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Kinetic analyses of biomass tar pyrolysis using the distributed activation energy model by TG/DTA technique

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Abstract Biomass tar pyrolysis behavior was investigated in absence and presence of catalyst-dolomite (10% mass) with different heating rates of 10, 20, 30 K min^{-1} under nitrogen atmosphere. Different kinetic methods such as distributed activation energy model (DAEM), Coats–Redfern method were used to analyze the TG/DTA data to identify reaction parameters. For Coats–Redfern method, first reaction order ($n = 1$) and two stages (volatilization and pyrolysis) reaction model was selected to calculate the kinetics parameters; for DAEM model, three different heating rates (10, 20, 30 K min^{-1}) were selected to obtain the activation energy distribution (E_a). The peak values of E_a curves for biomass tar volatilization process are nearly 250 and 200 kJ mol^{-1} in absence and presence of dolomite, whereas, the value of E_a for pyrolysis stage gradually increase and varied from 70 to 200 and 40 to 100 kJ mol^{-1} with the mass loss, respectively, in absence and presence of dolomite. The application of the new DAEM model can show the variation trend of activation energy for the whole pyrolysis process.

Keywords Biomass tar · Pyrolysis · Kinetic model · DAEM model · Dolomite

List of symbols

A	Pre-exponential factor (min^{-1})
E	Apparent reaction activity energy (kJ mol^{-1})
k	Rate constant (min^{-1})
R	Gas constant, 8.314 J mol^{-1} K^{-1}
t	Reaction time (min)
T	Sample temperature (K)
W_0	Sample mass at the start time (mg)
W_t	Sample mass at time t (mg)
W_∞	Sample mass at end time (mg)
β	Heating rate (K min^{-1})
α	Mass loss ratio

Introduction

With the depletion of fossil fuel sources as well as the global warming issues, the utilization of biomass is getting increased attention as a potential source of renewable energy, in which biomass thermochemical conversions (pyrolysis, gasification and combustion) are major utilization techniques [1, 2]. Pyrolysis reactions are the first step for all thermochemical biomass conversions, then produces gas, char and tar, so the research on pyrolysis behavior of biomass tar will favor the understanding the development of energy thermal conversion process. Usually, tar is an unavoidable product for these process, for example, tar from biomass pyrolysis is often called as "pyrolysis oil", which is the main aim product of this process; The concentration of tar in product gases can be from 0.1% (downdraft) to 20% (updraft) or greater for biomass gasification, and also the calculated low heating value of biomass tar stands for approximately 10% of the heat content in the product gases [3]. So tar utilization also has an important influence on the efficiency of energy resource.

Thermo-analytical tools such as thermogravimetry (TG) and differential thermal analysis (DTA) can play an important role on combustion behavior research. The use of

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thermal method for characterization of fuel such as coal, lignin or tar is certainly not new, and much work has been carried out to study the combustion process [4–7]. Nevertheless, only few investigations are currently available on the pyrolysis behavior of biomass tar [8–10] and also in coexistence with catalyst [9].

Biomass oil derived via slow pyrolysis process blended with ethanol and burned in a circular jet spray at atmospheric pressure was studied by Stamatov et al. [4]. It showed that biomass pyrolysis oil flames were shorter, wider and brighter than diesel fuel flames at the same conditions. Karaosmanoglu and Tetik [5] studied the characteristic of tar oil as combustion energy from biomass pyrolysis. It was found that pyrolytic oil was a carbon rich, hydrocarbon mixture bearing oxygen at a considerable ratio and containing ash, sulphur and nitrogen in very small quantities. Ambalae et al. [6] studied the pyrolysis and combustion behavior of heavy oil and its asphaltenes by TGA. Kök [7] applied TG/DTG techniques to characterize the pyrolysis and combustion properties of two heavy crude oils, in pyrolysis experiments, temperature ranges where distillation and cracking process were identified. Kök and Karacan [8] also studied the pyrolysis behavior and kinetics of six crude oils by DSC and TG/DTG. And also the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix was investigated by TG/DTA techniques, and four stages combustion kinetic model was applied [9]. On some degree, the property of biomass tar is similar to heavy oil, and can be regarded as one kind potential combustion oil, so it is quite promising for its evaluation as fuel from the view of kinetic process. However, biomass tar pyrolysis is extremely complicated and its pyrolysis behavior and mechanism still requires further study.

In this study, thermo-gravimetric analyzer was adopted to obtain information on the pyrolysis behavior of biomass tar in the absence and presence of catalysts, 10% (mass) dolomite was added in biomass tar, and pyrolysis behavior was studied. Coats–Redfern and distributed activation energy models (DAEM) were used to analyze the TG/DTG data. Three different heating rates (10, 20, 30 K min^{-1}) were selected to obtain the activation energy distribution (E_a). It showed that DAEM was more descriptive of the pyrolysis reaction.

Experimental

Sample and catalysts

The tar studied in this research was supplied from fowl droppings gasification process. The chemical analysis of the tar obtained by a CHN analyzer was shown in Table 1. In the presence of catalyst, for each sample, around 10% (mass) of catalyst (calcined dolomite) was added to the tar and mixed uniformly in order to see the effect of catalyst on tar pyrolysis behavior.

Table 1 Elemental composition of tar by CHN

C	45.2%
H	6.4%
N	6.20%
Ignition loss	42.2%

Table 2 Component of calcined dolomite

Composition	CaO	MgO	SiO_2	Fe_2O_3
(mass%)	55.90	39.98	4.05	0.07

Catalysts: Calcination of natural dolomite was carried out in muffle oven from room temperature to 1,000 °C with the heating rate 5 K min^{-1}, then kept at 1,000° for 2 h in air environment and used in this study. The component analysis of the calcined dolomite by energy dispersive X-ray spectrometer (EDX-700HS, SHIMADZU) is shown in Table 2, the main composition are CaO and MgO.

Thermogravimetry (TG/DTG) and differential thermal analysis (DTA) were performed with Rigaku Thermo Plus TG8120 thermo-gravimeter analysis system. The TG/DTG-DTA curves were obtained using the following experimental conditions: atmosphere. N_2; flow rate 50 mL min^{-1}; mass of tar sample was about 20–25 mg; heating rates: 10, 20 and 30 K min^{-1}; temperature range: 25–1,000 °C. During TG experiments, buoyancy such as effect temperature on balance, convection and/or turbulence and so on is the main source of error. So prior to experiments with the real tar, a blank run was carried out to check the satisfactory performance of the weighing module, and also to correct the buoyancy effect by running blank experiments. Each experiment was also performed more than twice for repeatability.

Kinetic theory

Different reaction models such as Arrhenius-type kinetic model [10–12], Coats–Redfern model [13–18], Horowitz–Metzger [19], DAEM [20–23] were developed and used on solid fuel such as coal, lignin combustion process by different researches. For our sample, biomass tar is one kind black and high viscosity liquid, can be regarded as one material whose properties are between liquid such as crude, heavy oil and solid such as coal, asphaltene, so the above reaction models also can be also applied in this process.

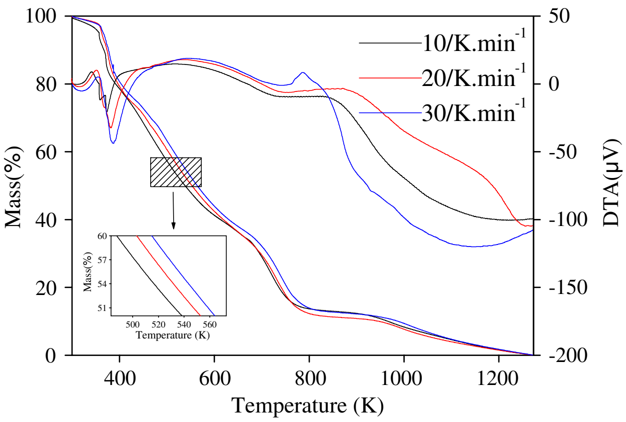

Fig. 1 TG/DTA curves of biomass tar with different heating rates

Coats–Redfern model

Our sample is a black liquid of high viscosity and can be regarded as a material whose properties lie between a liquid such as a crude heavy oil and a solid such as coal or asphaltene. Theoretically, the pyrolysis behavior of tar can be initiated when the temperature reaches some degree. However, the pyrolysis process is exceedingly complex and many competing reactions contribute to the thermal analysis curves, and also biomass tars from different sources have different combustion characteristics. TG/DTA curves of tar pyrolysis in the absence of catalyst were selected (the heating rate: 10, 20, 30 K min^{-1}) for the analysis of whole process (Fig. 1). It found that one endothermic peak appeared for all samples between 80 and 160 °C. Then one wide and gentle period appeared in the DTA curves. So, in conformity with the DTA curves, a two stage kinetic model was proposed and used in this study. The first stage is volatilization process, the endothermic peak lay in the volatilization of water and some smaller molecular compounds contained in tar, then will enter into pyrolysis stage. It is (i) volatilization, (ii) pyrolysis.

Because of the complex nature of the tar, its pyrolysis is often assumed to be a single reaction in which all the tar components are regarded as one group (a tar mixture) undergoing several simultaneous reactions: cracking, reforming, etc. The overall rate of tar disintegration is thus given by the sum of the rates of all the elementary individual reactions. This approach has been accepted by most researchers [7, 8, 13–18]. In this study, we also adopt this method, i.e. all the reactions involved in the pyrolysis process are lumped into one.

The calculation of kinetic data by thermogravimetry is based on the Eq. (1):

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \tag{1}$$

where k is reaction rate constant, $f(\alpha)$is reaction rate function.

In this study, all the reactions during the whole process are regarded as one lump, reaction order model was selected in this study, the calculation of kinetic data is based on the formal kinetic equation, then tar reaction rate function ($f(\alpha)$) including volatilization/pyrolysis can be expressed as Eq. (2).

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

where $\alpha = (W_0 - W_t)/(W_0 - W_\infty)$, it is volatilization/pyrolysis conversion rate, n is assuming reaction order, the correct presumed order should lead to the best linear plot. W_0 is the sample mass at start time (mg), W_t is sample mass at time t (mg). W_∞ is sample mass at the end time (mg). In this study, the first-order linear rate is adopted. Then combines with Arrhenius equation, by integral, if assuming $n = 1$ and $2RT/E \ll 1$; then the final style by Coats–Redfern method [7, 8, 13–18] can be available:

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

where A is pre-exponential factor, min^{-1}, E is apparent reaction activity energy, J mol^{-1}. $\beta = \mathrm{d}T/\mathrm{d}t$ (heating rate, K min^{-1}). The kinetic parameters could be obtained from TG/DTG data. Then, a plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ versus $\frac{1}{T}$ should give a straight line of slope $\frac{E}{R}$ and an intercept of $\ln\left(\frac{AR}{\beta E}\right)$. The criterion used for accepted values of E and A is that the $f(\alpha)$ should yield the best linear correlation coefficient.

DAEM model

The DAEM assumes that a number of parallel, irreversible and first-order reactions with different activation energies occur simultaneously. All the reaction activation energies had the same k_0 at the same conversion rate. The activation energy had a continuous distribution. The release of volatiles is given by:

$$1 - \frac{W_t}{W_0 - W_\infty} = \int_0^\infty \exp\left[-\frac{k_0}{\beta}\int_0^T \exp^{-E/RT}\mathrm{d}T\right] f(E)\mathrm{d}E \tag{4}$$

where W_0 is the sample mass at start time (mg), W_t is sample mass at time t (mg), W_∞ is sample mass at the end time (mg). E is apparent reaction activity energy (J mol^{-1}), β is the linear heating rate of the pyrolysis reaction heating rate (K min^{-1}), $f(E)$ is the distribution curve of the activation energy to represent the differences in the activation energies of many first order irreversible reactions. Usually, the pre-exponential factor is considered to be a constant over the temperature range studied. Then Eq. (4) can be simplified to Eq. (5) [20, 21]:

$$\frac{W_{\mathrm{t}}}{W_0 - W_\infty} = 1 - \int\limits_0^\infty \Phi(E,T) f(E)\mathrm{d}E \tag{5}$$

$$\Phi(E,T) = \exp\left[-\frac{k_0}{\beta}\int\limits_0^T \exp^{-E/RT}\mathrm{d}T\right] \tag{6}$$

by approximation, Eq. (6) can be simplified to

$$\Phi(E,T) = \exp\left[-\frac{k_0 RT^2}{\beta E}e^{-E/RT}\right] \tag{7}$$

Then it can be substitute with a step function at some special activation energy E_{s},

$$\frac{W_{\mathrm{t}}}{W_0 - W_\infty} = 1 - \int\limits_0^{E_{\mathrm{s}}} f(E)\mathrm{d}E. \tag{8}$$

Therefore, it can find the values of E at different $W_{\mathrm{t}}/(W_0 - W_\infty)$ levels from Eqs. (7) and (8), shown in Eq. (9), then it can find *f*(*E*) from experimental data.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) - \ln\left[-\ln\left(1 - \frac{W_t}{W_0 - W_\infty}\right)\right] - \frac{E}{R}\cdot\frac{1}{T}. \tag{9}$$

So by using Eq. (9), Arrhenius plots can be drawn for $\ln(\beta/T^2) \sim 1/T$. Different heating rates give different Arrhenius plots, theoretically, if two heating rates are used, a series of E values can be calculated from the slopes at different mass loss. Usually, three or more heating rates are used.

Results and discussion

Coats–Redfern method

According to Eq. (2), different reaction order will result different the expression style [17], in this study, first reaction order was selected, this handling method was accepted by most of researchers and Labs [2].

TG–DTA curves were produced for biomass tar and in the coexistence with 10% (mass) of dolomite, flow rate of N_2 (50 mL min^{-1}). Isothermal experiments were conducted from room temperature to 1,000 °C with different heating rates. An integrative plot of TG–DTA curves in N_2 environment with different heating rates was shown in Fig. 1 and 2, respectively. Analysis of the DTA curve of the tars showed that, the reaction trends of the two conditions (tar in absence or presence of dolomite) were similar, one endothermic peak appeared between 80 and 160 °C in the first reaction stage, then enter one relatively gently pyrolysis period. So for the calculation, two main stages are used, i.e. (i) volatilization, (ii) pyrolysis. From the calculation process, a plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ versus $\frac{1}{T}$ corresponding to the slope $\frac{E}{R}$ and an intercept of $\ln\left(\frac{AR}{\beta E}\right)$ also showed the obvious two stages (Fig. 3).

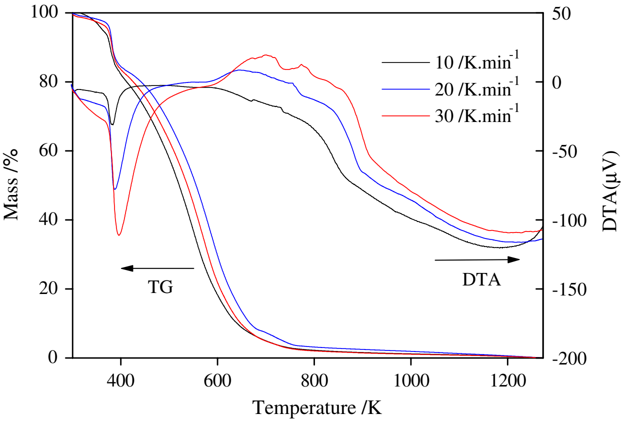

Fig. 2 TG/DTA curves of biomass tar with 10% (mass) dolomite at different heating rates

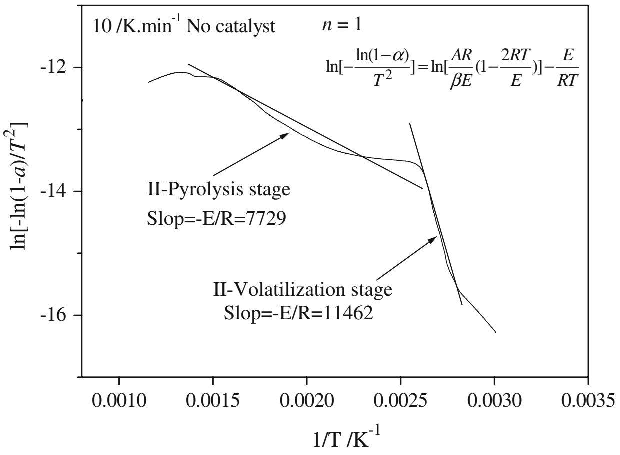

Fig. 3 Analysis of biomass tar pyrolysis without catalyst by Coats–Redfern method

The summary of the calculation results including apparent activation energy (E_{a}) and frequency factor (A) was shown in Table 3, the heating rates are 10, 20, 30 K min^{-1}, respectively, which provided the quantitative explanation for the TG and DTA curves of tar pyrolysis behavior in the absence and presence of catalysts. The values in the absence of catalysts of this study is in concordance with that reported by Williams and Ahmad [24], the activation energies were between 56, 74, 73, 58 kJ mol^{-1} for oil shale at different heating rates. A-boulkas et al. [25] obtained the mean values 85 ± 7 kJ min^{-1} for oil shale pyrolysis. From the results of Table 3, it showed that the apparent activation energy of volatilization stage was very higher. One possible reason to

Table 3 Results of biomass tar pyrolysis kinetic with Coats–Redfern method

Sample	β (K min^{-1})	Volatilization stage			Pyrolysis stage		
		E_a (kJ mol^{-1})	A (min^{-1})	R	E_a (kJ mol^{-1})	A (min^{-1})	R
Tar without catalyst	10	95.3	1.7×10^{5}	0.9917	60.1	1.7×10^{2}	0.9987
	20	110.5	4.1×10^{10}	0.9962	72.6	9.1×10^{3}	0.9965
	30	120.8	3.8×10^{14}	0.9968	89.3	1.8×10^{3}	0.9943
Tar + mass 10% dolomite	10	50.1	8.3×10^{11}	0.9985	38.1	8.3×10^{2}	0.9907
	20	58.6	7.2×10^{10}	0.9939	49.2	5.1×10^{3}	0.9983
	30	79.5	1.1×10^{14}	0.9928	62.1	8.9×10^{2}	0.9952

account for such observation is that some biomass internal oxygen was transferred into a liquid composition in form of water (around 10% in biomass tar) during biomass gasification. With the emulsions effect, these water is chemically dissolved in biomass tar, and could not form divided layer of water and oil, so it was more difficult to evaporate than pure water, and exhibited higher apparent activation energy in volatilization stage. The adding of solid dolomite reduced the higher apparent activation energy of the stage, main reason of this was on account of de-emulsification not catalysis. In pyrolysis stage, the apparent activation energy of biomass tar was greatly reduced with the adding dolomite. And also the heating rate has important influence on the activation energy.

DAEM method

The DAEM includes several first-order reactions and might be a better approach for modeling the real process. In this work a DAEM was evaluated from the set of three experimental runs in the thermo-balance, at different heating rates (10, 20, 30 K min^{-1}). For each run, and assuming a first order reaction, the nominal reaction rate constant k can be calculated at several identical volatile formation values but at different heating rates, and the Arrhenius plot can be considered as Eq. (8). In this case the activation energies were obtained from the Arrhenius plot at different levels of volatile formation. Thus, the same value of activation energy was obtained for the three heating rates, but its dependence on temperature varies with the operating conditions (i.e. heating rate). The distributed activation energy function, $f(E)$, is obtained by differentiating the volatile formation values from the activation energy values calculation, the procedure is summarized as: (1) Measure $W_t/(W_0 - W_\infty)$versus T using the three different heating rates. (2) Calculate the values of $\ln(\beta/T^2)$ and 1/T at the same $W_t/(W_0 - W_\infty)$. (3) Plot $\ln(\beta/T^2)$ and 1/T at the selected $W_t/(W_0 - W_\infty)$ ratio and then determine the activation energies E from the slopes. Then can get the relationship of $W_t/(W_0 - W_\infty)$ with E_a.

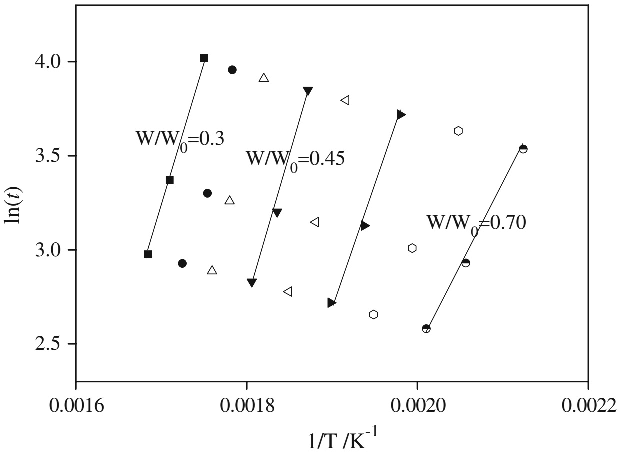

Fig. 4 Ln(t)–1/T plots at different mass loss level for biomass tar pyrolysis

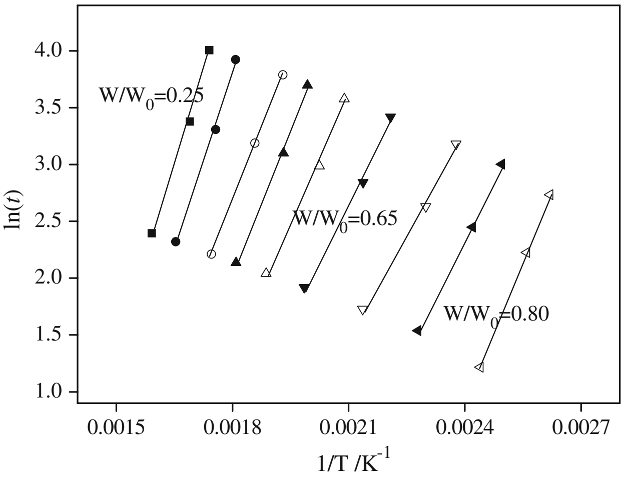

Fig. 5 Ln(t)–1/T plots at different mass loss level for biomass tar pyrolysis with dolomite (10% mass)

The results of biomass tar pyrolysis process in the absence and presence of dolomite are shown in Fig. 4 and 5.

The distribution of activation energies calculated from experimental results was shown in Fig. 6. For the two conditions (with and without dolomite), the E_a shape is

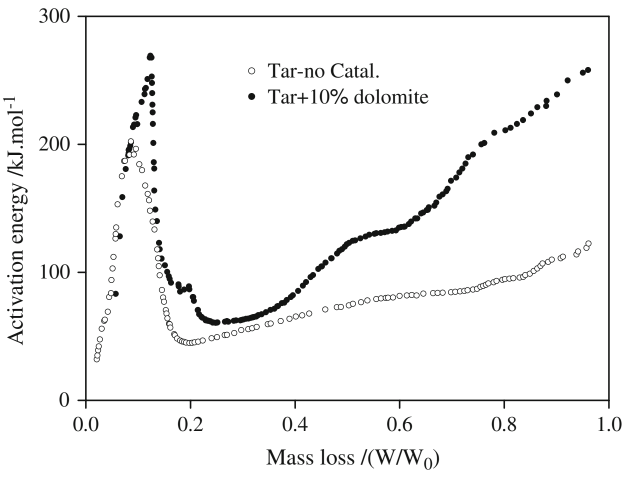

Fig. 6 Activation energy variation during biomass pyrolysis

nearly same. It can be divided into two parts clearly, the first one is present the shape of a normal Gaussian distribution (W/W$_0$ < 0.2). Then the E_a increases gradually. These results are also coincident with the two stages reaction model. The advantage of DAEM is that it can reflect the E_a distribution, more objectively reflect the real process.

Comparing the distribution of activation energies, it can find the adding of dolomite reduces the E_a for whole process. In summary, it can conclude that dolomite can greatly improve tar pyrolysis.

Conclusions

The thermo-gravimetric and derivative thermo-gravimetric analysis conducted in this study provided valuable information on the tar pyrolysis behaviour in absence and presence of dolomite.

By comparison the calculation result of different calculation model, Coats–Redfern method can be easily applied, and obtained one around E_a value, but DAEM can reflect the E_a distribution of whole pyrolysis process, was more descriptive of the pyrolysis reaction than Coats–Redfern. The coexistence of dolomite greatly improved the amount and speed of tar pyrolysis process, and the calculation results of E_a also gave the quantity explanation.

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