Study on the effect of drying conditions on the pyrolysis properties of rice husk

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Abstract. Drying can remove the moisture and volatile fraction from biomass to achieve the purpose of improving the pyrolysis performance of biomass feedstock. In this project, three different drying treatments (blast, vacuum and microwave) were applied to rice husk in order to investigate the effect of drying conditions on the pyrolytic properties of rice husk. Thermogravimetric experiments were performed on the materials at different heating rates (10℃/min, 20 ℃/min, 30 ℃/min). Then the TG and DTG plots were analyzed, and the kinetic parameters were solved and compared using the FWO method. Experimental studies have shown that the pyrolysis process of rice husk can be divided into three stages, namely the water loss stage, the pyrolysis stage, and the carbonization stage. At the same heating rate, the highest weight loss rate of rice husk was achieved after microwave drying, with a maximum weight loss rate of 97.1% at 20℃/min.In addition, with the increase in temperature rise rate, the characteristic temperature of rice husk of both blast drying and vacuum drying showed a changing trend of increase, and the TG and DTG graphs showed a movement toward the high-temperature side, while the characteristic temperature of rice husk after microwave drying was basically unchanged. The activation energy of all three dried rice husks was calculated by the FWO method to reach the maximum at a conversion rate of 0.6. The average activation energy of rice husks after microwave drying was much greater than that of the other two drying methods, indicating that microwave drying made rice husks more difficult to pyrolyze.

1 Introduction

With the rapid development of the global economy, energy consumption has increased dramatically, traditional non-renewable energy sources are becoming depleted, and the phenomenon of global warming is intensifying. Among renewable energy sources, biomass energy has attracted widespread attention and has been used at domestic and overseas because of its wide range of sources, environmental friendliness, and abundant reserves.[1] Pyrolysis is one of the most promising methods for the thermochemical conversion of biomass, which can be classified into electric heating, microwave heating, etc. according to the heating type.[2-3] Some scholars have shown that microwave pyrolysis has the advantages of high heating efficiency and non-contact heating, but the energy is not completely acting on the heated raw materials, resulting in relatively large energy losses. The drying treatment before biomass pyrolysis can improve the energy efficiency in the pyrolysis process.[4-7] Therefore, in this study, rice husk is selected as the research material, which is subjected to microwave drying, blast drying, and vacuum drying, and the effect of drying conditions on the pyrolysis characteristics of rice husk is investigated by performing thermogravimetric analysis of rice husk in a microcomputer differential thermal balance and calculating the kinetic parameters of pyrolysis using the integration method.

2 Materials and Methods

2.1 Materials and Instruments

The rice husk was taken from the rural area of Xinyang City, Henan Province, and crushed in a miniature electric grinder, and samples with a particle size of 100 μm or less were retained by sieving using a screen. The experimental raw materials were divided into three groups, and the first group used vacuum drying oven (Beijing Yiheng, DZF-6050) to dry for 12h; the second group used blast drying oven (Beijing Yiheng, DHG-9003) to dry for 24h; the third group used microwave oven (Midea M1-L213B) to dry for 5min.

2.2 Experimental methods

The instrument selected for thermogravimetric analysis was a microcomputer differential thermal balance （Beijing Hengjiu, HCT-1), as shown in Figure 1, including thermogravimetric (TG) and differential thermal (DTA) data acquisition systems. The TG

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measurement range is from 1 to 300 mg with an accuracy of 0.1μg; the temperature measurement range is from 25 to 1150℃with an accuracy of ±0.1℃, and the heating rate is from 0.1 to 70℃/min.The crucible material is Al_2O_3。

Fig. 1. Microcomputer differential thermal balance

After the power and cooling water are turned on and the machine is allowed to warm up for 30 min, about 10 mg of biomass is weighed and placed in the crucible. Nitrogen gas with a flow rate of 15 ml/min is introduced into the system, and the basic experimental parameters are entered into the thermal analysis software. The starting temperature was 25℃, the final temperature of pyrolysis was 900 ℃, and the ramping rates were set to 10 ℃/min, 20 ℃/min, and 30℃/min, respectively. The experimental system is automatically sampled, the TG curve and DTA curve are plotted by the computer, and the first-order derivative of the TG curve is done to derive the DTG curve.

2.3Theoretical Methods

The kinetics of pyrolysis is generally used to find the energy required for pyrolysis, the apparent activation energy E. In this experiment, the FWO method [8]is used to derive E under different conditions, and to visually compare the ease of pyrolysis of rice husk under different drying conditions by comparing the magnitude of E during pyrolysis of rice husk under different drying conditions.

The pyrolysis reaction of biomass can be described by the Arrhenius equation：

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

Where k is the rate constant; A is the prefactor, min^{-1}; E is the reaction activation energy, kJ/mol; R is the ideal gas constant, 8.314 J/(K • mol); T is the thermodynamic temperature,K.

And the kinetic equation for the non-homogeneous solid reaction：

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = \mathrm{k}(T) f(\alpha) \tag{2}$$

$$\alpha = \frac{\mathrm{m_0} - \mathrm{m_t}}{\mathrm{m_0} - \mathrm{m}_f} \tag{3}$$

The rate of temperature increase β is a constant，β=dT/dt

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{4}$$

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{B}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right) dT \tag{5}$$

Where α is the conversion rate of the pyrolysis feedstock; β is the heating rate, kJ/mol; $f(\alpha)$ is the reaction mechanism function of pyrolysis; $g(\alpha)$ is the conversion rate action function; t is time, s;

A further transformation of equation (5) yields,

$$\ln\beta = \ln\frac{AE}{RG(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{6}$$

The FWO method is performed by plotting the temperature T at equal α of the curve under different β about $\ln\beta \sim \frac{1}{T}$, After fitting, the slope of the graph line is 1.052E/R, which leads to E.

3Results and Analysis

3.1TG-DTG analysis

Taking the temperature rise rate of 10℃/min as an example, the TG and DTG curves of rice husk under different drying conditions are shown in Fig.2, which shows that the pyrolysis process of rice husk can be roughly divided into three stages:

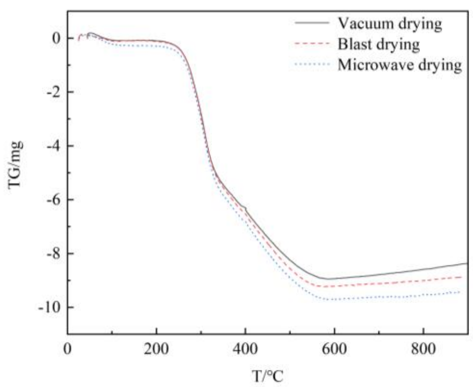
The first stage is the water loss stage, the temperature range is 30~100℃. The TG graph line decreases slightly, and the DTG graph line shows a very small weight loss peak, the weight loss rate can be understood as the water content of the sample, and the weight loss rate is below 1% because the water content of the material is very low after drying treatment.

The second stage is the pyrolysis stage with the temperature range of 100~500℃. The TG plot line decreases rapidly and the DTG plot line shows a more obvious shoulder-like peak.The initial stage of pyrolysis is mainly the separation of hemicellulose and cellulose pyrolysis, and the rate of weight loss is gradually accelerated with the increase of temperature, and the most intense weight loss occurs around 300℃, mainly the pyrolysis of cellulose into small molecule gas and large molecule condensable volatile fraction. The weight loss rate at this stage accounts for more than 80% of the total weight loss rate, so it is also the main stage of kinetic analysis.

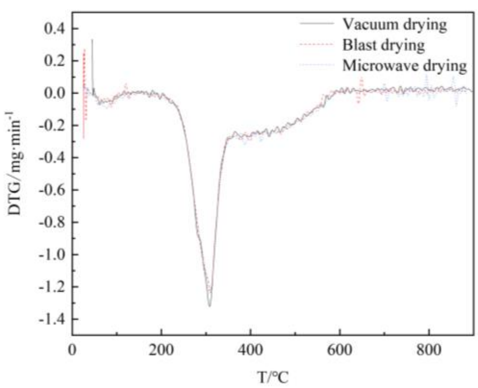
The third stage is the carbonization stage, the temperature interval is above 500℃. The pyrolysis has been completed, the TG graph line slowly decreases, the

DTG graph line gradually flattens and gradually tends to 0. The lignin in the sample slowly decomposes into solid carbon and ash.

The TG and DTG lines of rice husk under the three drying conditions have the same evolutionary trend, but there are also differences. In the TG line, the first stage of rice husk after microwave drying is more obvious than that under the other two drying methods, representing the most elimination of free water, adsorbed water and crystalline water in rice husk. The three lines in the first half of stage 2 almost overlapped, and the microwave drying graph line in the second half dropped more indicating that microwave drying was more favorable for the precipitation of volatile fraction. In the DTG plots, the plots of the three drying methods differed only in the peak of the shoulder peak. The vacuum drying plot had the lowest temperature and the largest peak area, and the Blast drying had the highest temperature and the smallest peak area.



(a)TG curve



(b)DTG curve

Fig.2. TG and DTG curves of rice husk under different drying conditions with heating rate of 10℃/min

3.2 Effect of drying conditions on the pyrolysis process of rice husk

In order to compare the differences of rice husk in each stage of pyrolysis under different pyrolysis conditions, several temperature characteristic points are defined as follows[9]. (1) Ignition temperature: It is the intersection of the point with the largest slope on the TG curve and the extension of the front step baseline. (2) peak temperature: the temperature corresponding to the point on the DTG curve with the largest absolute value of the peak. (3) Burnout temperature: the intersection point between the point with the largest slope on the TG curve and the extension line of the backstep baseline. The characteristic temperatures of rice husk under different drying conditions are shown in Fig. 3.

With the increase of the heating rate, all three characteristic temperatures of Blast drying and vacuum drying showed the same trend of change. The fire temperature of rice husk after Blast drying and vacuum drying increased by 6.1℃ and 5.3℃ on average, and the combustion temperature increased by 9.2℃ and 4.2℃ on average, and the TG line showed an overall shift toward high temperature measurement, and the peak temperature increased by 1.4℃ and 2.3℃ on average, and the DTG line showed a larger peak and higher peak area. The main reason for this change is: the increase in temperature rate makes the temperature gradient inside the sample becomes larger, and the diffusion of the product is blocked thus producing the phenomenon of thermal lag. However, the microwave drying of rice husk three characteristic temperatures basically do not change with the change in temperature rate, mainly because microwave drying increases the specific area of raw materials, enriching the void structure of the rice husk, these changes are conducive to the precipitation of volatile fraction in the pyrolysis process volatile fraction stays for a very short time.

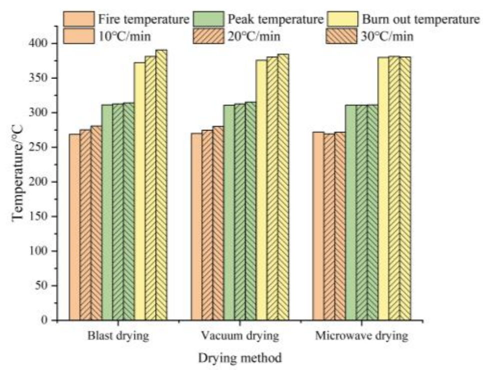
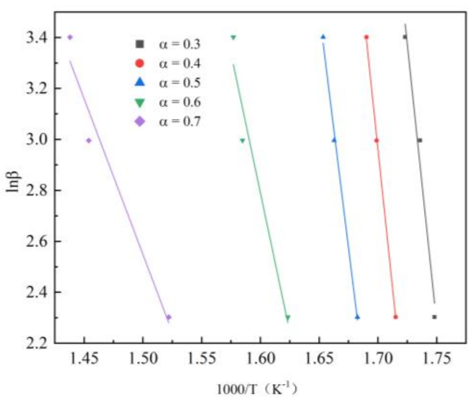


Fig.3. Characteristic values of rice husk temperature under different drying conditions

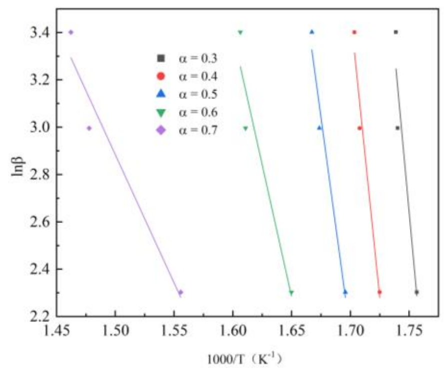
After calculation, it can be obtained that the weight loss rate of rice husk after microwave drying under the conditions of temperature rise rate of 10℃/min, 20℃/min and 30℃/min is 88.9%, 97.1% and 93.3% respectively, and the weight loss rate of rice husk after Blast drying is 82.2%, 93.8% and 87.5%, and the weight loss rate of rice husk after vacuum drying is 77.9%, 82.1% and 92.7%. The weight loss rate of rice husk after microwave drying at the same heating rate is always greater than the weight loss rate of rice husk after Blast drying and vacuum drying. The reason for this situation is due to microwave radiation to polarize the molecules and increase the kinetic energy, the cell wall pore structure will be destroyed, the fiber organization from dense to sparse, porosity increased, and the biomass macromolecules occur in different degrees of chemical bond breakage, which promotes the pyrolysis of cellulose[10]. In addition, the weight loss rate of rice husk after vacuum drying increased with the increase of the heating rate, and the trend of increasing and then decreasing after the increase of the heating rate appeared in the Blast drying and microwave drying.

3.3 Effect of drying conditions on the pyrolysis process of rice husk

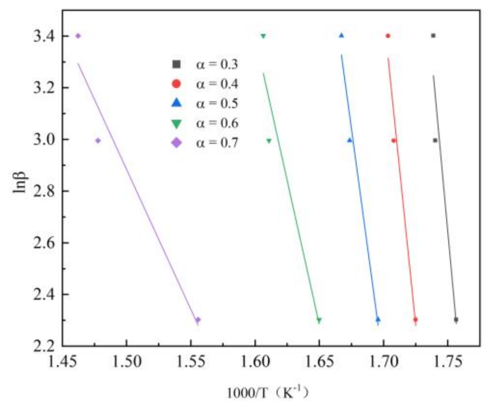
The apparent activation energy of rice husk under three drying conditions was calculated by using the FWO method, and the original data used the pyrolysis weight loss data of rice husk under three heating rates (10℃/min, 20 ℃/min, 30℃/min), and the fitted graphs were fitted by using Origin software, and the fitted graphs are shown in Fig.4. The activation energy was obtained by calculating the slope of five conversion lines and then taking the average value.



(a)Blast drying



(b)Vacuum drying



(c)Microwave drying

Fig. 4. Fitted straight line of FWO method at different conversion rates

Table 1. The activation energies under different drying conditions were calculated by FWO method.

Conversion rate/E(kJ/mol)	Blast drying	Vacuum drying	Microwave drying
0.3	96.42	85.51	131.66
0.4	172.68	176.24	339.83
0.5	293.84	289.25	537.41
0.6	346.55	380.93	655.95
0.7	346.23	370.64	521.36
Average E	251.14	260.51	437.24

From the above table, it can be seen that the apparent activation energy of all three dried treated rice husks reached the maximum value at the conversion rate of 0.6, which were 346.55 kJ/mol, 380.93 kJ/mol, and 655.95 kJ/mol, respectively. This is because when the conversion ratio is higher than 0.6, the apparent activation energy appears to decrease as the pyrolysis temperature increases and the main pyrolysis components such as internal cellulose and hemicellulose have been completely pyrolyzed and do not require more energy for pyrolysis. The average activation energies of rice husk after the three drying treatments were 346.55 kJ/mol, 380.93 kJ/mol, and 655.95 kJ/mol, respectively. The average activation energy values of rice husk after vacuum and Blast, both conventional drying treatments, are close, and the average activation energy of rice husk after microwave treatment is much greater than the former, because after microwave drying, the original structure of lignin in the material cellulose is destroyed, so that it separates from the internal tissue of biomass, thus increasing the energy required for pyrolysis, which leads to an increase in the average activation energy and makes pyrolysis more difficult. To sum up, the size of the difficulty of pyrolysis is Microwave drying > Vacuum drying > Blast drying.

4 Conclusion

Through the study and kinetic analysis of the pyrolysis process of rice husk under three drying conditions, the following conclusions were obtained：

(1)The pyrolysis process of rice husk can be divided into three stages: water loss stage, pyrolysis stage, and carbonization stage, among which the pyrolysis stage is the main stage of kinetic analysis.

(2)Under the same heating rate, the weight loss rate of rice husk after drying was the highest due to microwave drying enriched the void structure of rice husk, and the weight loss rate could reach 97.1% when the heating rate was 20°C/min. The weight loss rate of rice husk after microwave and blast drying showed a trend of increasing and then decreasing with the increase of the heating rate, while the rice husk after vacuum drying would increase with the increase of the heating rate.

(3)The characteristic temperature of rice husk after blast drying and vacuum drying increased with the increase of the heating rate, and the TG and DTG graphs showed a shift toward the high temperature side. As the original structure of lignin in the material cellulose was destroyed, the energy required for pyrolysis was increased, and the characteristic temperature of rice husk after microwave drying basically did not change with the increase of the heating rate.

(4)The FWO method calculates the average apparent activation energy of rice husk after blast, vacuum, and microwave drying as 346.55 kJ/mol, 380.93 kJ/mol, and 655.95 kJ/mol, respectively, indicating that microwave drying makes rice husk more difficult to pyrolyze.

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