Pyrolysis of Asphaltenes Derived from Residual Oils and Their Thermally Treated Pitch

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ABSTRACT: Thermogravimetric analysis (TGA) was employed to investigate the thermal stability of asphaltenes at different environments (inert and oxidizing atmosphere) and identify their refractory nature. TGA and differential scanning calorimetry were carried out at a temperature range of 50−700 °C, for asphaltene samples obtained from atmospheric residues, vacuum residues (VRs), and aromatic petroleum pitch samples, which were obtained from the cracking of VRs at different temperatures. The TGA results clearly indicate that thermal degradation of asphaltene takes place in a single process that starts around 350 °C and ends at 500 °C, giving ash contents of less than 2%. The derivatives of the TGA for the asphaltene samples suggest that the weight loss of composite material took place in two steps. The first step corresponds to the degradation of aliphatic side chains or easily oxidized hydrocarbons, while the second step corresponds to the degradation of the aromatic sheets or the stacked layers. TGA of asphaltenes in oxidizing atmosphere showed considerable changes in heat flow due to the destructive oxidation of the asphaltene molecular structure. The thermal stability or refractory nature of these asphaltenes have been calculated as heat of energy or enthalpy of the molecule, which corresponds to the $\pi-\pi$ interaction between the aromatic ring, hydrogen bonding, and alkyl chain size of the asphaltene molecule.

1. INTRODUCTION

Crude oil is constituted of four fractions: saturates, aromatics, resins, and asphaltenes (SARA fractions). The four fractions are normally classified based on the solubility and polarity of their components. Asphaltenes are commonly presumed to represent the most refractory fraction of crude oil and frequently associated with major operational problems in upstream and downstream industries. Asphaltene’s hypothetical molecular structure is composed of a polycyclic aromatic core containing various alkyl side chains. It is often viewed as a fraction of crude that is soluble in aromatic solvent (i.e., toluene and benzene) but insoluble in light paraffins (i.e., hexane, and heptanes). Therefore, asphaltenes are often defined as the dispersed colloids in the oil phase that are stabilized by polyaromatic molecules, particularly the resins fraction, which act as protective bodies for asphaltenes. If the resin-protective shields are removed or disturbed, asphaltenes normally precipitate.

To understand the impact of thermal stress on the asphaltene molecules, our research group conducted a number of studies on thermal cracking of heavy residues and reported that thermal cracking conditions influence the structure and properties of asphaltene. Analyses of the cracked products showed that increasing the cracking severity results in a notable decrease in the molecular size of the asphaltenes, significant increase in aromaticity, reduction in the H/S ratio, and concentration of metals (Ni and V) in the core aromatic ring of the asphaltene molecule. An X-ray diffraction (XRD) study indicated a decrease in cluster diameter as the severity of cracking increases, which was mainly attributed to the loss of aliphatic carbon in the side chains and the decrease in the number of aromatic sheets per stack. The study also illustrated an insignificant impact of thermal treatment on the layer distance between the aromatic sheets, the distance between the aliphatic chains (or naphthenic sheet), and the average diameter of the aromatic sheet. Moreover, a Fourier transform infrared (FTIR) study revealed the impact of thermal treatment on the different functional groups that exist in asphaltenes and reported obvious differences between asphaltenes exposed to thermal cracking and their parent asphaltenes from the vacuum residues (VRs). The FTIR results suggested that thermal treatment mainly affects the
paraffinic side chains in the molecular structure of asphaltenes, while changes in the aromatic core appear to be very limited.5 In a more recent study, AlHumaidan et al.2 used NMR analysis to identify and quantify the structural parameters and the functional groups from which the hypothetical average structure of different asphaltene molecules were derived. The NMR analysis revealed several valuable findings and developed better understanding about the nature of structural changes that asphaltene molecules undergo during the thermal cracking of VRs. For instance, the polyaromatic structure of asphaltenes in the parent VRs consists of peri-condensed cores interlinked through aliphatic bridges. It was observed that the peri-condensed polyaromatic cores were converted to cata-condensed polyaromatic as the reaction severity increases. The NMR analysis also confirmed that the observed reduction in the average molecular weight of asphaltene molecules, as reaction severity increases, is mainly due to cracking of the saturated parts of the asphaltene molecules, loss of sulfur and nitrogen located in the saturated parts, and shrinking in the aromatic core.5

The pyrolysis behavior of crude oils and its SARA fractions was investigated in a number of studies.6−12 They indicated that asphaltenes are the most difficult fraction to oxidize due to the high energy requirement and because they are the main contributors to coke formation. Kok and Karacan7 reported the changes in the strength of the bonds as volatilization of asphaltene, which might suggest that the kinetics of coking is not always satisfactorily applied. The second-order kinetics was also observed by Khulbe et al.,24 while Karacan and Kok6 analyzed the differential thermogravimetric data using Arrhenius-type reaction model and reported that asphaltene has the highest activation energy compared to aromatics and resins.

This TGA study is a complement to our previous studies2−5 and will focus on monitoring asphaltene thermal stability under different environments to identify the refractory nature of asphaltenes precipitated from residual oils and pitch samples, which are the byproducts of VR thermal cracking at different reaction conditions.

2. EXPERIMENTAL SECTION

2.1. Thermal Cracking Experiments. Vacuum residues were obtained from atmospheric distillation, followed by vacuum distillation of three Kuwaiti crude oils (Figure 1), namely, Ratawi–Burgan (RB), Lower-Fars (LF), and Eocene (EC). The properties of the three VRs are listed in Table 1. The atmospheric residue (AR: 355+ °C) and the vacuum residue (VR: 550+ °C) were obtained using 30 and 5 L capacity distillation units, respectively. The IBP value for the VR is 550 °C, since the vacuum gas oil is obtained at a boiling range of 355−550 °C. HT-Simdist (D-7169) was carried out for the VR fractions, and the 5% volume was obtained at 535 °C (±1 °C), which is mainly due to the overlapping fraction. Thermal cracking of the VRs was performed in a pilot plant emulating the Eureka process, a commercially proven thermal cracking process that produces cracked oil and aromatic petroleum pitch from vacuum residues.25,26 A schematic diagram of the thermal cracking pilot plant is reported in AlHumaidan et al.25 The cracking takes place in a 2 L semibatch pilot-scale reactor, which is equipped with a mixer and a nitrogen injector. The mixer (300 rpm) is used to ensure a uniform reaction temperature within the reactor, whereas the nitrogen injector (1 NL/min of preheated N2) is used to immediately strip the products after formation. The continuous stripping by nitrogen prevents overcracking of products and reduces the hydrocarbon partial pressure within the reactor, which shifts the reaction equilibrium toward product formation. The thermal cracking tests were carried out at three cracking temperatures (400, 415, and 430 °C) and a reaction time of 50 min. Each experimental run resulted in three products: cracked oil, off-gases, and a byproduct pitch (P). Analyses of the thermal cracking products indicated that asphaltene tends to concentrate in the pitch byproduct, while

Figure 1. Origin of the asphaltene samples used in the TGA.
Table 1. Properties of RB, LF, and EC Vacuum Residues

| property method | RB-VR | EC-VR | LF-VR |
|-----------------|-------|-------|-------|
| boiling range, °C | 550   | 550   | 550   |
| yield on crude, wt % | 31.2  | 40.2  | 36.3  |
| yield on crude, vol % | 26.6  | 40.8  | 32.4  |
| density at 15 °C, g/cm³ | D5002 | 1.0497| 1.0583| 1.0659|
| gravity, °API | D1250 | 3.2   | 2.1   | 1.2   |
| molecular weight, g/mol | 1174 | 1256.1| 1045.3|
| asphaltene, wt % | D6560 | 14.6  | 22.3  | 14.7  |
| CCR, wt % | D4530 | 25.98 | 29.17 | 31.76 |
| TAN, mg KOH/g | D664 | 0.878 | 2.751 |
| elemental analysis |       |       |       |
| C, wt % | D5291 | 83.6  | 83.2  | 82.5  |
| H, wt % | D5291 | 9.9   | 9.6   | 9.1   |
| N, wt % | D5762 | 0.6   | 0.7   | 0.5   |
| S, wt % | D5453 | 5.9   | 6.5   | 7.9   |
| Ni, ppm | D5708 | 69.9  | 75    | 106.4 |
| V, ppm | D5708 | 139.1 | 153.5 | 277.9 |
| composition (SARA), wt % |       |       |       |
| saturates | D2007 | 6.45  | 5.17  | 6.29  |
| aromatics | D2007 | 64.25 | 53.68 | 65.46 |
| resin | D2007 | 14.66 | 18.88 | 13.57 |
| aromatics | D6560 | 14.64 | 22.26 | 14.67 |

aRB-VR: Ratawi–Burgan vacuum residue; LF-VR: Lower-Fars vacuum residue; EC-VR: Eocene vacuum residue.

The origins of the asphaltene samples analyzed in this study are shown in Figure 1. They were precipitated from the crude oils, their atmospheric and vacuum residues, and the pitch products produced at three cracking temperatures. The pitch samples were dissolved in toluene at 1:1000 (pitch to toluene; w/w) ratio to separate coke from the pitch. Subsequently, toluene was distilled off from the filtrate (volume was reduced), and asphaltene samples were extracted according to the method described in the IP 143/90 (ASTM 6560) standard. Asphaltene molecular weights were determined by gel permeation chromatography (GPC) using chloroform as a solvent at room temperature. A Waters 1500 series GPC, equipped with a Waters 2487 dual UV absorbance detector, was employed for GPC analyses. The stationary phase was PL gel, and various polystyrene standards with molecular weights ranging from 891 to 42,300 Da were used to calibrate the instrument. More details about asphaltene extractions are given in Lababidi et al.² and AlHumaidan et al.³

2.2. Pyrolysis Analysis. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed using TGA/DSC 1 Mettler Toledo equipment. The temperature range was 50–700 °C, and the maximum decomposition temperatures (Tₘₐₓ) for the various asphaltene samples were determined at a heating rate of 10 °C/min in the presence of air at a flow rate of 30 mL/min. Selected samples were analyzed in the presence of oxygen, hydrogen, and He medium at a constant flow rate of 30 mL/min. The instrument was calibrated with high-purity indium and zinc pure metals. The asphaltene samples (10–15 mg)
were placed in 70 μL aluminum crucibles. Evaporation enthalpies were evaluated by peak area integration of the DSC profiles, and the results were compared for different asphaltene samples.

The thermal experiments in the DSC monitor differential heat flow of the samples, whereas the TGA/DTG measures the weight loss as a function of either temperature or time in a varied but controlled atmosphere. The kinetic data of the nonisothermal reaction that takes place during the heating of the samples may be analyzed using the thermoanalytical method. The reaction rate constant is defined as a function of temperature using the Arrhenius equation

$$k = A \ e^{-E_a/RT}$$

where $k$ is the reaction rate constant (s$^{-1}$), $A$ is the preexponential factor (s$^{-1}$), $E_a$ is the activation energy (J/mol), and $R$ is the universal gas constant, 8.314 (J/(mol K)). Using eq 1, the activation energy and the preexponential factor are estimated using the linear regression equation

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

The principal role of thermal analysis is to provide information on the oxidation behavior of various asphaltene samples. It is expected that two successive oxidation reaction regions are recognized from thermogravimetric and heat flow generation. Thus, to understand the asphaltene molecule, it is important to consider its thermal behavior and ascertain its characteristics under different environments. Apart from the other issues related to the asphaltene, the knowledge of kinetic parameters associated with thermal decomposition has been useful for understanding structural modifications.

3. RESULTS AND DISCUSSION

Thermal analysis was performed on 18 asphaltene samples (Figure 1) that were extracted from the residual oils (ARs and VRs) and the pitch byproducts from thermally cracking the VRs of Kuwaiti crude oils from three origins (LF, EC, and RB) at three different temperatures (400, 415, and 430 °C). The TGA curves of the LF asphaltene samples are shown in Figure 2a, while those of the EC and RB samples are shown in Figure 2b,c, respectively. The plots show that thermal degradation of the asphaltene samples starts around 350 °C and complete decomposition is achieved around 500 °C, with an ash content of less than 2%. It is also evident from the TGA curves that asphaltene samples derived from the residues are lighter than those derived from the cracked samples, and those subjected to the most severe conditions (P430) are the heaviest. The differences in weight losses with respect to temperature are more obvious for LF samples compared to those of EC and RB samples (Figure 2). This gives a clear indication that asphaltenes from different origins have different structures and compositions.

The derivatives of the thermogravimetric analysis curves, which indicate the rates of weight losses (in mg/s), for the LF samples, are plotted in Figure 3a. The plots show two minima, indicating that the weight loss of the composite material takes place in two stages. The first corresponds to the degradation of the weak aliphatic side chains ($α$-methyl and $α$-methine structures), while the second corresponds to the degradation of the heavier fractions.$^{5,27-29}$ The aliphatic side chains are easy to break, and their concentration is relatively high in the AR asphaltene samples compared to asphaltenes derived from VRs and the VR-cracked samples. After the removal of the weak side chains, energy increases to a level at which decomposition
of the heavy factions is initiated. This observation is clearly illustrated by the peak intensities’ trends in Figure 3a. The shift leads to higher temperatures and up to a lower rate of weight loss at higher cracking temperatures. Hence, it is evident from the TGA results that the asphaltene derived from the thermally cracked VRs have considerably lesser aliphatic side-chain fractions. Moreover, comparing the weight loss plots (Figure 3) shows that the atmospheric and vacuum residue samples (LF-AR and LF-VR) have different types of aliphatic side chains, which vary with temperature, as illustrated by the differences in weight loss curves around 400 °C. The effect of the side chains on the TGA curves was reported by Kopsch, who showed that enhancing the side chains by five $-\text{CH}_2-$ groups (methyl to hexyl pyrine) increases the evaporation temperature by 35–40 °C.

The TGA results discussed so far showed quite pertinent indications to the structural differences in the asphaltene samples. They provided additional relevance to previous characterization results in which we reported changes in the skeletal composition of the asphaltene molecules and the atomic arrangements of hydrogen and carbon atoms when subjected to various severity conditions. The shifting of temperature indicates the bond scission reaction where the lighter fraction of asphaltene cracks at a lower temperature, while the asphaltene core (aromatic sheet) cracks at a higher temperature.

The rates of weight losses for the RB asphaltene samples are illustrated in Figure 3b. It appears from the plots that the RB samples have only one functional group type along with the main core of asphaltene. Hence, they have a comparatively straightforward molecular structure compared to those of asphaltene from the LF and EC origins. These asphaltene are originated from Kuwaiti oil fields, and their structural changes and thermal stabilities are an indication of the geochemical parameters that are considered to be influenced exclusively by source or thermal maturity.

The TGA results (Figures 2 and 3) clearly prove that the differences in thermal behavior are mainly due to the constituent organic functional group of the asphaltene. Degradation at lower temperatures (on-set) gives evidence of the presence of a lighter fraction, while degradation at higher temperatures (end-set) indicates the decomposition of aromatic sheets or the stacked layers. The thermal behavior is also dependent on a large extent on the cleavage of the carbon–heteroatom (N, S, O, and metals) unstable bond thermolysis.

### 3.1. Reactivity of Asphaltene.

Asphaltenes subjected to thermal treatment are expected to have low hydrogen content, high aromaticity, and high degree of aromatic compression. This was verified by studying the gas–solid reactions of asphaltene through TGA runs under different reaction medium gases. In these experiments, weight changes of the asphaltene samples were monitored when subjected to pyrolysis using one inert gas (He) and two reactive gases (O$_2$ and H$_2$).

The TG curves for the asphaltene derived from the atmospheric residue (RB-AR) for the three different gas mediums are shown in Figure 4a. The curves show that there are two weight loss steps. The first step starts at around 150 °C and is mainly caused by the loss of moisture or very light hydrocarbons remaining in the sample. The second weight loss starts at around 350 °C, and it is due to burning of the solid carbon into their respective gases. The remaining weights at the end vary with the reactive gas used and the type of asphaltene. As shown in Figure 4a, the sample completely burns in an O$_2$-rich medium, while around 43% remains in the He and H$_2$ medium. Comparing the RB-AR and cracked RB-P430 asphaltene samples, the amounts of their residuals are 43 and 46%, respectively. For the O$_2$-rich medium, the sample is placed in an environment that will cause “accelerated” oxidation reaction. The O$_2$ TG curve in Figure 4a illustrates that the reaction starts by the absorption of O$_2$, which is indicated by the low rate of weight loss in the mid-temperature range (275–400 °C), followed by a rapid loss of weight indicating complete burning. These results are indicative of the reactivity of asphaltene as a function of temperature in various mediums (He, H$_2$, and O$_2$) at atmosphere pressure. The oxidation reaction of asphaltene is exemplified in eq 1a. It is a bond scission reaction that produces CO$_2$, CO, and water, together with sulfur, nitrogen, and metal (Ni and V) oxides that result from the constituent heteroatoms.

Chemical and thermal degradation of the asphaltene samples was further investigated by running the TGA experiments in He and H$_2$ environments. The anticipated reactions are given in eq 1b and 1c, respectively. In both cases, solid carbon particles were left behind in the sample pan. The inert medium isolates the effect of reactive gases and breaks down the bonds with no addition of atoms to the asphaltene molecule. On the other hand, the H$_2$ gas saturates the carbon atoms and produces saturated carbon soot. The three reactions (eq 1) are not easy to follow and are often used to verify the TGA experiments. However, postulating such reactions requires

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c02792)
additional experiments using TG/mass spectrometry (MS) and TG/GC/MS to separate and identify individual products.

\[
\text{asphaltene (C)} + \text{O}_2 \xrightarrow{\text{oxidation}} \text{CO}_2 + \text{CO}_2 + \text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O}
\]

(1a)

\[
\text{asphaltene (C)} + \text{He} \xrightarrow{\text{carbonization}} \text{HC} + \text{H}_2\text{O} + \text{C} 
\]

(1b)

\[
\text{asphaltene (C)} + \text{H}_2 \xrightarrow{\text{saturation+combination}} \text{HC} + \text{H}_2\text{O} + \text{saturated C}
\]

(1c)

Unlike the smooth O2 and He TGA curves, the H2 TGA curve shows high variations, especially below 350 °C (Figure 4a). The frequent fluctuation of the curve makes it difficult to generate the rate of weight loss for the H2 medium. This unstable behavior can be related to the highly reactive unsaturated olefin functional groups in the asphaltene samples. The oscillation at low temperatures is mainly attributed to H2 diffusion (adsorption and desorption), while at higher temperatures, the observed oscillation can be attributed to the saturation reactions (increase in weight) and the compression due to cracking reactions (reduction in weight).

The adsorptive capacity is also governed by physiosorption via \(\pi−\pi\) interactions and electrostatic attraction between asphaltene and hydrogen. There are several studies that have reported the low-temperature \(H_2\) saturation, particularly for the graphene that is readily chemically active for either functionalization. The low-temperature hydrogen reduction for graphene is well supported in the literature, where the hydrogen is analyzed with different spectroscopic techniques. Figure 4b illustrates the reactivity of the three types of asphaltenes in a \(H_2\)-rich medium. Variations in the TGA are reported for asphaltene samples derived from the cracked product (RB-P430 °C). The plots show also that the weight of the samples remains constant or increases up to 250 °C, followed by a significant weight loss around 400 °C. The initial weight gains, especially for the RB-P430 °C sample, give clear evidence that the asphaltene molecule undergoes two reaction steps (eq 1c). The weight gain takes place in the saturation reaction, while the weight reduction occurs due to the cracking reaction that induces dissociation of the \(\pi−\pi\) complex, which may help to hold the asphaltene macrostructure together. The asphaltene molecule is known for its instability, especially to temperature, where it shows major changes in parallel semiaxes in comparison to perpendicular semiaxes. The reaction mainly initiates with the asphaltene side-chain (aliphatic) cracking, which reduces the overall size but without significantly affecting the core of asphaltene.

3.2. Thermal Stability and Heat Flow. The stability and the structural properties of the precipitated asphaltenes were determined by means of differential scanning calorimetry (DSC) analysis that measures the energy generated during the TGA as asphaltene melting enthalpy.22 The method of heat flow calculation may also indicate whether a measurable exothermic reaction is taking place.

Since the reaction in oxygen-rich medium occurs rapidly, the actual sample temperature \(T_s\) increases faster than the preset heating rate of the instrument \(T_t\). Hence, heat flow curves may be generated from the temperature measurements of the sample and an empty reference crucible that are placed in the same atmosphere and temperature field. The difference between the two temperatures, \(T_s - T_t\), indicates a region where the exothermic reaction is taking place. Furthermore, plotting \(T_s\) versus \(T_t\) (see Figure 5) produces a curve that contains positive peak area. Integration of the peak area gives the amount of energy released and, hence, the heat of reaction of the asphaltene sample.

To understand the thermal behavior of different asphaltenes, their heat capacities at constant pressure, \(C_p\), can be calculated using the TGA and DSC analysis data. The enthalpy, or the amount of energy released, is defined as

\[
\Delta H = \int_{T_i}^{T_f} C_p \, dT
\]

Assuming constant heat capacities in the temperature range

\[
\Delta H = C_p \, \Delta T
\]

the heat capacity of the asphaltene sample, \(C_p\), can be determined by dividing the change in enthalpy, \(\Delta H\), estimated from the peak area of the heat flow plots, by the temperature range in which the heat is released. The enthalpy can be quantified as follows

\[
\Delta H = \frac{1}{m_i} \int_{T_i}^{T_f} [T_s - T_t] \, dT
\]
where \( T_1 \) to \( T_2 \) is the temperature range (50–693.5 °C) and \( m_f \) is the weight of the sample. Another quantity that will be used in the analysis is the centroid of the exothermic peaks, which can be calculated as follows

\[
C_{\text{peak}} = \frac{\int_{T_1}^{T_2} T_i \times [T_i - T_f]dT}{\int_{T_1}^{T_2} [T_i - T_f]dT} \quad (6)
\]

Heat flow plots for the oxidation of asphaltene samples, precipitated from the LF residues and their cracked products, are shown in Figure 5a. The plots show that the induction periods start at around 375 °C followed by distinct heat flow peaks, which depend on the fragmentation of different asphaltene structures. The oxidation processes for all samples were completed close to 530 °C. At a constant heating rate, the heat released by various asphaltenes depends on the molecular oxidation kinetics (fast or slow) and the physical–chemical processes involved in heat generation. The differences in the molecular structures of the five LF asphaltenes are evident in the size, shape, and position of the peaks. The heat flow at higher temperatures indicates that the asphaltene molecules are more refractory and they need a higher energy to decompose. This is clearly shown in Figure 5a, where the centroids of the peak areas are shifted up to higher temperatures for the asphaltenes of the cracked products.

The estimated enthalpies and heat capacities of the LF-AR, LF-VR, LF-P400, LF-P415, and LF-P430 asphaltenes are 232.78, 250.20, 245.00, 246.68, and 153.16 mW/mg and 0.918, 1.309, 1.288, 1.132, and 0.842 mW/(mg °C), respectively. The LF-VR asphaltene has the highest heat capacity and thus released more energy than the asphaltenes derived from cracked products. This is mainly due to the considerable energy required to break the C–C covalent bonds homolytically (free-radical mechanism) present in the asphaltene molecules derived from the LF vacuum residue. On the other hand, although the asphaltenes from cracked products are more refractory in nature, their oxidation reactions require lower energy but at higher levels.

Another important feature of the LF asphaltenes is that their oxidation reactions take place in multiple steps, which points to the complex reaction kinetics that starts with the dissociation of the free radicals followed by cracking of the aromatic core of the asphaltene molecules. Comparing the peak areas developed by different LF asphaltene samples (Figure 5a), the multiple peaks start diminishing out as the asphaltene samples become heavier. For the LF-VR, for instance, the initial peak is comparable to the second peak, while for the LF-P430 sample, the second peak resulting from the oxidation of the aromatic core dominates.

Heat flow plots for the asphaltene samples derived from cracked RB residues are shown in Figure 5b. The plots show that the oxidation reactions occur in a single step and narrower range (430–500 °C) compared to those of the LF asphaltenes. They provide further indication of the refractory nature of the RB asphaltenes and that the oxidation reaction involves cracking the heavy molecules. Another observation from Figure 5b is that the centroids of the peaks occur at the same oxidation temperature. The magnitude of peaks in Figure 5b is mainly related to the sample weights. However, the estimated enthalpies and heat capacities of RB-P400, RB-P415, and RB-P430 are 222.32, 217.0, and 101.44 mW/mg and 1.179, 1.284, and 0.557 mW/mg °C, respectively. Figure 6a compares the enthalpies of samples obtained from RB and LF. The figure clearly indicates that the significant change in enthalpy is mainly observed in the asphaltenes treated under the most severe operating condition (i.e., 430 °C).

Molecular structure differences of asphaltenes from different sources are further illustrated in Figure 6b. The plots compare the exothermic peaks resulting from the oxidation of the LF, EC, and RB asphaltenes extracted from cracked products at 415 °C. For the LF asphaltene, heat evolves at different temperatures, which explains the multiple-step reactions that start with the oxidation of various types of functional groups and end with the dissociation of the core. This behavior is less evident for the EC and the RB asphaltenes. The complexity of the oxidation reactions of the three samples (LF > RB > EC) is reflected in the estimated enthalpies and heat capacities. The enthalpies and heat capacities of LF-P415, EC-P415, and RB-P415 are 246.68, 77.29, and 217.0 mW/mg and 1.31, 0.36, and 1.28 mW/mg °C, respectively.

3.3. Kinetics of Asphaltene Oxidation. Studying the kinetics of the pyrolysis that occurred during the TGA is useful to understand the structural changes of the asphaltene molecules and to get more insight into the role of temperature in the degradation of asphaltenes. The kinetics of asphaltene oxidation reactions can be calculated according to the ASTM 698-79 method.\(^{37}\) At a constant heating rate during asphaltene pyrolysis (10 °C/min), the overall rate of the solid-state thermo-oxidation reaction is usually described as\(^{38}\)
\[
\frac{da}{dt} = A e^{-\frac{E_a}{RT}} f(\alpha)
\] 

(7)

where \(\alpha\) is the extent of reaction or the fraction of oxidized (converted or pyrolyzed) asphaltene as a function of temperature, \(A\) is the preexponential factor, \(E_a\) is the activation energy, \(T\) is the temperature, and \(f(\alpha)\) is the reaction mechanism function. The asphaltene conversion, \(\alpha\), can be estimated as

\[
\alpha = \frac{M_0 - M_f}{M_0 - M_i}
\] 

(8)

where \(M_0\) and \(M_f\) are the initial and final weights (mg) of the sample, respectively, while \(M_i\) is the weight of the samples at time \(t\).

The oxidation conversion of asphaltene samples derived from the three cracked residues under various conditions is plotted in Figure 7. They indicate that the bulk molecular losses (oxidations) start at about 350 °C and reached the maximum rate at around 500 °C. The conversion profiles confirm the differences between the residues (AR and VR) and their cracked fractions. They illustrate also the conversion differences between the asphaltenes derived from the three sources. Asphaltenes from cracked RB residues showed similar conversion curves (Figure 7a), which indicate that RB samples are the heaviest with a smaller number of side chains followed by the EC samples, then the LF samples.

For an \(n\)th-order reaction mechanism

\[
f(\alpha) = (1 - \alpha)^n
\]

(9)

Integrating eq 7 yields

\[
\int_0^\alpha \frac{da}{(1 - \alpha)^n} = A \int_T^{T_0} e^{-\frac{E_a}{RT}} dT
\]

(10)

where \(\beta = \frac{dT}{dt}\) is the rate of change of temperature, which is constant for the asphaltene pyrolysis experiments. For a first-order kinetics \((n = 1)\), the integration in eq 10 becomes

\[
-ln(1 - \alpha) = \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) e^{-\frac{E_a}{RT}}
\]

(11)

If \(\frac{2RT}{E_a} \ll 1.0\), eq 11 becomes

\[
-ln(1 - \alpha) = \frac{AR}{\beta E_a} - \frac{E_a}{RT}
\]

(12)

Equation 12 is a linear function that can be fitted to the experimental pyrolysis data for estimating the activation energy and the preexponential factor using the slope, \(\frac{-E_a}{RT}\) and \(\frac{AR}{\beta E_a}\), respectively. The slopes that represent the activation energies estimated for different samples at various conditions are shown in Figure 8. Due to the significant variations in the molecular changes, or the stability of the asphaltene molecules, the activation energies were calculated for three distinct temperature regions: 310–388, 400–455, and 460–505 °C. The aim was to achieve a coefficient of determination \(r^2 > 0.98\). The activation energies in each region are compared on that the steeper the slope, the more sensitive the reaction to changes in temperature.

It is evident from Figure 8 that the residues (AR and VR) have lower-temperature oxidation regions, where major mass losses occurred before 350 °C, while the LF residues show a more gradual decrease in mass at higher temperatures.
losses are due to the bond cracking. The results show also that there are no changes in asphaltene structure in the low-temperature range, except for the RB-430 °C-treated asphaltene, indicating that asphaltenes derived from RB have functional groups that are easier to decompose even at temperatures less than 350 °C (this is in contradiction to the conclusions derived before, e.g., Figure 8, that RB has fewer functional groups).

The mid-temperature region (400–455 °C) in Figure 8 shows that asphaltenes derived from AR and VR have considerably high activation energies compared to other samples, indicating easier structural changes due to the cleavage of weak chemical bonds, such as C-heteroatoms and C–C bond (alkyl side chains).39

Figure 9 illustrates that the estimated molecular activation energies for the thermal treatment of asphaltene samples increase with increasing severity. The wide variations in activation energies are attributed to the complex decomposition mechanism of the asphaltene molecule. Although the variations of activation energies for asphaltenes from the three origins (RB, EC, and LF) follow similar trends, the results in Figure 9 indicate that the LF and EC activation energies are comparable, while those of RB are slightly lower, especially the asphaltene-extracted RB residue cracked at 400 and 415 °C. Moreover, it is apparent from the oxidation kinetics results that carbon—carbon bond fission occurring during thermal degradation of the asphaltenes requires higher energy to oxidize π bonding to aromatic rings. Hence, asphaltene molecule pyrolysis is proportional to the temperature increase needed to overcome the energy barrier.

4. CONCLUSIONS

TGA was performed in asphaltene samples extracted from the residual oils and their thermally treated byproduct pitch to identify thermal, kinetic (average activation energies), and heat flow behaviors. The TGA results show that the thermal degradation of asphaltene occurs in a process that starts around 350 °C and ends around 500 °C, with an ash content of less than 2%. The difference in weight losses with respect to temperature was more notable in LF samples, compared to RB and EC samples, which indicates that asphaltenes from different origins have different structures and compositions. The derivatives of the DTG analysis, on the other hand, indicate that the weight loss of composite material occurred in two stages. The first one corresponds to the degradation of the weak aliphatic side chains, while the second step corresponds to the degradation of the core fractions and the aromatic sheets. The DTG derivative curves illustrate the threshold trend shifted toward higher temperatures as the severity of thermal cracking increases. This observation is mainly attributed to the considerably lesser aliphatic side-chain contents in the asphaltenes subjected to thermal treatment. The chemical and thermal degradation of asphaltene were further investigated by running the TGA experiments with a He and H2 medium. For the He case, the inert medium isolates the effect of reactive gases and breaks down the bonds with no addition of atoms to asphaltene molecules. On the other hand, the H2 gas saturates the carbon atoms, which makes the asphaltene molecules undergo two reactions: weight gain takes place in saturation reaction and weight reduction in cracking reaction. To further understand the thermal behavior of different asphaltenes, their heat capacity and enthalpy (amount of heat released) were calculated from the TGA data. The heat flow plots for the oxidation of asphaltene samples suggest that the induction period starts around 375–400 °C followed by distinct heat flow peaks and completes around 500–530 °C. The generation of heat flow at higher temperatures suggests that asphaltene is more refractory and requires higher energy to decompose. The estimated enthalpies obviously designate changes in heat flow for the asphaltene samples treated at the most severe cracking condition due to the molecular changes.

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