

Combustion characteristics and kinetics of bio-oil

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Abstract The combustion characteristics of bio-oils derived from rice husk and corn were studied by thermogravimetry analysis. According to the thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) curves of bio-oils in air and nitrogen atmosphere, we analyzed the combustion characteristics of different kinds of bio-oils in different atmospheres and worked out the combustion kinetics parameters of the bio-oil, providing reliable base data for the burning of bio-oil. The thermogravimetry indicated that the combustion process of bio-oil was divided into three stages. At the same time, the combustion process can be described by different order reaction models, and with the method of Coats-Redfern, the activation energy and frequency factor of different kinds of bio-oils were obtained.

Keywords bio-oil, combustion characteristics, combustion kinetics

1 Introduction

Bio-oil is the main product of biomass pyrolysis. The oxygen content and moisture of bio-oil are high, but its calorific value is lower than some other oils. It has many complex organic compounds which have large molecular weights. The sulfur and nitrogen contents in the oil are low and the ash is little, having a small impact on the environment [1]. Though the complexity of the bio-oil component gives it great potential utilization, it is also very difficult to use. As substitutes for fossil fuels, bio-oil can produce heat, electricity and chemicals. In the short-term it can be used in boilers and thermal power generation, and in the long-term it can be used in turbines and diesel engines. It is technically feasible to upgrade bio-oil to vehicle fuels, but this needs further development. Thus, the most direct application of bio-oil is as boiler fuel oil.

At present, there are few studies on bio-oil and there are also no clear assessment standards of bio-oil quality, so it is necessary to establish a quality evaluation standard for different kinds of bio-oils. In this paper, the combustion characteristics and chemical kinetics of bio-oils derived from rice husk and corn are studied by thermogravimetry, which can not only provide more reliable base data on the oil's burning but also provide reference for quality evaluation standards for bio-oil. The bio-oils used in this test are from the self-made small fast pyrolysis of biomass fluidized bed installations.

2 Bio-oil

Bio-oil is a complex organic mixture with high oxygen content, containing more or less solid carbon particles, and its color is brown to black, having a pungent odor [2]. Most of these compounds are large molecular weight organics, and there are hundreds of types of the compounds, almost including all types of oxygen-containing organics such as organic acids, alcohols, ketones, aldehydes, ethers, phenols, esters, etc. The density of bio-oil is 1200 kg/m³, larger than water, and its lower pH value is useful for the stability of bio-oil. The calorific value is smaller, for example, the calorific value of 25% moisture content bio-oil is about 17 MJ/kg, which is equivalent to 40% of the same the quality of gasoline or diesel. In addition, its viscosity is larger, and a study [3] shows that the viscosity of bio-oil decreases with increasing temperature below 353 K, and when the temperature is over 353 K, the viscosity of bio-oil increases as the temperature rises. So the heating temperature of bio-oil should not be more than 80°C and preservation should avoid contact with light and air.

Compared with gasoline and diesel, bio-oil is hugely different in its physical properties and chemical composition. Bio-oil contains much water, the existence of which seriously impacts on the calorific value and ignition characteristics of bio-oil and limits its preheating temperature, leading to a long fire delay ignition period, as well as

lowering the flame temperature of combustion [2]. The high oxygen content of bio-oil (about 45%–60%) makes its components become very complicated, leading to low stability [2]. Compared with oil, bio-oil has low sulfur and nitrogen content, as well as less ash, which makes less pollution. Compared with diesel's combustion, the cetane number of bio-oil is low, at about 5.6 [4], and its ignition characteristic is bad, but once ignited it could stably combust. Its combustion flame length is shorter than diesel's, but the width is larger. In addition, because of the formation of large carbon particles, the flame is very bright and the radiation heat transfer of the flame and surrounding objects is enhanced [5].

Based on the nature of bio-oil above, the combustion characteristics of bio-oils derived from rice husk and corn are studied by thermogravimetry in this paper, which can provide more reliable base data on the oil's burning. Thermogravimetric analysis can continuously measure the temperature, weight, differential thermal and some other information in the process of the combustion of bio-oil, with advantages such as accurate measurement, good repeatability, simple operation, facilitation of data processing, etc. and it can be operated in the impact of the elimination of proliferation. Now, thermogravimetry has become a powerful tool for studying the combustion kinetics characteristics of coal and oil etc, directing large-scale power station boilers and the engineering design of combustion devices [6]. The thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) curves of different kinds of bio-oils are studied under identical experimental conditions in this test. We analyse and compare the combustion characteristics of rice husk oil and corn oil, and establish their combustion kinetics model.

3 TG test

The bio-oils used in this test are from the self-made small fast pyrolysis of biomass fluidized bed installations. The test equipment was a TGA942 atmospheric thermogravimetric analyzer of France's Setaran corporation. The main technical parameters of this equipment were as follows: the thermal balance precision was 0.1 μg ; the biggest test weight was 200 mg; the range of temperature was from ambient temperature to 1600°C; the accuracy of temperature was 0.1°C; the heating rate was 0.01°C/min–99.99 °C/min. This test used the method of non-isothermal

weights, and the testing gases were air and high purity nitrogen of 99.999%; the velocity of the gas flow was 75 mL/min, the heating rate was 10°C/min. We raised the temperature from room temperature to 105°C and maintained it for about 5 min, then continued to heat it up to 800°C and maintained it for about 3 min. A blank test using the same conditions was needed after each test in order to eliminate systematic errors. The elemental compositions and characteristics of bio-oil are shown in Table 1.

4 Results and discussion

4.1 Analysis of combustion characteristics

The TG curves, the combustion rate curves (DTG curves) and DTA curves of the two bio-oils under the same test conditions are shown in Figs. 1, 2 and 3, respectively.

From the TG-DTG curves of the two bio-oils in air atmosphere we can see (Figs. 1(a) and 2(a)) that the weight-loss process of bio-oil can be divided into three phases in air atmosphere. In the first phase, bio-oil loses its weight fast—the weight loss is 50% in about 20 min, when the largest weight loss rate of the rice husk bio-oil reaches 8.6%/min, and the largest weight loss rate of the corn bio-oil reaches 10%/min or so. The buns peak, and the peaks in front of the figures can be seen as the volatilization of water and low boiling point compounds in the bio-oil [7], which occur before 400 K or so, and this shows that the bio-oil has higher moisture content and contains a lot of volatile components. In the second phase, the weightlessness becomes relatively slow, and the weight loss is 35% at about 700 K, which is due to the presence of oxygen in the air, and the decomposition of the volatilized bio-oil is inhibited. The third stage of weightloss is a less obvious peak at around 700 K to 750 K that can be seen as the combustion stage. At this stage the remainder of the bio-oil is fully burning and it is completely burnt at 800 K when the amount of remaining coke is very small.

From the TG-DTG curves of the two bio-oils in the nitrogen atmosphere we can see (Figs. 1(b) and 2(b)) that in the nitrogen atmosphere, the early weight loss of heating-oil is also fast, which is the same as the first phase of bio-oil under air atmosphere, and the largest weight loss rate of bio-oil reaches 9%/min or so in about 20 min. The two coterminous peaks can be seen as the volatilization of water and low boiling point compounds of the biological

Table 1 Elemental compositions and characteristics of bio-oil

bio-oil sample	element/wt-%					density ($\text{g}\cdot\text{mL}^{-1}$)	pH	viscosity /cp,40°C	HHV ($\text{MJ}\cdot\text{kg}^{-1}$)
	C	H	O	N	S				
rice husk	32.35	8.361	58.062	1.197	0.03	1.1	2.5	20–1000	12.94
corn	33.25	9.183	56.43	1.107	0.03	1.2	2.3	20–1000	13.85

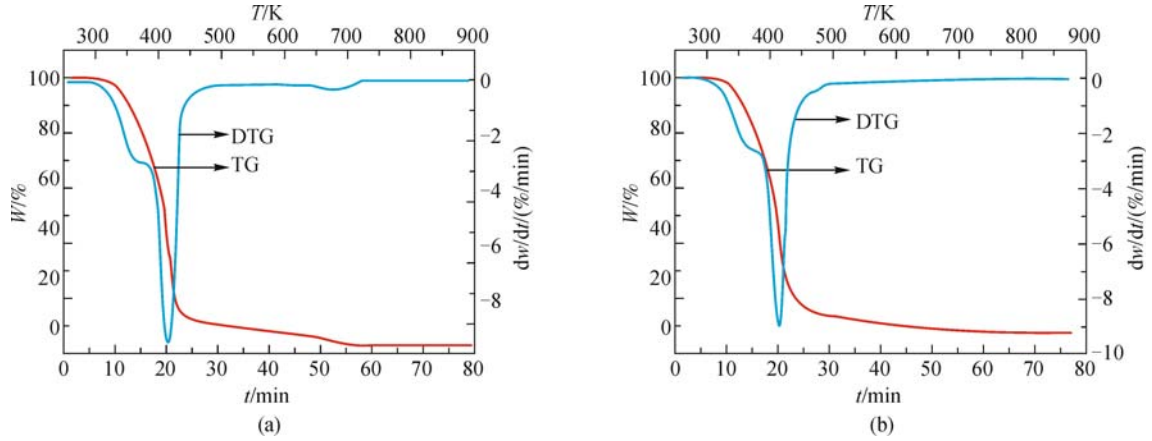


Fig. 1 TG-DTG curves of rice husk bio-oil under 10°C/min heating rate. (a) In air; (b) in nitrogen

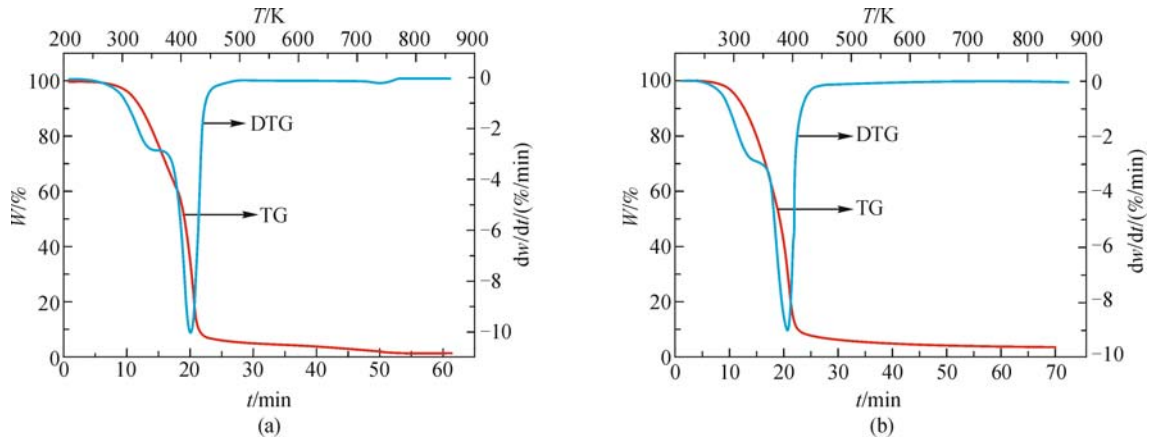


Fig. 2 TG-DTG curves of corn bio-oil under 10°C/min heating rate. (a) In air; (b) in nitrogen

oil. However, the bio-oil's weight-loss becomes slower in the latter heating stage, and the steady weight loss zone of the second half could be regarded as the pyrolysis phase, which is the volatilization and pyrolysis of macromolecule compounds. The remaining amount of coke in rice husk-oil is ultimately about 10%, and the remaining amount of coke in corn-oil is ultimately about 5%.

From the DTA curves in Fig. 3 we can see that in air atmosphere, the initial warming up stage of the two bio-oils is an endothermic reaction, which shows that the volatilization stage of water and low boiling point compounds of bio-oil is endothermic. Then it is an exothermic reaction that is the thermal decomposition process of larger components in bio-oils. The endothermic peak of bio-oil ends at 500 K, and its exothermic peak ends at 800 K. Similarly, in the nitrogen atmosphere, the initial warming up stage is also an endothermic reaction, and the endothermic peak ends at 450 K. A study [8] indicated that the reaction may move to a high temperature stage as the heating rate increases, which can also speed up the combustion rate and reduce the burning time, making the burning more easy.

From these curves, we analyze the main combustion parameters of bio-oil [9]: 1) the initial precipitated temperature of volatile T_0 ; 2) the largest weight loss rate of volatile $(d\alpha/d\tau)_{\max}$, that is, the peak of the DTG curve; 3) the peak temperature T_{\max} corresponding to $(d\alpha/d\tau)_{\max}$; 4) the average weight loss rate of volatile $(d\alpha/d\tau)_{\text{mean}}$, that is, the ratio of pyrolysis weight loss rate to pyrolysis time; 5) the largest weight loss of pyrolysis V_{∞} . The main combustion characteristic parameters of the two bio-oils are shown in Table 2.

4.2 Combustion kinetics analysis

The reaction of the bio-oil combustion process can be abbreviated as: A (liquid)→B (gas), and its kinetic equations can be described as follows:

$$\frac{d\alpha}{dt} = kf(\alpha) = Ae^{-E/RT}f(\alpha), \quad (1)$$

$$k = A\exp\left(-\frac{E}{RT}\right). \quad (2)$$

In the equations: α is the conversion rate, denoting the

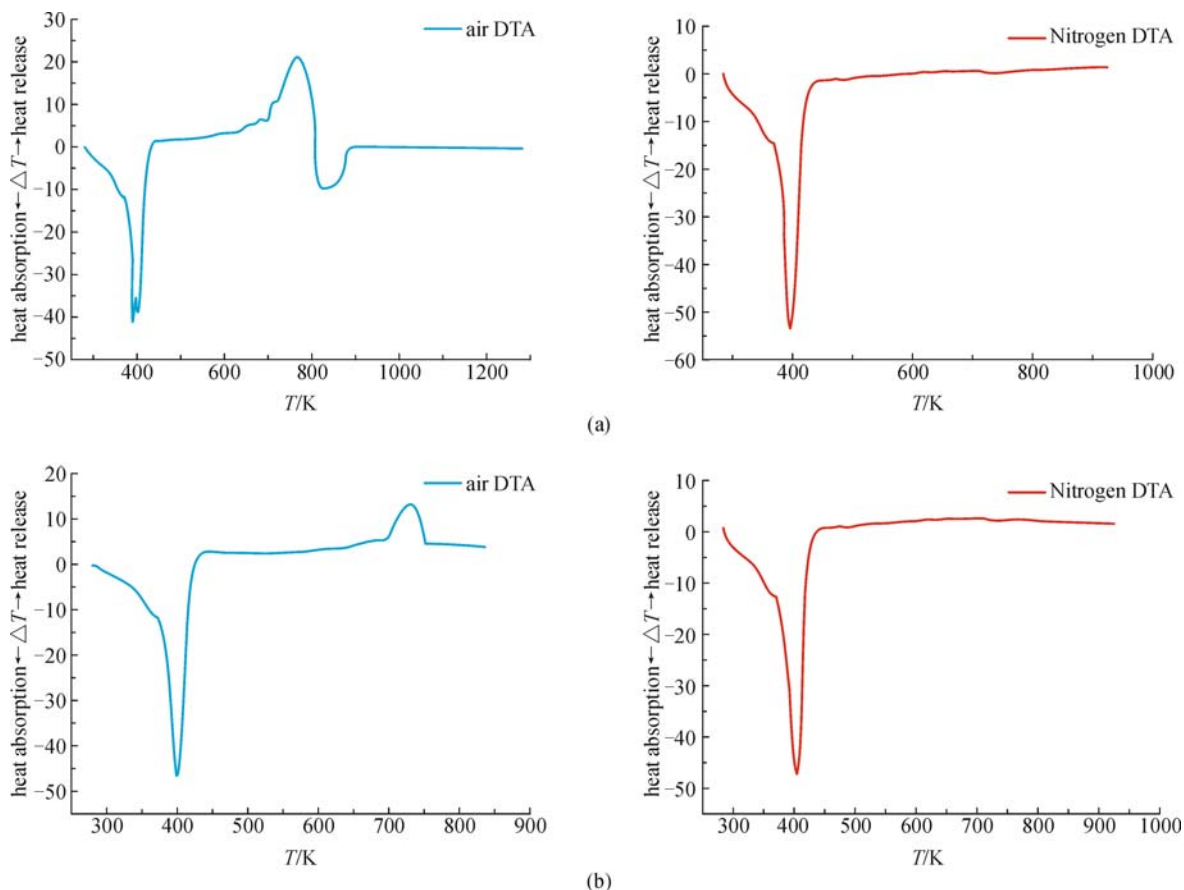


Fig. 3 DTA curves of two bio-oils under 10°C/min heating rate. (a) Bio-oil of rice husk; (b) bio-oil of corn

Table 2 Combustion characteristic parameters of bio-oil ($\beta = 10^\circ\text{C}/\text{min}$)

bio-oil sample		T_0/K	T_{\max}/K	$(d\alpha/d\tau)_{\max}/(\%/K)$	$(d\alpha/d\tau)_{\text{mean}}/(\%/K)$	V_∞
rice husk	air	365	395	-8.61	-0.923	96.95
	nitrogen	366	392	-8.93	-0.876	91.95
corn	air	367	393	-10.05	-0.938	98.45
	nitrogen	368	396	-9.13	-0.927	97.34

level of decomposition, and $\alpha = \frac{m_0 - m}{m_0 - m_\infty} \times 100\%$, m_0 and m_∞ respectively represent the initial and final mass of the sample; k is the constant rate of Arrhenius; E is the activation energy, J/mol; A is the frequency factor, s^{-1} ; R is the universal constant of gas, and $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$; T is the absolute temperature.

$f(\alpha)$ is the function relationship formula of the decomposition of the liquid and the reaction rate [10]. Generally, we assume that the function $f(\alpha)$ only has to do with the degree of response α , and nothing to do with temperature T and time t . For a simple reaction $f(\alpha) = (1 - \alpha)^n$, and n is the reaction order, so substituting $\beta = \frac{dT}{dt}$ into Eq. (1):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n. \quad (3)$$

Dealing with Eq. (3) using different methods can result in different expressions. We use the method of Coats-Redfern [11] to deal with Eq. (3), and through separation of variables, making integrals and taking approximations, we can obtain equations as follows:

$$n = 1; \ln \frac{-\ln(1 - \alpha)}{T^2} = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT}, \quad (4)$$

$$n \neq 1: \ln \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT}. \quad (5)$$

Table 3 Combustion kinetics parameters of bio-oil ($\beta = 10^\circ\text{C}/\text{min}$)

bio-oil sample	temperature range/K	n	fitting equation	correlation coefficient	$\ln A$ /min	E /(kJ/mol)
rice husk	280–430	$n = 1$	$Y = 3.13785 - 5953.97144X$	-0.98447	14.13225	49.50132
	430–655	$n = 2$	$Y = -2.28598 - 5093.82359X$	-0.92079	8.552389	42.35005
	655–850	$n = 1.5$	$Y = 27.13182 - 28409.65108X$	-0.97921	39.68889	236.19784
corn	280–430	$n = 1$	$Y = 2.52226 - 5668.32353X$	-0.98402	13.46749	47.12644
	430–655	$n = 2$	$Y = -3.03768 - 4762.23117X$	-0.90292	4.73338	39.59319
	655–850	$n = 1.5$	$Y = 19.60105 - 23126.42309X$	-0.98425	31.95237	192.27308

To the general reaction zone and most E , $2RT/E$ is much less than 1, so $(1 - \frac{2RT}{E}) \approx 1$, and then $\ln[\frac{AR}{\beta E}(1 - \frac{2RT}{E})]$ in Eqs. (4) and (5) can be seen as constant. So when $n = 1$, making a graph according to $g(\alpha) = \ln\frac{-\ln(1-\alpha)}{T^2}$ (Y axis) and $1/T$ (X axis); when $n \neq 1$, making a graph according to $g(\alpha) = \ln\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}$ (Y axis) and $1/T$ (X axis). We can get a beeline whose slope is $-R/E$ from the above two graphs (for the correct value of n). Then we can get the values of E and A through the slope and intercept. Through taking different values of n (1–3) and comparative analysis, we can get that the combustion process of bio-oil is a sub-reaction, and its reaction order and combustion characteristic parameters are shown in Table 3.

Table 3 shows that it is reasonable to describe the combustion kinetics of bio-oil by the kinetic model obtained through the method of sub-fitting. When the temperature range is 280 K–430 K, the reaction order is 1; when the temperature range is 430 K–655 K, the reaction order is 2; when the temperature range is 655 K–850 K, the reaction order is 1.5. The kinetics parameters through least squares are as follows: the frequency factor A of the rice husk bio-oil is, respectively, 1.373×10^6 , 5.179×10^3 , $1.725 \times 10^{17} \text{ min}^{-1}$ and the corresponding activation energy E is, respectively, 49.5, 42.4, 236.2 kJ/mol; the frequency factor A of the corn bio-oil is, respectively, 7.061×10^5 , 2.283×10^3 , $7.529 \times 10^{13} \text{ min}^{-1}$, and the corresponding activation energy E is, respectively 47.1, 39.6, 192.3 kJ/mol. From the view point of activation energy, the activation energy E of the third stage is higher than that of the first two phases, because the third stage is the burning stage, and the energy required to overcome it apparently increases and the activation energy also increases in performance [12]. Although the difference in organic components of biomass raw materials makes the combustion parameters of bio-oil obtained by pyrolysis slightly different, the combustion process is roughly the same. The activation energy E and the corresponding frequency factor A in this experiment provide necessary base data for the actual burning of bio-oil.

5 Conclusions

1) The combustion characteristic analysis of bio-oil shows that bio-oil is easy to volatilize and burn and the combustion process can be divided into three sections: the volatile endothermic stage, the transition stage and the burning exothermic stage. The corresponding DTG curve of bio-oil is also divided into three stages: the first stage is a narrow steamed peak, the second phase is a peak and the third stage is a wide steamed peak.

2) Using the method of Coats-Redfern, we can calculate the combustion kinetics parameters of bio-oil in air atmosphere, and determine the reaction order n and the corresponding activation energy E and frequency factor A in various temperature ranges. When the temperature range is 280 K–430 K, the reaction order is 1; when the temperature range is 430 K–655 K, the reaction order is 2; when the temperature range is 655 K–850 K, the reaction order is 1.5. In addition, the differences in activation energy E reflects the fact that different stages have different reaction mechanisms in the combustion process of bio-oil [12].

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