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Original Paper

Comparative pyrolysis kinetics of heavy oil and its SARA fractions using distributed activation energy model



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ABSTRACT

The pyrolysis behaviors of Qingdao vacuum residue (QD-VR) and its SARA (saturates, aromatics, reins, and asphaltenes) fractions were evaluated by thermo-gravimetric with mass spectrometer (TG-MS). The pyrolysis kinetics were determined by Friedman, one-parallel and four-parallel distributed activation energy model (DAEM), respectively. The results indicated that the pyrolysis behavior of QD-VR was similar to that of aromatics. For saturates, the release of H₂, CH₄, CO, and CO₂ occurred in 80–400 °C, while the temperature range for QD-VR and other fractions is 200–800 °C. The average activation energy (E_a) via Friedman method was 179.72 kJ/mol and increased with the conversion ratio. One-parallel Gaussian DAEM was more suitable to describe the pyrolysis process of the single SARA fractions, while four-parallel Gaussian DAEM was more suitable to describe the pyrolysis process of heavy oil. Furthermore, comparing the weighted E_a from one-parallel (227.64 kJ/mol) and four-parallel Gaussian DAEM (204.63 kJ/mol), the results suggested that during pyrolysis process of heavy oil, there was an interaction between the SARA fractions, which could reduce the E_a of heavy oil pyrolysis. Specifically, during heavy oil pyrolysis, resins and asphaltenes could increase the E_a of saturates and aromatics, while saturates and aromatics could decrease the E_a of resins and asphaltenes.

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1. Introduction

The depletion of conventional crude oil and the increasing demand for light oil products have prompted the global refining industry for heavy oil upgrading (Larter et al., 2008; Zhao et al., 2021). In addition, in order to make full use of heavy oil and reduce environmental problems, a large number of inferior petroleum residues (i.e., atmospheric residue, vacuum residue, oil slurry, and de-oiled asphalt) need to be processed into lighter fractions (Prajapati et al., 2021). However, heavy oil and inferior petroleum residues generally have the characteristics of low H/C ratio, high contents of heteroatoms (i.e., Ni, V, S, N, and O), resins and asphaltene, and thus leading to high coking tendency. For example, one of the problems in the residue thermal conversion are coke formation and fouling, which not only deactivate the solid catalyst, but also result in blockage for the refining equipment and pipes (Rahmani et al., 2002; Yi et al., 2009). Therefore, upgrading of these inferior petroleum residues into clean fuels has always been a hot

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and also a difficult issue during petroleum processing.

Pyrolysis of heavy oil and inferior petroleum residues is an important step in the production of high-quality gas, liquid fuels, and chemicals, which mainly involves thermal or catalytic processes, such as cracking, pyrolysis, coking, catalytic cracking, and hydrogenation, etc. Generally, heavy oil can be grouped into four group fractions, for instance, saturates, aromatics, resins, and asphaltenes, the so-called SARA fractions (Al-Saffar et al., 2001; Zhao et al., 2019). Therefore, quite a few researchers focused on the thermal behaviors and cracking activation energy (E_a) of heavy oil and its SARA fractions. Thermogravimetric analysis (TG) is one of the most widely used analysis methods to research the pyrolysis behaviors of fossil fuels (Fan et al., 2014; Gao et al., 2013; Li et al., 2020; Soria-Verdugo et al., 2020). According to the TG results, there are generally two kinds of methods to analyze pyrolysis kinetics. One kind is the model fitting (model-based) method, such as Coats-Redfern and Dolye methods. The other kind is model-free or iso-conversion method such as Flynn-Wall-Ozawa (FWO), Friedman, and Kissinger-Akahira-Sunose (KAS) method (Li et al., 2022).

Model-free methods can be used to accurately estimate the E_a under the condition of uncertain pyrolysis reaction mechanism

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(Mandapati and Ghodke, 2021). Hao et al. (2017a) calculated the kinetic parameters of oil sand bitumen and its SARA fractions by Friedman method and showed that the interaction between SARA fractions would affect the E_a value varying with the conversion ratio. Wei et al. (2018) studied that the oxidation kinetics of the SARA fractions of an extra-heavy crude oil by Arrhenius and FWO model. The results showed that saturates and resins could reduce the oxidation E_2 of asphaltenes oxidation, and aromatics could increase the oxidation E_a of asphaltenes oxidation. Trejo et al. (2010) compared pyrolysis kinetics of asphaltenes, resins, and sediments by an iso-conversional method based on Friedman's procedure and reported that the activation energy of asphaltenes ranged from 116.8 to 209.6 kJ/mol. Saitova et al. (2021) performed the thermodynamic and kinetic parameters for oxidation and pyrolysis of Yarega heavy crude oil asphaltenes and finding that asphaltenes from atmospheric residue and heavy parent oil had two pyrolysis stages, while only one stage was found for vacuum residue asphaltenes. Boytsova et al. (2017) investigated that pyrolysis kinetics of heavy oil and asphaltenes and found that the oil distillates and resins in the crude oil structure could prevent asphaltenes pyrolysis. Boytsova et al. (2018) conducted the pressure effect on the activation energy during asphaltene gasification by a first-order kinetic model and integral method and found that the E_a decreased with an increasing pressure. Wang et al. (2020) investigated that the pyrolysis kinetics of SARA fractions by the Arrhenius model and found that the addition of saturates, resins, and asphaltenes could reduce the high temperature pyrolysis E_a of heavy crude oil. In contrast. Kok and Gul (2013) studied the combustion characteristics and kinetics of two Turkish crude oils and their SARA fractions by KAS method and showed that each fraction followed its reaction pathways independent of the presence of other fractions. Karacan and Kok (1997) studied the pyrolysis characteristics of crude oils and its SARA fractions using TG/DSC methods and showed that the SARA fractions followed their own pyrolysis pathways without interaction. Liu et al. (2017) studied the interaction between the SARA fractions during pyrolysis and oxidation of heavy oil by TG and found that there were no interactions among saturates, aromatics, and resins during co-pyrolysis, whereas the interactions were significant during co-combustion. Concise review on the above studies showed that the pyrolysis behaviors of heavy oil and SARA fractions had received considerable attention in the literature. However, the pyrolysis behavior of SARA fractions especially SARA interactions during non-isothermal pyrolysis are still not fully understood. Also, the effects of SARA fractions on the pyrolysis behavior of heavy crude oil have not been well documented. In addition, in these studies, the heavy oil was regarded as a single component during the pyrolysis and the kinetic parameters were determined. It is well-known that the composition of heavy oil was complex and thus the pyrolysis involved multiple reactions, so heavy oil pyrolysis could not be simply treated as a single component. Therefore, an accurate kinetic model was necessary for clarifying the reaction mechanism and kinetics of heavy oil and its SARA fractions pyrolysis.

The distributed activation energy model (DAEM) was widely used in the analysis of complex reaction systems of fossil fuels (Miura, 1995). It assumes that there are a series of irreversible firstorder parallel reactions with different kinetic parameters (preexponential factor *A* and E_a) in the pyrolysis process, which has already been used to describe the pyrolysis characteristics of several carbonaceous fuels (Cai et al., 2014). DAEM was generally used to divide the pyrolysis process of biomass into three independent parallel reactions corresponding to three pseudocomponents (i.e., cellulose, hemicellulose, and lignin) to describe the pyrolysis characteristics of biomass (Li et al., 2008; Chen et al., 2016). Besides, DAEM has also been widely used in the study of pyrolysis of coal (Wang et al., 2017), sewage sludge (Soria-Verdugo et al., 2013), oil shale (Vyas et al., 2016). However, DAEM has not been extensively studied for the pyrolysis kinetics of heavy oils, especially for heavy oils with different compositions and their SARA reaction characteristics.

In this study, the pyrolysis performances of one heavy oil and its SARA fractions were comparatively evaluated by thermogravimetric mass spectrometer (TG-MS). The research on the pyrolysis performances of the samples mainly focused on the mass loss and corresponding gas release behavior. The kinetic parameters were calculated by the Friedman, one-parallel and four-parallel Gaussian DAEM model for complex heavy oil. By comparing the applicability and accuracy of these kinetics results, the pyrolysis behavior and kinetics of heavy oil and its SARA fractions in the whole temperature range were explored to provide new understanding of the pyrolysis. The experimental and analytic schemes are shown in Fig. 1.

2. Experimental

2.1. Characteristics of raw material

Qingdao vacuum residue (QD-VR) from China National Petroleum Corporation (CNPC) was selected as experimental feedstock. Its basic properties are presented in Table 1. According to the industrial standard of China Petroleum NB/SH/T 0509–2010, the SARA fractions, i.e., saturates, aromatics, resins, and asphaltenes were obtained, of which the specific procedure was previously described by Wu et al. (2014).

2.2. Pyrolysis experiment

The non-isothermal pyrolysis of QD-VR at four different heating rates (10, 20, 30, and 40 °C/min) and the non-isothermal pyrolysis of its SARA fractions at 20 °C/min were measured by TG (SII TG/DTA 7300, SETARAM, France). A minor amount of heavy oil sample (\sim 5 mg) was heated to 750 °C and maintained for 0.5 h to remove volatile matter. The preliminary tests justified that the mass of



Fig. 1. Schematic of experimental implementation and kinetic analyses.

Table 1

	Basic	proper	ties of	Qingdao	vacuum	residue
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Properties	Values	Properties	Values
Density (20 °C), g·cm ⁻³	1.025	n(H)/n(C)	$\begin{array}{c} 1.41 \\ \mu g \cdot g^{-1} \\ 51.12 \\ 46.13 \\ wt\% \\ 8.33 \\ 51.17 \\ 29.08 \\ 11.42 \end{array}$
Kinematic viscosity (100 °C), mm ² ·s ⁻¹	1329.01	Metal content	
Conradson carbon residue (CCR), %	17.15	Ni	
Elemental analysis	wt%	V	
C	84.74	SARA analysis	
H	9.96	Saturates	
N	3.64	Aromatics	
S	0.75	Resins	
O	0.91	Asphaltenes	

heavy oil sample less than 5 mg and the N_2 with a flow rate of 100 mL/min could minimize the effects of internal and external diffusion and thus to maximally keep heavy oil pyrolysis under the control of chemical reaction (Hao et al., 2017a). To ensure the repeatability and the correctness of the experimental data, each experiment was conducted three times.

Determination of evolved gases from TG was carried out continuously using the quadrupole mass spectrometer (LC-D200M PRO, TILON, USA). The generated gases entered the MS through a quartz capillary (<1000 mbar). According to the mass to charge ratios (m/z) of target gases, the gas components were detected. The MS scan range was 1–100 amu at a scan rate of 200 ms/amu.

2.3. Kinetics model

2.3.1. Friedman model

Friedman method is one of the model-free methods, which is an iso-conversional differential method. The advantage of using the Friedman method is that it does not require any knowledge of the reaction mechanism to determine the activation energy of the fossil fuels. However, it is important to note that the Friedman method has certain limitations and assumptions. For example, it assumes that the pyrolysis of the fuels is as a single component reaction and that the reaction order does not change with temperature. Meanwhile, it also requires accurate temperature measurements and the use of appropriate heating rates to increase the calculation accuracy.

Among the model-free method, the Friedman method was widely used to assess the pyrolysis E_a of fossil fuels. Many studies have shown that pyrolysis reaction as a first order reaction can better explain the pyrolysis reaction process (Heal, 1999; Alvarez et al., 2011; Schucker et al., 1983). The Friedman method involves plotting the logarithm of the conversion rate versus the reciprocal of the temperature, at a constant conversion level. The activation energy can then be calculated from the slope of the resulting line using the Arrhenius equation (Heal, 1999). The equation of Friedman method was given as (Alvarez et al., 2011):

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln A + \ln f(\alpha) - \frac{E_{\mathrm{a}}}{RT} \tag{1}$$

where β is the constant heating rate, α is the sample conversion rate at time *t*, *A* is the pre-exponential factor, $f(\alpha)$ represents the reaction mechanism model function, E_a is the activation energy of the reaction, *R* is the gas constant, and *T* is the absolute temperature at time *t*. By $\ln(\beta \cdot d\alpha/dt)$ to 1/T curve, the linear fitting of the same conversion point can be obtained, and the E_a can be determined by the slope of the corresponding line.

2.3.2. One-parallel Gaussian DAEM

The distributed activation energy model (DAEM) equation is widely used in the analysis of complex reactions and is developed on the assumption that many irreversible first-order or multi-order parallel reactions with different kinetic parameters occur simultaneously (Miura, 1995; Cai et al., 2014). Compared with Friedman method that assumes a single activation energy, it can provide a more accurate description of the thermal decomposition kinetics of complex materials. Meanwhile, it is very flexible, which can be applied to a wide range of materials and reaction conditions. However, the DAEM also has some limitations. It requires a significant amount of experimental data to determine the distribution of activation energies, which can be time-consuming and expensive. And the accuracy of the DAEM depends on the quality of the experimental data and the assumptions used to model the distribution of activation energies. The DAEM considers that there is an activation energy value for each reaction temperature at a constant heating

rate, as well as a distribution function $f(E_a)$ of activation energy values that vary with temperature. In most DAEM applications, the activation energy distribution curve is assumed to be the Gaussian function. In the DAEM equation of this study, we assumed that the reaction of heavy oil was a first-order reaction, and the DAEM equation could be expressed as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \int_{0}^{\infty} \frac{A}{\beta} \exp\left[-\frac{E_{\mathrm{a}}}{RT} \int_{T}^{I_{0}} \frac{A}{\beta} \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \mathrm{d}T\right] f(E_{\mathrm{a}}) \mathrm{d}E_{\mathrm{a}}$$
(2)

The E_a distribution is generally represented by the Gaussian distribution function, which can be descried by the mean E_a and the standard deviation σ , and the distribution function must meet the following conditions:

$$f(E_{\rm a}) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{(E_{\rm a} - E_0)^2}{2\sigma^2}\right) \tag{3}$$

$$\int_{0}^{\infty} f(E_{a}) dE_{a} = 1$$
(4)

If the fossil fuel was a single component, the pyrolysis could be regarded as one parallel reaction of one component. The oneparallel Gaussian DAEM could be used to assess its pyrolysis E_a . Eqs. (2)–(4) are combined to obtain the distributed E_a equation of one-parallel Gaussian DAEM, which can be expressed as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{\sqrt{2\pi\sigma}} \int_{0}^{\infty} \frac{A}{\beta} \exp\left[-\frac{E_{\mathrm{a}}}{RT} - \int_{0}^{T} \frac{A}{\beta} \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \mathrm{d}T - \frac{(E_{\mathrm{a}} - E_{0})^{2}}{2\sigma^{2}}\right] \mathrm{d}E_{\mathrm{a}}$$
(5)

2.3.3. Four-parallel Gaussian DAEM

Due to the complex composition of heavy oil, the pyrolysis of heavy oil can be regarded as a combination of parallel reactions of multiple components. According to the SARA of heavy oil, the process of heavy oil pyrolysis is divided into four independent parallel reactions corresponding to four pseudo-components, that is, saturates, aromatics, resins, and asphaltenes, by using the fourcomponent Gaussian DAEM, which can be expressed as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \sum_{i=1}^{4} w_i \frac{\mathrm{d}\alpha_i}{\mathrm{d}T} \tag{6}$$

Numerical optimization is carried out by the method of minimizing the value of the following objective function, which is shown in Eq. (7).

$$S = \sum_{i=1}^{n} \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T} \Big|_{i,\exp} - \frac{\mathrm{d}\alpha}{\mathrm{d}T} \Big|_{i,\mathrm{cal}} \right)^{2} < 5 \cdot 10^{-6}$$
(7)

When the *S* value does not change significantly with the increase of the number of iterations, the optimal fitting value is obtained.

In order to obtain accurate kinetic parameters, the fit deviation value was set as the standard for evaluating the model fitting degree. The lower the value, the higher the accuracy of the kinetic parameters. Its expression is as follows:

$$Fit(\%) = 100 \cdot \frac{\sqrt{S/n_d}}{(d\alpha/dT)_{\max}}$$
(8)

3. Results and discussion

3.1. Thermogravimetric analysis

3.1.1. Pyrolysis behaviors of the heavy oil and its SARA fractions

Fig. 2 shows the TG and DTG curves during the non-isothermal pyrolysis of QD-VR and its SARA fractions at a constant heating rate of 20 °C/min. The weight loss processes of QD-VR and its SARA fractions within the temperature range could be divided into two stages. The first stage was the distillation stage, which was mainly low boiling point hydrocarbons distillation and weak chemical bond breaking. The second stage was the thermal-cracking of heavy organics, for example, the fracture of C–C bond and C–heteroatom bond in alkanes, the fracture of alkyl side chain on cycloalkane ring or aromatic ring, the dehydrogenation and ring opening of cycloalkane ring and the dehydrogenation of aromatic ring structure, resulting in severe weight loss (Hao et al., 2017a).

According to the Fig. 2, the pyrolysis parameters of QD-VR and its SARA fractions are shown in Table 2. It was observed that the initial decomposition temperature (T_i) , final decomposition temperature (T_f) , the temperature at the maximum rate of mass loss (T_p) and the residual weight after pyrolysis experiment (M_f) of SARA fractions gradually increased. The T_i , T_f and T_p of QD-VR were lower than these of resins, but higher than these of aromatics, and the pyrolysis behavior of QD-VR was similar to that of aromatics. In other words, their thermal stability increased in turn due to the different composition and structure of QD-VR and its SARA fractions, which was consistent with the research results of other authors (Hao et al., 2017a; Alvarez et al., 2011). The saturate was mainly composed of alkanes and cycloalkanes, and its weight loss was mainly caused by distillation of low molecular weight compounds and pyrolysis of high molecular weight compounds. For other fractions, the aromatics mainly included aromatic hydrocarbons, and the complex and large-molecular components in heavy oil were mainly enriched in the resins and asphaltenes, leading to different energy for the pyrolysis reaction (Hauser et al., 2014).

Furthermore, the pyrolysis coke yields of saturates, aromatics, resins, and asphaltenes were 4.58, 10.17, 33.16, and 62.21 wt%, respectively, which was attributed to their degrees of condensation reactions. The greater the degree of condensation reaction, the more coke produced (Fals et al., 2018). Considering the SARA fractions, saturates mainly underwent cracking reaction, while aromatics, resins, and asphaltenes both underwent cracking reaction and condensation reaction. And their degrees of condensation



Fig. 2. TG-DTG curves of QD-VR and its SARA fractions at 20 °C/min.

Table 2	
Pyrolysis parameters of QD-VR and its SARA fractions at 20 °C/min.	

Sample	T _i , °C	<i>T</i> _p , °C	− <i>R</i> _p , %/min	T _f , °C	$M_{ m f}$, wt%
QD-VR	375.23	477.42	27.82	513.44	18.28
Saturates	223.71	432.63	21.95	485.09	4.58
Aromatics	371.12	476.54	31.36	517.53	10.17
Resins	390.34	478.65	21.39	527.45	33.16
Asphaltenes	414.55	475.74	11.56	533.46	62.21

M_f, the residual weight after pyrolysis experiment.

reactions followed the order of aromatics < resins < asphaltenes (Hao et al., 2017a). Meanwhile, the weighted coke yields determined by multiplying the coke yields of the SARA fractions with the percentage of the corresponding components of QD-VR were, in turn, 0.38, 5.20, 9.64, and 7.10 wt%, and added up to 22.33 wt%. By the comparison of the pyrolysis coke yield (18.28 wt%) of QD-VR and the sum of weighted coke yields (22.33 wt%) of the SARA fraction, it was suggested that there was an interactive effect between SARA fractions during pyrolysis process of heavy oil, which was consistent with the research results of Fang et al. (1996) and Hao et al. (2017a).

3.1.2. Evolution characteristic of gaseous products

The evolution characteristic of major gas products (H₂, CH₄, CO, and CO₂) of QD-VR and its SARA fractions during pyrolysis process were detected by TG-MS. Fig. 3 presents the evolution curves of major gaseous products including H₂, CH₄, CO, and CO₂ at 20 °C/min.

H₂ mainly came from the dehydrogenation of hydrogenated aromatic structures and the condensation of aromatic structures (Zou et al., 2017). The release of H₂ for QD-VR, saturates, aromatics, resins, and asphaltenes mainly occurred in the temperature range 172–489, 80–400, 151–516, 239–539, and 389–739 °C, respectively, which corresponded to the mass loss of QD-VR and its SARA fractions (Fig. 1). CH₄ release was attributed to the cracking of methyl and methylene located at aliphatic hydrocarbons and alkyl side chains attaching to aromatic or naphthenic rings (Hao et al., 2017b). Except saturates, the CH₄ release of QD-VR and its other fractions were similar, and all occurred in the temperature range 320–820 °C.

During QD-VR and its SARA fractions, elemental oxygen was mainly released in the form of CO and CO₂. Except saturates, two peaks in this temperature range can be observed in the evolution curve of CO and CO₂ for QD-VR and its SARA fractions. For saturates, the release of CO and CO₂ mainly occurred in 100-380 °C, which was generated from the cracking of carboxyl and ester groups with weak thermal stability. For QD-VR and its other fractions, the release of CO and CO2 mainly occurred in 300-600 and 200-560 °C corresponding to the first peak range, respectively. And the release of CO and CO2 mainly occurred in 648-800 and 600-780 °C corresponding to the second peak range, respectively. The differences in the number of peaks and temperature ranges corresponding to the main evolution intervals of QD-VR and its fractions may be ascribed to the differences in the types and quantities of oxygencontaining functional groups. The first evolving peak of CO and CO₂ was mainly attributed to the cracking and reforming of oxygencontaining heterocycles groups, while the second evolving peak was generated from the decomposition of carbonates in minerals (Nie et al., 2018).

TG-MS analysis revealed that the evolution curves of H₂, CH₄, CO, and CO₂ for QD-VR and its SARA fractions corresponded to their thermal-cracking pyrolysis temperature range. The differences in shape, intensity and temperature range of H₂, CH₄, CO, and CO₂ release curves were mainly attributed to the different composition



Fig. 3. The evolution curves of (a) H₂, (b) CH₄, (c) CO, and (d) CO₂ of QD-VR and its SARA fractions using TG-MS at 20 °C/min.



Fig. 4. Fitting straights of $\ln(d\alpha/dt)$ versus 1/T of QD-VR by Friedman model.

and structure of QD-VR and its fractions.

3.2. Pyrolysis kinetics analysis for the heavy oil and its fractions

3.2.1. Friedman model

The values of $d\alpha/dt$ and temperature corresponding to the specific conversion rate ranging from 0.1 to 0.9 at different heating rates (10, 20, 30, 40 °C/min) were taken to calculate the E_a and A of QD-VR by Friedman model. Fig. 4 shows that the fitting straights of $\ln(d\alpha/dt)$ versus 1/T at the specific conversion rate of 0.1–0.9. The A, the E_a , and the correlation coefficients R^2 are shown in Table 3. The correlation coefficients R^2 of the linear fitting results were greater

 Table 3

 The kinetic parameters of QD-VR obtained by Friedman model.

α	QD-VR		
	E _a , kJ/mol	<i>A</i> , s ⁻¹	R^2
0.1	106.60	1.24×10 ⁵	0.8919
0.15	141.36	3.66×10^{5}	0.8965
0.2	141.96	1.82×10^{6}	0.9866
0.25	175.12	2.12×10^{7}	0.9971
0.3	176.99	3.54×10^{8}	0.9976
0.35	182.19	4.31×10 ⁹	0.9943
0.4	184.28	3.37×10 ¹¹	0.9988
0.45	185.63	1.93×10 ¹³	0.9991
0.5	185.81	2.30×10 ¹³	0.9999
0.55	186.96	2.75×10 ¹³	0.9973
0.6	187.26	9.63×10 ¹³	0.9997
0.65	193.27	1.23×10^{14}	0.9991
0.7	194.71	3.35×10^{14}	0.9957
0.75	196.13	4.85×10^{14}	0.9927
0.8	198.95	1.57×10^{15}	0.9897
0.85	201.64	7.02×10^{15}	0.9616
0.9	216.42	1.61×10^{16}	0.9675
Average	179.72		

than 0.98, indicating that the Friedman model was suitable for calculating the kinetics of heavy oil pyrolysis as a single component reaction.

According to the slopes of $\ln(d\alpha/dt)$ versus 1/*T*, the E_a of each conversion rate can be calculated and the results are revealed in Fig. 5. The E_a range was 106.60–216.42 kJ/mol and its average E_a was 179.72 kJ/mol. The calculated E_a of QD-VR increased generally with the conversion rate increasing. This trend indicated that as the pyrolysis reaction progresses, the residual materials become more difficult to break and requires more energy. In the early stage of pyrolysis (the conversion rate less than 0.2), it may be the evaporation stage, and it was expected that weak connections, such as



Fig. 5. Activation energy as a function of conversion rates of QD-VR.

heteroatom chemical bonds in the chain, were first cut off in the low activation energy region. Subsequently, the side chain dissociation or random cleavage reaction that required more energy occurred, and finally, the main chain breaks as the reaction proceeded.

3.2.2. One-parallel Gaussian DAEM

Different from the traditional DAEM method (Miura differential method) requiring the data at different heating rates when calculating kinetic parameters (Cai et al., 2014), the improved DAEM method was used in this work to calculate the kinetic parameters at single heating rate, which avoided errors causing by equipment and operation. Meanwhile, the pattern search method was used to automatically search for $f E_a$), which avoided the error caused by artificially specifying the numerical range of E_a , improved the accuracy of the model, and realized the optimization of kinetic parameters. The experimental data at the heating rate of 20 °C/min of QD-VR and its SARA fractions were selected for analysis by the improved DAEM. The (d α /dt-T) curves were deconvoluted using Gaussian functions for each pseudo-component.

The one-parallel Gaussian DAEM was used to analyze their kinetics. Fig. 6 shows the deconvoluted pyrolysis rate curves of QD-



Fig. 6. Fitting curves of one-parallel Gaussian DAEM at 20 °C/min (a) QD-VR; (b) saturates; (c) aromatics; (d) resins; (e) asphaltenes.

Table 4

The kinetic	parameters and	evaluation	indexes of	OD-VR and	its SARA	fractions	from one-	parallel	Gaussian DAEM.
The minetic	parameters and	cranacion	macheo or	QD Intana	. neo on man	machono		paraner	oudoblair briblin

Sample	Pseudo-components	Ci	A_i , s ⁻¹	<i>E_i</i> , kJ/mol	Fit, %	R ²
QD-VR	1	9.4772	9.4×10 ¹¹	193.75	1.6682	0.8671
Saturates	1	5.1900	1.7×10^{11}	107.78	2.2936	0.9932
Aromatics	1	1.9531	4.9×10 ¹³	210.88	1.7276	0.9949
Resins	1	5.9306	9.1×10^{16}	268.75	0.8839	0.9988
Asphaltenes	1	11.1753	8.9×10 ²⁰	285.44	4.7273	0.9840

Table 5

Weighted *E*_{a-wt} of the SARA fractions of QD-VR from one-parallel Gaussian DAEM.

Sample	wt%	E _i , kJ/mol	Weighted <i>E_i</i> , kJ/mol
Saturates	8.33	107.78	8.98
Aromatics	51.17	210.88	107.91
Resins	29.08	268.75	78.15
Asphaltenes	11.42	285.44	32.60
Sum	100		227.64



Fig. 7. Fitting curves of four-parallel Gaussian DAEM at 20 °C/min.

VR and its SARA fractions at 20 °C/min, and the kinetic parameters are listed in Table 4. From Fig. 6(a), it can be seen that the DAEM prediction was not fitted with the experimental data of QD-VR pyrolysis and the fitting results showed poor correlation coefficients (R^2 =0.8671). However, from Fig. 6(b)–(e), it can be seen that the DAEM prediction was well fitted with the experimental data of saturates, aromatics, resins, and asphaltenes pyrolysis, and the fitting results showed good correlation coefficients (R^2 > 0.98). This phenomenon indicated the heavy oil pyrolysis could not be simply regarded as a single component, while the pyrolysis of SARA fractions could be treated as a single component. For SARA fractions, their E_a were in the order of saturates (107.78 kJ/mol) < aromatics (210.88 kJ/mol) < resins (268.75 kJ/mol) < asphaltenes (285.43 kJ/mol).

Meanwhile, the weighted E_a obtained by multiplying the E_a of the SARA fraction by the percentage of the corresponding component in QD-VR were shown in Table 5. In comparison to the average E_{a-av} (179.72 kJ/mol) of QD-VR obtained by Friedman model, the weighted E_{a-wt} was higher. This observation might be attributed to the interaction between SARA fractions during the pyrolysis process of oil QD-VR, rather than the simple superposition of pyrolysis behavior of the SARA fractions.

3.2.3. Four-parallel Gaussian DAEM

By analyzing the kinetic calculation of QD-VR and its SARA fractions by one-parallel Gaussian DAEM, it could be concluded that the pyrolysis of heavy oil was not a single component reaction, but a series of irreversible first-order parallel reactions with different kinetic parameters in the pyrolysis process. Therefore, according to the composition characteristics of QD-VR in Table 1, we assumed that the non-isothermal pyrolysis process of heavy oil was a combination of four independent pseudo-components parallel reactions, namely, simultaneous pyrolysis of saturates, aromatics, resins and asphaltenes. Meanwhile, four-parallel Gaussian DAEM was used to analysis the pyrolysis kinetic of QD-VR. The deconvoluted pyrolysis rate curves of QD-VR at 20 °C/min by the Gaussian multi-peak fitting method are shown in Fig. 7, with the corresponding kinetic parameters given in Table 6. It can be seen that the DAEM prediction was well fitted with the experimental data of QD-VR pyrolysis, and the fitting results showed good correlation coefficients (R^2 =0.98). The positions of four pseudo-components corresponding to saturates, aromatics, resins, and asphaltenes corresponded well to their thermal pyrolysis activities, namely "saturates > aromatics > resins > asphaltenes". Meanwhile, the E_a for four pseudo-components were in the following order of " $E_{a1} < E_{a2} < E_{a3} < E_{a4}$ ", which was consistent with the E_a results of the SARA fractions from Table 5.

Meanwhile, the weighted E_a determined by four-parallel Gaussian DAEM with the percentage (c_i), in turn, 30.19%, 59.03%, 81.95%, and 34.75%, and added up to 205.92 kJ/mol. In comparison to the average E_a (179.72 kJ/mol) of QD-VR obtained by Friedman model, the weighted E_a was higher. This observation might be attributed to that the Friedman model calculated the E_a value only in the conversion rate range of 0.1–0.9, but DAEM method calculated it in the whole conversion rate range (0–1) of heavy oil. Therefore, the E_a value obtained by four-parallel Gaussian DAEM could better reflect the pyrolysis E_a of heavy oil.

Furthermore, by the comparison of the weighted E_a from fourparallel Gaussian DAEM (205.92 kJ/mol) and that from oneparallel Gaussian DAEM (227.64 kJ/mol), it was suggested that

Table 6	
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Sample	Pseudo-components	Ci	A_i , s ⁻¹	<i>E</i> _{<i>i</i>} , kJ/mol	Fit, %	R^2
QD-VR	1	0.25	6.93×10^{9}	120.75	1.6679	0.9974
	2	0.2683	8.52×10^{12}	220.01	0.4871	0.9998
	3	0.3485	6.06×10^{15}	235.14	4.9366	0.9823
	4	0.1332	1.02×10^{20}	260.91	1.3690	0.9971



Fig. 8. Experimental data and DAEM prediction results for QD-VR at different heating rates of 10, 30, and 40 $^\circ C/min.$

there was an interaction between SARA fractions during pyrolysis process of heavy oil. This interaction could reduce the pyrolysis E_a

of heavy oil. In addition, it was observed that the E_a of pseudocomponent-1 (120.75 kJ/mol) and 2 (220.01 kJ/mol) of QD-VR were larger than the E_a of saturates (107.78 kJ/mol) and aromatics (210.88 kJ/mol) from Table 6. Meanwhile, the E_a of pseudocomponents 3 (235.14 kJ/mol) and 4 (260.91 kJ/mol) were smaller than those of resins (268.75 kJ/mol) and asphaltenes (285.44 kJ/ mol). This phenomenon indicated that during the pyrolysis of heavy oil, the existence of resins and asphaltenes increased the E_a of saturates and aromatics, while the saturates and aromatics decreased the E_a of resins and asphaltenes. Therefore, this might give the reason for that the E_a of heavy oil pyrolysis was between the E_a of aromatics and resins, which also reflected in the research results of Hao et al. (2017a) and Alvarez et al. (2011).

To further validate the accuracy of the four-parallel Gaussian DAEM, the kinetic parameters obtained at heating rate of 20 °C/min were used to predict the results at other heating rates (10, 30, and 40 °C/min) of QD-VR, as shown in Fig. 8. It can be seen that the DAEM prediction results at different heating rates were in good agreement with the experimental data. As a result, it indicated that kinetic parameters obtained by four-parallel Gaussian DAEM at a specific heating rate can be used to predict the pyrolysis behavior and kinetics of heavy oil. Through the above analysis and discussion, it can conclude that the four-parallel Gaussian DAEM can accurately describe the multi-component pyrolysis reaction of heavy oil, and also prove that the pyrolysis process of heavy oil is the interaction between SARA fractions, rather than a simple superposition of pyrolysis behavior of each fraction.

4. Conclusion

The pyrolysis behaviors and kinetic of Qingdao vacuum residue (QD-VR) and its SARA fractions (saturates, aromatics, reins, and asphaltenes) were analyzed and compared. The main conclusions can be drawn as follows.

- (1) By comparing the coke yields of QD-VR with the weighted coke yields of SARA fractions, it was found that there was an interaction between SARA fractions during heavy oil pyrolysis. The pyrolysis behavior of QD-VR was similar to that of aromatics.
- (2) The evolution curves of H₂, CH₄, CO, and CO₂ for QD-VR and its SARA fractions corresponded to their thermal-cracking pyrolysis temperature range. For saturates, the release of H₂, CH₄, CO, and CO₂ all occurred at 80–400 °C, and for QD-VR and its other fractions, the gases release variations with temperature were similar, and all occurred at 200–800 °C.
- (3) Compared with Friedman and DAEM, one-parallel Gaussian DAEM was more suitable to describe the pyrolysis process of the SARA fractions, and four-parallel Gaussian DAEM was more suitable to describe the pyrolysis process of heavy oil.
- (4) By the comparison of the weighted E_a from one-parallel Gaussian DAEM and that from four-parallel reaction Gaussian DAEM, there was an interaction between SARA fractions during pyrolysis process of heavy oil, which could reduce the pyrolysis E_a of heavy oil. The resins and asphaltenes could increase the E_a of saturates and aromatics, while the saturates and aromatics could decrease the E_a of resins and asphaltenes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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