

# Thermal treatment of Indonesian lignite washery tailing

## Part 2. Kinetic analysis

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**Abstract** Kinetic analysis of Indonesian lignite washery tailings (LWT) was studied in this paper. Two methods were compared to evaluate the activation energy  $E$  of LWT, i.e., iso-conversional methods and model-based method. The Flynn–Wall–Ozawa method and the Kissinger–Akahira–Sunose method were chosen to represent the iso-conversional method. The Coats–Redfern method was chosen as the model-based method. Furthermore, a complementary method of iso-conversional and model-based was also used to determine the kinetic mechanism of LWT. The results provide useful information for designing a combustion or pyrolytic system using LWT as feedstock.

**Keywords** LWT · Kinetics · Model based · Iso-conversional · Complementary method

## Introduction

In the first part of this study series, pyrolysis and combustion characteristics of LWT were studied by TG–FTIR. Its gaseous products of pyrolysis and combustion were also analyzed. It gives us information on how to control the process to obtain target products. For further understanding the thermal conversion mechanism of LWT, the kinetic parameter is very important. So in this part, the kinetic analysis of LWT was studied with various methods.

In the aspect of kinetics, two main mathematical methods are the iso-conversional (model-free) and model-based (model-fitting) methods [1]. Iso-conversional methods give an estimate of activation energy without model-based assumption, e.g., the Flynn–Wall–Ozawa (FWO) method [2, 3] and the Kissinger–Akahira–Sunose (KAS) method [4]. On the contrary, a reaction model must be postulated first in model-based methods. One of the most popular model-based methods is the Coats–Redfern (CR) method [5, 6]. Khawam and Flanagan [7] pointed out that using Coats–Redfern (CR) method can produce misleading results and the iso-conversional methods can only determine the activation energy. However, a kinetic triplet ( $A$ ,  $E$ , and model) is necessary to fully study any kinetic process. So they recommended a complementary use of iso-conversional and model-based methods in the analysis of kinetics.

In this study, both the iso-conversional methods (FWO and KAS methods) and the model-based method (CR method) were used to analyze the pyrolysis and combustion kinetics of LWT. The two methods were compared to see which one is more credible. In addition, a complementary use of iso-conversional and model-based methods was also used to determine the pre-exponential factors and the reaction models. The results of this study offer useful information for designing a combustion or pyrolytic system using LWT as feedstock.

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## Kinetic methods

In TG, the mass loss fraction is defined as:

$$\alpha = \frac{M_i - M}{M_i - M_f} \quad (1)$$

where  $M_i$  is the initial mass of the sample,  $M_f$  is the final mass, and  $M$  is the mass at certain time  $t$ .

In non-isothermal conditions, the rate of conversion can be described as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \longrightarrow \beta = dT/dt \frac{d\alpha}{dT} = \left(\frac{1}{\beta}\right)k(T)f(\alpha) \quad (2)$$

where  $f(\alpha)$  is the differential expression of kinetic model equation,  $k$  represents the constant of the reaction rate, and it is usually described by Arrhenius equation as:

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

where  $A$  is the pre-exponential factor (frequency factor),  $E$  is the activation energy, and  $R$  is the universal gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

### Model-based method (CR method)

Coats and Redfern proposed the integral method to calculate kinetic parameters as [5, 6]:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) \approx \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \approx \frac{ART^2}{\beta E} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \quad (4)$$

Assuming that  $f(\alpha) = (1 - \alpha)^n$ , Eq. 4 can be described as:

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{ART^2}{\beta E} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \quad (5)$$

The famous Coats and Redfern equation is obtained by taking logarithmic computation on both sides of Eq. 5: when  $n \neq 1$ ,

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \left[ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \quad (6)$$

when  $n = 1$ ,

$$\ln \left[ \frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \quad (7)$$

For most reaction,  $E/RT \geq 1$ , and  $1 - 2RT/E \approx 1$ . Thus, Eqs. 6 and 7 can be simplified as:

$$\ln \left[ \frac{G(\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (8)$$

Thus, based on Eq. 7, the plot of  $\ln(G(\alpha)/T^2)$  versus  $1/T$  can fit to a straight line. The value of  $A$  and  $E$  can therefore be obtained according to the intercept and slope of the line.

### Iso-conversional method (FWO and KAS methods)

According to Flynn–Wall–Ozawa (FWO) method, the activation energy  $E$  is thought to remain unchanged during the reaction. In order to get the approximate solution of the temperature integral in Eq. 4, a new parameter was proposed:

$$u = \frac{E}{RT} \quad (9)$$

Based on Eq. 9, Eq. 4 becomes:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} \int_u^\infty \frac{e^{-u}}{u^2} du = \frac{AE}{\beta R} \cdot P(u) \quad (10)$$

where  $P(u)$  (the temperature integral) does not have an exact analytical solution and Doyle proposed the approximated solution [8, 9]:

$$P(u) = 0.0048 \times e^{-1.0516u} \quad (11)$$

$$\lg P(u) = -2.315 - 0.4567 \frac{E}{RT} \quad (12)$$

Based on Eq. 12, the FWO equation can be obtained by using logarithms of both sides of Eq. 10 [2, 3, 10–14]:

$$\lg \beta = \lg \left( \frac{AE}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E}{RT} \quad (13)$$

Thus, plots of  $\lg \beta$  versus  $1/T$  at a fixed  $\alpha$  can be obtained based on different heating rates and the activation energy  $E$  can be obtained based on the slope of these lines.

Another widely used iso-conversional method is the Kissinger–Akahira–Sunose (KAS) method [4, 15]:

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{E} \right) - \frac{E}{RT} \quad (14)$$

Similar to FWO, in KAS method, the plots of  $\ln(\beta/T^2)$  versus  $1/T$  at a fixed conversion  $\alpha$  can be obtained based on different heating rates and the activation energy  $E$  can also be obtained according to the slope of these lines.

### A complementary method of iso-conversional and model-based analysis

A complementary method of iso-conversional and model-based was used in this study. Firstly, the activation energies were obtained by using both FWO and KAS methods. Then, the master plot method proposed by Gotor et al. [16] was used to predict the kinetic models of the pyrolysis and combustion processes.

**Table 1** Expressions for the most frequently used reaction mechanisms

Symbol	Mechanisms	$f(\alpha)$	$G(\alpha)$
Reaction order models			
$F_1$	First order	$1 - \alpha$	$-\ln(1 - \alpha)$
$F_2$	Second order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
$F_3$	Third order	$(1 - \alpha)^3$	$[(1 - \alpha)^{-2} - 1]/2$
$F_4$	Fourth order	$(1 - \alpha)^4$	$[(1 - \alpha)^{-3} - 1]/3$
Geometrical contraction models			
$R_1$	One-dimensional	1	$\alpha$
$R_2$	Two-dimensional	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
$R_3$	Three-dimensional	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
Random nucleation and nuclei growth models			
$A_2$	Two-dimensional	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
$A_3$	Three-dimensional	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
$A_4$	Four-dimensional	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
Nucleation models			
$P_2$	Power law, $n = 1/2$	$2\alpha^{1/2}$	$\alpha^{1/2}$
$P_3$	Power law, $n = 1/3$	$3\alpha^{2/3}$	$\alpha^{1/3}$
$P_4$	Power law, $n = 1/4$	$4\alpha^{3/4}$	$\alpha^{1/4}$
Diffusion models			
$D_1$	One-way transport	$0.5\alpha$	$\alpha^2$
$D_2$	Two-way transport	$[- \ln(1 - \alpha)]^{-1}$	$\alpha + (1 - \alpha) \ln(1 - \alpha)$

The master plot method is based on the integral kinetic equation. From the integral kinetic equation (Eq. 6), we can obtain the following one using a reference at point  $\alpha = 0.5$ :

$$G(0.5) = \frac{AE}{\beta R} P(u_{0.5}) \quad (15)$$

Dividing Eq. 10 by Eq. 15, one obtains:

$$\frac{G(\alpha)}{G(0.5)} = \frac{P(u)}{P(u_{0.5})} \quad (16)$$

The integral master plot method can be established by comparing the experimental plot of  $P(u)/P(u_{0.5})$  versus  $\alpha$  with theoretical plots of  $G(\alpha)/G(0.5)$  versus  $\alpha$  using various kinetic models (Table 1). According to Eq. 16, the experimental value of  $P(u)/P(u_{0.5})$  is equal to the theoretical value of  $G(\alpha)/G(0.5)$  at a fixed conversion  $\alpha$ . Therefore, the reaction kinetic model can be determined based on the comparison of the experimental and the theoretical master plots.

## Results and discussion

### Determination of activation energy with different methods

Three methods, i.e., CR, FWO, and KAS, were used to determine the apparent activation energy of LWT. Based on

the detail methods described in “[Model-based method \(CR method\)](#)” and “[Iso-conversional method \(FWO and KAS methods\)](#)” sections, the values of apparent activation energy using different methods were obtained (Tables 2 and 3). Table 2 gives the values using CR method, among which the linear correlation coefficients are all above 0.99, so the values are credible. According to Table 2, the activation energy  $E$  of stage II and III during pyrolysis is 22.87 and 260.51 kJ mol<sup>-1</sup> and their kinetic exponent  $n$  is 2.3 and 5.4, respectively. In combustion process, the activation energy  $E$  is 43.73 kJ mol<sup>-1</sup> and the kinetic exponent  $n$  is 1.2.

Figure 1 shows the plots for the determination of the activation energy using FWO and KAS methods. In theory, these plots should be straight lines as described in “[Iso-conversional method \(FWO and KAS methods\)](#)” section. However, the plots in Fig. 1 are obviously not straight. This is due to the temperature shift under the action of different heating rates, and this tendency can also be predicted according to the TG and DTG curves in the first part of this study series. Besides, Xiao et al. [17] analyzed the TG data of coal blends during combustion using KAS method and the plots showed the same tendency.

In pyrolysis process, according to the first part of this study series, the characteristic temperatures are basically consistent with each other at the heating rates of 25 and 35 °C min<sup>-1</sup>. In particular, for stage III, the peak temperature is nearly the same at these two heating rates. Thus,

**Table 2** Activation energy and Arrhenius pre-exponential factors from pyrolysis/combustion process using CR method

Process/stage	Heating rate/ $^{\circ}\text{C min}^{-1}$	Temperature zone/ $^{\circ}\text{C}$	$n$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$R$
<b>PYR</b>						
II	5	280–520	2.7	16.45	0.23	0.9921
	15	280–620	2.7	23.55	5.25	0.9901
	25	300–600	2.2	22.88	6.53	0.9911
	35	300–600	2.1	24.93	11.58	0.9917
	45	330–570	1.8	26.52	18.98	0.9949
	Average			2.3	22.87	
III	5	800–850	7	326.75	$1.34 \times 10^{17}$	0.9907
	15	740–830	6	263.93	$7.11 \times 10^{15}$	0.9907
	25	710–780	5	261.09	$7.45 \times 10^{15}$	0.9919
	35	710–780	5	256.81	$4.75 \times 10^{15}$	0.9919
	45	690–770	4	193.96	$1.37 \times 10^{12}$	0.9934
	Average			5.4	260.51	
<b>COM</b>						
II	5	250–410	1.5	65.07	$5.94 \times 10^4$	0.9921
	15	250–550	1.6	61.94	$5.65 \times 10^4$	0.9945
	25	250–550	1.3	46.92	$2.19 \times 10^3$	0.9923
	35	250–600	0.8	26.53	18.21	0.9980
	45	250–650	0.6	18.21	2.76	0.9975
	Average			1.2	43.73	

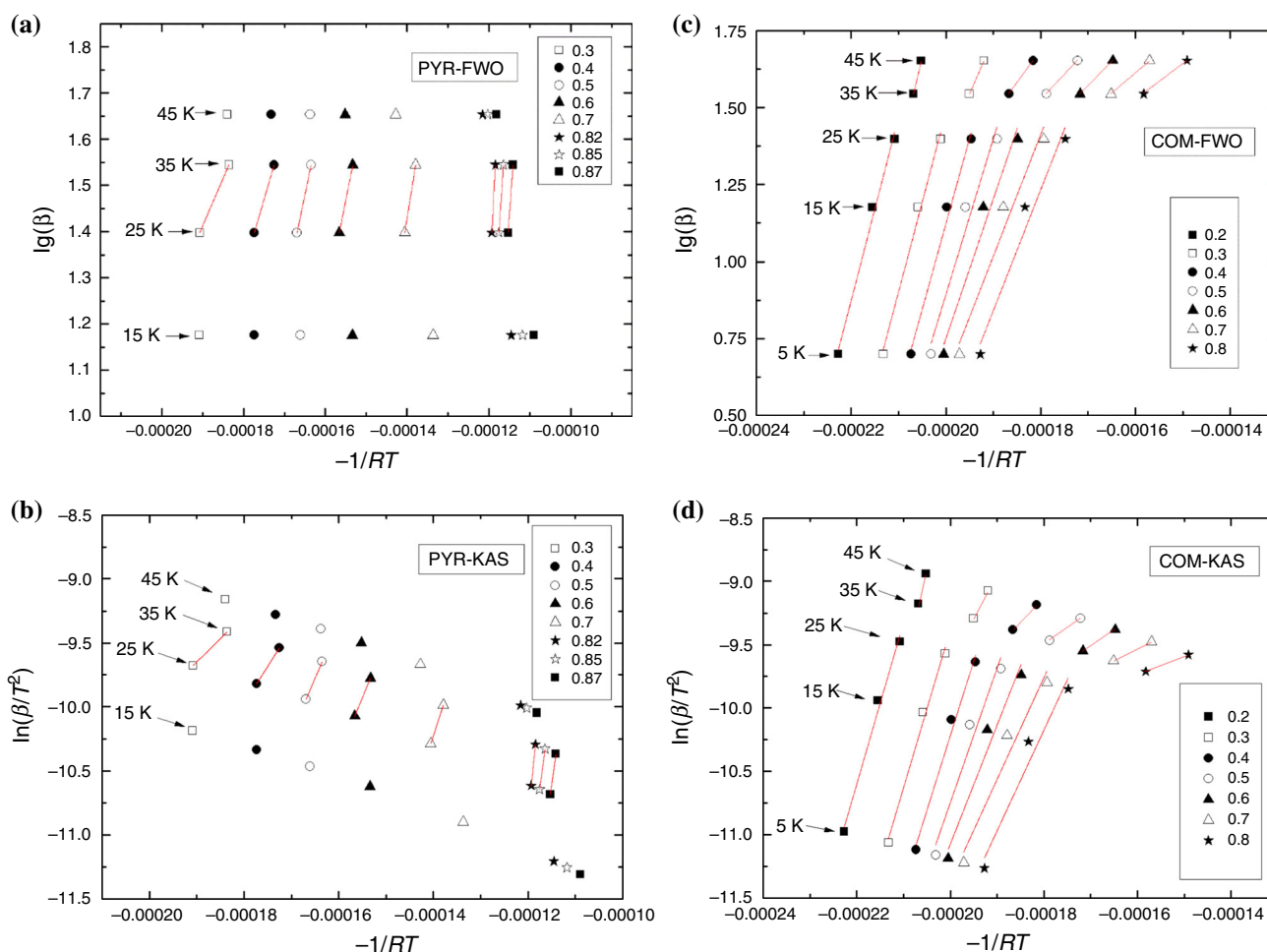
**Table 3** Activation energy from pyrolysis/combustion process using KAS and FWO methods

Conversion rate ( $\alpha$ )	KAS method $E/\text{kJ mol}^{-1}$	FWO method $E/\text{kJ mol}^{-1}$
<i>Pyrolysis</i>		
0.3	36.488	44.861
0.4	58.174	66.192
0.5	86.762	94.019
0.6	89.278	97.174
0.7	112.156	120.313
Average	76.572	84.512
0.82	365.089	363.178
0.85	278.611	281.199
0.87	262.213	265.931
Average	301.971	303.436
<i>Combustion</i>		
0.2	138.027	140.256
0.3	97.496	102.215
0.4	78.218	84.277
0.5	66.264	73.280
0.6	59.068	66.760
0.7	49.469	58.002
0.8	46.952	56.016
Average	76.499	82.972

data from 25 and 35  $^{\circ}\text{C min}^{-1}$  were chosen for the determination of activation energy and the results are given in Table 3. The average activation energies of stage II using FWO and KAS methods are 76.57 and 84.51  $\text{kJ mol}^{-1}$ , and they are 301.97 and 303.44  $\text{kJ mol}^{-1}$  in stage III. The values of activation energy using these two methods vary slightly, so these methods are credible.

In combustion process, as shown in Fig. 1, the data were separated into two groups for the determination of the activation energy. Just as mentioned in the first part of this study series, two kinds of rule were observed from the DTG curves of combustion. Therefore, the activation energies of these two groups were first obtained based on the slopes of plots in Fig. 1 and their average value was defined as the final activation energy of LWT during combustion. According to the data in Table 3, during combustion process, the activation energies of LWT using FWO and KAS methods are 76.50 and 82.97  $\text{kJ mol}^{-1}$ , respectively.

From the result in Tables 2 and 3, it is obvious that the value of activation energy using iso-conversional methods (FWO and KAS) is higher than that using CR method. Besides, Cui et al. [18] also compared CR with KAS methods when analyzing the activation energy of oil shale combustion and the activation energy obtained by KAS method was also higher than CR method. This is consistent with the



**Fig. 1** Plots for the determination of activation energy of pyrolysis/combustion process at different  $\alpha$  by FWO method and KAS method

**Table 4** Comparison of various activation energy values of pyrolysis/combustion for different fuels by iso-conversional method

Sample	$E/\text{kJ mol}^{-1}$	
	COM	PYR
LWT (stage II)	79.74	80.54
LWT (stage III)	–	302.70
Lignite (HX) [19]	80.92	–
Bituminous coal (ZQ) [19]	75.16	–
Oil shale (stage II) [18]	80	–
Oil shale (stage III) [18]	250	–
Chlorella (stage II) [20]	45	51
Chlorella (stage III) [20]	63	64
Wood chips [21]	24	29
Olive husk [21]	35	40
Pine seed shells [21]	26	34

conclusion in this study and proves that the result is correct. In addition, according to Wang et al. [19], the activation energy of a lignite during combustion was obtained as

$80.92 \text{ kJ mol}^{-1}$  (Table 4) using KAS method. This value is close to the average value  $79.74 \text{ kJ mol}^{-1}$  in this study, which illustrates that the method used in this study is correct. In a word, the activation energy obtained based on iso-conversional methods is believed to be more credible.

For CR method, the value of activation energy during combustion process is higher compared to pyrolysis process. However, when using iso-conversional methods, the activation energy of combustion and pyrolysis is nearly the same and the activation energy of combustion is slightly lower than that of pyrolysis. In order to evaluate which method is more credible, the comparison of various activation energy values of pyrolysis and combustion for different fuels was analyzed as shown in Table 4 [18–21]. In Table 4, it can be easily found that there are four fuels whose activation energy of combustion is slightly lower than pyrolysis. It is consistent with the conclusion in this study and proves that the iso-conversional method is accurate for analyzing the activation energy of pyrolysis and combustion.

The iso-conversional method has already been proved to be more accurate than CR method, and the activation energy obtained by FWO and KAS methods is very close, so the average values of the two methods were chosen as the final activation energy as given in Table 4. From Table 4, the LWT is found to have similar characteristics to the oil shale since they both have two main stages and the activation energy of each stage is also similar.

**Determination of kinetic model, kinetic exponent, and pre-exponential factor with the complementary method**

The activation energy of LWT has been obtained by iso-conversional methods; however, a whole kinetic mechanism still needs the kinetic model, kinetic exponent, and pre-exponential factor. Thus, a complementary method was used in this study to determine the three parameters.

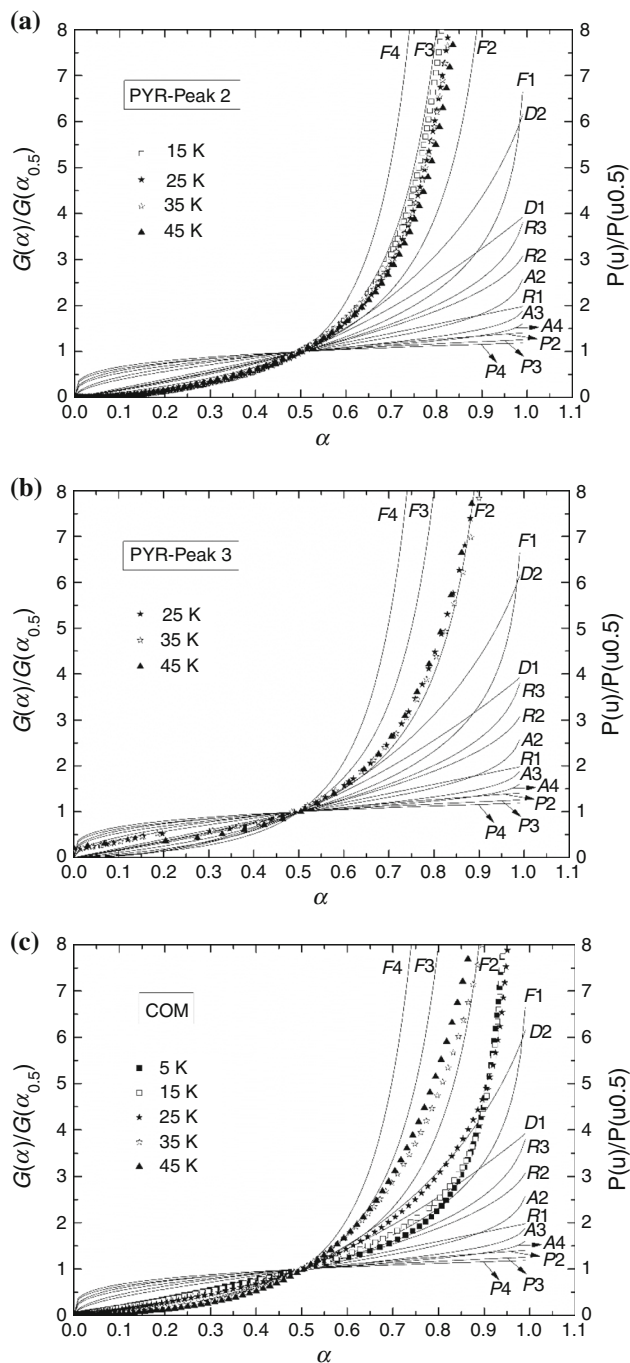
Firstly, the master plot method was used to determine the kinetic model. Detail method was described in “A complementary method of iso-conversional and model-based analysis” section, and the plots of  $G(\alpha)/G(0.5)$  versus  $\alpha$  from various reaction models (Table 1) and  $P(u)/P(u_{0.5})$  versus  $\alpha$  from experimental data are shown in Fig. 2. The parameter  $\alpha$  used here is defined as the degree of conversion at the analyzed stage. Comparing the experimental plots [ $P(u)/P(u_{0.5})$  vs.  $\alpha$ ] with the theoretical plots [ $G(\alpha)/G(0.5)$  vs.  $\alpha$ ], the kinetic model of pyrolysis at stage II is found to be between  $F_2$  and  $F_3$  and the model at stage III is close to  $F_2$ . In combustion process, two kinetic models were observed at different heating rates: One is between  $F_2$  and  $F_3$  and the other one is close to  $F_2$ . Thereby,  $n$ th-order model is the kinetic model of both pyrolysis and combustion of LWT, i.e.,  $f(\alpha) = (1 - \alpha)^n$ .

Secondly, the kinetic exponent  $n$  needs to be determined. Based on  $n$ th-order model and Eq. 10, one obtains:

$$G(\alpha) = \frac{AE}{\beta R} P(u) = \frac{(1 - \alpha)^{1-n} - 1}{n - 1} \tag{17}$$

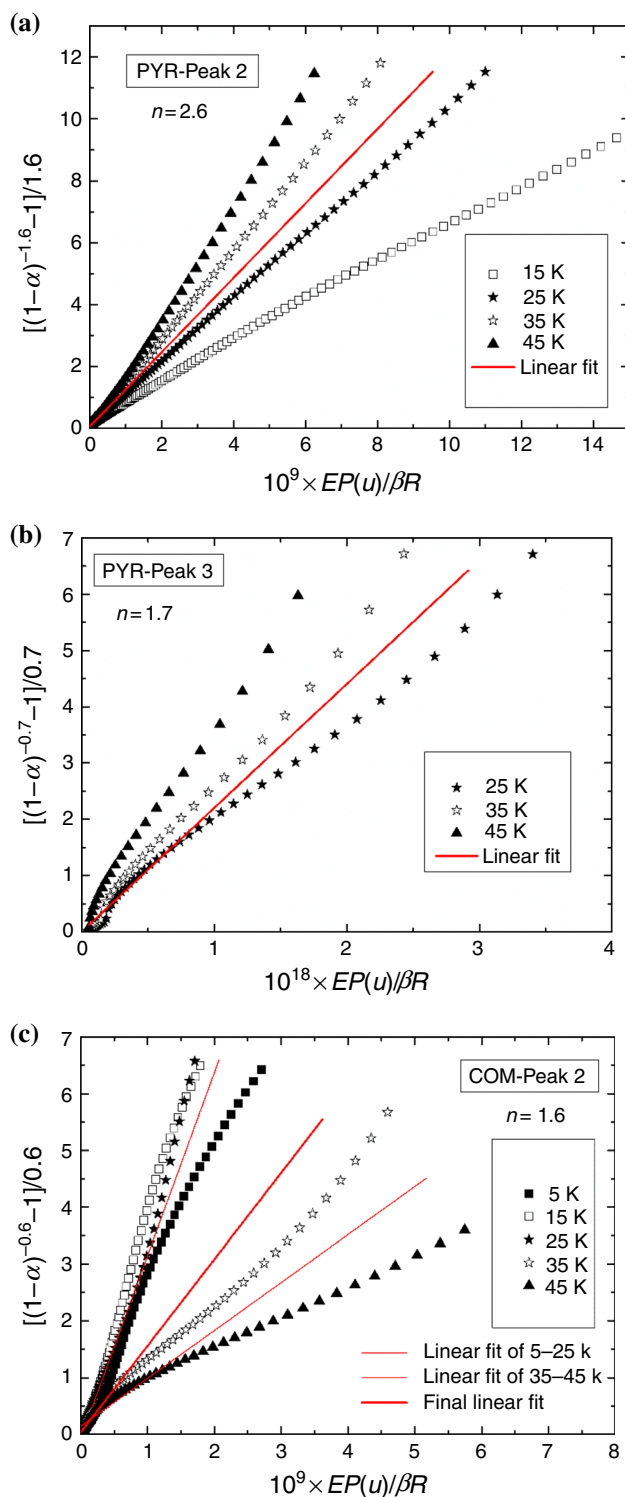
To obtain the optimal kinetic exponent  $n$ ,  $n$  was increased by 0.1 within the range showed in Fig. 2. Then, plot  $[(1 - \alpha)^{1-n} - 1]/(n - 1)$  versus  $EP(u)/\beta R$  and use linear fitting to these curves. The optimal  $n$  was defined as the one for which the correlation coefficient  $r$  reached its highest value. The results showed that the optimal  $n$  of pyrolysis at stage II, stage III, and the combustion process is 2.6, 1.7, and 1.6, respectively. The corresponding kinetic models are  $f(\alpha) = (1 - \alpha)^{2.6}$ ,  $f(\alpha) = (1 - \alpha)^{1.7}$ , and  $f(\alpha) = (1 - \alpha)^{1.6}$ , respectively.

Finally, the pre-exponential factor needs to be determined. Figure 3 shows the plots of  $[(1 - \alpha)^{1-n} - 1]/$



**Fig. 2** Theoretical plots of  $G(\alpha)/G(0.5)$  versus  $\alpha$  from various reaction models (Table 1) and experimental plots of  $P(u)/P(u_{0.5})$  versus  $\alpha$  from experimental data

$(n - 1)$  versus  $EP(u)/\beta R$  at various heating rates and their linear fitting lines. In combustion process (Fig. 3c), two linear fitting lines were observed and their average value was defined as the final line. Based on Eq. 17, the slopes of these lines were defined as the pre-exponential factor. The



**Fig. 3** Plots of  $[(1 - \alpha)^{1-n} - 1]/(n - 1)$  versus  $EP(u)/\beta R$  at various heating rates

pre-exponential factor  $A$  of pyrolysis at stage II, stage III, and the combustion process is obtained as  $1.20 \times 10^9$ ,  $2.20 \times 10^{18}$ , and  $1.52 \times 10^9 \text{ min}^{-1}$ , respectively.

## Conclusions

Model-based method (CR) and iso-conversional methods (FWO and KAS) were compared in this study to evaluate the activation energy  $E$  of LWT. The heating rate has an obvious effect on the kinetics of pyrolysis and combustion. The iso-conversional methods were proved to be more credible than model-based method.

The values of  $E$  of pyrolysis at stage II, stage III, and the combustion process are 80.54, 302.70, and 79.74  $\text{kJ mol}^{-1}$ , respectively. Compared to other fuels, the characteristics of LWT are close to oil shale based on their similar  $E$ .

A complementary method of iso-conversional and model-based was used in this study to determine the kinetic mechanism of LWT. Firstly, the kinetic model was determined using master plot method as:  $f(\alpha) = (1 - \alpha)^n$ . Then, the kinetic exponent  $n$  and the pre-exponential factor  $A$  were determined by plotting  $[(1 - \alpha)^{1-n} - 1]/(n - 1)$  versus  $EP(u)/\beta R$  and the two parameters got their optimal values when the correlation coefficient of the linear fitting line is highest.

The results show that  $n = 2.6$  and  $A = 1.20 \times 10^9 \text{ min}^{-1}$  for pyrolysis at stage II;  $n = 1.7$  and  $A = 2.20 \times 10^{18} \text{ min}^{-1}$  for pyrolysis at stage III;  $n = 1.6$  and  $A = 1.52 \times 10^9 \text{ min}^{-1}$  for combustion process.

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