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THERMOGRAVIMETRIC ISOLATION AND CHROMATOGRAPHIC CHARACTERIZATION OF VOLATILE FRACTIONS OF PETROLEUM

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Petroleum samples were analyzed by TG between 25–600°C. Mass loss was observed up to 500°C. The volatile fraction of petroleum samples in the range of 25–150°C were recovered by bubbling the outgoing gaseous products of the TG experiments in dichloromethane. Each volatile fraction obtained was analyzed by HRGC-MS for identification and quantification of the major components. Following this procedure the classification of the petroleum samples were done according to the obtained mass losses between 25–150°C (which varied from 1.76 to 21.89%) and according to their normal paraffin, aromatic and naphthene contents.

Keywords: *gas chromatography, petroleum, thermogravimetry*

Introduction

Characterization of petroleum samples has to include the separation and identification of their individual compounds. From Day [1], in 1897, to Karam *et al.* [2], in 1984, several petroleum analysis methods have been developed.

Crude petroleum analysis involves techniques that allow the fractioning of sample using classical liquid chromatography involving several steps. Kök *et al.* [3] studied crude petroleum and its fractions using pyrolysis analysis. Fractionation was done utilizing precipitation techniques and liquid chromatography in an open column permitting observation as to which fraction is the most important in coke formation. The mechanism of pyrolysis depends on the chemical composition of the crude petroleum sample. Kök *et al.* [4] studied the oxidation behavior of petroleum fractions using TG/DTG and liquid chromatography, obtaining four fractions: saturated hydrocarbons, aromatics, resins and asphaltenes (SARA). Two samples, medium and heavy petroleum, were separated according to their solubility in each eluent, but not according to their bullying point, which is closer to the petroleum refining process based on distillation in fractionation columns. Ambalae *et al.* [5] used TG analysis for a kinetic study of activation energy and coke formation reaction order of two crude petroleum and one asphaltene sample obtained by solvent extraction, filtration and distillation techniques. It can be seen that TG analysis is an important technique for petroleum heavy fractions evaluation, but it is not commonly used technique for crude petroleum fractionation and to collect the fractions that are separated by heating decomposition in the equipment, as intended in this work.

Regarding reference norms, Brazilian Association of Technical Norms (ABNT) prescribes NBR 9619 norms for distillation characteristic determination of some petroleum products; MB 890 norm for the boiling range temperature determination at reduced pressure for petroleum products that degrade when distilled at atmospheric pressure; and NBR 14156 for total vapour pressure in vacuum determination exerted by petroleum liquid and volatile products that contain air using vapour pressure automatized instruments. For volatile fraction analysis up to 220°C ABNT proposed NBR 11344 norm for percentages and distillation range of naphthans in crude petroleum commercially known as petroleum refinery product determination [6].

Among petroleum analysis ASTM methods [7] such as atmospheric equivalent temperature (AET) determination established by the ASTM D2892 and ASTM D5236-03 norms are frequently used standard methods in the world. While ASTM D2892 method is used for stabilized crude petroleum distillation to a final cut temperature of 400°C, ASTM D5236-03 method is used for distillation of different samples such as crude oils, petroleum distillates, residues and

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synthetic mixtures that contain heavy hydrocarbons with initial boiling points higher than 150°C.

ASTM also proposed D86-04b standard method which covers petroleum product distillation, however is not applied for samples that contain appreciable amount of residual material and D1160-03 method that deals with petroleum and derivatives distillation at reduced pressure. There are no ASTM methods to exclusively evaluate petroleum volatile fraction composition up to 150°C. Moreover, all above mentioned ASTM methods are expensive and time-consuming [8] as well as the ABNT methods, too.

There are many advances of complex mixture analysis, as petroleum and other samples. Thermal analysis techniques permit e.g. sample fractionation, such as chromatography [9]. Gonçalves *et al.* [10] used combined TG/DTA-GC/MS for characterization of asphaltenes obtained from Brazilian crude petroleum by pirolysis products analysis. It was concluded, combined TG/DTA-GC/MS requires adjustments and adaptations, which are not well developed. This makes the full analysis process functioning as an 'on-line' system and is impractical. However, the same authors state that gases generated in TG analyzer could be collected as an 'off-line' system. In another work Gonçalves *et al.* applied thermogravimetry to evaluate the thermal behaviour and the heavy distillation residues of different Brazilian crude oils [11] and to evaluate petroleum distillation residues [12].

Therefore, considering that in the petroleum refining process, the first fraction obtained consists of substances with a boiling point equal or below 150°C under atmospheric pressure and that there is not a specific standard method for such fraction analysis. This work reports the application of thermogravimetry on volatile fraction isolation to identify its chemical composition and to quantify the normal paraffin content by HRGC-MS.

Experimental

Sampling

Ten different crude petroleum samples supplied by Cenpes/Petrobrás (Brazil) were analyzed. Samples and their specifications are described in Table 1.

Table 1 API Degree* and crude petroleum samples classification

Petroleum sample	°API	Classification
P1	39.9	light
P2	37.7	light
P3	36.5	light
P4	25.9	heavy
P5	21.6	heavy
P6	19.6	heavy
P7	18.6	very heavy
P8	16.8	very heavy
P9	16.0	very heavy
P10	13.0	asphaltic

*°API=(141.5 g) – 131.5 being 'g' petroleum relative density at 15.6°C

Thermogravimetry

Thermal behaviour of different crude petroleum samples

Approximately 10 mg of crude petroleum placed to alpha-alumina crucibles were subjected to TG analysis. Mettler Toledo TGA/SDTA 851^e thermogravimetric analyzer operated from 25 to 1000°C at a heating rate of 15°C min^{-1} applying continuous nitrogen flow. (When the heating rate is too high, sample heating was not homogeneous which would not allow petroleum volatile fractions collection.)

From the TG curves the mass losses were determined between 25–150°C and each initial sample masses were defined for fractionation and petroleum volatile fraction collection up to 150°C.

The most volatile sample mass was fixed in 200 mg, previously defined in fractionation test. It was collected and analysed by GC-MS. The 500 mg mass was fixed for the less volatile samples. For samples with intermediate volatility, initial petroleum mass was calculated using a linear equation, relating mass loss percentage of each sample up to 150°C with initial masses fixed for samples having higher or lower volatility obtaining the necessary mass values for fractionation and volatile fraction for GC analysis.

Volatile fraction thermogravimetric isolation

The same thermogravimetric conditions described in 'Thermal behaviour of different crude petroleum samples' were used, but in temperature ranging from 25 to 150°C, then keeping it at 150°C for 5 min, ensuring volatilization of sample compounds from the crucible. In the gas outlet of the thermobalance a Pasteur pipette was connected, prepared in an 'L' form, which had its lowest diameter tip inserted in a 20 mL (15 cm·1.5 cm) test tube containing 1.5 mL of dichloromethane. Test tubes used were previously introduced in plastic bottles, slightly than the tubes. After putting water in the plastic bottles and sealing the test tube mouths with PVC film, the sets were placed in a freezer until ice had formed around the tube.

After the end of isotherm (150°C for 5 min), thermogravimeter heating and atmosphere gas were turned off. The Pasteur pipettes were removed from the exit of the thermal analyzer system, and was washed with 0.5 mL of dichloromethane, spilling the wash solvent in the interior of the test tube used to collect the liberated gases. Solution volume was completed until the 1.5 mL mark because there was evaporation of solvents contained in the test tube during gas collection. The test tubes were closed with cloth covers and were conditioned to the freezer for posterior sample chromatographic analysis.

Chromatographic analysis

Volatile fractions analysis by HRGC-MS-CI and HRGC-MS-EI

Petroleum volatile fractions samples collected at 150°C from TG equipment were analyzed HRGC-MS using GC17A Gas Chromatograph equipped with a Shimadzu QP-5050 mass spectrometer detector, with helium 5.0 as a carrier gas at a linear speed of 25 cm s^{-1}. Mass spectrometer was operated in positive-ion chemical ionization and electron impact ionization modes. Positive-ion chemical ionization mass spectrometry was performed with methane 4.0 as a reagent gas. The electron impact ionization mode operated at 70 eV. The injector was used in split mode, at a split rate of 1:20 and a temperature of 250°C. The interface temperature of the mass spectrometer was of 240°C. The column used was a HP-1 with a length of 60 m, 0.25 mm of internal diameter and 1 μm of film thickness of stationary phase. The oven operated with an initial temperature of 30°C, held for 5 min, then increased to 120°C at 3°C min^{-1}, and again increased to 280°C at 7°C min^{-1} and kept at this temperature for 15 min.

Results and discussion

Figure 1 shows TG curves for petroleum samples (mass approximately 10 mg) in temperature range from 25 to 600°C. Although experiments were performed until 1000°C, curves were shown till 600°C, once there were no events after this temperature.

Samples P1, P2 and P3, classified by °API system as light, presented the most accentuated mass loss among petroleum samples. While samples P1 and P2 presented mass loss stabilization at 480°C, the other samples presented at about 500°C.

Samples P4, P5 and P6, classified as heavy petroleum, and P7 classified as extra-heavy, show mass loss profile very similar throughout temperature range from 25 to 1000°C.

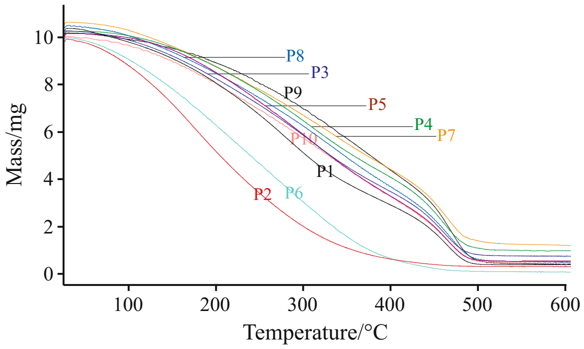

Fig. 1 TG curves obtained from P1 to P10 crude petroleum samples from 25 to 600°C

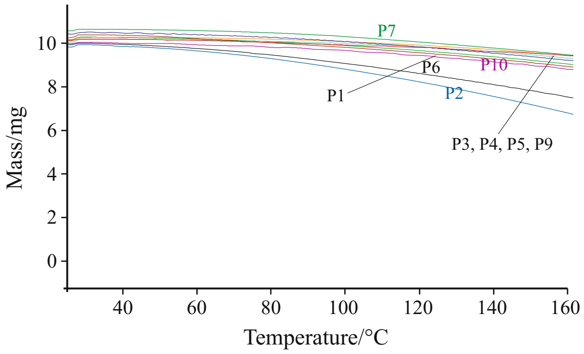

Fig. 2 TG curves for crude petroleum (P1–P10) samples in temperature range from 25–150°C

Samples P9 and P10, classified as extra-heavy and asphaltic, respectively, presented lower mass loss than samples P4, P5, P6 and P7, but they were slightly more volatile than extra-heavy petroleum sample P8.

Regarding mass loss from 25 to 150°C, Fig. 2 illustrates the results, where it is possible to observe that, at this temperature interval, P2 and P1 samples showed the highest mass loss and P7, P8 and P10 the lowest. P3, P5, P9, P4 and P6 samples presented inter-

Table 2 Mass losses (%) for each sample with an initial mass of about 10 mg in temperature range from 25 to 150°C, and initial masses proposals for each sample

Crude oil sample	Mass loss/%	Petroleum estimated initial mass for volatile fraction isolation up to 150°C/mg
P1	21.9487	261
P2	27.5657	200
P3	12.4249	416
P4	10.7067	387
P5	10.7256	385
P6	10.1656	440
P7	6.3633	500
P8	6.4827	435
P9	9.6494	399
P10	6.5247	500

Table 3 Absolute values and mass losses (%) for light fraction of crude petroleum samples isolation and collection

Sample of petroleum	Petroleum initial mass for volatile fraction isolation up to 150°C/mg	Mass loss/ mg	Mass loss/ %
P1	253.7247	44.46	17.52
P2	197.7514	43.29	21.89
P3	406.9119	30.65	7.53
P4	380.3248	24.45	6.42
P5	383.0594	24.19	6.31
P6	420.1009	21.45	5.10
P7	504.7183	8.88	1.75
P8	435.0975	12.29	2.82
P9	397.3337	23.33	5.87
P10	501.6736	11.59	2.31

mediate mass loss between the previous two groups. These facts are demonstrated by mass loss percentages at this temperature range, showed in Table 2.

Table 2 also shows crude petroleum masses used for thermogravimetric isolation of volatile fraction up to 150°C, for subsequent analysis by HRGC, which were calculated based on mass loss percentage presented for each sample. Experimental consideration that defined that initial mass of 200 mg is necessary to analyze the most volatile sample (P2) and 500 mg for the less volatile (P7). The other values being calculated relatively to these ones.

Table 3 shows volatile fraction masses collected for subsequent analysis by gas chromatography. Evaluation of data mass losses in Tables 2 and 3 indicates that low-volatile samples (P7) had a reduction in mass loss % of about 70%. High-volatile samples (P2), increasing sample mass from 10 to 200 mg showed reduction in mass loss % of about 20%.

Table 4 Volatile fraction at 150°C of P3 sample chemical composition determined by HRGC-MS-EI

Peak	Compound	*t*/min	Peak	Compound	*t*/min	Peak	Compound	*t*/min
01	2,2-dimethyl-butane	12.633	18	1,1,3-trimethyl-cyclohexane	32.050	35	2-methyl-undecane	47.833
02	3-methyl-pentane	13.492	19	2,3,4-trimethyl-hexane	33.775	36	*n*-dodecane	48.925
03	*n*-hexane	14.533	20	(o.m.p) xylenes	35.108	37	2,6-dimethyl-undecane	49.408
04	methyl-cyclopentane	16.383	21	*n*-nonane	36.125	38	4,6-dimethyl-undecane	51.083
05	benzene	18.025	22	1-ethyl-2-methyl-cyclohexane	36.875	39	*n*-tridecane	51.700
06	cyclohexane	18.733	23	1-propenyl-cyclohexane	37.658	40	2,6,10-trimethyl-dodecane	53.708
07	3-methyl-hexane	19.897	24	3-methyl-nonane	38.267	41	*n*-tetradecane	54.133
08	1,3-cyclopentane	20.842	25	3-ethyl-2-methyl-heptane	38.767	42	*n*-pentadecane	56.317
09	*n*-heptane	21.625	26	4-methyl-nonane	39.833	43	*n*-hexadecane	58.342
10	methyl-cyclohexane	23.350	27	1,1,2,3-tetramethyl-ciclohexane	39.908	44	2,6,10,14-tetramethyl-hexadecane	59.417
11	toluene	25.850	28	trimethyl-benzene	41.008	45	*n*-heptadecane	60.342
12	2,5-dimethyl-hexane	26.575	29	*n*-decane	41.533	46	*n*-octadecane	62.408
13	3-methyl-heptane	27.150	30	trimethyl-benzene	42.375	47	*n*-nonadecane	64.642
14	1,3-dimethyl-cyclohexane	27.575	31	4-methyl-decane	42.650	48	*n*-eicosane	67.192
15	*n*-octane	29.067	32	*n*-butyl-cyclohexane	43.275	49	*n*-heneicosane	70.175
16	1,4-dimethyl-cyclohexane	29.567	33	*n*-undecane	45.633			
17	ethyl-cyclohexane	31.650	34	pentyl-cyclohexane	47.217			

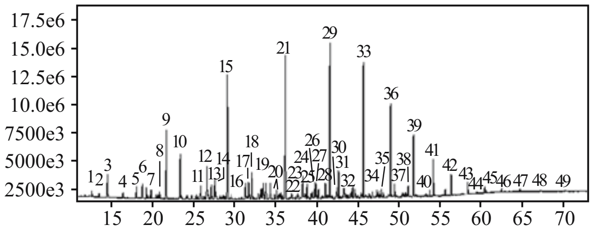

Fig. 3 HRGC-MS total ion chromatogram (TIC) and constituents identified in volatile fraction up 150°C of P3 sample

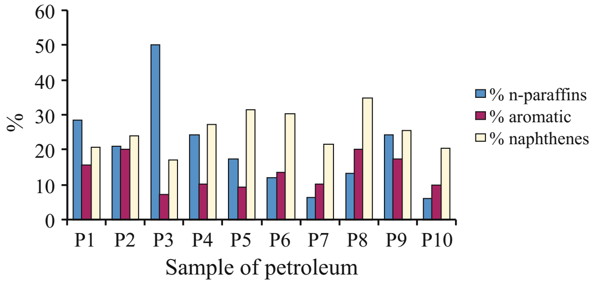

Fig. 4 Normal paraffins, aromatic and naphthenes composition (%) at volatile fractions up 150°C from P1 to P10 samples

Despite the samples total mass loss obtained from masses from 200 to 500 mg have been smaller than mass losses for 10 mg of these same samples, the amount of volatilized samples were enough for subsequent chromatographic analyses. The volatile fraction isolation of all petroleum samples proceeded using a thermal analyzer system operating from 25 to 150°C, 15°C min^{-1}, with 5 min of isotherm at 150°C. The relative standard deviations obtained for all evaluation of mass loss % were lower than 0.8%.

Figure 3 shows P3 sample chromatographic analyses by HRGC-MS, while Table 4 shows identified P3 volatile fraction substances up to 150°C. It was verified that normal paraffin composites, with 6 to 21 carbon atoms, were the major sample constituents, also being seen ramified hydrocarbons, naphthenes, *n*-alkanes (cyclic-alkanes) and aromatic groups.

The samples total normal paraffin quantification (Fig. 4) demonstrated that samples such as P1, P4 and P9, classified by degree API system as light, heavy and extra-heavy, almost all presented the same normal paraffin content. Therefore, there was no correlation between the samples chemical composition and mass loss by thermogravimetry or classification by degree API system.

Conclusions

Fractionation process of crude oil samples through thermogravimetric analysis presented great advantages regarding the usual procedures of distillation: it was fast, once it was possible to get the desired fraction in 15 min; it required only small amounts of a sample, not more than 500 mg; and it was efficient because it allowed a large number of samples to be analyzed daily, using only one equipment. Moreover, enough quantities of samples for posterior chromatographic analysis could be got through the adjustment of initial sample mass needed to be used in TG equipment.

More studies need to be done in different experimental conditions, but it seems that this method could be adopted by the petrochemical industry, in substitution of distillation methods, for petroleum volatile fractions analysis in temperature range from 25 to 150°C.

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