Mass loss evolution of bituminous fractions at different heating rates and constituent conformation of emitted volatiles

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Abstract
Bitumen is frequently used as energy source. To further understand bituminous combustion and emitted volatiles during its energy generation and conversion at the fraction level including saturates, aromatics, resins, and asphaltenes (SARA), an elemental analyzer, thermogravimetry coupled with mass spectrometer and Fourier-transform infrared spectroscopy (TG-MS-FTIR) were utilized to monitor the mass loss evolution, and confirm molecular structures of emitted volatiles, and track the whereabouts of main elements during each SARA fraction combustion. Results indicate that TG, DTG, and Gram-Schmidt (G-S) curves show two-stage characteristics, while the total ion chromatogram (TIC) curves present one-stage characteristic during each SARA fraction combustion. Also, as the heating rate is raised, TG, DTG, TIC, and G-S curves are shifted to higher temperature and the total emitted volatile amount is increased from saturates to asphaltenes. Molecular weights of main volatiles are distributed in the range of 12-64. The elemental species of volatiles are consistent with those of SARA fractions. Finally, the typical volatiles of saturates and aromatics are similar, and the release amount of CO and CO2 at stage II is larger than those at stage I. SO2 is released during the combustion of resins. SO2 and NO2 are identified in volatiles of asphaltenes.

KEYWORDS
bituminous fractions, constituent conformation, emitted volatiles, mass loss evolution, molecular structure, molecular weight distribution

1 | INTRODUCTION

Bitumen, as one of petroleum products, is produced in large quantities as the petrochemical industry is rapidly developed.1 Bitumen has been widely used as the energy source of metallurgical furnaces and kilns, the pavement binding material, building waterproof, etc.2,3 Bitumen consists of hydrocarbons, sulfur (S), nitrogen (N), oxygen (O), metal-containing compounds, etc.4 Generally, hydrocarbons and their derivatives are classified into four fractions, such as saturates, aromatics, resins, and asphaltenes (SARA).5 Chemical components of bitumen depend on the crude oil source and petroleum refining process. Therefore, bitumen includes complicated chemical compositions owing to a large number of carbon atoms and the existence of heteroatoms, for instance, S, N, etc.6

Recently, SARA fractions were often separated from bitumen to further study its various properties.7 Wang et al.8 found that SARA fraction contents showed obvious effects on rheological properties and chemical characteristics of bitumen. Shishebor et al.9 reported that aromatics and resins had their
maximum adhesion properties on silicon dioxide aggregate, while saturates had the minimum adhesion. Dai et al.\(^\text{10}\) found that the weathering caused the morphology changes of SARA fractions in different ways and at different speeds during the aging. Alam et al.\(^\text{11}\) pointed out that the addition of styrene butadiene styrene in bitumen did not change the asphaltenes content, but altered the contents of aromatics and resins.

Additionally, thermal properties and kinetics characteristics of SARA fractions were investigated by the thermogravimetry (TG),\(^\text{12}\) TG-differential scanning calorimetry (TG-DSC),\(^\text{13}\) and high-pressure DSC.\(^\text{14}\) TG-mass spectrometer-Fourier-transform infrared spectroscopy (TG-MS-FTIR),\(^\text{15}\) etc. Among them, TG-MS-FTIR is a useful tool to discuss thermal behaviors of various compounds as it continuously monitors the time-dependent evolution of volatiles and the mass loss process.\(^\text{15}\) Ahmad et al.\(^\text{16}\) used TG-FTIR-MS to study the bioenergy potential of Wolffia arrhiza according to its pyrolysis, thermal kinetic parameters and emitted gaseous products. Ye et al.\(^\text{17}\) analyzed the released gases using TG-FTIR-MS to monitor the chemical compositions and released gases. Luo et al.\(^\text{18}\) examined the devolatilization behaviors of superfine pulverized coal during its pyrolysis using TG-MS-FTIR. Yang et al.\(^\text{19}\) used TG-FTIR-MS to study the thermal degradation of cattlehide collagen fibers according to emitted volatile analysis. Kai et al.\(^\text{20}\) investigated effects of interactions between rice straw and polyethylene on the releasing process of volatile species during their copyrolysis based on TG-MS-FTIR.

However, the mass loss dynamic evolution of SARA fractions using both TG and DTG curves, as well as the releasing trend of total volatiles, was seldom monitored using both total ion chromatograms (TIC) and Gram-Schmidt (G-S) under different simulated combustion conditions. Further, the molecular structures of volatile constituents were rarely determined using TG-MS-FTIR in the SARA combustion processes at various heating rates. Finally, few researchers simultaneously qualitatively identified functional groups or molecules in volatiles at the characteristic temperatures during the SARA combustion processes. Therefore, the objective of this study is to comprehensively understand bituminous combustion characteristics and to confirm the constituents of emitted volatiles, and to track the whereabouts of main elements and heteroatoms during its energy generation and conversion at the SARA fraction level under different simulated combustion conditions.

In this study, the elemental analysis (EA) was performed to compare bituminous main element compositions and volatile constituents, tracking the whereabouts of main elements and heteroatoms during the SARA fraction combustion. To continuously and accurately obtain the information of mass loss evolution and emitted volatile at the same time, TG-MS-FTIR was utilized to characterize the dynamic releasing trend of volatiles using both TIC and G-S curves in the SARA combustion processes at the heating rates of 5, 10 and 15°C/min from 40°C to 800°C, respectively. Here, the different heating rates are used to simulate different combustion conditions of SARA fractions.

Simultaneously, the molecular weight distribution of emitted gaseous products was analyzed using MS, and functional groups or molecules in volatiles were qualitatively identified. Finally, test results from MS and FTIR were verified each other. Among them, MS could analyze molecular weights of ionized molecules and ionic groups.\(^\text{21}\) FTIR could identify the types of main functional groups or molecules in volatiles and quantified their release amount using the selected volatile indexes. Therefore, the constituents of main emitted volatiles were confirmed and the whereabouts trace of main elements and heteroatoms in bitumen was tracked. As a result, the combustion characteristics and emitted volatile constituents of bitumen were further understood at the SARA fraction level.

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

SBS modified bitumen was bought from Nanjing Petrochemical Refinery Co., Ltd. Elemental analysis of bitumen was performed using an elemental analyzer (PE 2400II type, Perkin Elmer). Also, SBS modified bitumen was utilized to prepare SARA fractions by means of chromatographic separation based on ASTM D4124-09. Table 1 summarized basic properties of SBS modified bitumen and its SARA fraction contents.

### 2.2 | Methods

Thermal decomposition and gaseous products were analyzed by TG-MS-FTIR combined test system. Among them, TG (STA409PC/P, Netzsch) was used to heat SARA fraction samples from 40°C to 800°C at three heating rates of 5, 10, and 15°C/min in air atmosphere, respectively. The purge gas was nitrogen which was input at a flow rate of 60 mL/min. The connected FTIR spectrometer (IZ10, Nicolet) and MS analyzer (QMS403C, Netzsch) were utilized to discuss emitted volatiles. The FTIR spectra were recorded in the range of 4000-500 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). The scanning range and cycle of MS were 2-202 amu and 105 seconds, respectively.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Mass loss evolution of each SARA fraction and releasing trend of volatiles

Test results of TG, TIC, and G-S of each SARA fraction are summarized to discuss their mass losses and changing trend
of volatile emission. Various structures of SARA fractions result in the differences in the release curves of volatiles, which indicates that the individual cracking pathway of each fraction is determined by its chemical nature.22

### 3.1.1 Mass loss evolution of saturates and releasing trend of volatiles

Test results of TG, TIC, and G‐S of saturates are used to discuss the mass loss and releasing trend of its volatiles as shown in Figure 1.

From TG and DTG curves of saturates in Figure 1, it is observed that there are two obvious combustion stages at different heating rates. When the heating rate is elevated, the mass loss is increased at stage I, but is lowered at combustion stage II. The reason for this is more light components of saturates are volatilized at stage I, and the imperfect combustion is increased at a higher heating rate. The peak temperature (Tp) occurs at around 390°C at stage I. The G‐S curve shows that the whole combustion includes a two‐stage release of volatiles. It is found that main thermal decomposition region is observed at stage I because saturates are an unstable fraction, which includes aliphatic chain structures as well as branching and cyclic alkanes. The oxidation combustion of its charring layer occurs at stage II. A lot of gaseous products are produced, and thus the residue is negligible.

However, a single peak is observed from TIC curve. This is because when the temperature is low, the micromolecular products are mainly released in the form of volatiles at stage I. When the temperature is further raised, the volatiles with relatively larger mass‐to‐charge ratios (m/zs) are emitted in the SARA combustion processes, but the release amount is so little that no significant peak appears at stage II. As a result, TIC curve shows a single‐peak characteristic.

The two obvious peaks on G‐S curves are found within the temperature range from 300°C to 600°C, which are corresponding to the two main mass loss stages on DTG curve at the heating rate of 5°C/min. The similar phenomenon occurs on TIC curves at the heating rate of 10°C/min and 15°C/min. The individual TIC peak appears at around Tp at stage I on DTG curve.

There is a one‐to‐one correspondence between every two peaks on G‐S and DTG curves in the saturate combustion process when the heating rate is 10°C/min. The strongest peak appears at stage I at the heating rate of 5°C/min, while the largest peak height and width occur at stage II at the heating rate of 10°C/min. This is attributed to various ion currents with different m/zs at the two combustion stages.

As the heating rate is increased, TG and DTG curves, as well as TIC and G‐S curves of emitted volatiles are all shifted to the higher temperature during the combustion of saturates. This is due to the fact that the combustion of saturates is more incomplete at a larger heating rate, leading to the rise
in peak temperature and the shift of TG curve to the higher temperature.

3.1.2 | Mass loss evolution of aromatics and releasing trend of volatiles

Test results of TG, TIC, and G-S of aromatics are used to discuss the mass loss and releasing trend of its volatiles as illustrated in Figure 2.

Figure 2 illustrates the TG and DTG curves, TIC and G-S curves of emitted volatiles in the aromatics combustion process at the heating rate of 5, 10, and 15°C/min. The mass loss of aromatics is increased at stage I, but is decreased at stage II as the heating rate is elevated. This is owing to the fact that the naphthenic aromatics contain hydrocarbon structures with lower molecular weights, which is easily cracked into a large number of micromolecules at stage I. However, aromatics are prone to dehydrogenate and condense into condensed nuclei aromatics at stage II.

As shown in Figure 2, the combustion interval becomes narrower at stage I, while becomes wider at stage II as the heating rate is increased from 5°C/min to 10°C/min. The reason for this is the oxidation combustion rate is decreased, and the dehydrogenation condensation rate is increased. The two-stage characteristics of G-S curves and the single-peak characteristics of TIC curves are shown at the three heating rates. The characteristic peaks on TIC curves of emitted volatiles in the aromatics combustion process appear at around \( T_p \) on DTG curves at stage I because the mass loss of aromatics is accompanied by the release of gaseous volatiles.

However, each peak on G-S curves of released volatiles occurs corresponding to that on TG and DTG curves in the aromatics combustion process at different heating rates. Moreover, it is found that the strongest peak occurs at stage II at the heating rate of 5 and 10°C/min, while the peak intensity at stage I on G-S curves is slightly larger than that at stage II at the heating rate of 15°C/min. Therefore, it is concluded that high molecular weight products are generated at stage II at the heating rate of 5 and 10°C/min, and light products are emitted at stage I, while the heavy constituents are generated at stage II. Moreover, the release amount of small molecular volatiles with smaller m/zs is more than that of macromolecular volatiles with larger m/zs at the heating rate of 15°C/min.
3.1.3 | Mass loss evolution of resins and releasing trend of volatiles

Test results of TG, TIC, and G-S of resins are used to discuss the mass loss and its releasing trend of volatiles as shown in Figure 3.

Figure 3 shows TG, DTG, TIC, and G-S curves of emitted volatiles in the resins combustion at the three heating rates, respectively. When the heating rate is elevated, the mass loss of resins is almost equal at the two stages. This is because of the fact that resins are sticky semi-solid and becomes more difficult to thermally decompose at stage I. Also, it is difficult for the generated charring layer and macromolecular products to combust at stage II at a larger heating rate. This is because resins contain polar aromatic rings and nonpolar paraffinic groups, which are significant to thermal stability.23

The peak on TIC curve appears at stage I, but the main peak of G-S occurs at stage II in the resins combustion process. This is because macromolecular volatiles are mainly shown on G-S curve, while the main release process of light volatiles is concentrated at the first peak on TIC curve. TG, DTG, TIC, and G-S curves are shifted to higher temperature when the heating rate is elevated owing to a large thermal lag. Therefore, both dehydrogenation condensation and side chain cracking occur at stage I. The charring layer combustion and colloidal condensation happen at stage II.

3.1.4 | Mass loss evolution of asphaltenes and releasing trend of volatiles

Test results of TG, TIC, and G-S of asphaltenes are utilized to discuss the mass loss and its releasing trend of gaseous products as shown in Figure 4.

Figure 4 presents TG, DTG, TIC, and G-S curves of produced volatiles in the asphaltenes combustion process. Two obvious combustion stages are distinguished on DTG curves at the three heating rates. The mass loss of asphaltenes at stage I is almost similar with that at stage II as the heating rate is elevated. This is attributed to the fact that asphaltenes are the most polar solid fraction with the maximum molecular weight in the bituminous system, thus is the most stable fraction. Therefore, the heating rate effect on TG changes of
asphaltenes becomes negligible. The imperfect combustion part of asphaltenes becomes more when the heating rate is raised.

TIC curves suggest that the whole mass loss process involves a two-stage dynamic evolution of gaseous products. However, only one peak is found on the G-S curve. The two obvious peaks on G-S curves are corresponding to the main mass loss stages on TG curves. When the heating rate is increased, TG, DTG, TIC, and G-S curves of emitted volatiles all show the shift to higher temperature during the combustion of asphaltenes. This is because the solid asphaltenes sample is not timely decomposed and volatilized as the heating rate is increased because of the lower heat transfer efficiency in asphaltenes, leading to the thermal hysteresis.

In conclusion, TG-DTG and G-S curves show two-stage characteristics, while the TIC curve presents a one-stage characteristic which is related to m/zs of emitted volatiles in each SARA fraction combustion process. As the heating rate is raised, TG-DTG, TIC, and G-S curves are shifted to higher temperature in each SARA fraction combustion process. The maximum release amount of volatiles occurs at around \( T_p \) at the main combustion stage of each SARA fraction. The mass loss is decreased at stage I, but increased at stage II in the order of saturates, aromatics, resins, and asphaltenes.

### 3.2 Molecular weight distribution of emitted volatiles using MS

Several representative \( T_p \)s on DTG curves is selected to study the molecular weight distribution of emitted volatiles. Furthermore, the injected gases of \( N_2 \) and \( O_2 \) are excluded when determining the molecular weights of volatiles according to MS test results.

#### 3.2.1 Molecular weight distribution of saturates volatiles

The molecular weight distribution of emitted volatiles at each combustion stage of saturates is given in Figure 5.

As shown in Figure 5, except for \( N_2 \), the ethene or CO with the m/z of 28 is found in the gaseous products during the combustion of saturates. Several kinds of micromolecular products such as \( H_2O \) (m/z = 18), CO and ethene (m/z = 28), methanol (m/z = 32), propylene or ketene (m/z = 42), \( CO_2 \) and acetaldehyde or propane (m/z = 44) are detected at stage I as the heating rate is 5°C/min. The generation of \( CO_2 \) is associated with the thermal decomposition of carboxylic acid, ester, and acid anhydride groups. Small molecular olefins such as ethane, propylene are main products of saturates which are easily oxidized to aldehydes and carboxylic acids.
Compared with the emitted volatiles at stage II at the heating rate of 5°C/min, the propanal, acetone, or butane (m/z = 58) are found at the heating rate of 10°C/min. In addition, acetic acid, methoxyethane, or methyl formate (m/z = 60) in the released volatiles disappear at stage I, but they are confirmed at stage II at the heating rate of 10 and 15°C/min. The flammable diacetylene (m/z = 50) disappears at stage II at the heating rate of 15°C/min, as well as CO₂ and CO is produced by the secondary combustion of flammable gases. Test results show that the thermal decomposition, as well as complete and incomplete combustion occurs during the combustion of saturates.

3.2.2 | Molecular weight distribution of aromatics volatiles

Figure 6 illustrates the molecular weight distribution of emitted volatiles at each stage in the aromatics combustion process. From Figure 6, different micromolecular volatiles such as H₂O (m/z = 18), methanol (m/z = 32), propylene, or ketene (m/z = 42), CO₂ and acetaldehyde or propane (m/z = 44) are detected at the heating rate of 5°C/min. CO₂ is generated from aliphatic and aromatic carboxy (–COOH) groups. The products of aromatics are attributed to the dehydroaromatization of cycloalkenes and olefins. Macromolecular compounds with m/z = 62 are found during the combustion of aromatics, which is different from saturates. These compounds include alcohol and dimethyl ether. However, the compounds such as propanol or acetic acid (m/z = 60) are not found at stage II when the heating rates are 5°C/min and 10°C/min. Compared with saturates, the released volatiles of aromatics contain more macromolecules. The reason is that aromatics mainly contain side chains which are difficult to break from aromatic rings and aromatic compounds.

3.2.3 | Molecular weight distribution of resins volatiles

The molecular weight distribution of emitted volatiles at each stage in the resins combustion process is presented in Figure 7. As shown in Figure 7, the positive ion mass [CH₂CN]⁺ (m/z = 20), [C₃H₄]⁺, [CH₂CN]⁺ (m/z = 40), and SO₂ or disulfides (m/z = 64) are found in the emitted volatiles from resins, which is different from aromatics. At around Tₚ on DTG curve during the combustion of resins, CO (m/z = 28) and CO₂ (m/z = 44) are generated due to the thermal decomposition of carbonyl structures and ether structures or oxygen-bearing heterocycles, respectively. The m/z = 64 is the base peak of SO₂ and disulfides. This is attributed to the presence of S heteroatom in the molecular structure of resins.
FIGURE 7  Molecular weight distribution of emitted volatiles in the resins combustion process

FIGURE 8  Molecular weight distribution of emitted volatiles in the asphaltenes combustion process
The S element, as one of heteroatoms, improves the thermal stability of resins, therefore resins act as a stabilizer for the asphaltenes, and thus plays an important role in the bituminous stability. The constituents of emitted volatiles are similar during the resins combustion processes at the three heating rates.

### 3.2.4 Molecular weight distribution of asphaltenes volatiles

The molecular weight distribution of emitted volatiles at each stage in the asphaltene combustion process is shown in Figure 8.

From Figure 8, the release of H2O is caused by the thermal decomposition of various oxygen-containing groups such as phenolic –OH. When compared with the resins, the positive ion mass [C12H3+ (m/z = 38), and SO or CH4 (m/z = 64) appear at around Tp on DTG curve during the combustion of asphaltenes. SO2 (m/z = 64) reacts intensely with H2O (m/z = 18) to form S (m/z = 32) which is flammable. S is also undergone the secondary combustion with O2 to form SO2. CH4 is generated from C–C bond breakage in aliphatic chains at stage I, whereas the release of CH4 is due to the breakage of strong bonds such as arylmethyl group and arylalkyl ether at stage II. The release of CO is attributed to the decomposition of ketones at stage I, while CO is the decomposition product of phenolic groups at stage II. The volatile kinds emitted from resins and asphaltenes are similar at the three heating rates because resins are often converted into asphaltenes. Therefore, the Tp of asphaltenes is higher and the thermal stability of asphaltenes is better.

The main molecular weight of SARA fraction volatiles is distributed in the range of 12-64, including H2O, CO2, CO, ethene, methanol and propylene or ketene, and acetaldehyde or propane. This suggests the main volatile kinds are similar in each SARA fraction combustion process. The same volatile emitted from saturates and aromatics is propanol or acetic acid, while the common products of resins and asphaltenes are SO2 and disulfides. Moreover, the m/zs of released volatiles become larger in the order of saturates, aromatics, resins, and asphaltenes, which is attributed to the molecular structures become more and more stable from the saturates to asphaltenes.

### 3.3 FTIR analysis of functional groups or molecules in emitted volatiles

In order to accurately identify volatile constituents and avoid the influence of ion fragmentations in MS, FTIR test results at Tp on DTG curves during the combustion of SARA fractions are discussed in the spectrum range of 400-4000 cm⁻¹.

#### 3.3.1 FTIR analysis of emitted volatiles in the saturates combustion process

FTIR spectra of emitted volatiles from saturates at each combustion stage at various heating rates are shown in Figure 9.

From Figure 9A, the characteristic bands at 3500-4000 cm⁻¹ represent the presence of H2O. The bands at 1680-1720 cm⁻¹ indicate the existence of oxygen-type compounds. The released H2O is derived from the bound H2O or oxygen-containing group decomposition during the combustion of saturates. When the temperature is up to 500°C at stage II, a small amount of H2O is produced, which possibly originates from more thermally stable oxygen-containing groups such as heterocyclic aromatic compounds.

The bands at 2060-2240 cm⁻¹ and 2240-2400 cm⁻¹ are typical absorption peaks of CO and CO2, respectively. CO is because of the bond breakages of C=O and C–O–C at stage I. The generation of CO2 is mainly contributed to the breakages of aliphatic bonds, oxygen-containing –COOH groups and partial weak aromatic bonds at stage II. CO2 is released at below 450°C at stage I due to the presence of aliphatic and aromatic –COOH groups. As the temperature further rises at stage II, more stable ether structures and

![Figure 9](image_url)
oxygen-bearing heterocycles are decomposed into CO\textsubscript{2}.\textsuperscript{31} The bands at 3500-4000 cm\textsuperscript{-1} are owing to the stretching of O–H bond. The bands at 3200-3000 cm\textsuperscript{-1} are because of the stretching vibration of aromatic C–H bond. The bands at 3000-2840 cm\textsuperscript{-1} are due to the stretching and bending modes of aliphatic C–H.\textsuperscript{32} This indicates that light hydrocarbons are released at stage I in the saturates combustion process.

However, as shown in Figure 9B, the release amount of volatiles is decreased significantly at stage II. The bands at 1500-1300 cm\textsuperscript{-1} are the characteristic peaks of methyl and methylene. The band at 1061 cm\textsuperscript{-1} is owing to the stretching vibration of C–O–C bond which indicates the existence of ether. The band at 950 cm\textsuperscript{-1} is corresponding to the out-of-plane deformation vibration of C–H bond at stage I as shown in Figure 9A, while it disappears at stage II as shown in Figure 9B.

Weak bands are observed at the wavenumber range of 737-615 cm\textsuperscript{-1} and 2400-2240 cm\textsuperscript{-1}, which are attributed to the deformation vibration and antisymmetric stretching of CO\textsubscript{2}, respectively. This indicates that more and more CO\textsubscript{2} is emitted at stage II as the heating rate is raised, which is because of the breakages of both –OH and side chains in aliphatic hydrocarbons, as well as the deacidification reaction of –COOH groups.\textsuperscript{33}

From Figure 9, it is observed that C=O groups are continuously produced from the combustion stage I to stage II. These similar phenomena are found at various heating rates. Both CO and CO\textsubscript{2} at stage II are more than those at stage I at the three heating rates, which suggests that the complete combustion part of saturates is predominant at various heating rates.

### 3.3.3 | FTIR analysis of emitted volatiles in the aromatics combustion process

Figure 10 provides FTIR spectra of emitted gaseous products at each aromatics combustion stage at various heating rates.

It is observed from Figure 10A that the release of main volatiles including CO, CO\textsubscript{2}, and H\textsubscript{2}O are increased at stage I. The formation of CO\textsubscript{2} and H\textsubscript{2}O is due to the breakage of –OH groups and the deacidification reaction of –COOH groups, as well as the dehydration reaction of –OH and –COOH free radicals, and the combination of –OH and hydrogen groups, respectively.\textsuperscript{33} The characteristic absorption peak at 1729 cm\textsuperscript{-1} is owing to the existence of oxygen-contained compounds.

Figure 10B illustrates the obvious stretching vibration peaks of C=O groups at 2060-2240 cm\textsuperscript{-1} and 2240-2400 cm\textsuperscript{-1} at stage II at the heating rate of 15°C/min, and C=O groups are easily oxidized to –COOH. The presence of C=O groups indicates that emitted gaseous products include alcohols, aldehydes, ketones, carboxylic acids, phenols, and esters. The band at 1700 cm\textsuperscript{-1} is attributed to C=O in –COOH group, aldehydes, ketones, ester, or amides. The band at 1600 cm\textsuperscript{-1} is due to C=C. The absorption peaks at 1460 cm\textsuperscript{-1} and 1376 cm\textsuperscript{-1} are because of aliphatic CH\textsubscript{2} and CH\textsubscript{3}.\textsuperscript{34}

Additionally, the obvious bands at 1500-1300 cm\textsuperscript{-1} and 3000-2800 cm\textsuperscript{-1} are because of the antisymmetric and symmetric stretching vibrations of methane and methyl, respectively. The strong characteristic peak at 3017 cm\textsuperscript{-1} indicates the presence of CH\textsubscript{4} at stage II. The CH\textsubscript{4} is possibly derived from the breakage of arylmethyl group at higher temperature.\textsuperscript{35}

Finally, Figure 10 shows that the release amount of CO and CO\textsubscript{2} is increased significantly during the combustion of aromatics, suggesting that C=O groups are generated continuously. Moreover, the release amount of CO\textsubscript{2} is more than that of CO. Therefore, the complete combustion dominates the aromatics combustion process.

### 3.3.3 | FTIR analysis of emitted volatiles during the combustion of resins

Figure 11 illustrates FTIR spectra of emitted volatiles at each combustion stage of resins at various heating rates.

It is seen from Figure 11 that when the heating rate is increased, similar characteristic peaks appear at the two
combustion stages at different heating rates, while the absorption peaks of released volatiles become stronger. This suggests more volatiles are emitted on the whole. From Figure 11, the strong absorption bands at 737-615 cm\(^{-1}\) and 2400-2240 cm\(^{-1}\) are because of the existence of CO\(_2\).

The bands at 3017 cm\(^{-1}\), 3000-2700 cm\(^{-1}\), and 3100-3000 cm\(^{-1}\) show the presence of short-chain methane, alkanes, and aldehydes, respectively. The obvious continuous characteristic bands at 4000-3500 cm\(^{-1}\) are ascribed to the release of H\(_2\)O, which is usually associated with phenolic OH groups and sample moisture.\(^{36}\) The appearance of absorption bands at 1720 cm\(^{-1}\) is due to the stretching vibration of C=O which is proved to the presence of aldehydes and ketones.\(^{37}\) As shown in Figure 12A, the spectrum intensity of characteristic band at 1475 cm\(^{-1}\) corresponding to SO\(_2\) is much higher at stage I than that at stage II.

Figure 11 shows that the release amount of CO\(_2\) is more than those of CO and SO\(_2\) during each combustion stage at the three heating rates. Further, the release amount of CO\(_2\) at the heating rate of 10°C/min is larger than those at the heating rate of 5°C/min and 15°C/min. This indicates that the combustion of resins is more complete at the heating rate of 10°C/min. The release amount of CO at stage II is more than that at stage I, while the release amount of SO\(_2\) at stage I is more than that at stage II at the heating rate of 5°C/min. This is because CO is attributed to the bond breakages of C=O and C–O–C at stage II, while SO\(_2\) is derived from the bond breakages of S=O on side chains at stage I as shown in Figure 11A. However, the release amount of SO\(_2\) is decreased in the resins combustion processes at various heating rates.

3.3.4 FTIR analysis of emitted volatiles in the asphaltenes combustion process

FTIR spectra of emitted volatiles at each asphaltenes combustion stage at the three heating rates are illustrated in Figure 12.

From Figure 12, FTIR spectra of emitted volatiles from asphaltenes are similar to those from other three bituminous fractions. The absorption intensity of FTIR spectra is increased in the asphaltenes combustion process as the heating rate is increased. The absorption peaks at 4000-3500 cm\(^{-1}\) and 1360 cm\(^{-1}\) are due to the appearance of H\(_2\)O generated by the dehydroxylation of asphaltenes. The absorption peak at 1475 cm\(^{-1}\) shows the characteristic stretching vibration of S=O, which indicates the existence of SO\(_2\) in emitted volatiles.\(^{38}\) When compared with Figure 12B, the absorption peaks at 3017 cm\(^{-1}\), 3000-2700 cm\(^{-1}\), and 3100-3000 cm\(^{-1}\) in Figure 12A are attributed to the presence of methane, aldehydes, and short-chain alkanes, respectively.

The bands at around 1750 cm\(^{-1}\) and 1724 cm\(^{-1}\) are because of C=O group in esters.\(^{39}\) CO results from the decomposition of phenolic groups.\(^{27}\) The band at 3450 cm\(^{-1}\) is assigned to the stretching vibration of –OH in alcohol, carboxyl acid, and phenol.\(^{32}\) Two characteristic bands at 1496 cm\(^{-1}\) and 1333 cm\(^{-1}\) are due to the stretching of C=C in aromatic benzene ring, and the bending of C–H, respectively.\(^{40}\) Moreover, the weak peak at 1545 cm\(^{-1}\) is because of the existence of NO\(_2\), which may derive from the thermal decomposition of nitrogen compounds.\(^{31}\)

From Figure 12, it is found that the release amount of SO\(_2\) and NO\(_2\) is relatively less than that of CO and CO\(_2\). This is attributed to the fact that the heteroatom contents of S and N in asphaltenes are lower. Also, the release amount changes of main volatiles are not obvious when the heating rate is increased from 5°C/min to 15°C/min. The reason for this is that asphaltenes are solid, and the heating rate shows few effects on its combustion. Finally, the contents of CO and CO\(_2\) at stage II are higher than those at stage I in the asphaltenes combustion process at the three heating rates. The reason is that it is more difficult for asphaltenes to combust at stage I at lower temperature, while more asphaltenes is combusted at stage II at higher temperature.
During the combustion processes of SARA fractions, the dominant emitted volatiles are CO, CO$_2$, and H$_2$O. The emissions of CH$_4$ and other light hydrocarbons are identified during the combustion of saturates and aromatics. Except for CO, CO$_2$, and H$_2$O, the common volatile of resins and asphaltenes is SO$_2$. The release amount of SO$_2$ is decreased in the resins combustion processes at the three heating rates.

3.4 Whereabouts trace of main elements and heteroatoms in bitumen

According to previous elemental analysis results in Table 1, it is known that the main elements in bitumen are C, H, O, N, and S. Test results of MS and FTIR show that no new heteroatoms are introduced during the SARA fraction combustion. Based on FTIR analysis results, in order to track the whereabouts of main elements and heteroatoms, we identify the constituents of emitted volatiles from SARA fractions. For this, main volatile indexes are calculated to compare their release amount in emitted volatiles of SARA fractions.$^{42,43}$

To compare the release amount of selected volatiles which contains the tracked elements, typical volatile indexes are calculated at different combustion stages of SARA fractions at the three heating rates as shown in Figure 13.

The integrated area between 2060 and 2240 cm$^{-1}$, 2240-2400 cm$^{-1}$, 1475 cm$^{-1}$, and 1545 cm$^{-1}$ is utilized to estimate the contents of CO, CO$_2$, SO$_2$, and NO$_2$, respectively. Since C=O groups contribute to the intensities of bands in the range of 2060-2400 cm$^{-1}$. The selected volatile indexes such as I$_{co}$, II$_{co}$, I$_{co2}$, II$_{co2}$, I$_{so2}$, II$_{so2}$, I$_{no2}$, and II$_{no2}$ are calculated as follows.

\[
I_{co} = \frac{S(2060 - 2240)}{S(40 - 4000)}
\]
\[
II_{co} = \frac{S(2060 - 2240)}{S(40 - 4000)}
\]
\[
I_{co2} = \frac{S(2240 - 2400)}{S(40 - 4000)}
\]
\[
II_{co2} = \frac{S(2240 - 2600)}{S(40 - 4000)}
\]
\[
I_{so2} = \frac{S(1475)}{S(40 - 4000)}
\]
\[
II_{so2} = \frac{S(1475)}{S(40 - 4000)}
\]
where \( S(s) \) is the integrated area value in the wavenumber ranges, and I and II represent the combustion stage, respectively.

From Figure 13A, it is found that calculated indexes of CO and CO\(_2\) are increased significantly during the combustion of saturates, indicating that the C=O groups are continuously produced from the combustion stage I to stage II. These similar phenomena are found at the three heating rates. The calculated indexes of both CO and CO\(_2\) at stage II are larger than those at stage I at the three heating rates, which suggests that the complete combustion of saturates occurs at different heating rates.

Figure 13B shows that calculated indexes of CO and CO\(_2\) are increased significantly during the combustion of aromatics, suggesting that C=O groups are generated continuously. Moreover, I\(_{CO}\) and II\(_{CO}\) of aromatics at different heating rates are larger than I\(_{CO}\) and II\(_{CO}\), respectively. Also, when comparing each two sets of indexes, the content of CO\(_2\) is larger than that of CO. This indicates that the release amount of CO\(_2\) is more than that of CO. Therefore, the complete combustion dominates the combustion process of aromatics.

Figure 13C shows that the calculated index of CO\(_2\) is obviously larger than those of CO and SO\(_2\) during each combustion stage of resins at the three heating states, indicating that the release amount of CO\(_2\) is more than those of CO and SO\(_2\). The release amount of CO at stage II is more than that at stage I, while the release amount of SO\(_2\) at stage I is more than that at stage II at the heating rate of 5\(^\circ\)C/min. This is because CO is attributed to the bond breakages of C=O and C–O–C at stage II, while SO\(_2\) is derived from the bond breakages of S=O on side chains at stage I. However, the index of SO\(_2\) is lowered at a higher heating rate due to the incomplete combustion of resins. This suggests that SO\(_2\) is derived from the heteroatom of S in resins.

From Figure 13D, it is found that the release amount of SO\(_2\) and NO\(_2\) is relatively less than those of CO and CO\(_2\), SO\(_2\), and NO\(_2\) are derived from heteroatoms of S and N in asphaltenes. This indicates that asphaltenes contain heteroatoms of S and N, and their contents are much less. Also, the release amount changes of CO, CO\(_2\), SO\(_2\), and NO\(_2\) are not obvious at different heating rates. The reason for this is that asphaltenes are solid, and the heating rate show fewer effects on the combustion of asphaltenes than those of other three fractions.

In conclusion, the main typical volatiles of saturates and aromatics are similar during each combustion stage at the three heating rates, and the release amount of CO and CO\(_2\) at stage II are larger than that at stage I. SO\(_2\) is released during the combustion of resins, which derives from the heteroatom of S in resins. SO\(_2\) and NO\(_3\) are identified in volatiles of asphaltenes, coming from S and N in asphaltenes.

4  CONCLUSIONS

In this study, the mass loss of each SARA fraction and releasing trend of volatiles, molecular weight distribution of emitted volatiles, and functional groups or molecules in emitted volatiles were discussed. Main conclusions are summarized as follows.

1. TG-DTG and G-S curves show two-stage characteristics in each SARA fraction combustion process, while the TIC curve presents a one-stage characteristic which is related to m/zs of emitted volatiles.
2. When the heating rate is raised, TG-DTG, TIC, and G-S curves are shifted to higher temperature in each SARA fraction combustion process. The maximum release amount of volatiles occurs at around \( T_p \) at the main combustion stage, indicating that each SARA fraction combustion process includes a volatilization process.
3. The release amount of different gaseous products is increased from saturates to asphaltenes when the heating rate is raised. The molecular weights of main volatiles are distributed in the range of 12-64, including H\(_2\)O, CO\(_2\), CO, ethene, methanol and propylene or ketene, and acetaldehyde or propane. This suggests the main volatile kinds are similar in each SARA fraction combustion process.
4. The same volatile emitted from saturates and aromatics is propanol or acetic acid, while the common products of resins and asphaltenes are SO\(_2\) and disulfides. The elemental species of volatiles are consistent with those of SARA fractions. As the heating rate is raised, the volatile release amount is increased, but the elemental species remain unchanged.
5. The dominant emitted volatiles are CO, CO\(_2\), and H\(_2\)O. CH\(_4\) and other light hydrocarbons are identified during the combustion of saturates and aromatics. Except for CO, CO\(_2\), and H\(_2\)O, the common volatiles of resins and asphaltenes are SO\(_2\), and its release amount is decreased during the combustion of resins at the three heating rates.
6. The main volatiles of saturates and aromatics are similar during each combustion stage at the three heating rates, and the release amount of CO and CO\(_2\) at stage II is larger than that at stage I. SO\(_2\) is released during the combustion of resins. SO\(_2\) and NO\(_2\) are identified in volatiles of asphaltenes, coming from S and N in asphaltenes.
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