

THERMAL BEHAVIOR OF REFINERY ATMOSPHERIC RESIDUE FROM SOME DIFFERENT OILS

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Thermogravimetry (TG) was applied to evaluate the thermal behavior of five refinery atmospheric distillation residues (ATR) obtained from different Brazilian crude oils. The asphaltenes were extracted of each sample and their influence on coke formation was studied. It was observed that they have a great contribution on carbonaceous residues formation during pyrolysis and that the heavier the ATR sample, the higher is the contribution of other heavy components present in ATR samples.

Keywords: distillation residues, petroleum, thermogravimetry

Introduction

Processing high-density petroleum feeds, that are nowadays very important in the scenario of fossil fuel supplies, brings naturally the challenge of dealing with abundance of heavy ends. Studies on thermal degradation of refinery heavy residues are quite important in a refinery process.

The petroleum refinement process is normally started by distillation units at atmospheric pressure. Different boiling temperatures separate the hydrocarbons and the distillation residue are called atmospheric residue (ATR), naturally a heavy residue. This heavy end of an atmospheric distillation is also submitted to thermal treatments to obtain lighter fraction, which has greater economical value.

Processing high-density petroleum feeds oil industry deals with abundances of heavy ends naturally coke precursors. On the other hand, the optimization of refining facilities to deal with such feeds brings economical competitiveness, since these oils have low prices in the international market.

The heaviest constituents of an atmospheric distillation residue are named asphaltenes [1]. The presence of asphaltenes in atmospheric residue is of considerable significance to thermal processing since asphaltenes are implicated in carbon deposition in the refinery units (coke precursors). Asphaltenes can be quantifying by treatment of petroleum residue with a low boiling liquid hydrocarbon such as *n*-heptane. Traditionally, the portion soluble in alkane is called maltene and the portion insoluble in alkane, but soluble in aromatic hydrocarbons, are asphaltene. The at-

mospheric distillation residue can contain a significant amount of asphaltene [2, 3].

The thermal decomposition of petroleum feedstock has received some attention in the literature. Karacan and Kök [4] studied the pyrolysis behavior of crude oils and their fractions isolated by SARA methodology. They used differential scanning calorimetry (DSC) and thermogravimetry (TG) and suggested that each fraction in whole crude oil follows its own reaction pathway independent of the presence of other fractions. Others researchers studied, by the same technique, the effect of the crude oil composition, characterized on the basis of light hydrocarbon, resins and asphaltenes contents on the pyrolysis kinetic of the crude [5–6]. Recently Yasar *et al.* [7], studying the effect of same crude oils components also by TG, suggested that the reactivity of saturates was strongly affected by presence of asphaltenes in the reaction environment.

The objective of this work is to gain additional insight into refinery residues pyrolysis. In this study was analyzed the thermal behavior of five different atmospheric residues proceeding from Brazilian oils with different API degrees that are processed in Brazilian refineries. The asphaltenes were extracted of each sample and their influence on coke formation was studied.

Experimental

Samples of atmospheric distillation residues (ATR)

The distillation residues (ATR) from Brazilian industrial refining facilities were provided by Petrobras (Brazilian

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Table 1 Characteristics of the samples

Samples	Density/20°C g mL ⁻¹	Relative density/°API	Carbon residue/% _{op} *	C/H
ATR12	0.9884	11.6	9.9	0.56
ATR13	0.9751	13.0	9.7	0.57
ATR16	0.9574	15.7	7.3	0.57
ATR19	0.9391	18.6	8.0	0.55
ATR28	0.8840	28.0	1.9	0.53

*ASTM 524-64 Ramsboton methodology

Oil Company) and used as received. The samples are chosen by different API degree (relative density) and their characteristics are described in Table 1.

API degree is a denomination established by American Petroleum Institute and defines the relative density of an oil or fraction. The API degree is high when the oil or fraction is light that is lighter oil higher API degrees. Petroleum and fractions with 30°API are considered light, between 22 and 30°API are mediums, between 10 and 22°API are heavy and smaller than 10°API are extra heavy oils. How higher API degree of oil higher is its economical value.

Atmospheric distillation residues with API degree smaller than 22° produce higher amount of carbonaceous residue during its thermal degradation because they have higher amount of heavy aromatic hydrocarbon.

Precipitation of asphaltenes samples

The methodology applied was based on the IPI-143, traditional method used to quantify asphaltenes in petroleum [8–9]. Each residue (10 g) was added to 400 mL of heptane and the mixture was shaken for about two hours at 60°C. Then allowed to cool and settle for 60 h. The solution was filtered to remove the precipitate. The solid fraction was submitted a Soxhlet extraction, first with *n*-heptane to verify the absence of maltenes. And after with toluene to isolated the asphaltenes. The toluene solution was evaporated at vacuum and 60°C to quantify the asphaltenes.

Elemental analysis

Elemental analysis of asphaltenes for C and H was carried out using a Perkin Elmer 240C analyser.

Thermogravimetric experiments

TG experiments were performed on a Netzsch STA-Lux 409 module in a 40 µL opened platinum pans using N₂ as purge gas. The temperature calibration was performed with indium, zinc and tin. The mass calibration was checked with calcium oxalate. Each sample (20 mg) was heated from room tempera-

ture to 600°C at 10 K min⁻¹ under dynamic nitrogen (50 mL min⁻¹) atmosphere. The sample mass, heating rate and flow gas were based on the results obtained in a previous paper [10].

Results and discussion

The different ATR samples were submitted at TG experiments as described before. Besides the amount of carbonaceous residue formed during the thermal decomposition of each sample, the TG curve give the initial and final temperatures (T_{onset} and T_{end}) of the lost mass; the amount of volatile material given off by distillation or sample cracking; and the temperature of the DTG peak, that represents the maximum reaction rate (T_{max}).

Six replicates of ATR28 sample under the same TG conditions (mass=20 mg, β =10 K min⁻¹ and N₂ flow rate=50 mL min⁻¹) have been recorded the reproducibility study. Table 2 describes the carbonaceous content taken from TG curves. It was observed that the result interval (μ) with 95% confidence is 0.7.

Figures 1 and 2 describe TG and DTG curves of ATR samples. All profiles are similar and mass loss of the two events (150–400 and 400–550°C) are observed. The first one probably is due to evaporation rather than cracking [5] and the second one is due to the cracking of high molecular mass compounds present in this kind of residues.

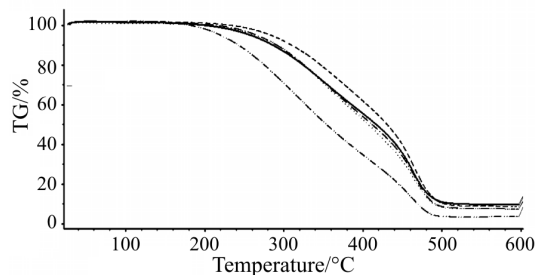
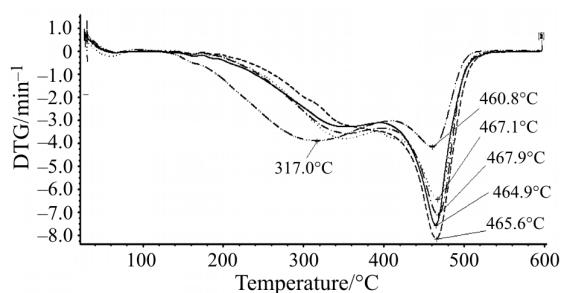
Table 2 Replicates of ATR28 (20 mg initial mass, β =10°C min⁻¹ and N₂ flow rate=50 mL min⁻¹)

ATR28	TG Carbonaceous residue at 600°C/%
1	3.4
2	3.2
3	2.6
4	2.3
5	2.4
6	3.9
Medium	2.97
SD	0.63
μ (95%)	± 0.67

SD – standard deviation

Table 3 Data taken from the TG and DTG curves of ATR samples (20 mg initial sample, $\beta=10\text{ K min}^{-1}$ and $50\text{ mL min}^{-1}\text{ N}_2$ flow rate)

Sample	TG			DTG	
	Carbonaceous residue at $600^\circ\text{C}/\%$	Volatile material at $150\text{--}400^\circ\text{C}/\%$	$T_{\text{onset}}/^\circ\text{C}$	$T_{1\text{max}}/^\circ\text{C}$	$T_{2\text{max}}/^\circ\text{C}$
ATR12	9.6	46	273	350	465
ATR13	8.5	40	287	351	466
ATR16	7.3	48	283	352	467
ATR19	7.3	47	277	353	468
ATR28	3.4	67	228	317	461

**Fig. 1** TG curves of — ATR12, --- ATR13, ... ATR16, - - - ATR19, - · - ATR28 samples (sample mass: 20 mg, $\beta=10\text{ K min}^{-1}$, flow rate= 50 mL min^{-1} of N_2)**Fig. 2** DTG curves of — ATR12, --- ATR13, ... ATR16, - - - ATR19, - · - ATR28 samples (sample mass=20 mg, $\beta=10\text{ K min}^{-1}$, flow rate= 50 mL min^{-1} of N_2)

At the ATR28 sample the higher amount of mass loss and the smaller T_{onset} was observed (Table 3). This result is in accordance with its high API gravity (28°API) and its high amount of light hydrocarbons, that produce small amount of carbon residue (Table 2).

As expected in the DTG curves two T_{max} ($T_{1\text{max}}$ and $T_{2\text{max}}$) were observed to all samples. The $T_{2\text{max}}$ values were similar to all samples, but the $T_{1\text{max}}$ to ATR28 sample was lower than the others. It is explained by the same reason detailed before; as it had a great amount of light hydrocarbons that quickly evaporate when temperature is increasing.

The asphaltenes of each sample were extracted and quantified by the methodology described before. As expected, the content of asphaltenes increases when the API degree samples decrease (Table 4).

Table 4 Content of asphaltenes extracted from each ATR sample (10 mg)

Samples	Content of asphaltenes/%
ATR12	7.3
ATR13	7.1
ATR16	6.8
ATR19	4.3
ATR28	0.2

Table 5 Elemental analysis of asphaltenes extract from different RAT samples

Samples	C/%	H/%	C/H
ATR12	86.78	9.91	0.7
ATR13	86.77	9.85	0.7
ATR16	87.04	9.16	0.8
ATR19	87.83	8.87	0.8
ATR28	nd	nd	nd

nd – not determined, the amount of sample was not sufficient to elemental analysis

To confirm if the asphaltenes extracted are aromatic substances, the samples were submitted to an elemental analysis. The asphaltenes elemental analysis indicated the C/H relation molar is very close to one, typical value of aromatic compounds (Table 5). These results confirmed the asphaltenes isolation.

The extracted asphaltenes samples were analyzed in the same TG conditions of ATR samples. The TG of asphATR 12, 13, 16 and 19 (Fig. 3) showed an appreciable mass change between 400 and 600°C and the maximum rates of lost mass in DTG curves are between 468 and 477°C (Fig. 4). These results are consistent with the literature about thermal decomposition of asphaltenes from different origins [4, 7, 11].

AsphATR28 sample, showed a different curve in the low temperature region ($200\text{--}350^\circ\text{C}$). It can be attributed to the volatilization of some paraffin hydrocarbon that co-precipitated with the asphaltenes [12]. How the ATR28 sample has very small amount of asphaltenes, the paraffin becomes prominent more than in the other ATR samples.

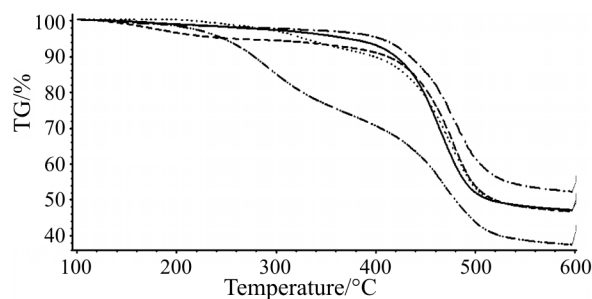


Fig. 3 TG curves of — ATR12, --- ATR13, ... ATR16, - - - ATR19, ··· ATR28 samples (sample

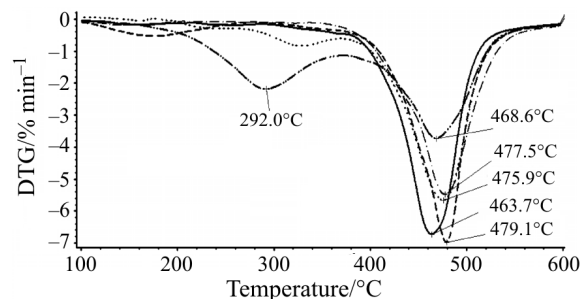


Fig. 4 DTG curves of — ATR12, --- ATR13, ... ATR16, - - - ATR19, ··· ATR28 samples (sample mass=20 mg, $\beta=10$ K min^{-1} , flow rate=50 mL min^{-1} of N_2)

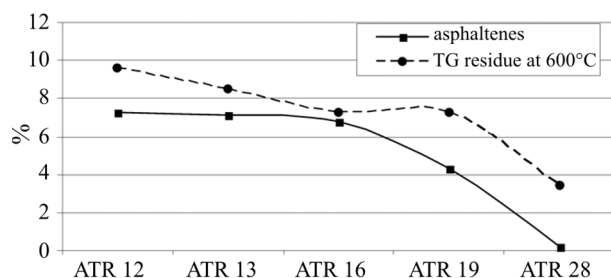


Fig. 5 Comparison of TG residues at 600°C and asphaltenes content of each ATR sample

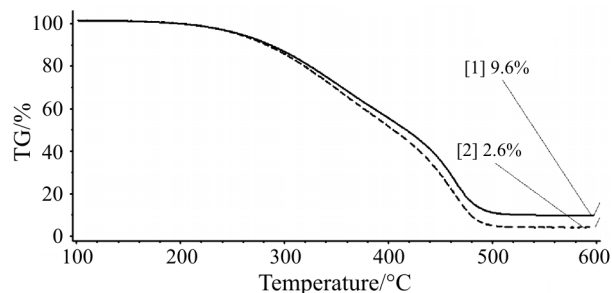


Fig. 6 TG curves of — whole ATR12 and --- without asphaltenes, (sample mass=20mg, $\beta=10$ K min^{-1} , flow rate=50 mL min^{-1} of N_2)

Figure 5 compares the amounts of carbonaceous residues at 600°C taken from TG curves with the asphaltenes content of its ATR sample. The TG residue decreases when the amount of asphaltenes decreases.

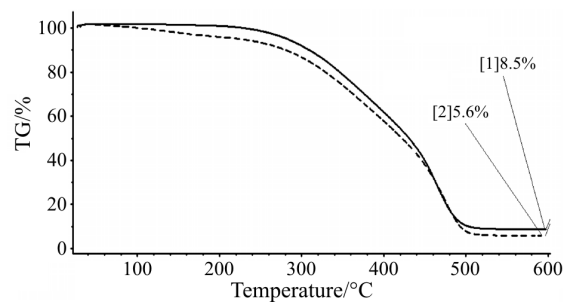


Fig. 7 TG curves of — whole ATR13 and --- without asphaltenes, (sample mass=20 mg, $\beta=10$ K min^{-1} ,

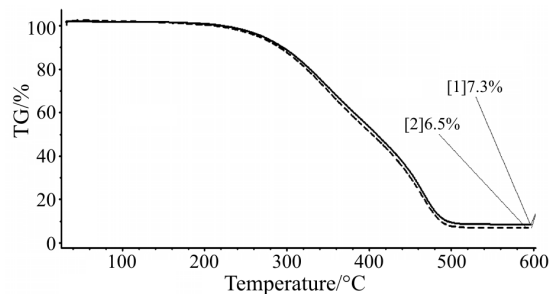


Fig. 8 TG curves of — whole ATR16 and --- without asphaltenes, (sample mass=20 mg, $\beta=10$ K min^{-1} , flow rate=50 mL min^{-1} of N_2)

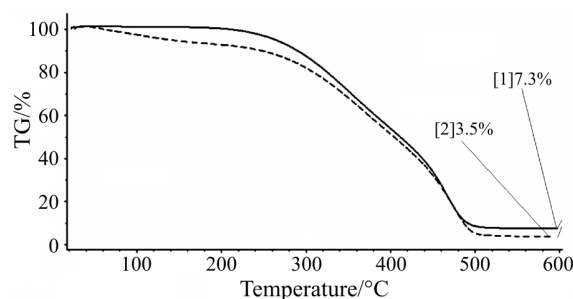


Fig. 9 TG curves of — whole ATR19 and --- without asphaltenes, (sample mass=20 mg, $\beta=10$ K min^{-1} ,

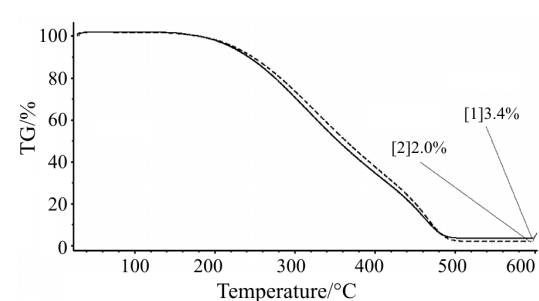


Fig. 10 TG curves of — whole ATR28 and, --- without asphaltenes, (sample mass=20 mg, $\beta=10$ K min^{-1} , flow rate=50 mL min^{-1} of N_2)

The TG curves of ATR samples after asphaltenes extraction were compared with their respective original samples (Figs 6–11). There was a carbonaceous residue reduction observed in ATR12, ATR13 and ATR19 sam-

ples. Little difference was registered in ATR16 and finally an insignificant difference was detected at ATR28 sample, that has a small amount of asphaltenes.

Conclusions

The thermogravimetry has been shown to be a viable technique to the evaluation and comparison of various atmospheric residues from distillation process in refinery.

The thermal decomposition of extracted asphaltenes from samples with 12 to 19°API is similar with that observed in the literature. The extracted asphaltenes from the lighter sample (28°API) lost mass at low temperature region (200–350°C). It was attributed to paraffin volatilization that co-precipitate with the asphaltenes. The little amount of asphaltenes (0.2%) is the responsible for this event.

It was observed that the asphaltenes are the greater responsible in the pyrolysis residues formation, but as heavier as the ATR sample, higher is the contribution of other heavy components.

Acknowledgments

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