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Kinetic study of corn straw pyrolysis: Comparison of two different three-pseudocomponent models

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Abstract

With heating rates of 20, 50 and 100 K min^{-1}, the thermal decomposition of corn straw samples (corn stalks skins, corn stalks cores, corn bracts and corn leaves) were studied using thermogravimetric analysis. The maximum pyrolysis rates increased with the heating rate increasing and the temperature at the peak pyrolysis rate also increased. Assuming the addition of three independent parallel reactions, corresponding to three pseudocomponents linked to the hemicellulose, cellulose and lignin, two different three-pseudocomponent models were used to simulate the corn straw pyrolysis. Model parameters of pyrolysis were given. It was found that the three-pseudocomponent model with *n*-order kinetics was more accurate than the model with first-order kinetics at most cases. It showed that the model with *n*-order kinetics was more accurate to describe the pyrolysis of the hemicellulose.

Keywords: Corn straw; Pyrolysis; Three-pseudocomponent model

1. Introduction

Current energy consumption of biomass accounted for about 14% of total world energy consumption, second only to coal, oil, and natural gas, and developing countries accounted for 75% of the biomass utilization (Peter, 2002; Matti, 2004). Increasing the use of biomass for energy generation purposes is of particular interest nowadays because they allow mitigation of greenhouse gases and provide means of energy independence (Leung et al., 2004; Lai, 2005; Adnan et al., 2006). The pyrolysis, basically a polymeric structure cracking process, converted the lignocellulosic materials into volatile fraction and char. The volatile fraction (gas or liquid, depending on its molecular weight) can be used as a fuel or as a chemical synthesis source. On the other hand, the solid fraction presented several applications, like as a domestic fuel, in the production of activated carbon, or as a reducing agent in metallurgy (Fisher et al., 2002; Demirbas and Bala, 2006). Understanding pyrolysis kinetics was important for the effective design and operation of the thermochemical conversion units. It was always a fundamental step for these conversion processes. Thermoanalytical techniques, in particular thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), allowed this information to be obtained in a simple and straightforward manner.

Several researchers (Atul and Rajeswara, 1999; Blasi et al., 2000; Cao et al., 2004; Cai and Liu, 2008; Zabaniotou et al., 2008) have intensively investigated the kinetics of biomass pyrolysis. The pyrolysis process of the biomass was interpreted in terms of a simple first-order reaction with Arrhenius kinetics by Aiman and Stubington, while Thurner and Mann have approximated the pyrolysis process by two competitive first-order reactions. Thermogravimetric studies showed that each kind of biomass had unique pyrolysis characteristics, by virtue of the specific proportions of the components present in it. There was

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no detectable interaction among the components during pyrolysis. Orfao et al. (1999) assumed that the biomass components react independently and, therefore, that the global thermal behaviour reflected the individual behaviour of the components, weighed by the composition. Meszaros et al. (2004) advised to use a three-pseudocomponent model to simulate biomass pyrolysis.

The objective of this study was to investigate the pyrolysis of different parts of corn straw and to determine the decomposition kinetics by comparison of experimental and modeled data. The data were analyzed using two different three-pseudocomponent models to simulate corn straw pyrolysis.

2. Experimental

2.1. Materials

Corn straw was collected from Harbin farm. The following four samples were prepared: (a) corn stalks skins (corn stalks without their cores); (b) corn stalks cores (corn stalks without their skins); (c) corn bracts; and (d) corn leaves. All samples were meshed to small particles with range from 0.60 to 1.0 mm. The average sizes of all samples closed to 0.77 mm. Table 1 gives the proximate and ultimate analysis of these samples. Four of the samples had similar carbon, hydrogen, oxygen, volatile and fixed carbon values but had differences in the content of ash, nitrogen and sulphur on a dry basis and on an ash-free basis.

2.2. Equipment and procedures

The thermogravimetric experiments were carried out in a Mettler-Toledo TGA/STDA851. The inert gas used for the pyrolysis was nitrogen with a flow rate of 150 ml min^{-1}. In this work, heating rates of 20, 50 and 100 K min^{-1} were selected for these samples. Three thermogravimetric experiments were carried out for each biomass sample in the entire range of biomass decomposition, 40 to about 900 °C. A blank experiment was conducted to exclude a buoyancy effect. The initial mass of the samples used was in a range of 14–40 mg.

3. Analytical methods

DTG curves of biomasses frequently contain shoulders and tailing, as shown below in this work. This indicated that more than one reaction was involved and that the biomass consisted of components with different reactivity for pyrolysis. To consider this, the approach of Varhegyi et al. (1997) was chosen to describe the overall decomposition by means of independent parallel reactions and thus by independent components. In this work, it was assumed that the biomass consists of three pseudocomponents, and the pyrolysis rate was then described by

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \sum_{i=1}^{3} \frac{\mathrm{d}a_i}{\mathrm{d}t} = \sum_{i=1}^{3} c_i A_i \exp\left(-\frac{E_{A,i}}{RT}\right) f(a_i) \tag{1}$$

The variable a is the degree of transformation. The subscripts i represent the different pseudocomponent of the biomass. Parameters c_i, E and A are the coefficient, express the contribution of the partial processes to the overall mass loss, the activation energy and the pre-exponential factor and R is ideal gas constant.

This assumption of three pseudocomponents was consistent with the nature of most biomasses which were often composed of hemicellulose, cellulose and lignin. In fact, three pseudocomponents represented a pool of fractions of the main biomass components. This was the definition of pseudocomponent used in previous studies (Varhegyi et al., 1997; Hu et al., 2007) and applied again in this work. In this research, to explain analysis result more clearly, hemicellulose, cellulose and lignin were used to represent three pseudocomponents, respectively. Depending on the reaction order n, the following kinetic equations were used for each pseudocomponent:

$$\begin{aligned}\frac{\mathrm{d}a_i}{\mathrm{d}t} &= A_i \exp\left(-\frac{E_{A,i}}{RT}\right)(1-a_i)^{n_i} \\ &= A_i \exp\left(-\frac{E_{A,i}}{RT}\right) \exp\left\{-\frac{A_i}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_{A,i}}{RT}\right)\mathrm{d}T\right\} \\ n_i &= 1\end{aligned} \tag{2}$$

Table 1
Proximate and ultimate analysis

Samples		Corn stalks skins	Corn stalks cores	Corn bracts	Corn leaves
Proximate analysis (wt.%) (as dry and ash-free basis)	Moisture (as received basis)	10.00	11.60	11.00	11.00
	Volatiles	83.61	84.95	84.78	83.68
	Fixed carbon	16.39	15.05	15.22	16.32
	Ash (as received basis)	2.44	1.80	2.73	6.99
Ultimate analysis (wt.%) (as dry and ash-free basis)	C	49.38	49.54	48.02	49.28
	H	5.84	6.03	5.78	5.67
	O	44.28	43.72	45.51	44.12
	N	0.48	0.65	0.62	0.87
	S	0.03	0.06	0.07	0.06
Gross calorific value (MJ kg^{-1})		17.19	17.60	16.52	16.31