# STUDY ON PYROLYSIS KINETICS OF WALNUT SHELL

*H. R. Yuan*[1,2] *and R. H. Liu*[1*]

[1]Biomass Energy Engineering Research Centre, School of Agriculture & Biology, Shanghai Jiao Tong University
2678 Qixin Road, Shanghai 201101, P.R. China
[2]Planting Industry Service Centre of Yanqing County of Beijing City, Yanqing, Beijing 102100, P.R. China

Slow pyrolysis of walnut shell which is a cheap and abundantly available solid waste was carried out using thermogravimetric analysis. The effects of raw material heating rate on the pyrolysis properties and kinetic parameters were investigated. A two-step consecutive reaction model were used to simulate the pyrolysis process. The kinetic parameters were established by using the pattern search method. Comparison between experimental data and the model prediction indicated that the two-step consecutive reaction model can better describe the slow pyrolysis of walnut shell as the formation of an intermediate during the pyrolysis process was taken into account.

*Keywords: kinetics, pattern search method, pyrolysis, walnut shell*

## Introduction

The walnut is one type of the dried fruits, and is mainly produced in Asia, Europe and North America. With the expansion of walnut demand, walnut wastes (in particular walnut shell) has increased markedly. The walnut shell belongs to the group of nutshells, a class of highly insoluble species and can be used to produce chemicals such as activated carbons [1], lignin [2] and carbon molecular sieve [3].

The walnut shell is a high-potential biomass energy source that is $CO_2$ neutral. Pyrolysis is considered to be one of the promising thermal approaches in converting biomass to energy [4–7]. However, it is a highly complex process that is influenced by many factors, such as the properties of raw materials and the operating conditions [8–9]. At present, the research of walnut shell pyrolysis is scarcely found in literatures.

The use of TG has the advantage of a fast and repeatable data collection of pyrolysis rate, which facilitates a deep investigation of the kinetic parameters [10, 11]. In this work, the slow pyrolysis experiments have been performed by a thermogravimetry analyzer. The kinetic analysis of the pyrolysis of the walnut shell has been also investigated. The study results will be responsible for the optimization of the pyrolysis reaction processes, giving insight into the pyrolysis mechanisms and aiding in engineering efforts.

## Experimental

### Materials

The walnut shell has been obtained from the market. The walnut shells were dried at 105°C for 40 h to remove the moisture and kept in desiccator for further testing. The pre-dried samples were crushed and sieved to 0.154 mm. The ultimate analysis and ash content of the walnut shell sample are shown in Table 1.

**Table 1** Ultimate analysis and ash content of walnut shell

| Sample | C/% | H/% | O/% | N/% | ash/% |
|---|---|---|---|---|---|
| Walnut shell | 47.67 | 5.67 | 46.32 | 0.34 | 0.69 |

### Methods

Thermogravimetry

The slow pyrolysis of walnut shell has been carried out using a thermogravimetric analyzer (Perkin-Elmer pyris 1). Approximately, 2 mg sample was placed in a platinum pan, which was suspended by a platinum wire. The furnace was heated from ambient temperature to a programmed temperature of 823.15 K at a constant heating rate (5, 10, 20, 30, 40 K min$^{-1}$). Purified nitrogen (99.9% purity) at a constant flow rate of 20.0 mL min$^{-1}$ was used as the purge gas to provide an inert atmosphere for pyrolysis and to remove any gaseous and condensable products evolved, thus minimizing any secondary vapor-phase interactions. The sample mass was measured continuously by a microbalance as a function of time or temperature.

Kinetic model

The primary pyrolytic rate of biomass may be considered to be the sum of rates of the main components. Each component contributions to the formation of the pyrolytic rate, that is, to a certain extent, proportional to its contribution to the composition of the raw material. Normally, the main components of biomass are

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\*     Author for correspondence: liurhou@sjtu.edu.cn

lignin and holocellulose (including cellulose and hemicellulose). Each component converts to the respective ultimate product via intermediate [12]. Here the two-step consecutive reaction model has been used to describe the slow pyrolysis of the walnut shell. The reactions of the pyrolysis process, therefore, can be simplified to two steps, i.e., from raw material to intermediate and primary volatile, and from intermediate to ultimate char and secondary volatile. The basic assumptions involved are:

- the reaction is a pure kinetic controlled process,
- the pyrolytic reactions follows first-order reaction and
- there are no secondary reactions among the gaseous products.

Therefore, the kinetic model for the description of the kinetic rate of the walnut shell sample can be schematized by Fig. 1.

$$\text{raw material} \xrightarrow{k_1} (1-x)\text{intermediate} + x\text{volatile(I)}$$
$$\xrightarrow{k_2} (1-y)\text{char} + y\text{volatile(II)}$$

**Fig. 1** Pyrolysis reaction scheme of the walnut shell sample

In Fig. 1, $k_1$ and $k_2$ represent the first-step and second-step reaction rate, respectively.

From the above analysis, the kinetic equations were given as follows:

$$\frac{dw_R}{dT} = -\frac{A_1}{\beta}\exp\left(-\frac{E_1}{RT}\right)w_R \qquad (1)$$

$$\frac{dw_{V(I)}}{dT} = x\frac{A_1}{\beta}\exp\left(-\frac{E_1}{RT}\right)w_R \qquad (2)$$

$$\frac{dw_I}{dT} = (1-x)\frac{A_1}{\beta}\exp\left(-\frac{E_1}{RT}\right)w_R - \frac{A_2}{\beta}\exp\left(-\frac{E_2}{RT}\right)w_I \quad (3)$$

$$\frac{dw_C}{dT} = (1-y)\frac{A_2}{\beta}\exp\left(-\frac{E_2}{RT}\right)w_I \qquad (4)$$

$$\frac{dw_{V(II)}}{dT} = y\frac{A_2}{\beta}\exp\left(-\frac{E_2}{RT}\right)w_I \qquad (5)$$

$$\frac{dw}{dT} = \frac{d(w_R + w_I + w_C)}{dT} =$$
$$-x\frac{A_1}{\beta}\exp\left(-\frac{E_1}{RT}\right)w_R - y\frac{A_2}{\beta}\exp\left(-\frac{E_2}{RT}\right)w_I \qquad (6)$$

In the above equations, $w_R$, $w_I$, $w_V$ and $w_C$ are the mass fraction of the raw material, the intermediate, the volatile and the char. And the residual mass fraction $w$ was given by the sum of the raw material, intermediate and char ($w_R + w_I + w_C$).

The initial condition is

$$w_R = w = 1, \ w_I = w_V = w_C = 0 \text{ at } T = T_0 \qquad (7)$$

## Results and discussion

### TG and DTG curves

Figure 2 shows the TG-DTG curves for slow pyrolysis of the walnut shell sample at the heating rates of 5, 10, 20, 30 and 40 K min⁻¹. Generally, the slow pyrolysis process of the biomass sample can be separated into four stages [13, 14]. They are a release of physically adsorbed water, a trace of mass loss of the sample, a major loss of mass (larger and reflects the evaporation of volatile matter) and a slow further loss of mass. Here, we analyse a major loss of mass stage. From the Fig. 2, we can see that the main pyrolysis occurs between 423 and 673 K. Volatile matter yield amounts to about 85% in this stage. The maximum pyrolysis rate occurs within 602–643 K when the heating rate is ranged from 5 to 40 K min⁻¹.

DTG curves indicated that the heating rate was greater, the DTG curve was more steep, and the peak temperature was lagging behind. In other words, with



**Fig. 2** TG and DTG curves for slow pyrolysis of the walnut shell sample at various heating rates

the increase of heating rate, the starting and ending temperatures were slightly moved to the high-temperature direction at every step. At the same time, the area of peak of DTG was slightly increased. At the same time, the heating rate will influence heat transfer difference and temperature difference between specimen and testing point, as well as the outer of specimen and internal specimen.

*Estimation of kinetic parameters*

In the calculation, the form of the objective function to optimize kinetic parameters is

$$\text{O.F.} = \sum_{j=1}^{n_s} \sum_{i=1}^{n_d} (w_{cal,ij} - w_{exp,ij})^2 \qquad (8)$$

where $i$ represents the experimental data at time $t$ of the experiment at heating rate $j$, $n_d$ is the number of point of experiment data, $n_s$ is the number of heating rates, $w_{exp,ij}$ is the residual mass fraction experimentally and $w_{cal,ij}$ is the calculated residual mass fraction. $w_{cal,ij}$ can be calculated by the classical fourth-order Runge–Kutta method.

In order to determine the kinetic parameters minimizing O.F. value, a certain optimization technique will be used. It is difficult to obtain information about gradient or higher derivations of the objective function without explicit expression. Therefore, the optimization algorithm should be derivative-free, robust with respect to local optima and should be required as least function evaluations as possible to find the optimum. In this study, the pattern search method has been used. Detailed information about the pattern search method can be found in the literature [15].

Using data from the pyrolysis thermograms at the heating rates of 5, 10, 20, 30 and 40 K min$^{-1}$, the kinetic parameters of the two-step consecutive model were established. To obtain the values of the kinetic parameters, a program coded in Matlab was developed by using the pattern search method. The kinetic parameters were given below: $A_1 = 5.03 \cdot 10^7$ s$^{-1}$, $E_1 = 120.158$ kJ mol$^{-1}$, $A_2 = 6.19 \cdot 10^{12}$ s$^{-1}$, $E_2 = 154.414$ kJ mol$^{-1}$.
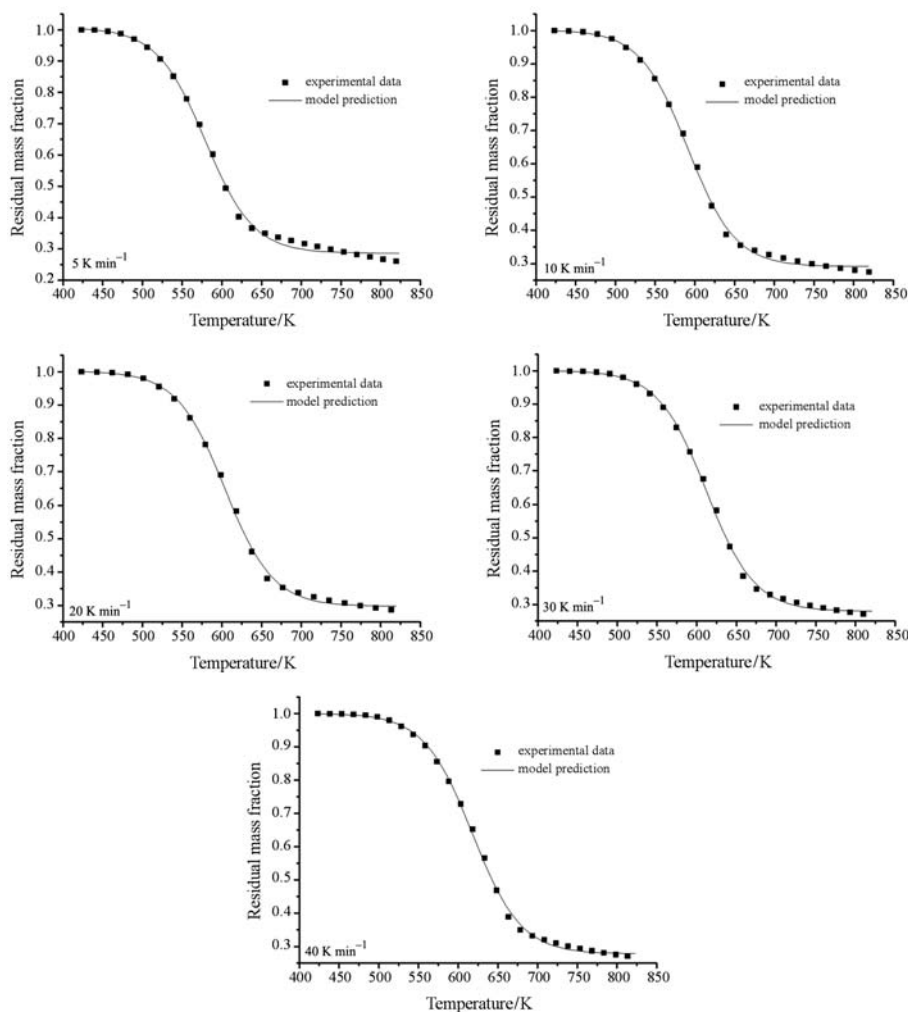


**Fig. 3** Comparison between experimental data and model prediction

Figure 3 shows the comparison of predicted pyrolytic conversion under different heating rates with the experimental data. Figure 3 illustrates that the two-step consecutive model could fit the experimental data sufficiently well because the formation of the intermediate during the pyrolytic process were taken into account.

## Applications

In general, compared to conventional precursors (e.g., coal and lignite) subjected to pyrolysis for producing fuels or chemicals [16], walnut shells are renewable and abundantly available in reasonable quantities and this favors dispersed use. Although walnut shell has a low energy density, it is easier to pyrolyze because of its low decomposition temperature.

For slow pyrolysis with a heating rate less than $100$ K min$^{-1}$ (compared to fast pyrolysis with high heating rates of $1000–10000$ K min$^{-1}$), relatively high yields of char ($10–40\%$) are expected. As fuels, char prepared from agricultural solid wastes usually has a high-heating value. It burns with a hot flame, with no smoke and emits very few polluting substances such as sulfur dioxide [17]. Char can also be pulverized and used in industrial char-oil fuel injection. The properties of char as a reducing agent make it ideal for smelting metals and steel manufacturing [18]. Another main application of char is to be used as precursor for the preparation of activated carbon [19], which is widely used for air pollutant removal and wastewater treatment. These activated carbons have potential applications in both gaseous and aqueous phase adsorption.

## Conclusions

The two-step consecutive reaction model kinetic parameters used in the explanation of thermal decomposition process of walnut shell can be determined easily from nonisothermal TG data of sample and through a pattern search method. The obtained the kinetic parameters were $A_1=5.03\cdot10^7$ s$^{-1}$, $E_1=120.158$ kJ mol$^{-1}$, $A_2=6.19\cdot10^{12}$ s$^{-1}$, $E_2=154.414$ kJ mol$^{-1}$ by the pattern search method. Reconstructed of TG curves with the determined kinetic triplet at different heating rates matches good to the TG curves with the experimental data. Determined kinetic parameters can be used for design and control of thermal decomposition process.

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