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CONTRIBUTION OF THERMAL ANALYSIS FOR CHARACTERIZATION OF ASPHALTENES FROM BRAZILIAN CRUDE OIL

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Abstract

The thermal decomposition of asphaltenes is mainly responsible for the formation of coke in petroleum processing. Phenomena involved are not clearly understood, because of the difficulties to characterize such heavy components. This paper reports the application of thermal analysis techniques to study the thermal behavior of asphaltenes from Brazilian oil. The approach involves kinetic studies of the thermal decomposition of asphaltenes under controlled conditions by thermogravimetry (TG), characterization of volatile fractions by thermogravimetry and differential thermal analysis coupled with gas chromatography/mass spectrometry (TG-DTA/GC/MS) and by gas chromatography/mass spectrometry (GC/MS) in the volatile recovered. The coke formed was also studied after being decomposed into smaller molecules using selective oxidation.

Keywords: asphaltenes, pyrolysis, thermogravimetry and coupled techniques

Introduction

Petroleum asphaltenes, chemically defined as the heptane-insoluble, toluene-soluble fraction of heavy oils [1], are a complex mixture of polycyclic aromatic molecules with long alkyl side chains. They contain an appreciable amount of sulfur, nitrogen and oxygen in their structure.

Asphaltenes are a class of material of considerable importance in refining processes, since their presence may cause some problems in thermal and catalytic transformation of petroleum residues [2].

The thermal decomposition of petroleum asphaltenes has received some attention primarily because of the tendency of asphaltenes to form high yields of coke under thermal conditions and to be responsible for catalyst deactivation. So, one of the keys of residue processing lies in understanding the chemistry of coke formation at different temperatures. However, most of the studies have been focused on the elucidation of the chemical structure of asphaltenes and on the nature of the volatile material produced, being missed a deep analytical attention to the solid pyrolysis products.

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Analysis of pyrolysis products from petroleum asphaltenes using different techniques, has been extensively reported. Pyrolysis coupled with gas chromatography/mass spectrometry is a usual technique for this purpose [3–6]. Thermogravimetry (TG) has been used only to study the thermal stability of asphaltenes without identification of the pyrolysis products [7–9].

Speight [10] studied the thermal decomposition of asphaltenes from 300 to 900°C, and observed the occurrence of low molecular mass species in the volatile products. The most complex aromatic systems remain as non-volatile residue (45%) normally called coke. It could not retrieve from the literature any contribution focusing characterization of the coke formed. That is probably due to the difficulty in employing analytical techniques to the pyrolysis residue.

The aim of this work is to present the contribution of thermal analysis to study asphaltenes from a Brazilian oil. The kinetic of decomposition was obtained by thermogravimetry which has been used for a numbers of years in polymer chemistry [11]. The technique was here employed to study of coke formation. Volatile products were analyzed by coupling thermogravimetric technique with gas chromatography and mass spectrometry. References on the employment of these coupled methods to analyze petroleum fractions were not found in the literature. In another experiment, volatile products were recovered from TG equipment to be analyzed by gas chromatography and mass spectrometry (GC/MS). The pyrolysis residues obtained by TG at different temperatures were submitted to ruthenium(VIII) ion catalyzed oxidation technique (RICO).

Experimental

Figure 1 shows the schematic research pathway to study the investigations on the thermal behavior of asphaltenes.

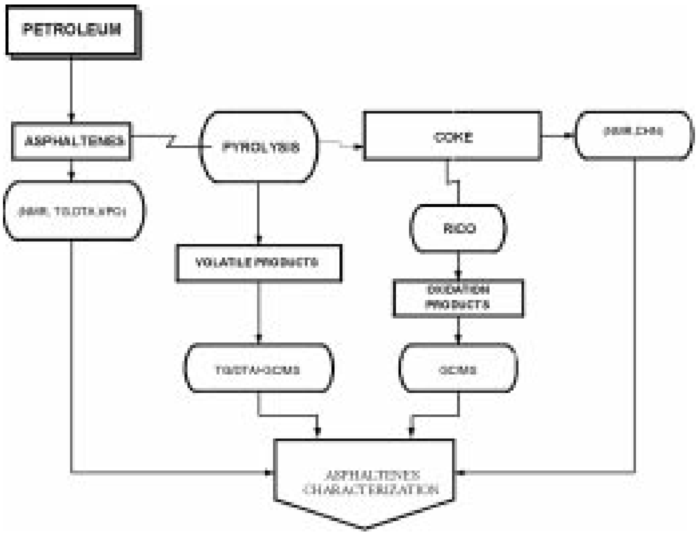

Fig. 1 Research pathway to characterize the thermal behavior of asphaltenes

Asphaltenes extraction

The asphaltenes employed in the study have been precipitated from a Brazilian oil (16.1 °API, 6.1% of asphaltenes, 0.77% of sulfur, 0.55% of nitrogen) by the conventional method [12], i.e., addition of 40 ml of *n*-heptane to 1 g of oil. After filtration, the precipitate was washed in a Soxhlet with *n*-heptane until no yellow color was visible in the washed fraction. The solvent was then changed to toluene for the extraction of asphaltenes. After their extraction, the solvent was evaporated in a rotary evaporator at 40°C operated under reduced pressure. The solid was dried at 40°C under vacuum.

Thermogravimetric experiments

The TG experiments were performed using the TA-2100 thermal analyzer system equipped with a TG-951 module from TA-Instruments. The sample (10 mg) was heated from room temperature to 1000°C at 10°C min^{-1} under nitrogen and air (100 ml min^{-1}) atmosphere. Non-isothermal kinetic experiments were carried out using approximately 10 mg of asphaltenes and heating rates of 2, 5, 10 and 20°C min^{-1}. The calculations were performed using a software of the TA-Instruments (TGA-Kin v.4) according to Flynn and Wall [11].

Volatile products

The analysis of volatile products from the pyrolysis of asphaltenes was carried out by coupled techniques on a Shimadzu system: DTG-50 H coupled with a CG14BC QP-5000 module. The sample (0.7 mg) was heated at 10°C min^{-1} under helium atmosphere (50 ml min^{-1}) from room temperature to 700°C in the TG-DTA (DTG-50H). The stream of gases generated on heating the sample were directly introduced to a chromatograph coupled to a mass spectrometer equipped with a heated interface (250°C) and a trap (Tenax-TA 60–80 mesh). The trap was at –70°C during the pyrolysis, and after it was heated at 300°C. The volatile materials were separated in a 1 m column coated with Tenax-TA 60–80 mesh to be analyzed by quadrupole mass spectrometer (CG14BC QP-5000).

Another experiment, was carried out by trapping the volatile products coming out TG-951 in CH_2Cl_2, and analyzing them by syringe injection in a CG/MS (HP-5988 A system).

Solid products

The pyrolysis residues were obtained in large quantities using a TG-951 from TA Instruments. About 300 mg of asphaltenes were rapidly heated under nitrogen (100 ml min^{-1}) from room temperature up to 320, 380, 400, 440, 480, 550 and 580°C respectively. Each of the final temperatures were maintained fixed for 10 min. After this, the oven was cooled at 50°C min^{-1} with air in the external part of the equipment.

Ruthenium-ions catalyzed oxidation (RICO)

The RICO reaction was performed using an adaptation from literature [13–14]. The procedure consists of stirring, 150 mg of asphaltenes or pyrolysis residues obtained at each temperature, at 40°C for 24 h with CCl_4 (20 ml), $NaIO_4$ (3.4 mg), H_2O (30 ml), acetonitrile (20 ml) and $RuCl_3 \cdot H_2O$ (7 mg). The resulting two layers are separated and the organic phase, after being concentrated, was mixed with excess of ethereal diazomethane. The ethereal solution was analyzed submitted by a gas chromatography/mass spectrometry (GC/MS) for methyl ester analysis. The analysis was performed on a HP-5988 A system. Samples were injected in splitless mode using a 5%-phenyl 95%-methyl siloxane capillary column (30 m×0.25 cm×0.25 μm) and helium as carrier gas. Mass spectrometer was operated in electron impact ionization mode (70 eV) and scanned from 15 to 450 *m*/*z*.

Results and discussions

The thermal behavior of Brazilian asphaltenes when heated at a constant rate from room temperature to 1000°C under nitrogen can be described in two steps based on the TG results (Fig. 2). In the first step (30–250°C) asphaltenes lose about 5% of mass probably due to the presence of residual solvent from extraction. In the second step (250–550°C) asphaltenes drastically decompose to produce 45% of coke. This behavior has been cited for others petroleum asphaltenes [15–16].

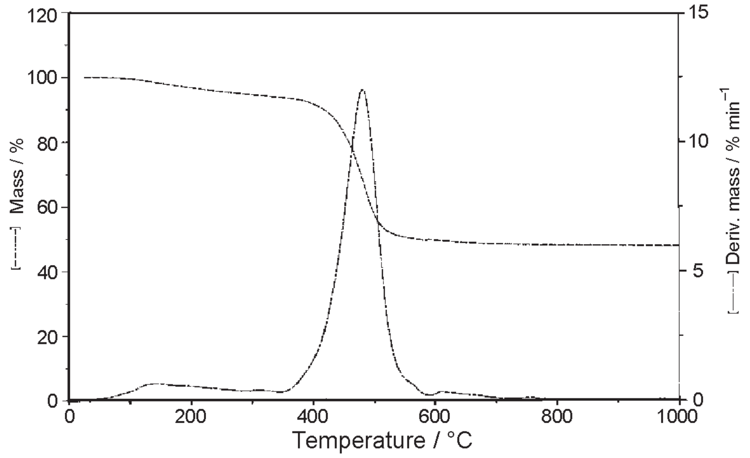

Fig. 2 TG curve of Brazilian asphaltenes under N_2 atmosphere (100 ml min^{-1}) at heating rate of 10°C min^{-1}

When air was introduced at 700°C it can be observed a drastic loss of mass due the oxidation of the coke formed during the previous stage (Fig. 3).

The technique chosen for kinetic measurements was thermogravimetry. As a rule, kinetic investigations are carried out isothermally at various temperatures, how-

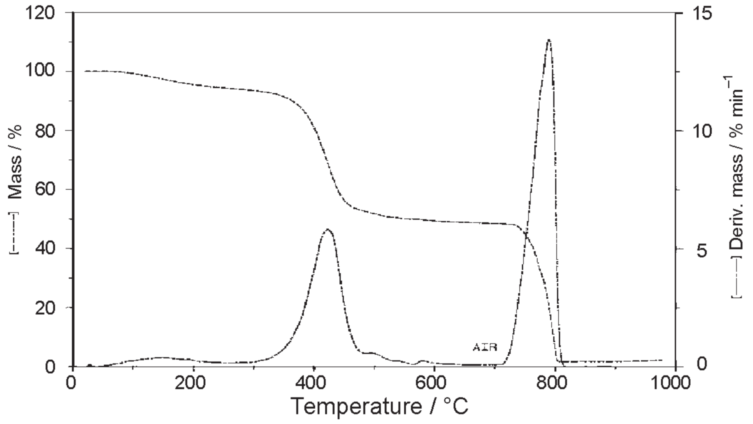

Fig. 3 TG curve of asphaltenes in N_2 and air atmosphere (100 ml min^{-1}) with a heating rate of 10°C min^{-1}

ever with complex samples, like asphaltenes, there are some problems associated with the interpretation of the chemical changes occurring during the heat up period. These difficulties can be overcome by using non-isothermal techniques [11].

This method is based on the evaluation of the TG curves at least four different heating rates. The pyrolysis region is called up to evaluation (Fig. 4).

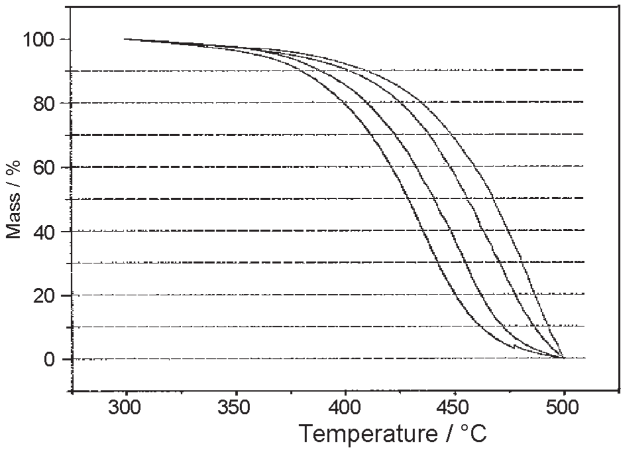

Fig. 4 TG curve of asphaltenes performed at heating rate: 2, 5, 10 and 20°C min^{-1}

The plot in log heating rate *vs*. temperature of constant conversion is presented in Fig. 5. A series of such lines created from the four curves shown in Fig. 4 by plotting data at different conversion levels. The lines have the same slope showing that the decomposition mechanism was independent of the conversion level. The angular coefficient of the straight lines is the activation energy (E_a) at different conversion levels (Table 1).

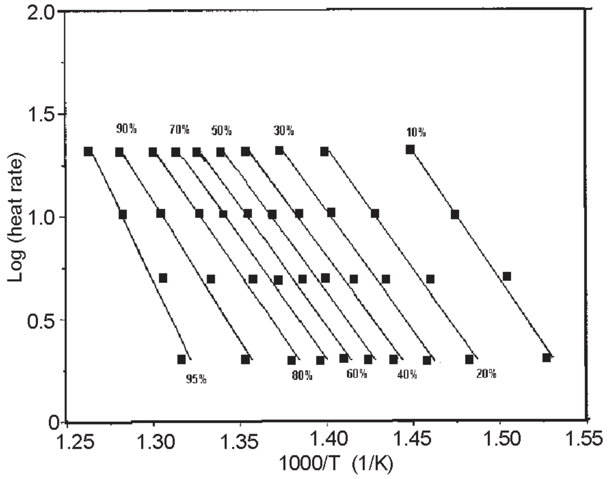

Fig. 5 Pyrolysis of asphaltenes: heating rate *vs*. 1000/K at different conversion levels

Table 1 Pyrolysis of asphaltenes: kinetic parameters at different conversion levels

Conversion/%	E_a/kJ mol^{-1}	Log(preexp. factor min^{-1})
10	217.6	15.57
20	198.0	13.83
30	192.8	13.36
40	190.2	13.12
50	193.3	13.28
60	201.7	13.44
70	207.5	13.88
80	231.0	14.26
90	298.3	15.82

Figure 6 presents the plot of percent conversion *vs*. time. It was observed that 150 min are sufficient to convert asphaltenes in 100% of coke when it was submitted at 400°C. At 440°C only 20 min are necessary and at temperatures higher than 480°C asphaltenes are quickly converted in coke.

Knowing more about the thermal decomposition conversion of asphaltenes, the pyrolysis residues of them were obtained in a larger quantity using TG equipment. TG was chosen to attain pyrolysis residues from asphaltenes because it permits a good control of the inert atmosphere and oven heating.

Asphaltenes and their pyrolysis residues obtained at different temperatures were characterized by elemental analysis and cross polarization/magic angle spinning (CP/MAS) ^{13}CNMR (Table 2). It was observed that at higher pyrolysis temperatures, lower the hydrogen and aliphatic carbon contents were obtained for the pyrolysis residues. These results do not lead to anything that was not expected previously.

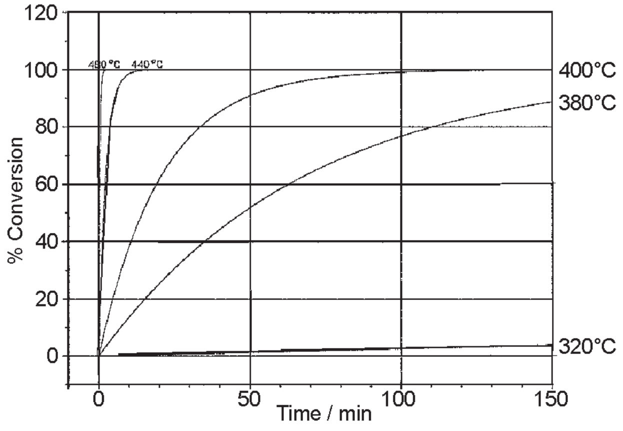

Fig. 6 Pyrolysis of asphaltenes: conversions *vs*. time

Table 2 Elemental analysis and ^{13}CNMR of asphaltenes and coke samples

Sample	C/m%	H/m%	N/m%	C/%			
				Total aromatic	Aliphatic	Arom. tri-subst.	Arom. tetra-subst.
Asphaltenes	85.8	8.4	1.8	55.5	44.5	27.7	27.8
320	85.9	7.8	2.3	60.9	39.1	36.4	24.5
380	86.2	7.6	2.5	66.8	33.2	31.6	35.2
400	86.3	7.2	2.5	67.8	32.2	40.6	27.2
440	85.7	6.2	2.7	75.5	24.5	42.1	33.4
480	87.4	4.7	3.2	82.3	17.7	44.1	38.2
550	86.0	3.1	3.3	97.8	2.2	33.1	64.7
580	86.4	2.7	3.3	99.0	1.0	31.3	67.7

So, to improve knowledge on these systems, asphaltenes and their pyrolysis residues obtained at each temperature were oxidized with ruthenium(VIII) ion. This reagent converts, selectively and efficiently, alkyl aromatics into alkanoic acids [13]. After the formation of acids they were mixed with excess of ethereal diazomethane and submitted to gas chromatography/mass spectrometry (GC/MS) in order to identify the correspondent methyl esters. It was observed three homologous series: methyl esters of linear carboxylic acids ranging from C_6 to C_{27}, small amounts of dimethyl esters were also present in a homologous series, ranging from C_4 to C_{17} and benzene dicarboxilic acids from C_{10} to C_{12} (Fig. 7).

To try a complete picture of the phenomena, characterization of volatile species generated in pyrolysis has been started, to be developed together with coke characterization.

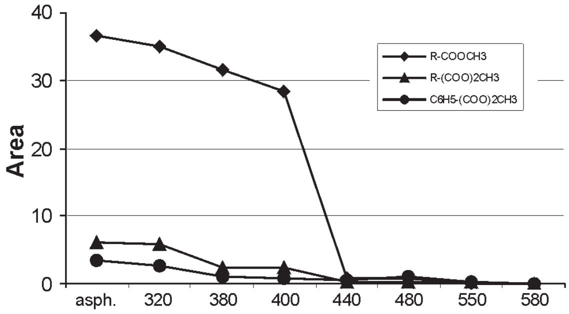

Fig. 7 Total esters from RICO reaction of asphaltenes and cokes at different temperatures

The first approach for identification of pyrolysis products of the asphaltenes from Brazilian crude oil was done by thermal methods of analysis coupled to GC/MS. Besides mass loss by TG, differential thermal analysis (DTA) informs about heat flow in comparison to a reference material. This approach aimed mainly the identification of very small products, which could be lost in more-than-one-step procedures. However, available equipment was not suitable for analysis with better resolution.

About the pyrolysis profile, it was observed in the TG curve (Fig. 2) of asphaltenes a small mass loss between 100 and 250°C. This volatile material was identified as toluene, the solvent used during asphaltenes extraction.

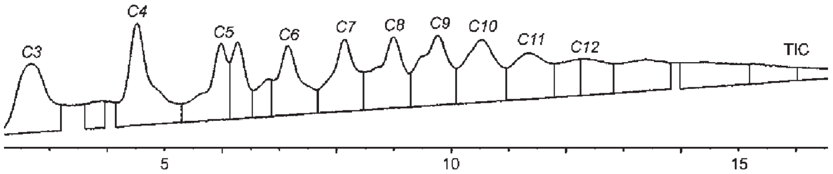

Fig. 8 Total ion chromatogram in a one-meter packed column from on-line analysis of gaseous products of asphaltene pyrolysis

Pyrolysis of asphaltenes corresponded to the remarkable mass loss that begins to occur more pronouncedly at 400°C. The GC/MS analysis (Fig. 8) of this volatile material identified a series of straight chain of normal alkyl ranging from C_3 to $C_{10.}$

This result indicated limitations of the apparatus employed *n*-alkyl chains longer than these were expected [3]. However, it worked well for lighter components. Another experiment, in which gaseous products from pyrolysis procedure were recovered by bubbling in CH_2Cl_2, accounted for the heavier components. The solution obtained this time can be analyzed by syringe injection in a gas chromatograph coupled to MS.

The majority of the sample is constituted of straight chain alkanes ranging from C_{13} to C_{33} with maximum in C_{17} and olefins from C_{14} to C_{24}. Naphthalenes, fluoranthenes and pyrenes were also identified in the solution analyzed but are present in

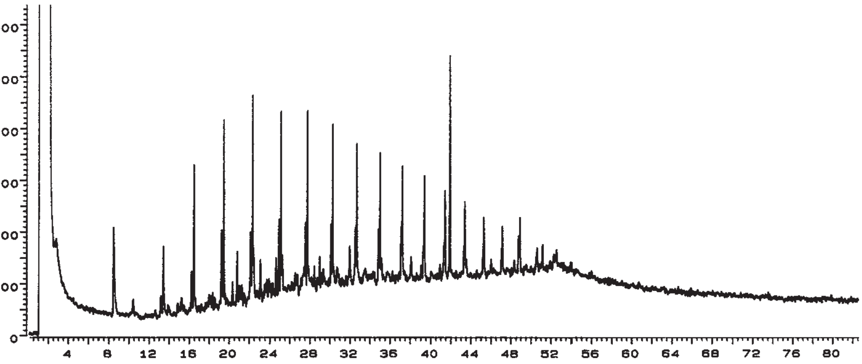

Fig. 9 Total ion chromatogram in a thirty-meter capillary column of volatile pyrolysis products recovered in CH_2Cl_2

lower content than the acyclic hydrocarbons. Figure 9 presents the total ion chromatogram showing a characteristic profile of the presence of a series of *n*-alkanes as it could be initially supposed.

It could be concluded that most of light material is lost in trapping procedure, and the heated interface employed for direct transfer from one apparatus, are not enough to prevent losses of the heavier species.

Conclusions

Thermogravimetry is a useful technique to study the coke formed during pyrolysis of asphaltenes. Kinetic studies observed that thermal decomposition of asphaltenes is a first order reaction and coke formation is quickly at temperatures higher than 440°C.

Coupled techniques are useful to get information about light materials and trapping procedure to get information about heavier species. Further studies will focus on combination of the results and on analytical solutions for these difficulties.

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