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Thermal Decomposition Mechanism and Kinetic Parameters of Semen Ziziphi Spinosae Based on Thermogravimetric Analysis

W.X. Fan[2], X.F. Lu[1,2], X.L. Meng[3], Y.R. Lan[3], B.Z. Song[2], Q.L. Ma[1] and L.P. Chang[1,*]

[1]State Key Laboratory Breeding Base of Coal Science and Technology, Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, Shanxi Province, P.R. China
[2]Shanxi Agriculture University, Taigu 030801, Shanxi Province, P.R. China
[3]Shanxi University of TCM, Taiyuan 030024, Shanxi Province, P.R. China

*Corresponding author: Tel/Fax: +86 351 6010482, E-mail: lpchang@tyut.edu.cn

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Semen Ziziphi Spinosae, which was firstly recorded in "Shennong Bencao Jing", has long been used in traditional Chinese medicine. Large-scale cultivation and processing is the main direction of future development of Semen Ziziphi Spinosae. To improve the pharmacodynamics of Semen Ziziphi Spinosae, we must upgrade it by heating before using, but some thermosensitive materials contained in it can be changed in this process. The thermal decomposition and kinetics during continuous heating Semen Ziziphi Spinosae are the key factors. In this work, pyrolysis tests of Semen Ziziphi Spinosae were performed under non-isothermal TGA in order to determine its thermal degradation behavior. The kinetic parameters in this process were evaluated by using three different models, including iso-conversional models (KAS and FWO) and CR model. Good agreement with the experimental data from TGA test was observed for all models, especially CR model. The different calculating values of activation energy at different conversion between KAS model and FWO model implies the complexity and multi steps of Semen Ziziphi Spinosae pyrolysis.

Keywords: Semen Ziziphi Spinosae, Thermal decomposition, Kinetic model, Activation energy.

INTRODUCTION

Semen Ziziphi Spinosae has been firstly recorded in "Shennong Bencao Jing", named Suan Zao Ren. There are many active components in Semen Ziziphi Spinosae for the treatment of insomnia and palpitation, *etc*., and it has been used as a traditional Chinese medicine[1,2]. GAP (Good Agricultural Practice for Chinese Crude Drug) standardized cultivation and processing of Semen Ziziphi Spinosae are the trend of further development. The thermosensitive components in Semen Ziziphi Spinosae may be destroyed in the upgrading process by heating if operating temperature is inappropriate. It should be the key factors to understand the thermal decomposition and kinetics during continuous heating Semen Ziziphi Spinosae.

At present, biomass pyrolysis is the hotspot of studies both at home and abroad[3-6]. Because of the complexity of the pyrolysis process, the reaction mechanism and activation energy become the focus on study the kinetic behaviour. The activation energy is one of the important kinetic parameters of biomass pyrolysis, the accuracy of results is different from alternative calculations[7-9] (*e.g.*, KAS, FWO and CR model). Similar to biomass, the decomposition properties of Semen Ziziphi Spinosae in the pyrolysis process through its kinetic behaviour are investigated. Because the plurality thermogravimetric curve to solve distributed activation energy can avoid the limitation of the single activation energy view of Semen Ziziphi Spinosae complex reaction, the activation energy and the conversion relationship become the research trend in kinetic studies. The distributed activation energy, which can greatly improve the calculation accuracy, is discussed in the paper.

The purpose of this paper is to present a complete kinetic study of Semen Ziziphi Spinosae pyrolysis, including a kinetic approach *via* thermogravimetric measurements and determination of the kinetic parameters with help of three different modeling methods. These models of pyrolysis kinetics are KAS model, FWO model and CR model. The obtained results will be compared to the experimental data in order to check the validity of the model performance.

EXPERIMENTAL

Preparation of sample: Semen Ziziphi Spinosae taken from Shanxi province in China was used as the experimental sample. It was crushed and grinded to a particle size range of 50-80 mm by a mill made from Huatong Machinery Factory.

Thermogravimetric analysis (TGA): Thermogravimetric analysis is the most commonly applied technique in solid-phase thermal degradation studies and it has gained the widespread currency in thermal studies of biomass pyrolysis. Thermogravimetric analysis technique mainly measures the decrease in substrate mass caused by the release of volatiles, or devolatilization, during thermal decomposition. In TGA, the mass of a substrate being heated at a specific rate is monitored as a function of temperature or time. Taking the first derivative of such thermogravimetric curves (-dm/dt), known as derivative thermogravimetry (DTG), provides the maximum reaction rate. Pyrolysis tests were performed in a NETZSCH STA 409C thermogravimetric analyzer from Germany. The operating conditions of TGA are shown in Table-1.

TABLE-1
OPERATING CONDITIONS OF TGA TEST

Item	Operating parameter
Sample quality (mg)	20-25
Working pressure (atm)	1
Protecting gas	N_2 (99.99 %)
Working gas	Air
Gas flow rate (mL/min)	100
Temperature range (°C)	30-500
Heating rate (β) (°C/min)	10, 20, 30

Kinetic model: The complex TG/DTG curves of Semen Ziziphi Spinosae pyrolysis show the diversity of Semen Ziziphi Spinosae' composition. Their mass loss rate curves contain partially overlapping peaks and three models (KAS and FWO iso-conversional models, CR model) are typically used to analyze their pyrolysis process.

KAS model is one of best iso-conversional methods used widely in the biomass pyrolysis, it can be mathematically expressed as eqn. 1.

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E}{R}\left(\frac{1}{T_m}\right) - \ln\left[\left(\frac{E}{AR}\right)\int_0^\alpha \frac{d\alpha}{f(\alpha)}\right] \quad (1)$$

where, α is conversion, β is heating rate, A is pre-exponential factor, E is activation energy. For the specified value of conversion, the activation energy can be obtained by the slope of the curve $\ln\left(\frac{\beta}{T_m^2}\right)$ *versus* $\frac{1}{T_m}$. Doing so for the whole range of conversion (0-1) will produce the activation energy for the progressing values of conversion.

Another one of the most commonly methods for the computation of the kinetic parameters based on thermogravimetric analysis is the FWO model. It can be mathematically expressed as eqn. (2).

$$\log\beta = \log\left(A\frac{E}{Rg(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \quad (2)$$

In the FWO method, the plots of log β *versus* $\frac{1}{T}$ for different heating rates produce parallel lines for a fixed degree of conversion. The slope $\left(0.4567\frac{E}{R}\right)$ of these lines is proportional to the apparent activation energy. The value of log A is given by the intercept of this line with the *y*-axis, log β.

The integral method based on the Coats and Redfern (CR) equation is a popular non-isothermal model-fitting method that requires an assumption to be made regarding the value of the reaction order. Coats and Redfern model expression is eqn. 3

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad n = 1$$
$$\ln\left[\frac{(1-\alpha)^{1-n}-1}{(n-1)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad n \neq 1 \quad (3)$$

A straight line can be obtained from single heating rate data by plotting the left-hand term *versus* T^{-1}. From the slope of the line -E/R and its intercept ln(AR/βE), E and A can be derived. The attractiveness of the CR method resides in its ability to directly furnish A and E for single heating rate.

Eqn. 3 can be simplified by recognizing that for customary values of E if the term 2RT/E«1.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \qquad n = 1$$
$$\ln\left[\frac{(1-\alpha)^{1-n}-1}{(n-1)T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \qquad n \neq 1 \quad (4)$$

RESULTS AND DISCUSSION

Thermal decomposition curve: The TG and DTG curves obtained for the Semen Ziziphi Spinosae pyrolysis at different heating rate are shown in Fig. 1. The first thermal decomposition of Semen Ziziphi Spinosae started at about 130 °C, followed by a loss of weight in the temperature range of 130 and 250 °C and the second thermal decomposition of Semen Ziziphi Spinosae started at about 250 °C, followed by a major loss of weight in the temperature range of 250 and 430 °C. Heating rate influenced the temperature ranges of the pyrolysis process. An increase of the heating rate tended to delay thermal degradation process towards higher temperatures, most probably due to thermal lag as at a given temperature. The higher heating rate implies that the Semen Ziziphi Spinosae reaches that temperature in a shorter time. Thermal degradation rates increased with the increase of heating rate.

Evaluation of activation energy using iso-conversional models: The iso-conversional models used in this study in order to calculate the kinetic parameters of the pyrolysis of biomass material are the KAS and FWO methods.

Based on the KAS model, the activation energy of the various conversion value during pyrolysis of Semen Ziziphi Spinosae is calculated. Fig. 2a shows the linear plots of $\ln\left(\frac{\beta}{T^2}\right)$ *versus* $\frac{1}{T}$. Activation energy can be evaluated from the slope of the appropriate linear plot and the values are listed in Fig. 2b. It can be seen that the highest value of activation energy of the first thermal decomposition of Semen Ziziphi Spinosae is close to 240 kJ/mol and the highest value of activation energy of the second thermal decomposition of Semen Ziziphi Spinosae close to 120 kJ/mol. This implies that pyrolysis progresses through multi-step kinetics with various apparent activation energies.

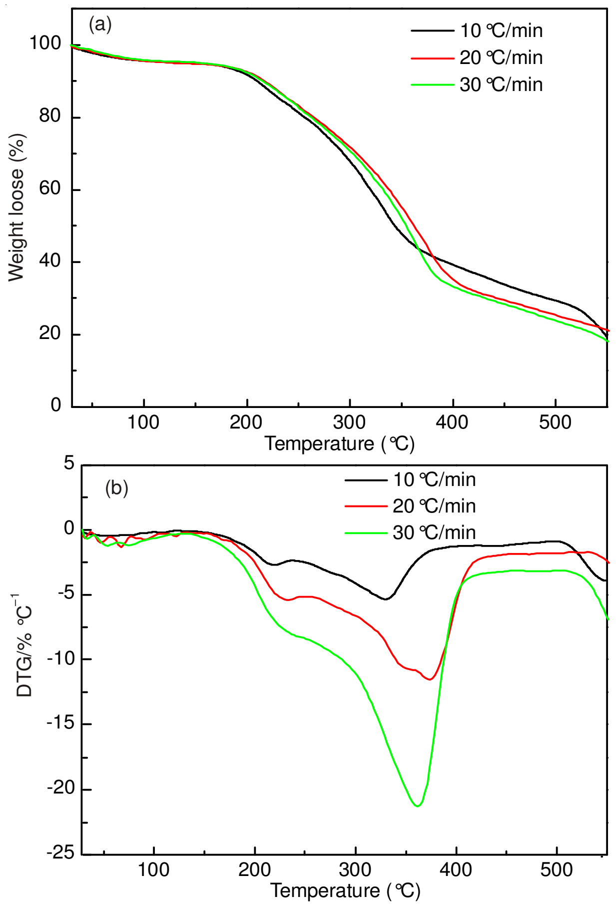

Fig. 1. TG (a) and DTG (b) curves of Semen Ziziphi Spinosae at different heating rate

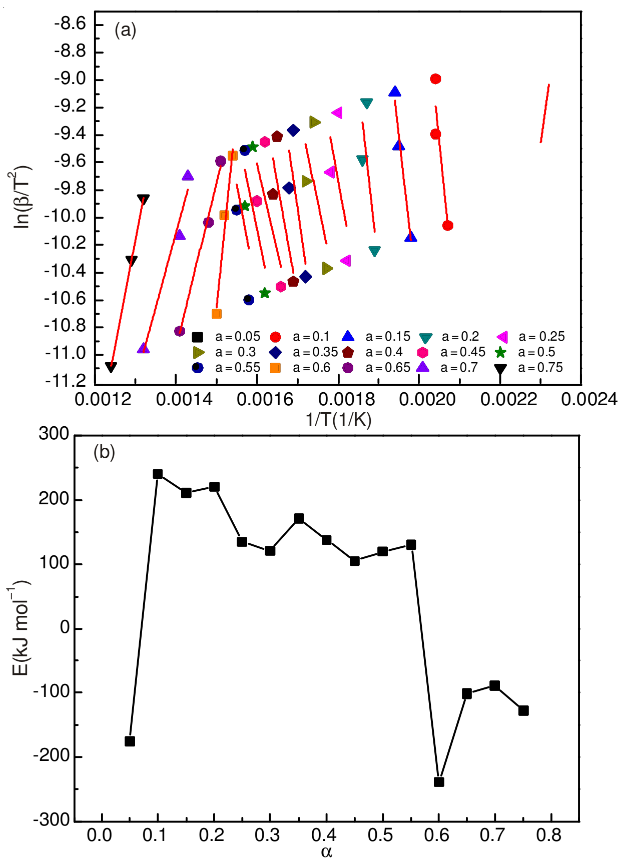

Fig. 2. Estimation of activation energy using the KAS method for the pyrolysis of Semen Ziziphi Spinosae

Kinetic data are also been calculated using FWO method. Fig. 3a shows the linear plots of log β *versus* $\frac{1}{T}$. The activation energy for each value of conversion can be obtained from the slope of the curve. These values are listed in Fig. 3b, in which the correlation coefficient is close to 1. The values of activation energy calculated using the FWO method and KAS method show a similar trend, but the calculated values of FWO method are significantly bigger than KAS method.

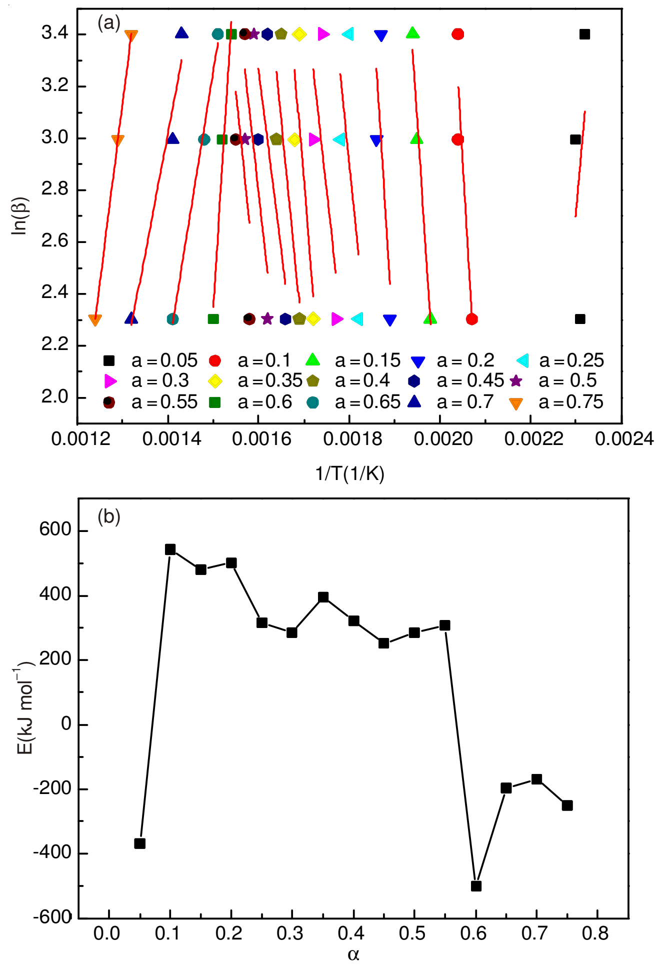

Fig. 3. Estimation of activation energy using the FWO method for the pyrolysis of Semen Ziziphi Spinosae

Given a fixed degree of conversion, $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ or $\ln\left[\frac{(1-\alpha)^{1-n}-1}{(n-1)T^2}\right]$ is plotted *versus* $\frac{1}{T}$ for each heating rate and generates a set of straight lines with the slope -E/R. The frequency factor A is calculated by inserting -E/R into the intercept. Estimation values of activation energy using the CR (a, n = 1; b, n = 3) method for the pyrolysis of Semen Ziziphi Spinosae are showed in Fig. 4. The values of kinetic parameters are listed in Table-2. It can be found that when the reaction order is larger, the correlation coefficient is closer to 1 and the activation energy should be closer to the actual value.

TABLE-2
KINETIC PARAMETERS FOR THE PYROLYSIS OF SEMEN ZIZIPHI SPINOSAE AT DIFFERENT HEATING RATE

Reaction order	β (°C/min)	Fitting straight line y = a + bx	E (kJ/mol)	A	R^2
n=1	10	y=-10.0-2134.5x	17.7	1.0	0.89064
	20	y=-9.5-2467.9x	20.5	3.7	0.96486
	30	y=-9.3-2559.7x	21.3	7.0	0.96254
n=3	10	y=-4.1-4785.0x	39.8	813.8	0.98961
	20	y=-4.5-4628.9x	38.5	1018.8	0.99051
	30	y=-5.3-4130.7x	34.3	618.8	0.99080

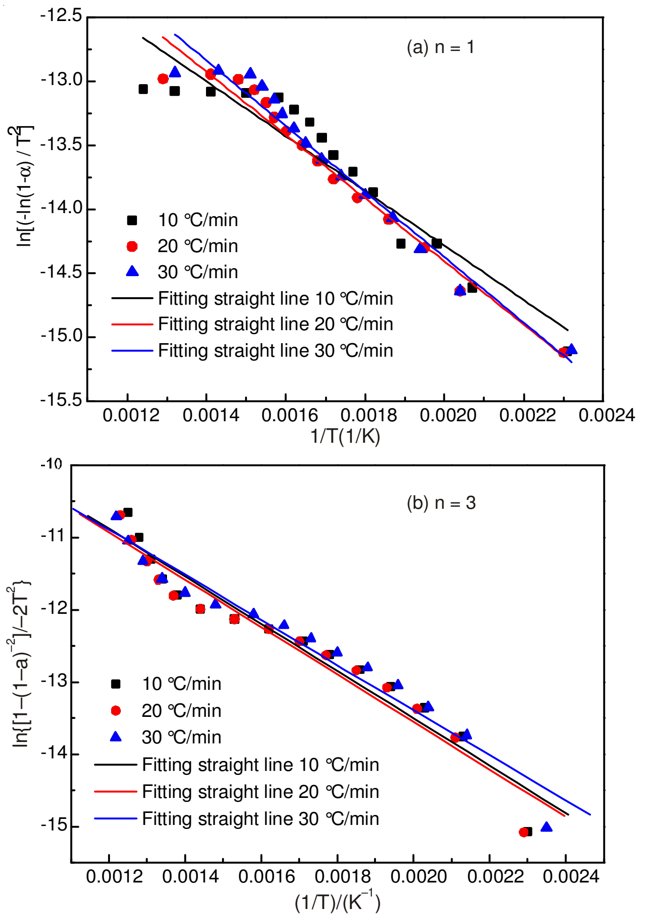

Fig. 4. Estimation of activation energy using the CR method for the pyrolysis of Semen Ziziphi Spinosae

With the increase of heating rate, the activation energy changes also obviously. Therefore, the heating rate is considered one of the important factors affecting the mechanism and process of Semen Ziziphi Spinosae pyrolysis.

Fig. 5 shows the simulation results of the pyrolysis of Semen Ziziphi Spinosae using the calculated values from CR model. In all case, the variable order method shows an overall better accordance with the values obtained from TGA experiment when reaction order n is 3, but it is not very accurate to predict the behavior at lower temperature. Therefore, the reaction order n as a parameter plays an important role in CR model.

If E and A obtained through the CR method, which is much more suitable for the pyrolysis process of Semen Ziziphi Spinosae, the model can be evaluated based on the kinetics

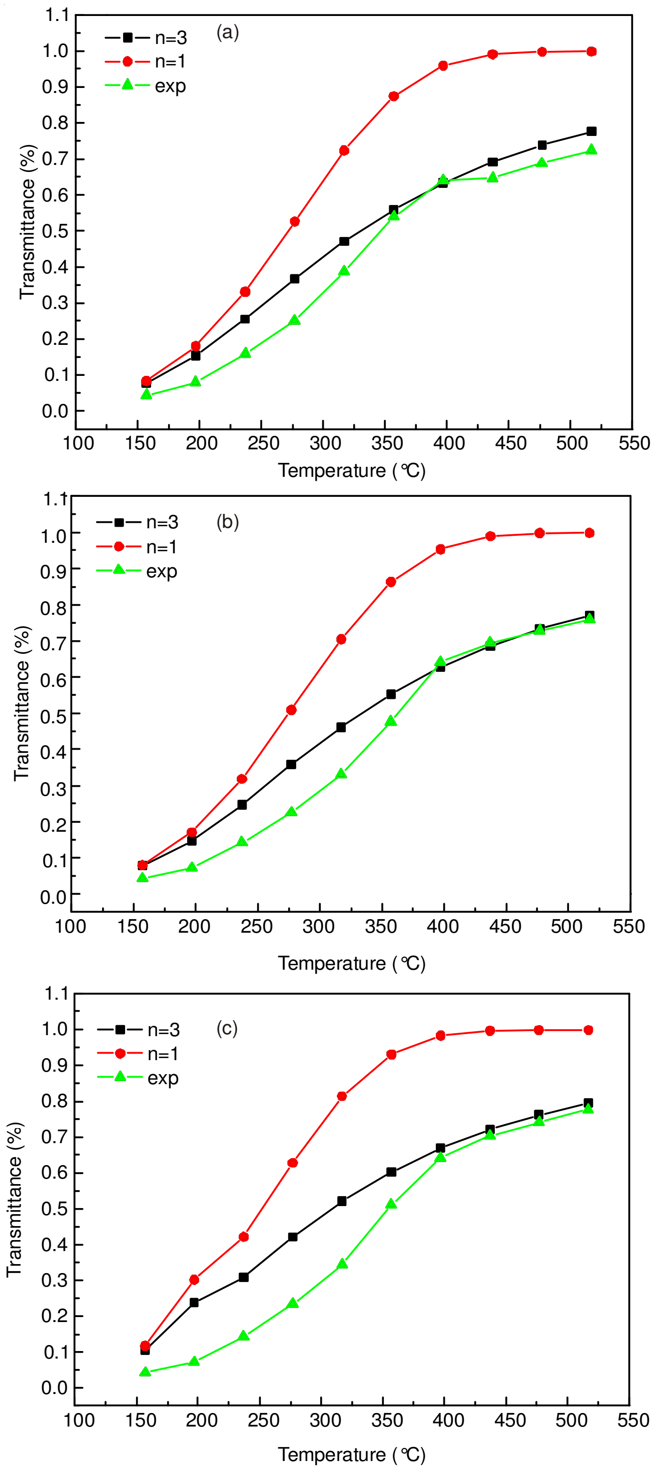

Fig. 5. Simulation results of Semen Ziziphi Spinosae pyrolysis using the kinetic data calculated from CR method at different heating rate of (a) 10 °C/min, (b) 20 °C/min, (c) 30 °C/min

mechanism function of $f(\alpha) = (1-\alpha)^n$ or $G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)}$.

Fig. 6 shows a simulation of the pyrolysis of Semen Ziziphi Spinosae using three models. The increase of the heating rate seems to have no effect on the predictive behaviour of the model, while CR model shows a better accordance with the values obtained from TGA data.

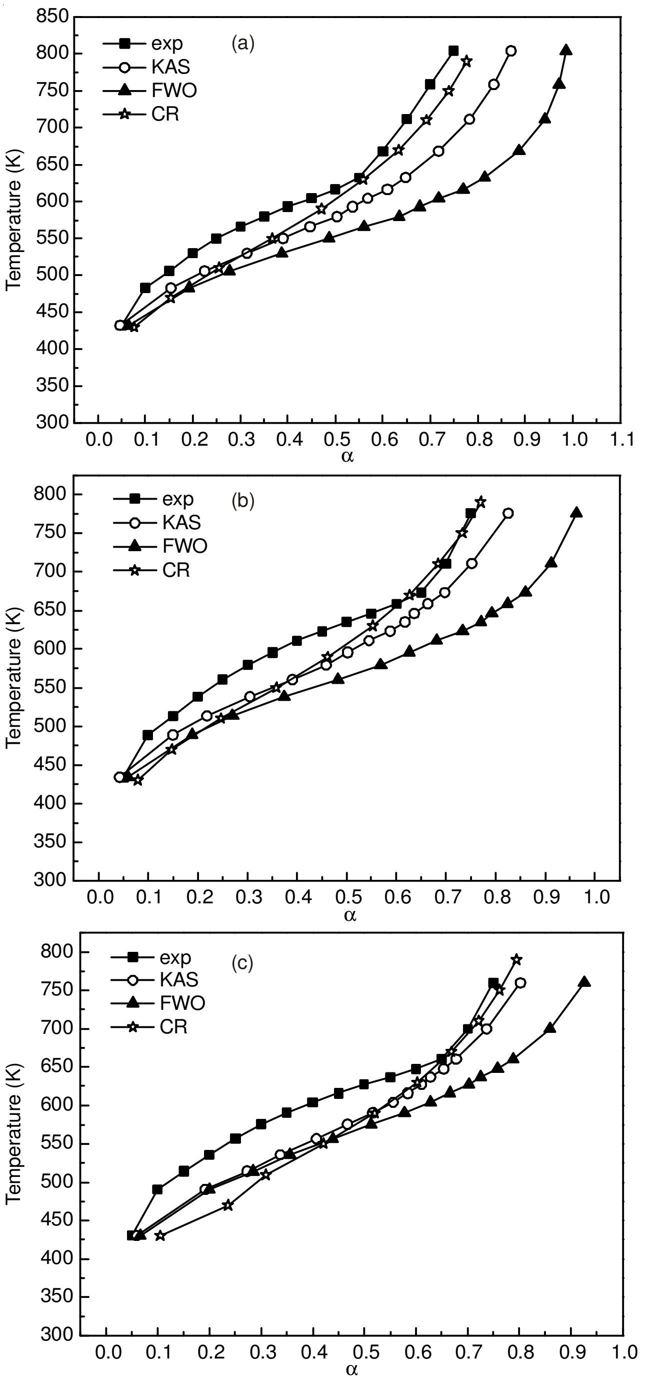

Fig. 6. Simulation results of Semen Ziziphi Spinosae pyrolysis using the kinetic data calculated from KAS, FWO and CR method at different heating rate of (a) 10 °C/min, (b) 20 °C/min, (c) 30 °C/min

Conclusion

The processing mechanism and kinetic parameters of Semen Ziziphi Spinosae pyrolysis based on TG/DTG tests were studied. Semen Ziziphi Spinosae pyrolysis is a comprehensive expression of a complex series of reactions of molecular bond breaking. Semen Ziziphi Spinosae pyrolysis mainly occurs in the temperature range of 150 and 430 °C. The values of activation energy calculated using KAS method is close to 100-200 kJ/mol and the activation energy calculated using the FWO method shows a similar trend to KAS method, but the calculated values by FWO method are significantly higher than KAS method. During pyrolysis of Semen Ziziphi Spinosae, its active component undergoes the oxidation and decomposition process, KAS model can well explain the oxidation process and FWO model can well explain the decomposition process. Activation energy obtained through CR model (n = 3) is about 40 kJ/mol, which should be closer to the actual. Thermal processing of Semen Ziziphi Spinosae follows three models well.

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