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Thermogravimetric determination of coke from asphaltenes, resins and sediments and coking kinetics of heavy crude asphaltenes

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ABSTRACT

Thermal analysis of asphaltenes and resins from heavy crude was carried out to understand the way in which they decompose to form coke. Sediments extracted from hydrotreated crude were also analyzed. It was found that asphaltenes produced 47 wt.% of coke, resins 9 wt.% of coke, and sediments decompose quickly toward coke giving the highest yield (66 wt.%). In the case of asphaltenes and resins a free radicals based mechanism is operating when labile points in alkyl chains are broken leading to condensation reactions. Thermal analysis of sediments obtained from hydrotreated crude revealed that they have high tendency to form coke. A non-isothermal technique using various heating rates was applied to study kinetics of asphaltene cracking toward coke formation. An iso-conversional method based on Friedman's procedure was used to calculate the reaction kinetic parameters from thermogravimetric analysis during asphaltene cracking and a set of activation energies and pre-exponential factor was obtained as the reaction progresses. Activation energy ranged from 29.2 to 52.4 kcal/mol.

1. Introduction

Petroleum is a complex fluid containing many components ranging from low to high molecular weight. Most of them are kept soluble in the fluid under reservoir conditions but may precipitate as solid materials such as asphaltenes or sediments at some stage in storage, transportation, and refining of crude oil. During catalytic hydroprocessing, the formation and deposition of these solids on catalyst reduce its activity and eventually block the pores. In the case of heavy or extra heavy crude oils significant amount of these high molecular weight components is available that leads to high viscosity of petroleum. It is well recognized that these heavy components are the main cause for all the problems during petroleum handling. Thus, understanding the influence of heavy components on oil properties as well as on solid formation and deposition is of high concern.

Thermal decomposition of petroleum asphaltenes has gained attention primarily because of the asphaltene tendency to form coke, which is responsible for catalyst deactivation (Fig. 1). Usually, coke is formed from carbenes, which are insoluble in benzene or toluene but soluble in carbon disulfide; and carboids, which are insoluble in any organic solvent. Carboids are condensed, cross-linked polymers in which the greatest part of the carbon atoms is aromatic. Experimental tests performed at 450 °C have indicated that dibenzyl produces 1% of carboids after 40 min while α-methylnapthalene requires 400 min. The conversion of condensed aromatics without side chains to advanced condensation products is even slower, *e.g.*, naphthalene requires 670 000 min. These findings may be explained by the fact that hydrocarbons possessing alkyl chains or bridges form free radicals much more easily than those species lacking alkyl chains [1]. Pyrolysis of asphaltenes is considered as depolymerization in parallel with thermal decomposition of functional groups. When asphaltenes are heated prior to gasification, their volatile compounds are released leaving a residue [2]. Primary pyrolysis products include light hetero-atomic and hydrocarbon gases, alkanes, cycloalkanes and single-ring aromatics [3]. Apart from this, deactivation also depends on the nature as well as textural properties of the hydroprocessing catalysts [4,5].

In recent years, the application of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to study the pyrolysis behavior of fossil fuels has gained wide acceptance among researchers. For example, Abu-Khamsin et al. [6] investigated the spontaneous ignition potential of a light crude oil in an adiabatic packed bed reactor. Al-Saffar et al. [7] studied the behavior of a light crude oil and its SARA (Saturates, Aromatics,

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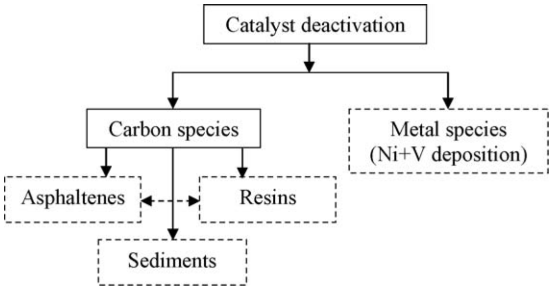

Fig. 1. Catalytic deactivation and its responsible species.

Resins, Asphaltenes) fractions. Karacan and Kök [8] also performed the thermal decomposition of Bati Raman and Garzan crudes and their fractions by TGA. All they concluded that pyrolysis mechanism depends on the chemical nature of the constituents and each fraction in the whole crude oil follows a reaction pathway independent of the other fractions. Kök et al. [9] have carried out tests in which SARA fractions from Turkish crude oils were separated and analyzed by TGA under air atmosphere to quantitative determine the intervals of evaporation, oxidation, and combustion in each fraction. Asphaltenes are the most difficult fraction toward oxidation due to their very high energy required whereas saturates are easily oxidized because of their low energy required. However, among the SARA fractions, asphaltenes contribute the most to coke formation. Douda et al. [10] observed that asphaltenes from Maya crude analyzed by TGA showed a considerable decomposition in the range of 300–680 °C with the maximum at 478 °C.

Various reports have dealt with obtaining kinetic parameters from either crude oil/residue or asphaltenes, *e.g.*, kinetic parameters during thermal cracking of petroleum residues were reported to be adjusted by first order reaction and coke formation to be a consequence of reactions involving asphaltenes [11]. Gonçalves et al. [12] also fitted experimental data to first order reaction while coke formation was very fast at temperatures higher than 440 °C. Kök and Karacan [13] observed that as crude oils become heavier the cracking activation energy increases and depends on asphaltenes content. However, correlation between coke yield and the amount of asphaltenes in crude oils was not good.

TGA experiments are carried out isothermally at various temperatures; however, with complex samples such as asphaltenes some problems are associated with the interpretation of chemical changes occurring during the heating period. These difficulties can be overcome by using non-isothermal techniques [12]. Friedman's procedure [14] is considered as an iso-conversional method that can be applied to complex chemical reactions with different mechanisms at several stages of reaction studied in non-isothermal way to obtain activation energies and pre-exponential factors as a function of asphaltene conversion. Based on iso-conversional methods, a series of activation energies for asphaltenes were obtained by Schucker [15] depending on volatilized fraction. Activation energies were higher at higher conversions. In contrast, Shih and Sohn [16] found that the activation energy was almost constant at different conversion of asphaltenes.

It is then observed that after separation of the heavier fraction of crude oil thermal characterization needs to be carried out in order to explore its behavior without catalysts. Thus, the aim of this research is to discuss the thermal decomposition of virgin asphaltene and resin fractions obtained from heavy crude oil and of sediment from hydrotreated heavy crude as well as its influence on coke formation. Activation energies and pre-exponential factors of asphaltenes cracking reaction were also obtained by using the Friedman's procedure.

Table 1
Physical and chemical properties of the heavy crude.

Property	Value
Density 20/4 °C	0.9815
API gravity	12.23
Total S, wt.%	5.25
Total N, wppm	4978
Asphaltenes, wt.%	21.8
Ramsbottom carbon, wt.%	15.85
Metals, wppm	
Ni	87
V	448
Elemental composition, wt.%	
C	82.58
H	11.40
O	0.22
Distilled volume at 538 °C, vol%	51.3

2. Experimental

2.1. Precipitation of asphaltenes and resins

Mexican heavy crude was used to separate asphaltenes by precipitation with solvent. The main properties of this crude are shown in Table 1. A pressurized system with heating and stirring was employed to precipitate asphaltenes with *n*-heptane as solvent. Precipitation conditions were defined previously to have similar asphaltene content and quality as those of asphaltene obtained with standard method as reported elsewhere [17], *i.e.*, crude-to-solvent ratio of 1:5 (w/v), nitrogen pressure of 25 kg/cm^2, temperature of 60 °C, stirring rate of 750 rpm, and contact time of 0.5 h. After precipitation, the mixture was settled, vacuum-filtered on a funnel and finally dried. Precipitated asphaltenes were washed with 100 mL of *n*-heptane. In order to obtain resins free of asphaltenes as possible, asphaltenes were washed in Soxhlet equipment overnight under *n*-heptane reflux. A colored liquid mixture was obtained from Soxhlet washing which is composed by *n*-heptane plus adsorbed resins. Resins are considered as natural stabilizing agents for asphaltenes as reported by Koots and Speight [18] and are adsorbed on asphaltenes surface precipitating along with them [19]. For this reason, resins were recovered by distillation of the liquid mixture and further analyzed by TGA. Fig. 2 shows the experimental methodology applied in this study.

2.2. Sediment samples

Sediments were obtained from hydrotreated crude based on the ASTM D-4870 method. Hydrotreating of heavy crude oil was carried out at the following conditions: 70 kg/cm^2 of hydrogen pressure, hydrogen-to-oil ratio of 5000 ft^3/bbl, LHSV of 0.5 h^{-1} and temperature of 410 °C.

2.3. Thermogravimetric analysis

10 mg of sample was used for TGA experiments in a Perkin-Elmer analyzer model TGA-7HT. Nitrogen (99.999%) was used as carrier with a flow rate of 50 mL/min by following the ASTM E-1131 method. In the case of asphaltenes, four different heating rates were used for obtaining kinetic parameters; *i.e.*, 4, 8, 12, 16 °C/min. Resins and sediments were analyzed only at heating rate of 4 °C/min. Gas carrier and its flow rate were the same as in the case of asphaltenes. For all cases, the temperature interval ranged from room temperature up to 900 °C. For comparison purposes, thermograms from asphaltenes, resins and sediments were recorded at heating rate of 4 °C/min. In addition, asphaltenes

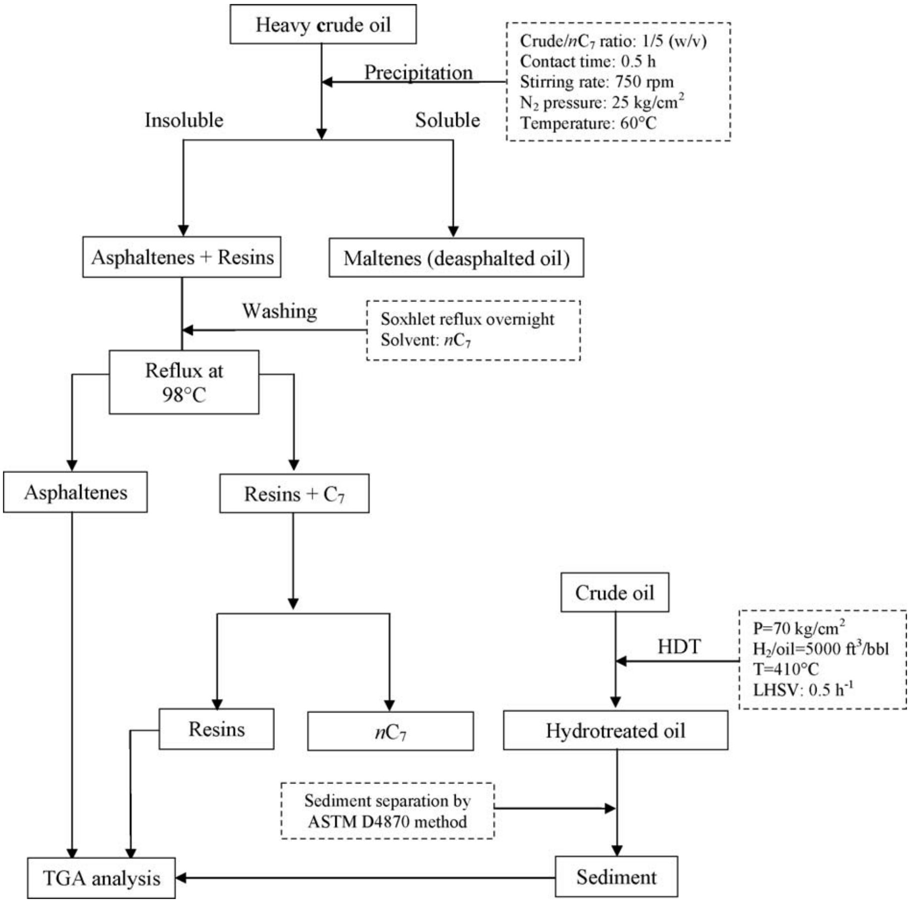

Fig. 2. Experimental methodology for obtaining asphaltenes, resins and sediments.

decomposition was analyzed under different gas atmospheres for comparing the coke yield behavior, *i.e.*, hydrogen, nitrogen and air at heating rate of 4 °C/min and 50 mL/min of gas flow.

3. Kinetic analysis of asphaltene cracking by Friedman's procedure

A non-isothermal technique using various heating rates has been applied to the determination of kinetics of asphaltene cracking. TGA data were analyzed by using the Friedman's procedure [14] and kinetics was fitted to first reaction order. According to Schucker [15], thermal decomposition of heavy components can be written as follows:

$$A \xrightarrow{k} aC + (1-a)V \tag{1}$$

where A is the reactant, C is coke, V the volatile fraction, and a is a stoichiometric coefficient. Taking into account this reaction, it is possible to derive the following kinetic expression for volatile products [16]:

$$\frac{1}{Vo}\frac{dV}{dt} = k_o e^{-E_A/RT}\left[1-\frac{V}{Vo}\right] \tag{2}$$

where Vo is the total amount of volatilized material. The linear transformation of Eq. (2) gives

$$\ln\left[\frac{1}{Vo}\frac{dV}{dt}\right] = \ln(k_o) - \frac{E_A}{RT} + \ln\left[1-\frac{V}{Vo}\right] \tag{3}$$

If the stoichiometry of the reaction is assumed to remain constant during the process, for simplification Eq. (3) can be rewritten as

$$x = \frac{V}{Vo} \tag{4}$$

$$\ln\left[\frac{dx}{dt}\right] = \ln[k_o(1-x)] - \frac{E_A}{RT} \tag{5}$$

x is considered as the volatilized fraction that corresponds to asphaltene conversion in thermal decomposition.

To use Eq. (5) with the results obtained in this work, different values of conversion (x) were selected, ranging from 0.1 to 0.9 at equal intervals. The values of dx/dt and T were determined for each conversion value at each heating rate by using the first derivative from TGA tests. It is to be remembered that four heating rates (4, 8, 12 and 16 °C/min) were used to obtain kinetic parameters for asphaltenes. Thus, by applying linear regression to Eq. (5), a series of activation energies (E_A) and pre-exponential factors (k_o) are obtained as function of volatilized asphaltenes (x). The left-hand side of this equation is the rate of weight change as it was directly obtained from the time derivative of the TGA.

4. Results

4.1. TGA of asphaltenes, resins and sediments

The two main polar components of crude, *i.e.*, resins and asphaltenes, and sediments obtained from hydrotreated crude oil were analyzed by TGA. Thermograms were recorded at 4 °C/min for comparison purposes. As initial experiment asphaltenes were

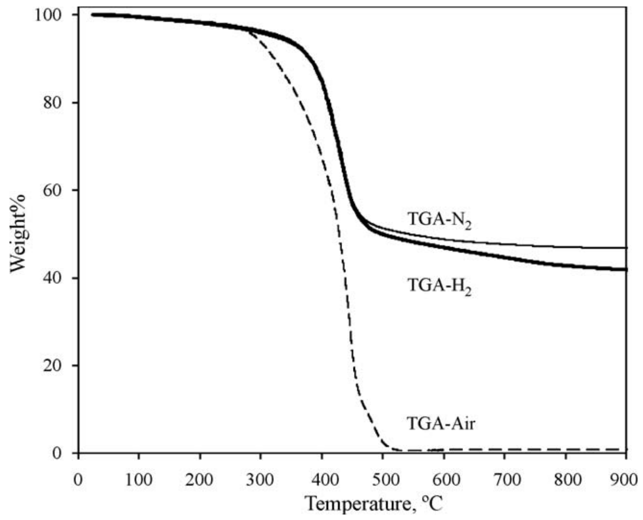

Fig. 3. Effect of thermal liquefaction of asphaltenes in different atmospheres.

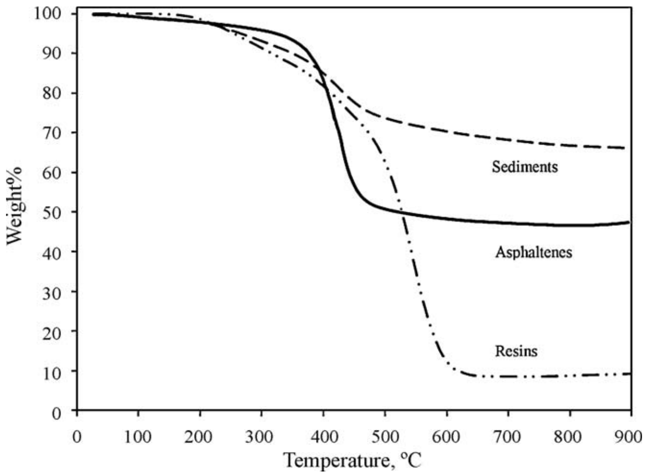

Fig. 5. TG curve of asphaltenes, resins and sediments under nitrogen atmosphere at heating rate of 4 °C/min.

heated in different atmosphere (air, hydrogen and nitrogen) but only in presence of air it is possible to burn off 100% of asphaltenes as shown in Fig. 3. The role of air is to start oxidation reaction; therefore, the decomposition rate is very fast at higher temperature (*ca.* 400 °C). The wide difference in the weight loss in different environment confirms the refractory nature of asphaltenes, which is relatively insensitive to the temperature. Similar results were reported by Savel'ev et al. [20] using inert and oxygen atmospheric thermal transformations of virgin Argentinean asphaltenes from Rafaelita and Toribia fields.

Fig. 4 shows the derivative weight curves for asphaltenes at 4 °C/min under nitrogen, hydrogen and air atmospheres. The purpose of analyzing asphaltenes decomposition under hydrogen was to illustrate the changes that asphaltenes could undergo during upgrading processes, *i.e.*, hydroprocessing, where high partial pressure of hydrogen is commonly used. It was observed that the behavior of asphaltenes toward coke formation is very similar when comparing nitrogen with hydrogen ambiances even the maximum weight loss for asphaltenes under nitrogen and hydrogen flows occurred at 430 and 431 °C, respectively. When air is employed as a TGA reaction medium, asphaltenes are completely burned off having a maximum weight loss at 443 °C. Asphaltenes did not show any change in their weight up until 230 °C. From 230 to 390 °C, smooth weight decrease is observed followed by fast reduction of weight in a relatively narrow range (390–470 °C). A small shoulder is seen at ∼472 °C which could mean decomposition of heavier asphaltenes with higher molecular weight or very highly associated asphaltenes. Total volatilization is achieved at 530 °C; asphaltenes at this temperature were fully burned off by the presence of oxygen in air.

Since the decomposition of resins is high (*ca.* 90% weight loss) and sediment formation is dependent on the balance between resin and asphaltene and reaction conditions [21], whose formation can be controlled by proper catalyst design and use of aromatic solvent [22–24], thus, the major concern remains about the asphaltenes and its thermal decomposition.

Asphaltenes were then examined by TGA in nitrogen ambiance (Fig. 5). The results do not show any appreciable change up to about 300 °C indicating that the structure remains almost intact. However, it is observed from Fig. 6 that a small change is detected at ∼370 °C resulting in a small weight loss due to the elimination of alkyl groups located in peripheral sites of asphaltenes. This behavior has been reported before [8,25]. According to our results, asphaltenes are responsible for around 47 wt.% of coke when suffering thermal decomposition. More significant changes in asphaltenes are observed at temperatures higher than 400 °C as shown in Fig. 6 and the maximum weight loss is seen at ∼430 °C. In this stage intermolecular associations and weaker chemical bonds are destroyed such as sulfur bridges. Asphaltenes are not only converted into coke but also expected to

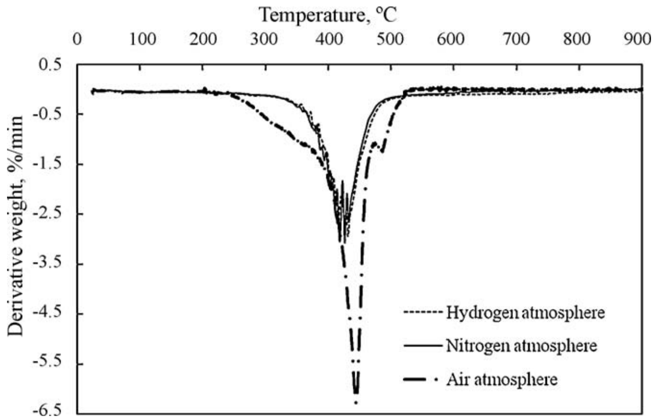

Fig. 4. Rate of weight loss for asphaltenes under hydrogen, nitrogen and air atmosphere at heating rate of 4 °C/min.

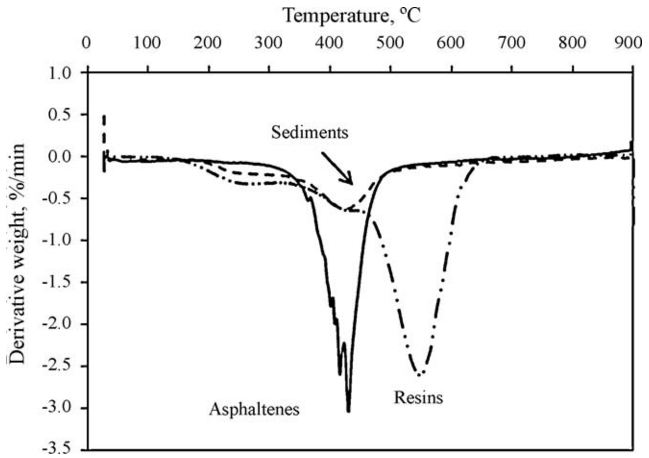

Fig. 6. Rate of weight loss for asphaltenes, resins and sediments under nitrogen atmosphere at heating rate of 4 °C/min.

be transformed into lighter compounds such as gases, oils and resins. Above 450 °C temperature asphaltenes are subjected to very severe conditions making condensation reactions to form coke as final residue.

Coke yield from resins is almost 10 wt.% during thermal decomposition as shown in Fig. 5, which exhibits a weight loss beginning at around 200 °C. In this temperature range (<200 °C) the weight loss was ~5 wt.% whereas 85 wt.% of resins is lost from 200 to 600 °C. Finally, coke (~10 wt.%) is obtained as final residue from 600 °C. Since resins are lighter than asphaltenes and are considered to keep the asphaltene solubility in the medium, it is also expected that they have more and longer alkyl chains compared with asphaltenes. These alkyl chains are labile points when resins are heated at high temperature giving more volatile compounds such as gases. After 200 °C resins suffer continuous decomposition up to around 600 °C. Fig. 6 shows significant weight loss to start at 400 °C with a maximum at ~540 °C. During thermal decomposition of resins, not only gases and oils are released but also condensation reactions occur by free radicals mechanism, especially at 400 °C and higher temperatures. If free radicals are formed in alkyl labile points they could be neutralized by adding to other free radicals and forming condensed and bigger structures such as asphaltenes. These new asphaltenes further generate coke at higher temperatures where free radicals reaction is predominant; however, as many of lighter compounds present in resins have been volatilized in the initial stages only a few amount of formed asphaltenes remains during the course of the reaction to finally decompose toward coke which appears in less amount compared with original asphaltenes. This could explain why resins continuously change in a wide range of temperature (200–600 °C) and why a broad range of reaction temperatures as such is not observed even for original asphaltenes. It has been reported by Phillips et al. [26] that asphaltenes can be produced from resins decomposition by thermal reactions and further condensation, which support the results discussed above.

Sediments are thought to be a structure having a high degree of condensation. Attached aromatic cores of sediments are a few alkyl chains that may be susceptible to breakdown by heating as observed in Fig. 5. Almost 5 wt.% of mass is lost from room temperature to 200 °C. From 200 to 500 °C the mass loss was ~25 wt.% and finally from 500 up to 900 °C sediments did not experience significant weight loss. Volatilization occurs at ~200 °C and the maximum weight loss is around 420 °C (Fig. 6). It is to be expected that sediments having highly condensed structures that are able to form coke. Results obtained by TGA confirmed this fact since 66 wt.% of coke is formed from sediments. What probably occurs during thermal decomposition of sediments is the complete removal of any alkyl chain to leave exclusively large aromatic and condensed cores. It has been observed by solid NMR that sediments obtained from hydroprocessed crude at 410 °C showed a small peak located between 10 and 40 ppm corresponding to alkyl carbons; however, sediments obtained from hydrotreated crude at 420 °C show that practically all alkyl carbons have disappeared remaining only aromatic carbons in the range of 100–160 ppm [27]. This could explain why the maximum weight loss is observed at ~420 °C in Fig. 6. As a summary of TGA experiments, Table 2 shows the coke yield from each fraction at heating rate of 4 °C/min and asphaltenes at different heating rates. The temperature, at which the weight loss is maximum, is also represented in this table. It is observed in the case of asphaltenes that temperature where maximum weight loss occurs increases as heating rate also increases. At the highest heating rates this T_{max} is the same indicating that reactions take place very fast and gases are readily released. The average coke yield at different temperatures is 47 wt.%.

Table 2
Coke yield from asphaltenes, resins, and sediments at heating rate of 4 °C/min.

Fraction	Coke yield, wt.%	T_{max} weight loss, °C
Asphaltenes	47.4	427
Resins	9.3	536
Sediments	66.3	418

Coke yield from asphaltenes at different heating rates

Heating rate, °C/min	Coke yield, wt.%	T_{max} weight loss, °C
4	47.4	427
8	46.3	445
12	46.7	450
16	47.4	450

4.2. Kinetic analysis of asphaltenes coking

Among thermal methods, DSC and TGA have great significance being applicable to obtain kinetics of thermal reactions. The advantage of these techniques is the ease of sample preparation, its simplicity and the avoidance of errors linked to the choice of a kinetic model. On the other hand, some drawbacks are found when using thermoanalytical methods, for example, the weight loss depends on the heating rate in the case of TGA by which the concentration of final products could show differences if distinct heating rates are applied [28]. One important assumption to be taken into account when TGA is carried out is that reverse reactions are supposed to be neglected. Another important assumption is that diffusion is not the controlling step. If diffusion has no influence in the reaction, activation energy is almost constant at each volatilization value; otherwise activation energy will tend to increase very rapidly particularly at high volatilization values [29]. For this reason, reverse reactions are neglected and it is assumed that diffusion does not control the reaction in order to perform kinetic analysis from TGA data. It has been demonstrated that although these assumptions calculation of activation energy based on TGA is in good agreement with that obtained by other methods such as distributed activation energy model (DAEM) [2].

In this work, a model-free kinetic approach based on the iso-conversional Friedman's procedure was used to analyze data obtained by TGA. Friedman's procedure gives simultaneously the activation energy and the pre-exponential factor (frequency factor) by assuming a value of the reaction order and calculating the activation energy without the knowledge of the rate dependence on conversion. Thermal behavior of asphaltenes is shown in Fig. 7 at different heating rates from room temperature to 900 °C under nitrogen atmosphere. From TGA results, three stages can be observed. In the first stage (25–300 °C) asphaltenes remain

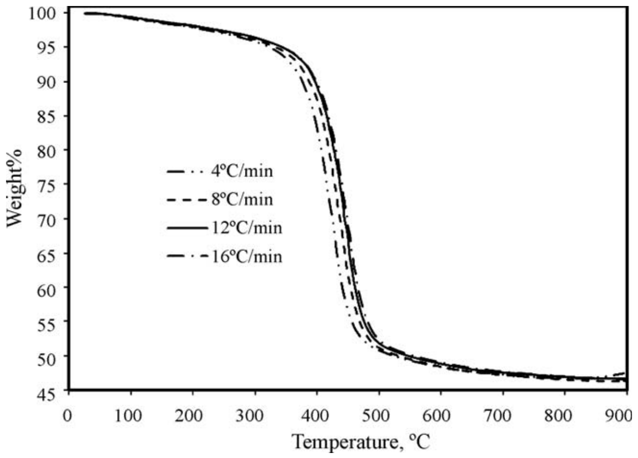

Fig. 7. Weight loss of asphaltenes at different heating rates.

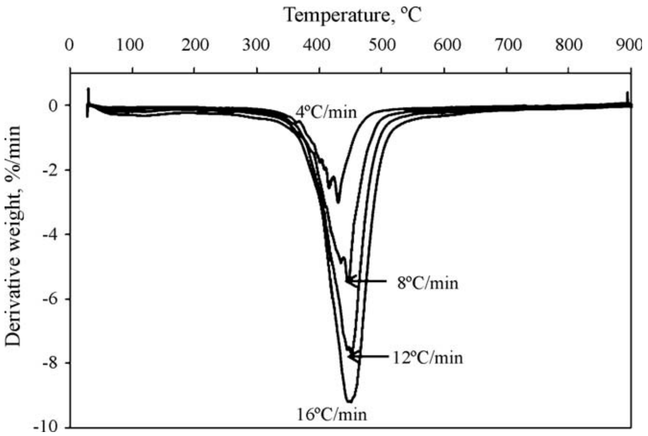

Fig. 8. Rate of weight loss of asphaltenes at different heating rates.

without significant changes and only ~5 wt.% of its mass is lost. In the second stage (300–500 °C) approximately 45 wt.% of the asphaltene mass is lost during reaction. Finally, in the third stage (500–900 °C) no more mass loss is observed and coke yield is 47 wt.%. All curves showed the same trend, but for the second stage the temperature at which the weight loss is maximum was slightly higher at the highest heating rate (16 °C/min). Slow heating rates will produce more coke whereas products of fast heating rate are mostly liquids and gases. At the highest heating rate reactions take place very fast and gases are readily released diminishing the weight of the sample more notoriously than at lower heating rates.

The rate of weight loss as function of temperature is depicted in Fig. 8. At the lowest heating rate (4 °C/min) some small peaks are observed. In this case, asphaltene sample is heated gradually and components are removed according to their nature, *i.e.*, short alkyl chains or sulfur-bonds are destroyed easily. After that, other components are also eliminated and different peaks appear. When increasing the heating rate, small peaks are reduced in number indicating that sudden decomposition due to higher temperatures is taking place. At the highest heating rate, only a big peak is observed because of the fast rupture of alkyl chains which releases gases as products of decomposition. Formation of free radicals is also quick and coke appears in a few minutes after reaction has begun. It is seen from Fig. 8 that weight loss of asphaltenes is the highest at ~450 °C at higher heating rates.

Fig. 9 presents the volatilization of asphaltenes against temperature where a typical thermogram for each heating rate is obtained. The *Y*-axis expresses the fraction of the original sample weight which has been volatilized as a function of temperature. Each curve approaches an asymptotic value at higher temperatures and volatile fractions (*x*). Coke is considered as the remaining material when heating has finished (900 °C). In all cases, asphaltenes were responsible for 47 wt.% coke during thermal decomposition.

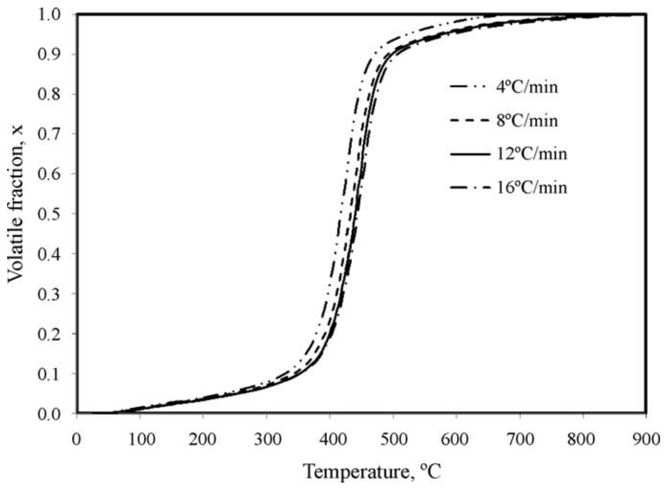

Fig. 9. Volatile fraction evolution of asphaltenes from heavy crude at different heating rates.

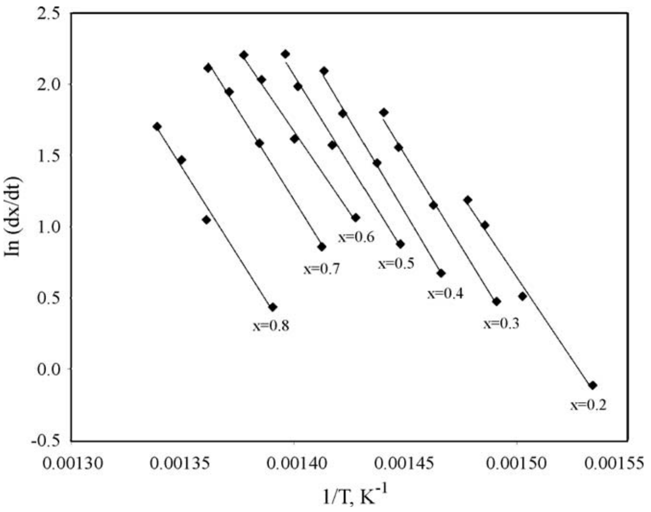

Fig. 10. Arrhenius plot at different volatilized fractions (*x*).

It is known that asphaltenes contain complex molecules made of polycyclic aromatic rings linked to naphthalene rings and alkyl chains along with hetero-elements. The molecular forces acting on asphaltenes are intermolecular associations and weaker chemical bonds which are destroyed or weakened at moderate temperature. Alkyl chains may be broken and some gases are released at this step. However, at higher temperature (>450 °C), the stronger chemical bonds are broken and molecular skeletons are destroyed releasing a big amount of gases due to decomposition of asphaltenes.

Fig. 10 shows the Arrhenius plot of $\ln(dx/dt)$ versus $1/T$. Only some values of conversion (0.2–0.8) are shown. On the basis of this plot, conversion-dependent activation energy values were obtained with good correlation coefficients as shown in Table 3. The values of 90% conversion are uncertain, likely due to the difficulty associated with obtaining accurate values of dx/dt near the completion of the reaction. As can be seen from Fig. 9, asymptotic curves are obtained as volatilized fraction is higher than 0.9. Differences in E_A values likely reflect changes in the strength of bonds. An increase in activation energy is observed as conversion increases (from 0.1 to 0.4) which could indicate that more complex molecules are broken which require more energy to react. It can be observed that activation energy is almost the same at conversions in the range of 0.5–0.8 with exception at 0.6; however, in this range E_A values were smaller than those in the range of 0.1–0.4. Constant values of E_A may indicate that the same

Table 3
Activation energy and pre-exponential factors as function of asphaltene conversion.

Conversion, *x*	E_A, kcal/mol	k_o, min^{-1}	r^2
0.1	39.9	5.58×10^{13}	0.996
0.2	46.1	2.58×10^{15}	0.996
0.3	50.9	6.07×10^{16}	0.998
0.4	52.4	1.25×10^{17}	0.999
0.5	49.9	1.52×10^{16}	0.996
0.6	45.5	4.58×10^{14}	0.997
0.7	49.6	4.94×10^{15}	0.998
0.8	49.0	1.20×10^{15}	0.993
0.9	29.2	1.67×10^{8}	0.974

rate-controlling step is occurring at these stages. Earlier studies by Collett and Rand [30] suggested that an increase in the heating rate caused the major reactions to occur at higher temperatures and therefore the increase in the activation energy reflected a change in the nature of the rate-controlling step.

From the results presented here, it is demonstrated that thermogravimetric analysis is very useful when studying kinetics of pyrolysis of asphaltenes. However, more information about reaction mechanism and products could be obtained if TGA is coupled to other techniques such as gas chromatography/mass spectrometry to obtain more insights about the composition of heavy structures.

5. Conclusions

Thermal analysis of the two main polar components present in heavy crude (∼12° API) was carried out. It was found that asphaltenes formed 47 wt.% of coke during cracking reaction, while resins are responsible only of 9 wt.% of coke formation. The temperature range in which resins react is wider compared with that of asphaltenes. Asphaltenes formed in this way contribute to the generation of free radicals and in consequence condensation reactions take place at higher temperatures. Sediments separated from hydrotreated crude showed that their highly condensed structure can yield up to 66 wt.% of coke. Alkyl chains are lacking in sediments and aromatic cores are the most abundant species in their structure.

Thermogravimetric analysis (TGA) was combined with Friedman's procedure to provide further insights about the kinetics of asphaltene decomposition from heavy crude. Kinetics of asphaltene cracking was well fitted to first order. The values of activation energies and pre-exponential factors reflect changes in the strength of bonds as volatilization of asphaltenes occurred. This could mean that kinetics of coking is not always well represented by simple kinetic mechanisms.

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