Thermal Characteristics, Kinetic Models, and Volatile Constituents during the Energy Conversion of Bituminous SARA Fractions in Air

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ABSTRACT: To understand the thermal characteristics, non-isothermal kinetic models, and volatile constituents during the energy conversion of bituminous materials at the fraction level, differential scanning calorimetry−mass spectrometry tests were performed on bituminous four fractions, including saturates, aromatics, resins, and asphaltenes (SARA). Then, three-dimensional (3D) nonisothermal kinetic models of SARA fractions were established and volatile constituents of SARA fractions were discussed. Results indicate that when the heating rate is increased, the decomposition temperature ranges in each stage increase and the initial decomposition, peak, and burn-out temperatures of each SARA fraction all shift to high temperatures. Also, the whole energy conversion processes of SARA fractions are mainly exothermic reactions. Additionally, the energy conversion mechanism in each stage of saturates and aromatics accords with different nonisothermal kinetic models. However, the energy conversion mechanisms of resins and asphaltenes are similar and both accord with the 3D diffusion models. Further, the established nonisothermal kinetic models in each decomposition stage of SARA fractions are feasible to describe the energy conversion processes of SARA fractions. The released small molecular volatiles from saturates and aromatics increase when the heating rate is increased, but the macromolecular volatiles are decreased. The opposite is true for resins, but all volatiles emitted from asphaltenes are increased. Finally, the heating rate has little influence on the constituents of emitted gaseous products from SARA fractions but shows an effect on the release amount of volatiles from SARA fractions. The main common volatiles of SARA fractions are CO₂, H₂O, methanol, hydrazine, propyne, acetaldehyde, and propane. This study contributes to further reveal the energy conversion mechanisms of bituminous materials.

1. INTRODUCTION

Bitumen is obtained industrially from petroleum distillation and mainly composed of hydrocarbons, its derivatives, and heteroatoms, including oxygen, nitrogen, sulfur, etc. Bitumen is often separated into saturates, aromatics, resins, and asphaltenes (SARA). The bituminous initial decomposition temperature is about 200 °C, which indicates that bitumen is a flammable material at high temperatures. Bitumen is often used as important industrial fuels and energy resources except for pavement binder, waterproof materials, etc. Bitumen is also used as a substitute for coal in the metallurgy industries. Additionally, bitumen is flammable and easily ignited because of thermal radiation, heat convection, and heat conduction in a fire, releasing lots of heat and toxic volatiles. Therefore, the energy conversion characteristics, nonisothermal kinetic properties, and emitted volatiles of bitumen have been studied.

Additionally, differential scanning calorimetry (DSC) is one of the important methods to discuss the heat flux variation and kinetic reaction of polymeric materials. Moreover, mass spectrometry (MS) can analyze the compositions by the mass/charge ratio (m/z) of gaseous products, which are decomposed from polymeric materials. Therefore, DSC−MS is often utilized to investigate the thermal properties of various polymers. Not only the thermal effects of samples are studied but also the evolved gaseous products are identified and quantitatively analyzed. As a result, some researchers also used the DSC−MS technology to discuss the thermal properties of bituminous materials.

Zhao et al. discussed the combustion behavior of bituminous SARA fractions using the thermogravimetry (TG)−MS method in a simulated air environment and pointed out that the combustion process was divided into several stages at a heating rate of 15 K/min according to the
mass loss rates in different temperature ranges. Shi et al. investigated the thermal effects of bituminous SARA fractions based on DSC test results and found that the heat released from SARA fractions was increased from saturates, aromatics, and resins to asphaltenes in turn. Wu et al. reported the bituminous combustion properties at four heating rates using TG and found that the combustion process of bitumen includes three main stages. Zhao et al. analyzed the combustion properties of bituminous SARA fractions using TG–MS technology at 15 °C/min, and the distributed activation energy model (DAEM) and Coats–Redfern integral model (CRIM) were utilized to confirm the activation energy of SARA fractions.

Moreover, Zhang et al. studied the thermal decomposition behaviors of bituminous SARA fractions using TG tests and reported that the thermal stability of each SARA fraction successively was increased from saturates, aromatics, and resins to asphaltenes. Freitag et al. studied the low-temperature oxidation reactions of SARA fractions separated from two crude oils in the temperature range between 130 and 230 °C. It was found that there were at least seven groups of fundamental reactions to seriously affect the oxidation rates of crude oils. Kapadia et al. pointed out that the pyrolysis, aquathermolysis, and oxidation mechanisms coexisted in the in situ combustion processes of bitumen. Zanoni et al. developed the multistep kinetic mechanisms for bituminous combustion, including five-step, four-step, three-step, and two-step models. Recently, Xia et al. investigated the energy conversion properties and produced volatiles of SARA fractions and reported that some toxic volatiles were emitted from SARA fractions.

Currently, it is noted that a few studies have been performed on bituminous energy conversion performances at the SARA fraction level using DSC–MS at various heating rates. Previous studies mainly reported the energy conversion performances of bitumen at different heating rates. The nonisothermal kinetic models of SARA fractions were seldom discussed to discover the energy conversion mechanism of bitumen. The dynamic evolution and constituent identification of emitted volatiles were also not analyzed in detail. The objective of this study is to understand the energy conversion properties, nonisothermal kinetic models, dynamic evolution, and constituent identification of bituminous volatiles from the aspects of SARA fractions. Thus, this study contributes to further reveal the energy conversion mechanisms of bitumen at its SARA level.

In this study, the energy conversion of SARA fractions was characterized using DSC–MS under different nonisothermal heating conditions. Further, the nonisothermal kinetic models of SARA fractions were established to discuss the thermal kinetic characteristics of SARA fractions. Finally, the dynamic evolution and constituent identification of emitted volatiles were studied using the total ion current (TIC) and ion histogram based on MS analysis during the energy conversion of SARA fractions, further revealing the energy conversion mechanism of bituminous materials from the SARA aspect.

2. MATERIALS AND METHODS

2.1. Raw Materials. Bitumen was supplied by Refinery of Nanjing Petrochemical Co., Ltd., China with a ductility of 29 cm at 5 °C, a penetration of 57 dmm at 25 °C, a Brookfield viscosity of 2.15 Pa·s at 135 °C, a density of 1.04 kg/m³, a softening point of 80.1 °C, and a flash point of 316 °C.

2.2. Methods. 2.2.1. Preparation of SARA Fractions and Their Molecular Structures. Bitumen was used to obtain SARA fractions using the chromatographic separation method according to ASTM D4124-09. The asphaltenes were black powder solids with a content of 15.1%. The content of yellow sticky aromatics was 27.5%. The content of colorless saturates was 9.1%. The content of brown viscous resins was 48.3%. The molecular structures of SARA fractions are shown in Figure 1.

As illustrated in Figure 1a, saturates were mainly saturated hydrocarbons, including cycloalkanes and alkanes. Saturates mainly consisted of nonpolar linear, branched, and cyclic alkanes. From Figure 1b, aromatics were a more stable fraction and contained two more aromatic rings, which were slightly more polarizable. Figure 1c indicates that resins were one of the polycyclic hydrocarbon compounds with N and S. The composition of resins was complexed and their structure was diverse. When the temperature was higher, resins were transformed into asphaltenes. Asphaltenes were one of the aromatic hydrocarbon compounds, as shown in Figure 1d. Asphaltenes were the most stable fraction in SARA fractions. More information about the differences of SARA fractions is given in ref 30.

2.2.2. DSC–MS Tests. DSC–MS tests were conducted on a DSC test system (STA409PC/PG type, Netzsch, Germany), which was connected with a mass spectrometer (QMS403C type, Netzsch, Germany). Each sample mass was approximately 16 mg. The samples were heated from 313 to 1073 K in air at the heating rates (β) of 5, 10, and 15 K/min. The compressed gases composed of 21% oxygen, and 79% nitrogen was injected at a flow rate of 50 mL/min. The purge gas was N₂ to protect the released gaseous products at a flow rate of 15 mL/min. The capillary transfer line of MS was heated to 573 K. The scanning range of m/z was from 2 to 202. The three heating rates corresponded to the scanned times of 87, 44, and 29, respectively.

In this study, the linear baseline method is mainly used to calculate the area of endothermic or exothermic peaks on the DSC curve by a professional operator using the analysis software of the TG/DSC test system. That is, the inflection points on the left and right sides of endothermic or exothermic peaks are connected to regard as the baseline. The area between the baseline and endothermic or exothermic peaks on
the DSC curve is calculated to obtain the enthalpy based on the curvilinear integral.

3. RESULTS AND DISCUSSION

3.1. Thermal Characteristics during the Energy Conversion of SARA Fractions. To study the energy conversion characteristics of SARA fractions, DSC tests are performed at the three heating rates. DSC test results of four SARA fractions are illustrated in Figure 2, and the peak temperature ($T_p$), decomposition temperature ($T_r$) range, and enthalpy ($E_n$) values in different combustion stages are provided in Table 1.

From Table 1 and Figure 2a, the DSC curve of saturates shows three characteristic peaks, and three peaks are exothermic peaks. Peak 1 is caused by the oxidative cracking process of saturates, which releases light gaseous products and heat. Peak 2 is due to the breakage of side chains from the alkyl side chains and the secondary cracking of short-chain alkanes with low molecular weights. The exothermic peak 2 is also due to the oxidation process. That is, these volatiles react with $O_2$ to produce heat, and the partial heat is transferred back to continue the production of gaseous volatiles. Finally, the coke-like residues are combusted and a large amount of heat is emitted, leading to peak 3.

Additionally, as shown in Figure 2b, peak 1 and peak 2 on DSC curves of aromatics indicate that complex endothermic and exothermic reactions occur during its energy conversion, respectively. Peak 1 is attributed to the release of some hydrocarbon volatiles and gases with low molecular weights during the thermal decomposition of aromatics, but which do not burn due to their lower concentrations. Then, the exothermic peak 2 appears, and some heat is emitted because of the combustion of the charring layer generated by the condensation of aromatics. Moreover, the exothermic peak 1 is because of the low-temperature oxidation and oxidative cracking process during the combustion of aromatics; then, the coke-like residues are formed. Also, peak 2 is a high-temperature oxidation process where the coke-like residues are further combusted.

As given in Table 1 and Figure 2c, a larger exothermic peak 1 appears in the energy conversion process of resins. The exothermic peak 1 is due to the oxidative cracking process and high-temperature oxidation reactions in the energy conversion process of resins. Finally, it is found from Figure 2d that DSC curves of asphaltenes show single peak characteristics, suggesting that the energy conversion of asphaltenes directly produces the charring layer, which then burns out, releasing a lot of gaseous products and heat. This is because of the high-

Figure 2. DSC test results of SARA fractions under different nonisothermal heating conditions.

Table 1. DSC Analysis Results under Different Nonisothermal Heating Conditions

| heating rates | items    | saturates | aromatics | resins | asphaltenes |
|---------------|----------|-----------|-----------|--------|-------------|
|               | stage 1  | stage 2   | stage 3   | stage 1| stage 1     |
| 5 K/min       | $T_p$ (K)| 637       | 666       | 764    | 746         | 831         | 823         | 819         |
|               | $T_r$ (K)| 586–565   | 659–699   | 699–871| 738–749    | 749–936     | 716–921     | 708–903     |
|               | $E_n$ (kJ/kg) | −53.7     | −40.4     | −161.1 | 14.9       | −302.9      | −733.0      | −702.9      |
| 10 K/min      | $T_p$ (K)| 616       | 651       | 801    | 741        | 861         | 863         | 871         |
|               | $T_r$ (K)| 568–628   | 628–718   | 718–933| 731–756    | 756–976     | 706–981     | 706–996     |
|               | $E_n$ (kJ/kg) | −28.9     | −144.2    | −342.7 | 60.9       | −477.9      | −1311.8     | −1591.2     |
| 15 K/min      | $T_p$ (K)| 619       | 679       | 804    | 738        | 868         | 882         | 931         |
|               | $T_r$ (K)| 889–644   | 644–764   | 764–939| 700–768    | 768–1005    | 707–1071    | 682–1029    |
|               | $E_n$ (kJ/kg) | −34.9     | −202.1    | −146.6 | 88.4       | −504.7      | −2152.2     | −1820.0     |
is the gas constant (8.314 J/(mol·K)). The kinetic mechanism function, $f$ is the conversion ratio, $T$ is the temperature, $\alpha$ is the conversion ratio, $f$ is the heating rate (K/min), and $E$ is the activation energy.

The conversion ratio ($\alpha(T)$) during the energy conversion process is described by eq 2.\textsuperscript{33}

$$\alpha(T) = \frac{\int_{T_i}^{T_f} \left(\frac{dT}{\alpha} \right) dT}{H_f} = \frac{H_f}{H_0}$$  \hspace{1cm} (2)

where $T_i$ is the initial temperature of the energy conversion process, $T_f$ is the final temperature of the energy conversion process, $H_f$ is the released heat at $T_i$ and $H_0$ is the total released heat.

Then, the plot of $\ln\left(\frac{\alpha}{f(\alpha)}\right)$ vs $1/T$ at each $\alpha$ is fitted according to the least-squares principle to show a series of straight lines. $A$ and $E$ are obtained based on the intercept and slope of each regression line, respectively. The $\frac{d\alpha}{dT}$ is obtained by eq 3 based on DSC test results.

$$\frac{d\alpha}{dT} = \frac{\alpha_{i+1} - \alpha_i}{T_{i+1} - T_i} (i = 1)$$

$$= \frac{\alpha_i - \alpha_{i-1}}{2(T_i - T_{i-1})} + \frac{\alpha_{i+1} - \alpha_i}{2(T_{i+1} - T_i)} (i = 1, \ldots, n - 1)$$

$$= \frac{\alpha_i - \alpha_{i-1}}{T_i - T_{i-1}} (i = n)$$  \hspace{1cm} (3)

The theoretical expressions of common kinetic mechanism functions ($f(\alpha)$) are summarized in Table 2.
Table 4. Nonisothermal Kinetic Models in Each Decomposition Stage during the Energy Conversion of SARA Fractions

| SARA fractions | heating rates | decomposition stage | energy conversion models |
|----------------|---------------|---------------------|-------------------------|
|                | 5 K/min       |                     |                         |
| saturates      | 1             | $\frac{da}{dT} = 0.5 \exp(105.26 - 43092.76)(1 - a)^{-1}$ |
|                | 2             | $\frac{da}{dT} = 0.5 \exp(139.87 - 43015.43)(1 - a)^{-1}$ |
|                | 3             | $\frac{da}{dT} = 15.51 - 15047.59(1 - a)$ |
|                | 1             | $\frac{da}{dT} = 0.5 \exp(77.52 - 49418.52)(1 - a)$ |
| aromatics      | 10 K/min      | $\frac{da}{dT} = 0.5 \exp(63.49 - 45045.07)(1 - a)^{1/3}[1 - (1 - a)^{-1}]^{-1}$ |
|                | 3             | $\frac{da}{dT} = 0.5 \exp(41.40 - 38035.89)(1 - a)^{1/3}[1 - (1 - a)^{-1}]^{-1}$ |
|                | 1             | $\frac{da}{dT} = 0.5 \exp(25.46 - 18474.96)(1 - a)^2$ |
|                | 5 K/min       | $\frac{da}{dT} = 0.5 \exp(17.96 - 17971.40)(1 - a)^2$ |
| resins         | 10 K/min      | $\frac{da}{dT} = 0.5 \exp(120.08 - 89398.60)(1 - a)^3$ |
|                | 15 K/min      | $\frac{da}{dT} = 0.5 \exp(120.08 - 89398.60)(1 - a)^3$ |
| asphaltenes    | 10 K/min      | $\frac{da}{dT} = 0.5 \exp(66.05 - 52566.45)(1 - a)$ |
|                | 15 K/min      | $\frac{da}{dT} = 0.5 \exp(13.04 - 13002.74)(1 - a)$ |
|                | 5 K/min       | $\frac{da}{dT} = 0.5 \exp(49.84 - 45081.75)(1 - a)^3/4[1 - (1 - a)^{-1}]^{-1}$ |
|                | 10 K/min      | $\frac{da}{dT} = 0.5 \exp(49.15 - 47716.02)(1 - a)^3/4[1 - (1 - a)^{-1}]^{-1}$ |
|                | 15 K/min      | $\frac{da}{dT} = 0.5 \exp(45.84 - 45757.67)(1 - a)^3/4[1 - (1 - a)^{-1}]^{-1}$ |
|                | 5 K/min       | $\frac{da}{dT} = 0.5 \exp(54.03 - 48283.14)(1 - a)^3/4[1 - (1 - a)^{-1}]^{-1}$ |

To confirm the most probable mechanism functions in each decomposition stage of SARA fractions, the approach degree of a linear relationship between $\ln \left( \frac{da}{dT} / f(\alpha) \right)$ vs $1/T$ is a good evaluation method after being fitted by the least-squares principle. Thus, the maximum correlation coefficient ($R^2$) is taken as a criterion for judging whether the selected $f(\alpha)$ is the most probable mechanism function in each decomposition stage of SARA fractions. The maximum correlation coefficients and the corresponding most probable mechanism functions in each decomposition stage of SARA fractions are given in Table 3.

As shown in Table 3, it is observed that the most probable mechanism functions in each decomposition stage of saturates and aromatics are different. This implies that the energy conversion of saturates and aromatics is very complicated in different decomposition stages at different heating rates. As the temperature increases, the molecular chains are gradually cracked due to intense decomposition reactions, producing many gaseous products to release. At the same time, a lot of free radicals are also generated. When the concentration of free radicals is increased, the thermal pyrocondensation reactions occur, and many recombinant components are produced.

However, the most probable mechanism functions of resins are the same as those of asphaltenes at 5, 10, and 15 K/min, indicating that the thermal decomposition mechanisms of resins and asphaltenes are similar. This is because resins are viscous semisolid and asphaltenes are fragile powder solid. The heating rate shows little influence on the energy conversion of resins and asphaltenes. Additionally, some hydrocarbon components in resins and asphaltenes are similar and have similar thermal decomposition mechanisms. In particular, the mechanism functions of saturates accord with F2 in its three decomposition stages at 15 K/min. This suggests that the whole energy conversion process of saturates belongs to the two-order chemical reaction mechanism and follows the chemical reaction law (two-order) and that $f(\alpha) = (1 - a)^2$ is its decomposition mechanism function.

Additionally, the mechanism decomposition of aromatics in stage 1 at 5 K/min is the same as that at 10 K/min, both accord with F3 (three-order chemical reaction) mechanisms,
and \( f(\alpha) = (1 - \alpha)^3 \) is their decomposition mechanism function. Finally, it is found that the decomposition mechanisms of resins are the same as those of asphaltenes at 5, 10, and 15 K/min. All accord with D5 (three-dimensional, 3D diffusion) mechanisms, and \( f(\alpha) = 3/2(1 - \alpha)^{\frac{3}{2}}(1 - \alpha)^{\frac{1}{3}} - 1 \) is their decomposition mechanism function.

After the most probable mechanism functions in each decomposition stage of SARA fractions are confirmed and the E and A are calculated, the nonisothermal kinetic models of SARA fractions in each decomposition stage at the three heating rates are established, as summarized in Table 4.

To verify the rationality of developed nonisothermal kinetic models in each decomposition stage of SARA fractions, the comparisons between the calculated results by eq 3 based on DSC tests and the established nonisothermal kinetic models in each decomposition stage of SARA fractions are illustrated in Figures 3—6, respectively. Among them, the 3D plots of \( \frac{dT}{dT - \alpha - T} \) are based on established kinetic models at any \( T \) and \( \alpha \) during each decomposition stage of SARA fractions, and the scatter plots are obtained according to eq 3 as \( \alpha \) is increased from 0.1 to 0.9 at an interval of 0.1.

From Figure 3, it is noted that the calculated results based on the established nonisothermal kinetic models of saturates are consistent with those according to eq 2 based on the DSC test at 5, 10, and 15 K/min. Further, it is observed that the fitting curves of \( \frac{dT}{dT - \alpha - T} \) are closer to the calculated results in stage 1, stage 2, and stage 3 at 10, 15, and 5 K/min, respectively. These indicate that the most suitable kinetic mechanisms in the three decomposition stages of saturates are the RSNG model \((n = 1)\), two-order chemical reaction model, and 3D diffusion model, respectively, as shown in Table 2. All of these energy conversion kinetic models show unimodal characteristics. \( \alpha \) and \( T \) are the parameters of the shape and location that mainly determine the nonisothermal kinetic curves. The Avrami–Erofeev equation is the most suitable mechanism function to describe the energy conversion processes of saturates at any \( T \) and \( \alpha \) at 10 K/min because the \( R^2 \) is the maximum value in the three stages at the three heating rates.

![Figure 3](https://pubs.acs.org/acsomega/2020/5/20836)  
**Figure 3.** Comparisons between calculated results by established kinetic models and eq 2 based on the DSC test of saturates (a), (d), and (g) in stage 1; (b), (e), and (h) in stage 2; and (c), (f), and (i) in stage 3 at different heating rates.

![Figure 4](https://pubs.acs.org/acsomega/2020/5/20836)  
**Figure 4.** Comparisons between the calculated results by established kinetic models and eq 2 based on the DSC test of aromatics (a), (c), and (e) in stage 1 and (b), (d), and (f) in stage 2 at different heating rates.

Figure 4 shows that the most suitable kinetic mechanisms of aromatics in each decomposition stage are the three-order chemical reaction and RSNG model \((n = 1)\) at 5 and 15 K/min, respectively. The 3D plots of \( \frac{dT}{dT - \alpha - T} \) of different kinetic mechanism functions exhibit unimodal characteristics during the energy conversion processes of aromatics. The shape of the main peak depends on the values of \( T \) and \( \alpha \). The 3D plot trends at different \( \alpha \)’s are almost diverse from each other. As shown in Table 3, the fitting correlation coefficient of the most probable mechanism functions of aromatics is 0.98539 at 10 K/min in stage 1, which follows the D1 model (one-dimensional diffusion mechanism). This indicates that the energy conversion of aromatics is a diffusion-controlled mechanism with a decelerated shape, which follows the parabolic rule. The decomposition mechanism function is \( f(\alpha) = \alpha^2/2 \).

Figures 5 and 6 illustrate the 3D plots of \( \frac{dT}{dT - \alpha - T} \) of different kinetic mechanism functions during the energy conversion process of resins and asphaltenes. By comparing the combustion mechanism functions of resins and asphaltenes, it is found that their kinetic models are similar at 5, 10, and 15 K/min. The shape or location of each plot is determined by the parameters \( \alpha \) and \( T \). However, each plot is a part of the complete curve that is subjected to the 3D diffusion mechanism.

It is observed from Figures 3—6 that there is a higher correlation between the calculated results by eq 3 based on DSC tests and the established nonisothermal kinetic models in each decomposition stage of SARA fractions. Additionally, the model residuals are almost close to zero and do not show any pattern, which indicates that the established nonisothermal kinetic models reflect the good functional relationship among \( \frac{dT}{dT}, \alpha \), and \( T \). These models are suitable to describe the
conversion of saturates at 5, 10, and 15 K/min are provided in Figure 7.

From Figure 7, as the heating rate is increased, the released molecular ions with the m/z range of 2–60 increase, but the emitted ions with the m/z range of 60–202 decrease. This is because saturates contain alkanes and cycloalkanes that are easily decomposed to produce short-chain alkanes such as ethane, propane, butane, etc. As the temperature is further increased, some relatively stable constitutions begin to decompose and some large lightweight components are released.

As shown in Figure 7, the released amount of CO$_2$, propane, or acetaldehyde with an m/z of 44 reaches the largest value at 10 K/min. However, when the heating rate is increased, the volatilization amount of propanol or acetic acid with an m/z of 60 increases. In conclusion, the released volatiles from saturates include CO, CO$_2$, H$_2$O, ethylene, etheneone, diacetylene, formaldehyde, glyoxal, propanol, methoxyethene, propylene, methyl formate, acrolein, aceton, acetaldehyde, butane, acetic acid, etc. These volatiles are derived from low-temperature oxidation, decomposition of saturates, and high-temperature oxidation.

3.3.2. Dynamic Release Process and Main Constituents of Volatiles from Aromatics. Figure 8 illustrates the relative abundances of mass spectra of evolved volatiles from aromatics at 5, 10, and 15 K/min.

Similar to saturates, it is seen from Figure 8 that the release amount of small molecules with the m/z range of 2–60 increases but the molecules with the m/z range of 60–202 decrease with an increase in heating rate. The reason for this is that aromatics are relatively stable naphthenic-aromatic compounds. Moreover, aromatics are a kind of sticky liquid and a lighter component in SARA fractions. Gaseous products are evolved from aromatics owing to the breakage of side chains in arenes and dehydrogenation condensation, including H$_2$O, CO$_2$, CO, methanol, hydrogen peroxide, methane, acetaldehyde, ethylene glycol, ethylene, propyne, methoxy, propane, acetic acid, methyl formate, ethane, etc.

As shown in Figure 8, the main volatile species released from aromatics at the peak temperature are more than those from saturates, and the m/z tends to increase. The release amount of main common volatiles with the m/z of 44, 60, and 62 increases. These volatiles contain CO$_2$, acetic acid, acetaldehyde, propane, methyl formate, ethylene glycol, methoxy, ethane, etc. These volatiles are due to the combined effects of low-temperature oxidation, deposition of aromatics, and high-temperature oxidation.

3.3.3. Dynamic Release Process and Main Constituents of Volatiles from Resins. The relative abundances of mass spectra of evolved volatiles from resins at 5, 10, and 15 K/min are provided in Figure 9.

In contrast with saturates and aromatics, it is found from Figure 9 that the release amount of small molecular ions with the m/z range of 2–60 decreases, but the ions with the m/z range of 60–202 increase. The reason is that resins are viscous semisolid, and the molecular structure is more stable than those of saturates and aromatics. As a result, the cross-linking condensation reaction occurs to produce coke or asphaltenes with macromolecular structures. Finally, the further combustion of coke is dedicated to releasing many volatiles, including CO$_2$, N$_2$O, NO$_2$, SO$_2$, disulphides, propane, 2-furonitrile, ethanol, aniline, formic acid, acetaldehyde, etc. Particularly, when the heating rate is increased, the intensities
of ions with the m/z of 18, 44, and 64 increase, indicating that the volatility of resins increases. The released volatiles are CO₂, H₂O, methanol, hydrazine, propyne, acetaldehyde, propane, etc. These volatiles are released because of the combination of the deposition of resins and high-temperature oxidation.

3.3.4. Dynamic Release Process and Main Constituents of Volatiles from Asphaltenes. The relative abundances of mass spectra of evolved volatiles from asphaltenes at 5, 10, and 15 K/min are shown in Figure 10.

From Figure 10, when the heating rate is increased, the released ions with the m/z range of 2–202 increase. This is because asphaltenes have a macromolecular structure with structural stability in SARA fractions. The release amount of small molecular and macromolecular volatiles increases simultaneously when the heating rate is increased. In conclusion, released gaseous products from asphaltenes mainly include H₂O, CO₂, SO₂, disulfides, propane, naphthalene, acetaldehyde, methyl mercaptan, acetonitrile, etc. In particular, as the heating rate is increased, the release amount of volatiles with the m/z of 18, 44, 48, and 64 tends to increase, including CO₂, H₂O, methyl mercaptan, acetonitrile, disulfides, SO₂, acetaldehyde, propane, etc.

From Figures 7–10, it is found that the heating rate has little influence on the constituents of emitted volatiles from SARA fractions; however, it shows an effect on the release amount of volatiles from SARA fractions. The main common volatiles of
SARA fractions are CO, H$_2$O, and acetaldehyde. Individually, the released volatiles from saturates include CO, ethylene, ethenone, diacetylene, formaldehyde, glyoxal, propanol, methoxyethane, propylene, methyl formate, acrolein, acetone, butane, and acetic acid. The released volatiles from aromatics include CO, methanol, hydrogen peroxide, methane, ethylene glycol, ethylene, propyne, methoxy, propane, acetic acid, methyl formate, and ethane. The released volatiles from resins include methanol, hydrazine, propyne, and propane. The released volatiles from asphaltenes include methyl mercaptan, acetonitrile, disulfides, SO, SO$_2$, and propane. This is mainly due to the high-temperature oxidation during the energy conversion of asphaltenes, which is consistent with TG analysis results.

4. CONCLUSIONS

The energy conversion characteristics and nonisothermal kinetic models of SARA fractions, as well as dynamic evolution and main constituents of released gaseous products, were studied. The main conclusions obtained are as follows.

1. As the heating rate is increased, the DSC curve of each SARA fraction shifts to high temperatures and the temperature of SARA fractions increases rapidly, and the total released heat from low to high is saturates, aromatics, asphaltenes, and resins. The whole energy conversion of asphaltenes, which is consistent with TG analysis results.

Figure 9. Relative abundances of mass spectra of emitted gaseous products during the energy conversion of resins.

Figure 10. Relative abundances of mass spectra of emitted gaseous products during the energy conversion of asphaltenes.
conversion processes of SARA fractions are mainly exothermic.

(2) The exothermic and endothermic reactions of saturates and aromatics are more intense than those of resins and asphaltenes at different heating rates. The energy conversion processes of saturates, aromatics, resins, and asphaltenes include three stages, two stages, one stage, and one stage, respectively.

(3) The energy conversion mechanisms in each decomposition stage of saturates and aromatics are different at the three heating rates and accord with different nonisothermal kinetic models. However, the energy conversion mechanisms of resins and asphaltenes are similar and both accord with the 3D diffusion models.

(4) The decomposition kinetic mechanism of resins is similar to that of asphaltenes at the three heating rates. The established nonisothermal kinetic models in each decomposition stage of SARA fractions are suitable to describe the energy conversion processes of SARA fractions.

(5) The released small molecular volatiles from saturates and aromatics increase as the heating rate is increased, but macromolecular volatiles decrease. Small molecular volatiles from resins decrease, but macromolecular volatiles increase. Small molecular and macromolecular volatiles emitted from asphaltenes increase.

(6) The heating rate has little influence on the constituents of emitted volatiles from SARA fractions; however, it shows an effect on the release amount of volatiles from SARA fractions. The main common volatiles of SARA fractions are CO2, H2O, and acetaldehyde.

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Notes
The authors declare no competing financial interest.

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