the key phases of combustion. Therefore, this study aims to investigate and develop a method to evaluate and predict the combustion behaviour and the combustion efficiency of various kind of biomass via simple characterisations of biomass. Thermogravimetric analysis (TGA) technique is employed for combustion study, followed by kinetic modelling employing Coats Redfern integral method.

2. Materials and method

2.1. Sample preparation

In order to study the activation energy required for combustion of different types of biomass, and with the aim of validating the proposed methodology using a sufficiently large number and wide range of samples, a total of 11 types of biomass samples had been used in this study, including industrial wastes (mulberry wood, peach wood, poplar wood and spruce wood) and agricultural wastes (corn straw, miscanthus straw, oilseed rape, sesame straw, wheat straw, sorghum straw and sorghum leaf). Corn straw, miscanthus straw, wheat straw and sorghum were obtained as a whole plant, while the rest were received as chips or coarse particles. Firstly, the 4 kinds of whole-plant biomass samples were ground into coarse particles using a Retsch SM 200 cutting mill with 8mm sieve size. After that, all biomass samples were ground into fine powder of less than 200 microns using the Retsch ZM200 centrifugal mill.

2.2. Thermogravimetric analysis

The thermal properties of biomass samples were examined following a non-isothermal method using a thermogravimetric analyzer equipped with differential scanning calorimeter (TGA-DSC, NETZSCH STA449F3, Germany). All samples were heated from room temperature to 900℃ at heating rates of 5℃/min and 17.5℃/min, respectively. An air atmosphere (80 vol% Nitrogen and 20 vol% Oxygen) was used to study and understand the combustion characteristics of biomass. The experiments were repeated 3 times to ensure accuracy and repeatability within ±3%. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained to determine the initiation temperature (T_i) and the local minimum point between two peaks (T_{lm}). There are two steps in a biomass combustion process: the first step is attributed to total decomposition of hemicellulose and cellulose as well as partial decomposition of lignin, whilst the second one is associated with the decomposition of the remaining lignin and combustion of the char residue [9]. The initiation temperature (T_i) is commonly used to indicate the start of the first step of combustion and is achieved after the release of moisture at which mass loss rate of the sample reaches 1 wt% min^{-1} for the first time[6]. Correspondingly, the local minimum point between two peaks (T_{lm}) refers to the lowest temperature between two peaks and it marks the end point of the first step of combustion.

2.3. Kinetics model

The Coats–Redfern integral method was adopted in this study to calculate the kinetic parameters of the first step of biomass combustion. It is acknowledged that several methods are available for calculating kinetic parameters [7],

however, fundamentally every kinetic model obeys the same Arrhenius equation and the conversion rate equation described as below:

$$K(T) = A exp(-\frac{E}{RT})$$ (1)

$$\frac{d\alpha}{dt} = A e^{-E/RT}(1-\alpha)^n$$ (2)

Where T is the absolute temperature, R is the universal gas constant, A is the frequency or pre-exponential factor, E is the activation energy of the reaction, n is the order of reaction and t is the time. Conversion rate α is defined as the mass change of biomass sample at time t (min) which represents the relationship between initial mass m_0, final mass m_f and current mass m_t of the system, as given below:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$ (3)

For constant heating rate of β, $\beta = dT/dt$ is constant, therefore, following equation can be obtained:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \times \frac{dt}{dT} = \frac{d\alpha}{dt} \times \frac{1}{\beta}$$ (4)

Substituting Eq. (4) into Eq. (2) will result the following:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT}(1-\alpha)^n$$ (5)

Eq. (5) can be integrated and expressed in logarithmic form to yield following equations:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = ln\left[\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right] - \frac{E}{RT} \text{ (for n} \neq 1)$$ (6)

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right] - \frac{E}{RT} \text{ (for n=1)}$$ (7)

For most system $\frac{RT}{E} \gg 1$, and $1 - \frac{2RT}{E} \approx 1$. Thus, Equations (6) and (7) can be further simplified as:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \text{ (for n} \neq 1)$$ (8)

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \text{ (for n=1)}$$ (9)

In the Coats-Redfern method [8] used for obtaining the activation energy (E) and pre-exponential factor (A), the left side of equation(8) and (9) are plotted against 1/T respectively, which leads to a regression line. E and A can be obtained from the slope and the interception of the line, respectively.

3. Results and discussion

3.1. Thermogravimetric analysis

In order to study the characterisation of combustion behaviour, DTG analysis of 11 biomass samples were investigated in air environment introduced at a flow rate of 20ml/min. The samples were subjected to constant heating rates of 5°C/min and 17.5°C/min, respectively in different sets of test. The DTG curves showing the mass loss rate of 11 biomass samples at 5°C/min heating rate are presented in Fig. 1. It should be noted that similar trend was observed for the tests involving17.5°C/min heating rate. The initiation temperatures were in the range of 224.39°C and 260.33°C, whilst the local minimum temperature was within 360.36 to 382.74°C for all samples tested. The difference in ignition and end temperatures of the first stage of combustion process is the consequence of decomposition and interactions between organic components (hemicellulose, cellulose and lignin) and inorganic minerals (ashes) of different biomass samples [10].

The temperature interval of the first stage is the difference between initiation temperature and local minimum temperature between two peaks. This represents the temperature range at which the first stage of combustion is taking place. On account that the heating rate for each combustion run in the TGA is constant, the temperature intervals also represent the time intervals, i.e. the time period at which the first stage of combustion is taking place.

Table 1 details the combustion properties of all biomass samples tested. A larger time interval means that the sample requires a longer time to burn and this is undesirable, particularly in pulverised fuel (PF) power plants where samples take only a few seconds to travel from feeding point to flu gas stack. On the other hand, a smaller temperature interval suggests faster combustion of biomass which also means a higher reaction rate. Apparent from Table 1, spruce wood with the shortest temperature interval of 107.47℃ is the most reactive while sesame straw is the least reactive with the longest temperature interval of 155.86℃. The first stage of combustion is of prime importance as it involves the decomposition of hemicellulose and cellulose [9], which is responsible for the major release of volatiles thus promoting the heterogenous combustion of the residue solid and thus improves burnout.

Table 1. Burnout temperature interval of biomass

| Sample	Initiation temperature (℃)	Local minimum point between two peaks (℃)	Temperature interval - the First Stage (℃)
Corn Straw	238.06	365.34	127.27
Miscanthus	252.14	365.34	113.19
Mulberry	247.50	362.85	115.35
Oilseed	238.85	380.26	141.40
Peach Wood	248.39	380.23	131.84
Poplar Wood	243.34	362.83	119.49
Sesame Straw	224.39	380.26	155.86
Sorghum Top	250.02	382.74	132.72
Sorghum	232.85	367.82	134.96
Spruce	260.33	367.80	107.47
Wheat Straw	236.56	360.36	123.79
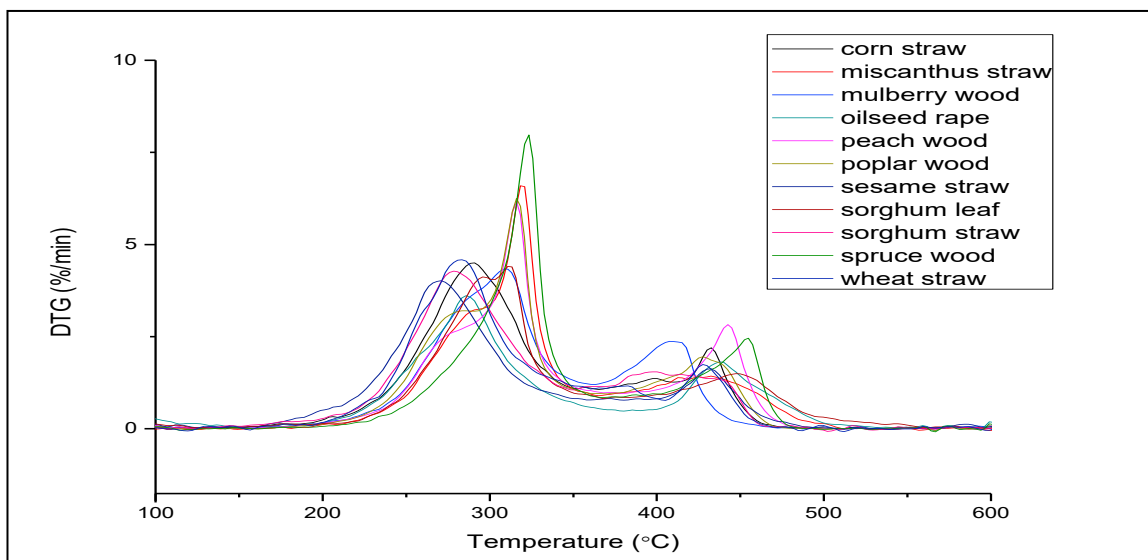
Fig. 1. DTG curves of biomass samples at 5℃/min heating rate

3.2. Kinetic Studies

Kinetics parameters of activation energy (E) and pre-exponential factor (A) were calculated from equation (9)

and are listed in Table 2. These kinetic parameters provide a comprehensive characterisation of the biomass thermal conversion process and an in-depth understanding of kinetic profile. The E and A values determined are within the normal range of biomass as reported in literature [11]. Moreover, the high correlation coefficient of the tests (at least 0.9085) suggests that first order kinetic model is feasible and the kinetic parameters obtained are reliable.

Table 2. Kinetics parameters by Coats Redfern method

Sample	Heating rate (°Cmin^{-1})	Temperature (°C)	Activation Energy (kJmol^{-1})	Pre-exponential factor (s^{-1})	R^2
Corn Straw	5	206-402	41.33	2736380.92	0.9487
	17.5	206-379	45.01	4931657.52	0.9545
Miscanthus	5	206-425	43.62	3554062.13	0.9492
	17.5	206-405	45.01	3683050.64	0.9357
Mulberry	5	206-400	44.13	4861598.91	0.9645
	17.5	215-388	48.07	8047405.81	0.9560
Oilseed	5	206-400	27.90	121081.15	0.9191
	17.5	206-370	32.38	298212.60	0.9399
Peach Wood	5	206-400	41.27	2236889.21	0.9571
	17.5	206-405	39.96	1238085.59	0.9497
Poplar Wood	5	206-400	44.69	5343765.26	0.9578
	17.5	215-396	47.37	6861061.78	0.9637
Sesame Straw	5	206-400	31.49	350961.10	0.9085
	17.5	206-397	35.38	662924.60	0.9319
Sorghum Top	5	206-400	39.43	1511431.14	0.9402
	17.5	206-388	38.75	1035058.00	0.9205
Sorghum	5	206-400	38.65	1611695.72	0.9421
	17.5	206-449	41.44	2519014.68	0.9413
Spruce	5	206-400	44.79	4436527.01	0.9364
	17.5	232-422	48.27	6318891.62	0.9481
Wheat Straw	5	206-400	40.50	2562334.43	0.9383
	17.5	206-405	38.56	1162303.96	0.9447

3.3. Relationship of pre-exponential factor versus burnout temperature interval

The relationships between temperature intervals of the first stage of combustion and pre-exponential factors (A) with heating rates of 5℃/min and 17.5℃/min are presented in Fig. 2. The value of A is inversely proportional to the temperature interval, which means that a larger A value corresponds to a smaller temperature interval and hence larger reactivity. The relationship was tested under 2 different heating rates to establish the relationship, its accuracy and reliability. It was observed that a larger heating rate led to an increase of temperature interval. However, an inversely proportional relationship between temperature interval and pre-exponential factor still persisted even when the heating rate was changed. It can be determined from Arrhenius equation that A is proportional to reaction rate constant (k) which quantifies rate of chemical reaction. Thus, the inverse relationship between temperature interval and pre-exponential factor is theoretically established as an indicator of reactivity, as illustrated in Fig. 2.

Combustion efficiency in coal-fired power stations can be significantly improved by enhancing combustion of fuels to achieve more complete combustion. The burnout of fuel depends on furnace temperature, residence time of fuel in furnace, etc and it was found that the higher the furnace temperature, the higher the carbon burnout [12]. The

furnace temperature range in power plants is commonly 1350-1700℃ [12] which is much higher than the burnout temperature range of biomass. This then suggests that the residence time of fuel in furnace (or the combustion period) is a more crucial factor than the furnace temperature in affecting the efficiency of power plants. However, given that the residence time of fuel in a power station furnace is around 2-3s [12], a faster burning fuel would lead to a more complete burnout and thus larger boiler efficiency. Therefore, biomass with shorter temperature intervals for the first step of combustion will lead to greater decomposition of hemicellulose and cellulose thus resulting in enhanced heterogenous combustion of the resulting char, thus giving a higher burnout rate and combustion efficiency. Thus, Fig. 2 is useful in evaluating and predicting the temperature interval for the first step of biomass combustion (and thus combustion efficiency) based on a simple kinetic studies using TGA. Potentially, it provides a numerical method to understand and predict the combustion behaviour, especially combustion efficiency of various types of biomass in a power station.
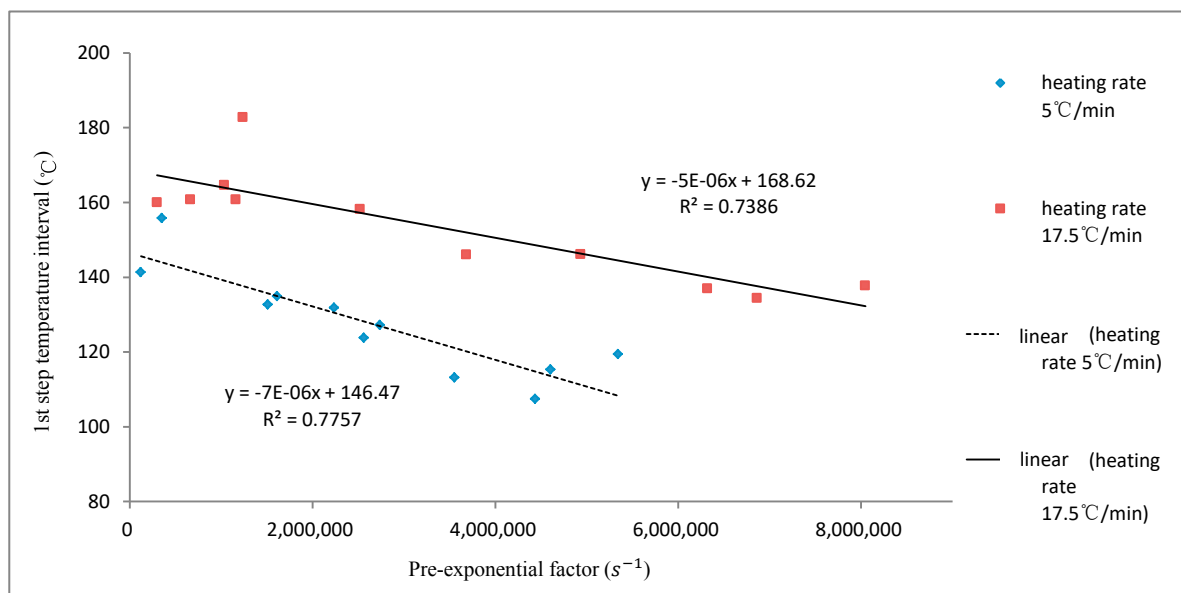

Fig. 2. The relationship between temperature interval and A value

4. Conclusion

In this study, the relationship between kinetic parameters and combustion behaviour of biomass was investigated using TGA. A wide matrix of kinetic data including pre-exponential factors and activation energy were determined using Coats Redfern integral method whilst the burnout temperature intervals were determined from the DTG curves. It is concluded that pre-exponential factor is inversely proportional to the temperature interval of the first stage of combustion of biomass. This relationship is useful in understanding and potentially predicting the combustion reaction rate and efficiency of various types of biomass in a power plant. It is meaningful for designing, modeling and developing thermo-chemical systems for different biomass samples.

Acknowledgements

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