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Heat/mass transfer characteristics and nonisothermal drying kinetics at the first stage of biomass pyrolysis

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Abstract Biomass pyrolysis can be divided into three stages: moisture evaporation, main devolatilization, and continuous slight devolatilization. This present study focuses on the heat and mass transfer characteristics of biomass in the first pyrolysis stage, which takes place in the range of room temperature to 150 °C. Thermalgravimetric experiments of rice husk and cotton stalk were performed by a synchronic thermal analyzer (TG/DSC). Four nonisothermal drying models were obtained from common isothermal drying models in order to describe the drying behavior of agricultural products. The moisture content of biomass decreased rapidly as the temperature increased and an apparent water loss peak was observed in the temperature range of 65–75 °C. DSC could be regarded as the superposition of three parts: heat flow from moisture evaporation, heat flow from the heat capacity of unevaporated moisture, and heat flow from the heat capacity of dry base biomass. The heat requirements for the dehydration of 1 kg rice husk and cotton stalk were 251 and 269 kJ, respectively. Nonisothermal drying models were evaluated based on the coefficient of determination (R^2) and reduced chi-square (χ^2). Page model was found to be the best for describing the nonisothermal drying kinetics. The values of activation energy were determined to be 9.2 and 15.1 kJ/mol for rice husk and cotton stalk, respectively.

Keywords Biomass · Heat and mass transfer · Nonisothermal drying · Activation energy

Introduction

The first stage of biomass pyrolysis corresponds to moisture evaporation [1], which takes place in the range of room temperature to 150 °C. Owing to the relatively low temperature, biomass has not undergone thermal decomposition, and volatile matter has not been released. Heat and mass transfer in this stage could be expressed as follows: biomass continues to heat up at the constant heating rate and the moisture diffuse rapidly toward the surface to satisfy the need for moisture evaporation.

Subsequent stages of biomass pyrolysis correspond to thermal decomposition of organic components (cellulose, hemicellulose and lignin) [2]. In recent years, extensive experiments have been performed to study the decomposition characteristics and reaction kinetics of biomass. Many pyrolysis parameters, such as heating rate [3], particle size [4], gas atmosphere [5], flow rate [6], catalyst [7], moisture content [8], and sample mass [9], have also been actively studied. However, these studies are mainly focused on the main devolatilization stage (150–450 °C). The characteristics of biomass in the first pyrolysis stage are usually ignored and sometimes eliminated.

The moisture content of biomass material is an important property used in the pyrolysis utilization of biomass, because the moisture levels not only have a considerable effect on the storage, transport, and energy density of biomass [10], but also significant affect biomass performance and reliability in the decomposition process as well as the design of pyrolysis reactors. Previous studies have shown that high-moisture-content biomass has a much lower net energy density by mass, due to the noncombustibility of the water. Transport is less efficient, as a fraction of the load is water, which required energy to evaporate in the ensuing utilization. Storage is also less

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efficient, with less net energy available. What is worse, the humid environments caused by moisture evaporation of materials would possibly make biomass mildew and deterioration in long-term storage.

Particularly, the water included in biomass would also recondense in pyrolysis liquid product (bio-oil). The presence of water has some negative effects on the oil properties. It reduces the calorific value and increases the ignition difficulties as well as diminishes the stability of bio-oil [11].

As a consequence, drying pretreatment of biomass material to pyrolysis is usually desirable and in some cases essential, in order to minimize the effect of moisture on biomass pyrolysis. Therefore, it is necessary to research the biomass characteristics, such as heat transfer, mass transfer and nonisothermal drying kinetics, during the moisture evaporation stage.

Currently, only a few literatures involve moisture evaporation in biomass pyrolysis research. He et al. [12] performed TG/DSC experiments on biomass using a synchronic thermal analyzer and obtained the heat requirements of different pyrolysis stages. The results showed that 1 kg wheat stalk (dry base) absorbed 243 and 558 kJ when the temperature was increased from room temperature to 440 and 773 K, respectively. Artiaga et al. [13] divided the DSC curves of biomass pyrolysis into two stages: drying stage (room temperature 200 °C) and pyrolysis stage (200–500 °C). In addition, they indicated that the heat energy absorbed during the drying stage was used not only for water evaporation but also warming-up biomass. Cai et al. [14] described the dehydration process of wheat stalk and corn stalk with the Weibull model and determined the heat flow from water contributions. In their calculations, the constant specific heat capacity of water was assumed.

Investigation of the drying kinetics and its parameters contributes to further information of heat and mass transfer [15]. As biomass is linear heating in the thermogravimetric analyzer, the moisture continuously absorbs energy and then evaporates. However, not all water molecules can be turned to vapor and released. Only the water molecules that have obtained sufficient energy for gasification can undergo the transition [16]. This level of gasification energy can be regarded as the activation energy required for biomass to dry. Previous study has shown that the higher the drying activation energy the more heat requirement in the drying process [17].

The range of this study is limited to the first stage of biomass pyrolysis, on which a scarce attention has been focused. In this present work, rice husk and cotton stalk, two of the main agricultural products waste in China, were used as experimental biomass materials. TG/DSC experiments were performed by a synchronic thermal analyzer for a quantitative understanding the relationship between heat transport and mass transport. In the following section, a method was presented to fit the TG data of water evaporation to the nonisothermal drying models which derived from some isothermal drying models. Moreover, the heat flow from moisture evaporation, unevaporated moisture and dry base biomass were calculated.

Experimental

Materials

Rice husk and cotton stalk were obtained from local farm. The varieties of rice husk and cotton stalk used in this study are *Oryza sativa* ssp. indica and *Gossypium hirsutum*, respectively. Prior to the experiments, the materials were ground in a high speed rotary cutting mill. The particles with the size of 0.125–0.3 mm were chosen for experiments. The results of ultimate and proximate analyses are listed in Table 1.

Thermal analysis

The pyrolysis experiments were using a synchronic thermal analyzer (SDT Q600, TA, USA), which simultaneously provides true mass change (TG) and true differential heat flow (DSC) on the same sample. For each experiment, about 5 mg of the material was chosen and a heating rate of 20 °C/min with a nitrogen flow rate of 100 mL/min was adopted. A computer connected to the thermal analyzer automatically recorded the mass changes and heat flow, and then processed the data. A blank experiment was performed under the same conditions before the actual experiment to eliminate the influence of system error on the experiment result. All experiments were repeated three

Table 1 Ultimate and proximate analyses of biomass

Sample	Ultimate analysis/%					Proximate analysis/%			
	[C]	[H]	[N]	[O]	[S]	M	V	FC	A
Rice husk	45.32	5.56	0.49	32.85	0.15	6.31	61.08	16.98	15.63
Cotton stalk	39.76	5.87	1.06	39.12	0.22	6.95	68.69	20.39	3.97

times, and the mean of the two closer values were considered.

Nonisothermal kinetics analysis

The first stage of biomass pyrolysis can be regarded as the nonisothermal drying process of biomass at a linear heating rate. Isothermal drying kinetics has been studied extensively. Table 2 lists four common isothermal drying models. To examine the nonisothermal drying process, it is necessary to convert the mathematical models in Table 2 into nonisothermal drying models.

On the basis of the TG data for drying, the moisture ratio (*MR*) was calculated using the following equation:

$$\mathrm{MR} = \frac{M - M_\mathrm{e}}{M_0 - M_\mathrm{e}} \tag{1}$$

where M is the moisture content at temperature T, M_0 is the initial moisture ratio, and M_e is the moisture ratio at the end of the drying process. Given that the mass loss rate approaches zero at 150 °C in DTG curve, this study takes 150 °C as the drying ends temperature, at which M_e equals 0 and thereby MR can be simplified to

$$\mathrm{MR} = \frac{M}{M_0} \tag{2}$$

The nonisothermal TG data for materials were converted to the corresponding MR data according to Eq. 2. In this case, MR was a function of temperature, while the MR of the isothermal drying model was a function of time under a given temperature.

The relationship between drying constant K and temperature T could be described by the Arrhenius-like formula [17]:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where k_0 is the pre-exponential factor, E is the drying activation energy, R is the universal gas content, and T is the absolute temperature.

The temperature/time relationship under programmed heating can be described as

$$T = T_0 + \beta t \tag{4}$$

Table 2 Four common isothermal drying kinetics models

Model number	Model	Model equation	Model parameters
1	Page	$\mathrm{MR} = \exp(-kt^n)$	k n
2	Newton	$\mathrm{MR} = \exp(-kt)$	k
3	Logarithmic	$\mathrm{MR} = a + b\exp(-kt)$	a k b
4	Henderson	$\mathrm{MR} = a\exp(-kt)$	a k

Table 3 Four nonisothermal drying kinetics models

Model number	Model	Model equation
1	Page	$\mathrm{MR} = \exp\left[-k_0 \exp\left(-\frac{E}{RT}\right)\left(\frac{T-T_0}{\beta}\right)^n\right]$
2	Newton	$\mathrm{MR} = \exp\left[-k_0 \exp\left(-\frac{E}{RT}\right)\frac{T-T_0}{\beta}\right]$
3	Logarithmic	$\mathrm{MR} = a + b\exp\left[-k_0 \exp\left(-\frac{E}{RT}\right)\frac{T-T_0}{\beta}\right]$
4	Henderson	$\mathrm{MR} = a\exp\left[-k_0 \exp\left(-\frac{E}{RT}\right)\frac{T-T_0}{\beta}\right]$

where T_0 is the initial drying temperature and β is the heating rate.

The equations above were introduced to Table 2 to obtain the nonisothermal drying models listed in Table 3.

Model fitting

Nonisothermal drying models (Table 3) were fit to the TG data, and the model parameters were determined using nonlinear regression analysis. The parameters used to evaluate goodness of fit were the coefficient of determination (R^2) and the reduced chi-square (χ^2) between the experimental and predicted MR values. The reduced chi-square (χ^2) is calculated as following:

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(\mathrm{MR}_{\mathrm{pre},i} - \mathrm{MR}_{\mathrm{exp},i}\right)^2}{N - n} \tag{5}$$

where $\mathrm{MR}_{\mathrm{pre},i}$ and $\mathrm{MR}_{\mathrm{exp},i}$ are experimental and predicted moisture ratios, respectively, N is number of observations, and n is number of drying constants. The best model describing the nonisothermal drying characteristics of rice husk and cotton stalk was chosen as the one with the highest coefficient of determination and the least reduced chi-square.

Results and discussion

Thermogravimetric curve analysis

The results of the thermogravimetric experiments are presented in Figs. 1 and 2 for rice husk and cotton stalk, respectively. It can be observed that, biomass pyrolysis process consists of three stages: moisture evaporation (Stage I), main devolatilization (Stage II), and continuous slight devolatilization (Stage III) [18]. In the first process of mass loss (Stage I), the moisture content drops rapidly as the temperature rises. An apparent mass loss peak is observed in the temperature range of 65–75 °C, which due to considerable moisture evaporation. When the

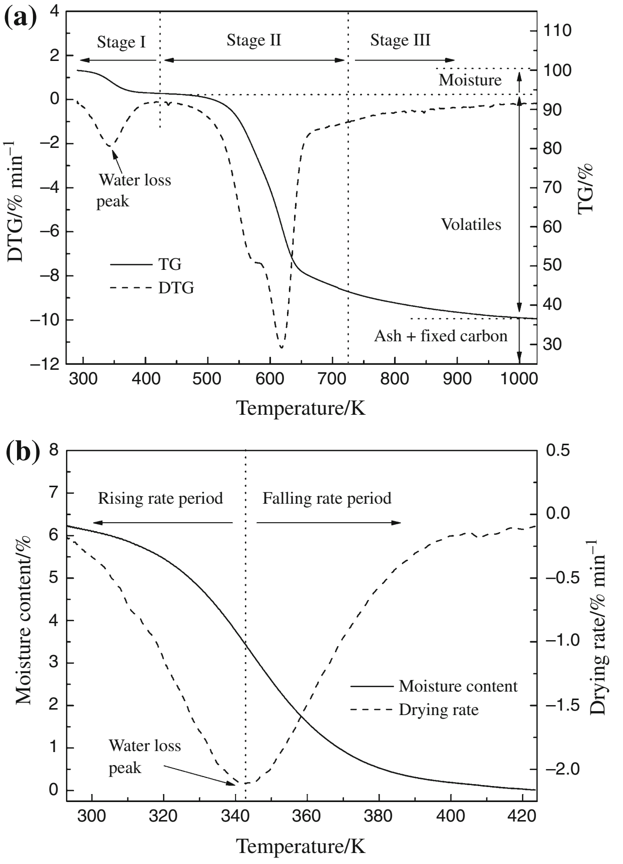

Fig. 1 Thermogravimetric curve of rice husk at heating rate of 20 °C/min **a** TG/DTG curve of pyrolysis process (Stage I, Stage II, Stage III); **b** variation of moisture content and drying rate with temperature in the first pyrolysis process (Stage I)

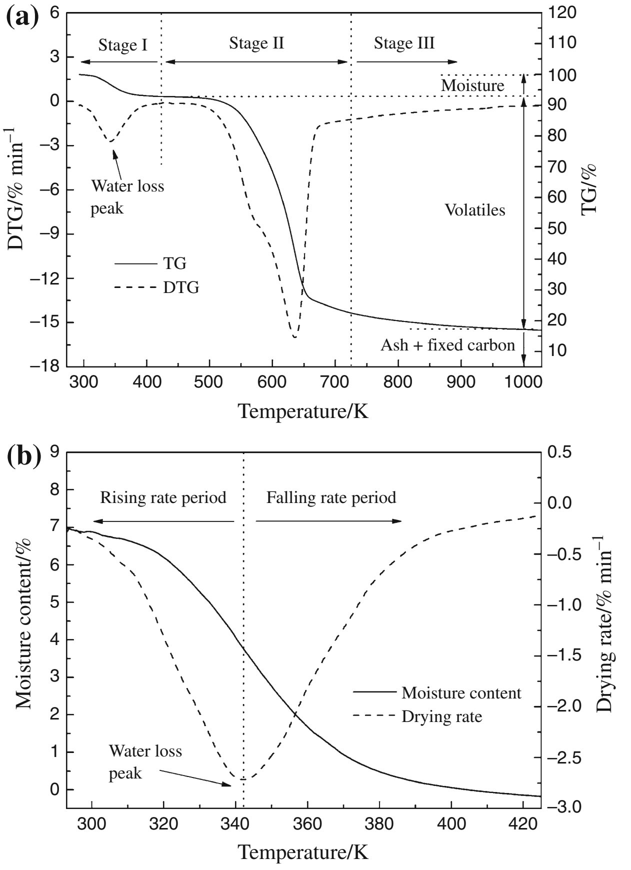

Fig. 2 Thermogravimetric curve of cotton stalk at heating rate of 20 °C/min **a** TG/DTG curve of pyrolysis process (Stage I, Stage II, Stage III); **b** variation of moisture content and drying rate with temperature in the first pyrolysis process (Stage I)

temperature approaches 150 °C, the TG/DTG curves become flat and the thermal decomposition of organic ingredients of biomass gradually begins. Therefore, 150 °C is generally regarded as the temperature at which dehydration ends.

When the temperature exceeds 150 °C, a slow process of depolymerization and restructures occur with slight mass loss of materials. Afterward, the materials go through a complex thermal chemical reaction. A large amount of volatile matter is released and the TG curve drops sharply [19]. Numerous studies have focused on this main devolatilization process [20]. The final pyrolysis process involves the slow decomposition of residues (mainly lignin), in which the TG curve is relatively flat [21].

It is particularly noted that, free water in biomass is basically removed after the moisture evaporation stage. However, the pyrolysis gas released from the subsequent stages of biomass pyrolysis always contains a large amount of water vapor. This is because the crystallized water of biomass is released under high temperature and a lot of water is generated from a series of thermal chemical reactions of the organic components.

Heat and mass transport

Moisture transport characteristics

Figures 1b and 2b show the relationship between moisture content and temperature in the first biomass pyrolysis stage (Stage I in Figs. 1a, 2a) for rice husk and cotton stalk, respectively. It is obvious from Figs. 1b and 2b that the constant rate period was absent and apparent water loss peaks take place at 69 and 72 °C for rice husk and cotton stalk, respectively. Therefore, taking the water loss peak as the demarcation point, the moisture evaporation stage can be divided to rising rate period and falling rate period.

The change in water loss rate is closely related to the bonding force between water and biomass. Water in materials can be identified as two categories based on different bonding methods: free water (adhering to the grain surface of materials and existing in pores of diameters greater than 10^{-5} cm) and bound water (coagulated, adsorbed, or penetrating into the pores and cells inside the grains of biomass). Free water has a weak bonding force with the materials and evaporates before the temperature reaching 90 °C. However, bound water is distributed inside the materials, with strong bonding force, and would be completely separated only at the temperature above 120 °C.

During the rising rate period, free water rapidly diffuses outward under the temperature and steam pressure gradient to satisfy the need of surface water for gasification. A substantial amount of water escapes as steam and the drying rate increase rapidly. Therefore, before the appearance of the water loss peak, this drying process can be regarded as the evaporation of free water in biomass.

As the drying process continues, less free water on the biomass surface is available and the bound water participates in the diffusion process. The rate starts to decrease and the falling rate period begins, which often happens in the later drying stage for many agricultural products [17]. In this period, the drying rate is dominated by the moisture diffusion from the inside to the surface of the biomass. Due to the more resistance, bound water needs more energy and time to escape. When the evaporation of bound water is complete, the drying rate approaches zero.

The water loss trend of cotton stalk is quite similar to rice husk. However, the water loss rate of cotton stalk is greater than that of rice husk, which is possibly related to the internal structure and surface density of the materials. The time required in falling rate period is much longer than that in rising rate period. It is noted that these times are not fixed. They depend on energy supplied, which rest with the heating rate of TG.

Heat transfer characteristics

The heat requirement in the first stage of biomass pyrolysis can be determined through the integration of DSC curve. The DSC curves and heat requirements are shown in Fig. 3. It is obvious from Figs. 1, 2, and 3 that the DSC and DTG curves clearly have a correspondent relationship. The endothermic peak in DSC curve appears around the water loss peak in DTG curve and the heat flow changes along with the change in drying rate. The result of DSC integration indicates that the heat requirements of rice husk and cotton stalk during the moisture evaporation stage are 253 and 282 kJ/kg, respectively.

In the paper of He et al. [13], the energy requirements to raise a biomass sample from room temperature to the reaction temperature have been obtained. In their calculations, 243, 214, 208, and 211 kJ were required during the drying stage (room temperature 157 °C) and 523, 459, 646 and 385 kJ were required to increase the temperature from 30 to 400 °C, for 1 kg of dried wheat straw, cotton stalk, pine, and peanut, respectively. However, these results were based on dried biomass and the effect of moisture evaporation on the energy requirement of wet biomass was ignored. Compared with the results of wet biomass (rice husk and cotton stalk) in this study, it can be concluded that the heat requirement in the moisture evaporation stage accounts for probably more than 50% of total heat requirement in the pyrolysis process. That is, a considerable amount of energy required during the entire pyrolysis process is not used for thermal decomposition, but for moisture removal in raw biomass materials.

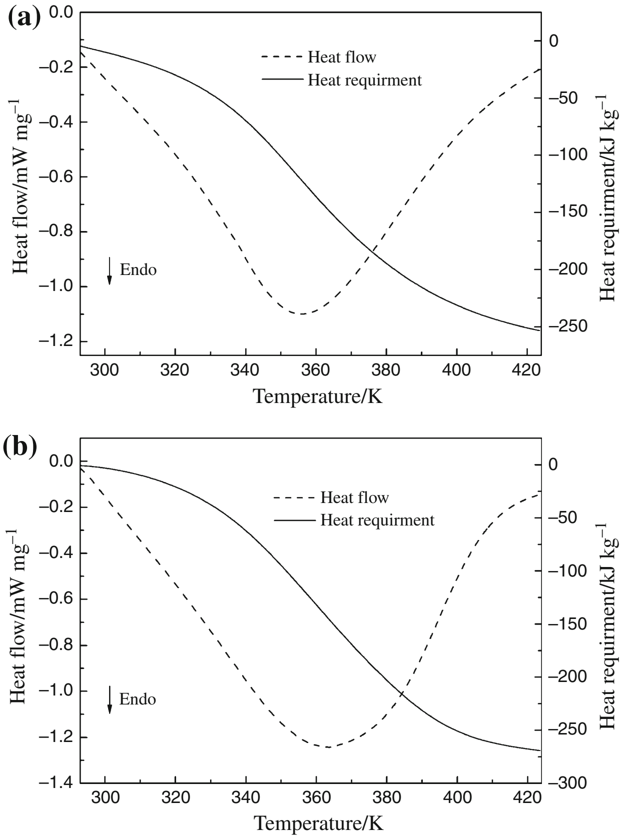

Fig. 3 DSC and heat requirement curve of **a** rice husk and **b** cotton stalk

Nonisothermal drying kinetics

The four mathematical models in Table 3 were used to evaluate the relationship between moisture ratio and drying temperature of biomass. The model constants were estimated using Origin8.0 software (OriginLab Inc., USA) according to the nonlinear modeling procedure. The details of statistical analysis for four models are presented in Table 4. Acceptable R^2 of greater than 0.98 are obtained for four models fitted to all drying runs. As observed in Table 3, Page model yields higher R^2 and lower χ^2 values

Table 4 Statistical results from nonisothermal drying models for biomass

Model	Rice husk		Cotton stalk	
	R^2	χ^2	R^2	χ^2
Page	0.9993	0.00006	0.9996	0.00007
Newton	0.9861	0.00031	0.9835	0.00021
Logarithmic	0.9825	0.00011	0.9882	0.00016
Henderson	0.9906	0.00009	0.9913	0.00015

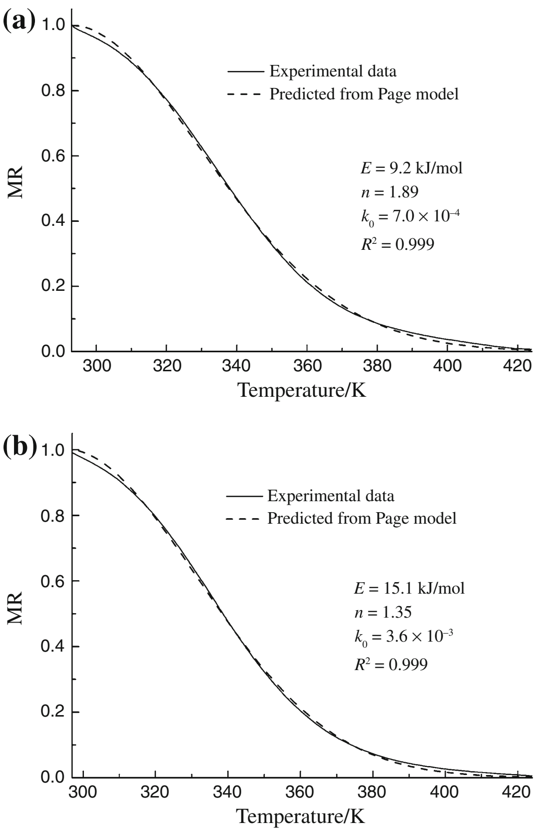

Fig. 4 Comparison of experimental and predicted moisture ratio by Page model: **a** rice husk, **b** cotton stalk

than the other three models. Therefore, Page model provides the best results in describing the nonisothermal drying characteristics of rice husk and cotton stalk.

Figure 4 shows the variations of experimental and predicted moisture ratios by Page model with drying temperature. According to Table 4 and Fig. 4, Page model satisfactorily fits the drying kinetics of rice husk and cotton stalk. Similar results have been reported for wheat straw in the literature [17].

The parameter values such as the drying activation energy of Page model are also presented in Fig. 4. The calculated values of activation energy for rice husk and cotton stalk are 9.2 and 15.1 kJ/mol, respectively. The drying activation energy of cotton stalk is higher than that of rice husk. The above-mentioned DSC experiment results have also shown that heat requirement of cotton stalk is higher than that of rice husk. This phenomenon indicated that cotton stalk with higher drying activation energy needs more heat for drying than rice husk. These results are consistent with the previous study in the literature [17].

Relationship between heat and mass transfer

Moisture transport is always accompanied by energy transfer. In this section, the relationship between heat and mass transfer is presented.

Two factors are contributory to the heat flow of biomass: biomass (dry base) and water. The heat capacity of dry base biomass changes minimally as temperature increases. Hence, the change in heat flow of dry base biomass is minimal under programmed heating. However, the heat flow from the water contribution is complex. On one hand, moisture is evaporating, and on the other, the unevaporated moisture is absorbing heat to increase its temperature. Thus, the heat flow of raw biomass can be decomposed into three components: the first corresponds to water evaporation, the second to unevaporated water, and the third to dry base biomass.

Therefore, total heat flow

= heat flow from the water contributions + heat flow from the dry base biomass contributions
= heat flow from water evaporation + heat flow from the heat capacity of unevaporated water + heat flow from the heat capacity of dry base biomass

The above-mentioned equation can be expressed as follows:

$$\begin{aligned} Q &= Q_{\mathrm{we}} + Q_{\mathrm{wc}} + Q_{\mathrm{s}} \\ &= r\frac{\mathrm{d}M}{\mathrm{d}t} + MC_{\mathrm{pw}}\frac{\mathrm{d}T}{\mathrm{d}t} + (1 - M_0)C_{\mathrm{ps}}\frac{\mathrm{d}T}{\mathrm{d}t} \\ &= \beta\left(r\frac{\mathrm{d}M}{\mathrm{d}T} + MC_{\mathrm{pw}} + (1 - M_0)C_{\mathrm{ps}}\right) \end{aligned} \tag{6}$$

where $\mathrm{d}T/\mathrm{d}t$ is the heating rate β, K/s; Q is the total heat flow from biomass per unit sample mass, W/kg; Q_{we} is the heat flow from water evaporation per unit sample mass, W/kg; Q_{wc} is the heat flow from heat capacity of unevaporated water per unit sample mass, W/kg; Q_{s} is the heat flow from heat capacity of dry base biomass per unit sample mass, W/kg; C_{pw} is the specific heat capacity of water, J/(kg K); C_{ps} is the specific heat capacity of biomass, J/(kg K); r is the evaporation enthalpy of water, J/kg.

Since Page model predicts the experimental data of water evaporation very well, the moisture content of biomass in Eq. 6 can be replaced as follows:

$$M = M_0\mathrm{MR} = M_0\exp\left[-k_0\exp\left(-\frac{E}{RT}\right)\left(\frac{T-T_0}{\beta}\right)^n\right] \tag{7}$$

Origin 8.0 software was used to calculate the differential of M (dM/dT). The variations of r, C_{ps} and C_{pw} with temperature (20–150 °C) are very small. Thus, r of 2.418×10^6 J/kg, C_{ps} of 4.187 J/(kg K), and C_{pw} of 0.9 J/(kg K) for biomass, were assumed.

The calculated results of heat flow and heat requirements from the three components are shown in Figs. 5 and 6 for rice husk and cotton stalk, respectively. It is clear from Figs. 5a and 6a that the heat flow from the heat capacity of unevaporated water is almost negligible compared with that from water evaporation. When the temperature exceeds 100 °C, the heat requirement of water evaporation is lower than that of dry base biomass owing to a substantial amount of water has evaporated. Figures 5b and 6b show that the calculated heat requirements for drying rice husk and cotton stalk are 290 and 303 kJ/kg, respectively. The percentages of the three components in the total heat requirements are listed in Table 5. It is proved that heat required for water evaporation is clearly far greater than that in the other two components. Considering the important role played by moisture, the study on the heat and mass transfer of biomass should not ignore the effect of the moisture evaporation, which is of key importance not only for a quantitative understanding of the process but also in the design of biomass pyrolysis reactors.

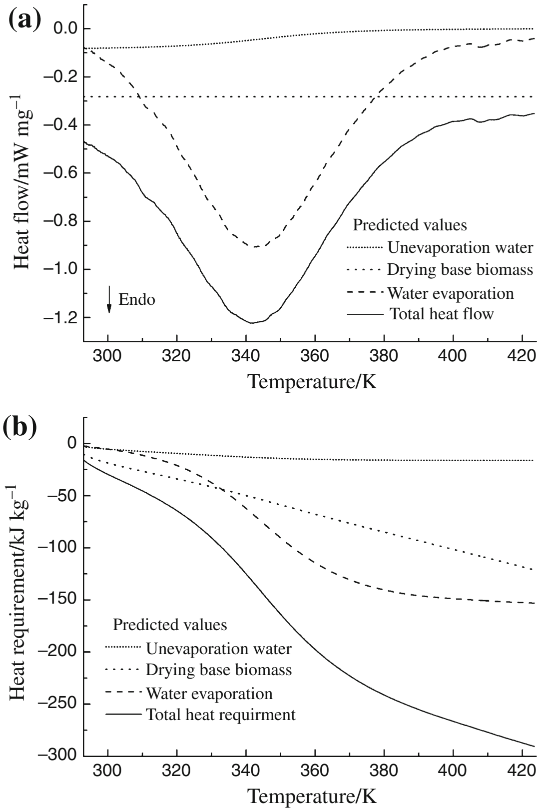

Fig. 5 Calculation of heat flow (**a**) and heat requirement (**b**) of rice husk during the first pyrolysis stage

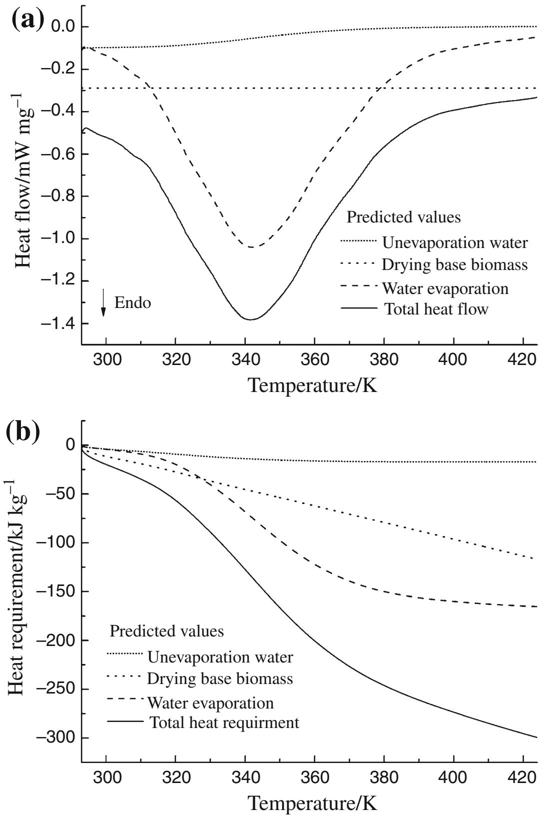

Fig. 6 Calculation of heat flow (**a**) and heat requirement (**b**) of cotton stalk during the first pyrolysis stage

Table 5 The percentages of the three components in the total heat requirements

Sample	Water evaporation/%	Unevaporated water/%	Dry base biomass/%
Rice husk	51	43	6
Cotton stalk	56	39	5

Comparison of experimental and calculated results of heat requirement, it can be found that the calculated heat requirements of rice husk and cotton stalk are, respectively, 16 and 11% higher than the experimental requirements. This difference may be attributed to three factors: (1) the moisture content of biomass is considerably affected by the environment, so that it may absorb some heat before the thermal analyzer began working; (2) baseline drift inevitably occurs during the experiment, and calculation error would occur when calibrating the baseline and determining the peak area; (3) data error for the model also affects the calculated result. Nevertheless, the calculated results approach the experimental values and reflect properly the changing trend of heat flow and requirement, which indicate the reliability of the calculation.

Conclusions

The moisture evaporation stage is the first process of biomass pyrolysis. As the temperature rises, the moisture content rapidly decreases, and an apparent mass loss peak appears in the range of 65–75 °C. Moisture transport is accompanied by heat transfer. DSC can be regarded as the superposition of heat flow from water evaporation, heat flow from the heat capacity of unevaporated water, and heat flow from the heat capacity of dry base biomass. The heat requirements of rice husk and cotton stalk are 251 and 269 kJ/kg, respectively, the main part of which corresponds to water evaporation.

Four nonisothermal drying models were developed to fit the experimental data of *MR* versus temperature for rice husk and cotton stalk. Page model is the best model for describing the nonisothermal drying process, with the highest R^2 and the lowest χ^2. The values of drying activation energy are 9.2 and 15.1 kJ/mol for rice husk and cotton stalk, respectively.

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