



In-depth investigation on the pyrolysis kinetics of raw biomass. Part I: Kinetic analysis for the drying and devolatilization stages



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HIGHLIGHTS

- ▶ Two different stages were shown in the pyrolysis process of biomass.
- ▶ Nonisothermal Page model is the best model for describing the drying kinetics.
- ▶ DAEM is not adequate for kinetics analysis in the first stage of biomass pyrolysis.
- ▶ Three ranges of activation energy are identified for the whole pyrolysis process.

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ABSTRACT

An in-depth investigation was conducted on the kinetic analysis of raw biomass using thermogravimetric analysis (TGA), from which the activation energy distribution of the whole pyrolysis process was obtained. Two different stages, namely, drying stage (Stage I) and devolatilization stage (Stage II), were shown in the pyrolysis process in which the activation energy values changed with conversion. The activation energy at low conversions (below 0.15) in the drying stage ranged from 10 to 30 kJ/mol. Such energy was calculated using the nonisothermal Page model, known as the best model to describe the drying kinetics. Kinetic analysis was performed using the distributed activation energy model in a wide range of conversions (0.15–0.95) in the devolatilization stage. The activation energy first ranged from 178.23 to 245.58 kJ/mol and from 159.66 to 210.76 kJ/mol for corn straw and wheat straw, respectively, then increasing remarkably with an irregular trend.

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1. Introduction

The moisture content of fresh biomass can be very high. After a long period of natural stacking or sun drying, the moisture content generally ranges between 0.05 and 0.15 kg of water/kg wet matter. These raw materials are the most common feedstocks for pyrolysis utilization. After undergoing forced drying at 105 °C for 12 h, for example, the moisture content of biomass can reach below 2%. Numerous pyrolysis studies have used this dry-basis biomass for experimental research and kinetic analysis (Dong et al., 2012; Sonobe and Worasuwanarak, 2008; White et al., 2011). Nevertheless, pyrolysis study should be performed on raw biomass, because water is its natural component and has an important influence on biomass pyrolysis (Demirbas, 2004). The drying data of the whole pyrolysis process should also be considered. Previous studies have shown that the whole pyrolysis process of raw biomass obtained by TGA presents different stages (Cai and Liu, 2007; Chen

et al., 2012a; Kumar et al., 2008). The process includes the drying stage and the devolatilization stage, in which the latter is sometimes further divided into main devolatilization and continuous slight devolatilization sections (White et al., 2011).

The devolatilization stage is a well-known biomass pyrolysis process that generally occurs in the temperature range of 150–700 °C. Knowledge on pyrolysis kinetics is essential in predicting pyrolysis behavior and in designing the suitable reactor (Damartzis and Zabaniotou, 2011). Many models have been proposed to determine the kinetic parameters in the devolatilization stage (Vyazovkin et al., 2011). These models have shown excellent performance in the temperature range of 200–450 °C or in the conversion range of 0.15–0.80. The distributed activation energy model (DAEM) is a simple and accurate model for this process (Cai and Liu, 2008; Li et al., 2009; Shen et al., 2011; Sonobe and Worasuwanarak, 2008; Varhegyi et al., 2010). DAEM is used to study the thermal decomposition kinetics of several biomass materials. However, types of raw biomass, such as agricultural wastes without forced drying, have not been tested by DAEM. Therefore, the first aim of the current study is to gain further understanding of the pyrolysis characteristics of raw biomass.

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The drying stage is the first mass loss process of biomass pyrolysis, which takes place within the range of room temperature to 150 °C (Cai and Liu, 2007). However, from the literature point of view, little attention has been given to this stage, because the biomass used in the pyrolysis study is not composed of raw materials but of dried materials. Thus, water evaporation is either absent or very weak in the pyrolysis process (Sonobe and Worasuwannarak, 2008). Meanwhile, when raw biomass is used in pyrolysis experiments, water mass is generally subtracted from the overall sample mass. The kinetic analysis is carried out beginning with the temperature at which the drying stage is finished (Zeng et al., 2011). Therefore, the second aim of the current study is to determine the kinetic analysis in the drying stage and obtain the distribution of activation energies of the entire pyrolysis process.

Moreover, pyrolysis models, such as DAEM, are not adequate for kinetic analysis in the drying stage. The kinetic results obtained by the pyrolysis models at low conversions are surprising and sometimes unacceptable. For example, the activation energy values were 67–74 kJ/mol for corn stover in the conversion range of 0.05–0.1 (Yang et al., 2011), and 215 and 235 kJ/mol for birch and pine at a conversion rate of 0.05 (Shen et al., 2011). According to numerous drying studies in literature, the activation energy in the drying process is very low, generally less than 30 kJ/mol (Chen et al., 2012b; Erbay and Icier, 2010). Damartzis et al. (2011) noted that the results of the kinetic calculation are not credible at low conversion (below 0.2). These cases were left out in their work to avoid an erroneous interpretation of the phenomena. Therefore, this study performed the kinetic analysis by stages. The third aim of the current study is to evaluate an appropriate kinetic model to describe the nonisothermal drying process.

The overall aims of this study are to conduct kinetic analysis on the whole pyrolysis process and to obtain the activation energy distribution corresponding to different solid conversions. The next study will focus on the physical meaning of the activation energy.

2. Methods

2.1. Materials

Two typical agricultural wastes (corn straw and wheat straw), coming from the suburb of Hefei City in China, were used as materials in this study. These materials were ground in a high speed rotary cutting mill and then naturally stacked in the room without forced drying. The particles with the size of 0.125–0.3 mm were chosen for experiments. The proximate analysis of the straw was performed in accordance with the ASTM D3172–07a standard practice (ASTM, 2009). The ultimate analysis was carried out using an elemental analyzer (Vario Macro, Elementar, Germany), from which the carbon, hydrogen, and nitrogen contents were obtained and oxygen was estimated by the difference. The results are listed in Table 1. It can be observed that the moisture contents are 0.087 and 0.072 kg water/kg wet matter for corn straw and wheat straw, respectively.

Table 1
Ultimate (dry basis) and proximate analysis (wet basis) of straw.

Sample	Ultimate analysis (% db)				Proximate analysis (% ar)			
	[C]	[H]	[N]	[O]	Moisture content	Volatile matter	Fixed carbon	Ash
Corn straw	41.67	6.15	0.72	45.28	8.67	70.83	14.87	5.53
Wheat straw	43.56	5.87	0.71	39.37	7.20	67.69	15.53	9.58

2.2. Thermogravimetric analysis

Pyrolysis experiments were performed using a thermogravimetric analyzer (TGA Q500, TA, USA). In each experiment, the sample was thinly distributed in the crucible and about 10 mg in mass was used in order to avoid the effect of mass and heat transfer during the pyrolysis process. The heating rates were controlled at 5, 10, 20 and 30 °C/min from 30 to 700 °C, with a nitrogen flow rate of 100 mL/min. A blank experiment was performed under the same conditions before the actual experiment to eliminate the effect of system error on the experiment result.

2.3. Kinetics analysis in drying stage

Drying is a complex process of heat and mass transfer; it is difficult to understand in the microscopic level because mathematical descriptions have many deficiencies. Therefore, in practice, effective models are necessary for mechanism analysis and process prediction. Thin layer drying equations have been widely applied in mathematical modeling of drying because of the ease of use and sufficiently good results they produce. The three types of thin layer equations are theoretical, semi-theoretical, and empirical models. Theoretical models include many assumptions that cause considerable errors, while the empirical models strongly depend on the experimental conditions. Their application is less than that of the semi-theoretical models, which need fewer assumptions and give more information on the drying behaviors. The semi-theoretical drying models are used in this study, and their nonisothermal forms are listed in Table 2 (Cai and Chen, 2008). The Page and Newton models are derived by analogues with Newton's law of cooling, while the other two models were derived from Fick's second law of diffusion. Additional information of the physical meaning and application of these models can be found in the literature and in our previous study (Chen et al., 2012a; Erbay and Icier, 2010).

In these models, T_0 is the initial drying temperature (°C), T is the temperature at any time (°C), β is the heating rate (°C/min), and t is the drying time (min), k_0 is the pre-exponential factor (1/min), R is the universal gas content, E is the activation energy (kJ/mol), and a , b , n are the drying constants.

The moisture ratio (MR) of biomass was calculated using the following equation:

$$MR = \frac{M - M_e}{M_0 - M_e} \quad (1)$$

where M is the moisture content at temperature T , M_0 is the initial moisture content, and M_e is the equilibrium moisture content.

Two types of water, namely, free water and bound water, were distributed in biomass. Free water has a weak bonding force with the materials, whereas bound water has strong bonding force. The first stage of biomass pyrolysis is a nonisothermal drying process with a constant heating rate. When the temperature gradually increased, the free water was first released before 90 °C, and then the bound water began to evaporate. When the temperature approached 150 °C, the mass loss of biomass was very small, and most of the water was removed. The values of M_e were relatively

Table 2
Drying models for the first stage of biomass pyrolysis.

Model	Nonisothermal model equation
Page	$MR = \exp[-k_0 \exp(-\frac{E}{R(T+273.15)}) (\frac{T-T_0}{\beta})^n]$
Newton	$MR = \exp[-k_0 \exp(-\frac{E}{R(T+273.15)}) \frac{T-T_0}{\beta}]$
Logarithmic	$MR = a + b \exp[-k_0 \exp(-\frac{E}{R(T+273.15)}) \frac{T-T_0}{\beta}]$
Henderson	$MR = a \exp[-k_0 \exp(-\frac{E}{R(T+273.15)}) \frac{T-T_0}{\beta}]$

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