

THERMOGRAVIMETRIC INVESTIGATION ON PREDICTION OF THERMAL BEHAVIOR OF PETROLEUM DISTILLATION RESIDUES

Maria Luisa A. Gonçalves^{1*}, Deusa A. Pinto da Mota², Ana Maria R. F. Teixeira² and M. A. G. Teixeira³

¹Universidade Federal Fluminense-Instituto de Química/CNPq, Niterói, RJ, Brasil

²Universidade Federal Fluminense-Programa de Pós Graduação em Química, Niterói, RJ, Brasil

³Centro de Pesquisas da Petrobras (CENPES/Petrobras), Rio de Janeiro, RJ, Brasil

Thermogravimetry (TG) is a potential tool to evaluate petroleum distillation residues, obtained in the crude oil distillation. Analyses were done at different heating rates, mass samples and gas flow rates. No differences were observed in the yields of the products formed during the pyrolysis at different analytical conditions. Linear correlation was found between the results of the TG and the standard methods for the prediction of the light fraction rates given by the pyrolysis.

Keywords: distillation residues, heavy fractions, petroleum, thermal analysis, thermogravimetry

Introduction

Petroleum is a mixture of aliphatic, aromatic and naphthenic hydrocarbons. The petroleum refinement process is normally started by distillation units, first at atmospheric pressure and, after at reduced pressure. The volatile fractions, in both cases, have greater economical value. The distillation residues produced are called atmospheric residue (ATR) and vacuum residue (VR), respectively. These refinement residues are also submitted to thermal treatments. Examples are delayed coking, viscoreduction and thermal-catalytic cracking. In the case of the non-catalytic process, they are based on pyrolysis reactions that are based on thermal behavior. In the case of catalytic solutions, they are carried out at high temperatures and the thermal cracking is a competition for the catalytic cracking.

Consequently, in the petroleum industry, the previous knowledge of the potential of a feedstock to produce light material is an important aspect of the refinement. This point is easily solved in the crude oil case, where the standard distillation tests predict the light material yield that will be produced during the refinement [1–3]. As for the refinement residues, the evaluation is harder. As they are submitted to thermal processes, the standard methods do not present the actual yield of the light fractions given off [4].

The thermal analysis techniques are being applied, more frequently, for the petroleum and petroleum products characterization. Bae [5] investigated the thermo-oxidative behavior and fuel forming properties of various crude oils by thermogravimetry and classified them

according to their oxidation characteristics. Other researchers studied, by the same technique, the effect of the oil composition, characterized on the basis of light hydrocarbon, resins and asphaltene contents on the pyrolysis kinetic of the crude [6–9].

Petroleum products have been also studied by thermal techniques in the investigation of problems concerning the evaporation of volatile components from heavy fractions, determination of the thermal stability under atmospheric and oxygen conditions, and the kinetics of these processes [10–12].

Nevertheless, the literature presents few references applying thermal analysis to petroleum distillation residues. Some publications use these techniques only to characterize the thermal behavior of refinement residue [13–15]. A possible reason is the difficulty in obtaining direct results from these techniques. However, in a previous paper [16], it is shown that it is possible to obtain correlations for the distillation curve of heavy feedstock for delayed coking using this technique, an example of how treated data from TG can be useful.

Refinement residue pyrolysis occurs through the formation of radical species that will undergo recombination or degradation to form substances. Since the level of activation energy is enough to form several possible intermediates, the conditions to which the reactional mass is submitted could influence the intermediates formed and, as a consequence, different product profiles could be obtained. Experimental conditions can also affect the measured yields, as a function of temperature, in distillation. One of the objectives of this work is to find

* Author for correspondence: maleixo@infolink.com.br

out if experimental conditions would bring different product profiles during the refinement residues pyrolysis. If so, physical-chemical understanding about the phenomena involved could be of great help to optimize industrial operations. TG was considered a very convenient technique to evaluate the yield of volatile and non-volatile pyrolysis products as a function of the reaction conditions, because of the ease of variation of mass, heating rates and gas flow rates.

In this investigation the results obtained by TG, were correlated with the results obtained by standard methodologies. To analyze this correlation the standard test Ramsbottom (RCR) [17] was selected, which measures the potential of carbonaceous products formation (coke) and the standard distillation methodologies that define the yields of volatile products in each temperature [2, 4].

Experimental

Samples

The atmospheric residue (ATR) and vacuum residue (VR) from distillation refinery units have been evaluated. Additionally, some fractions were analyzed to complete the understanding of the phenomena involved, including a residue of industrial deasphalting (ASFR) and middle distillation fractions, namely decanted oil (DO) and heavy gas oil (HGO). All of the fractions and residual employed in this work were ob-

tained from the same Brazilian feedstock (16°API crude oil) from Brazilian Oil Company (Petrobras) industrial refining facilities. The characteristics of the samples are described in Table 1.

Thermogravimetric experiments

TG experiments were performed on a Netzsch STA-Lux 409 module in 300 μL opened platinum pans using N_2 as purge gas. The temperature calibration was performed with indium, zinc and tin. The mass calibration was done with calcium oxalate.

Low and high heating rates (2.5, 5, 10 and 20 K min^{-1}) and sample masses (10, 15, 20, 30, 50 and 100 mg) have been varied in order to examine their influences in the volatile and solid pyrolysis products yields.

The purge gas flow was varied between 50 to 180 mL min^{-1} (the minimum and maximum flow permitted in the Netzsch equipment) to allow the observation of the differences related to the dispersion of the gaseous pyrolysis products.

Results and discussion

As it was told before, it is possible to change some experimental conditions like sample mass, heating rate and gas flow during the TG runs. Such circumstances were evaluated, on VR sample, to examine their influences on the volatile and solid pyrolysis products

Table 1 Characteristics of the samples

Test	Sample	DO	HGO	ATR	VR	ASFR
density (g mL^{-1}) ASTM 4052		1.0652	0.936	0.9848	1.006	1.058
RCR (% <i>p/p</i>) ASTM 524		6.7	0.4	9.9	17.9	29.3
asphaltenes (% <i>p/p</i>) IP 143		no	0.1	2.7	7.5	18
distillation standard method		Temperature/ $^{\circ}\text{C}$				
		(1)	(2)	(2)	(2)	(2)
	T_{initial}	200	239	242	386	387
	2% (v/v)	242				
	5% (v/v)	279	322	340	418	412
	10% (v/v)	314	351	377	502	480
	20% (v/v)	342			560	
	30% (v/v)	361	409	450		
	40% (v/v)	379		513		
	50% (v/v)	397	442	585		
	90% (v/v)	495	524	660		
	92% (v/v)	505				
	95% (v/v)	526	543	684		
	T_{end}	595	591	715	569	536

(1) – simulated distillation ASTM D-2887 [2], (2) – simulated distillation at high temperatures HT750 [4], no – no observed

yields, if different conditions result differences in the composition of volatile and solid materials.

Figure 1 describes the TG curves of VR sample at different heating rates, in inert gas flow (50 mL min⁻¹ nitrogen) using the same initial sample mass (20 mg). The curve profile is similar to the one was found in the literature for petroleum heavy residues [15]. The content of carbonaceous residue varied from 16.6 to 15.7% (Table 2).

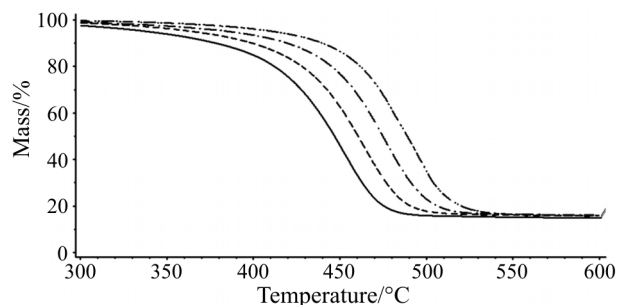


Fig. 1 TG curves of the VR sample: 20 mg, N₂ flow of 50 mL min⁻¹, at heating rates of — 2.5 K min⁻¹, --- 5.0 K min⁻¹, - - - 10.0 K min⁻¹ and - · - · 20.0 K min⁻¹

Table 2 Data taken from the TG curves of VR sample at different heating rates

Heating rate/ K min ⁻¹	Volatile material/%	Carbonaceous residue at 600°C/%
2.5	85.2	16.8
5	84.1	15.9
10	83.5	16.5
20	84.3	15.7

Twelve replicates of VR sample under the same experimental conditions (mass=20 mg, $\beta=10$ K min⁻¹ and flow rate=50 mL min⁻¹) have been recorded for reproducibility studies. As average, 16.1% residue formed. From the two medium determinations 2% differences was allowed as a non-significant variation of the content of the residual material formed at 600°C. Analyzing the data of Table 2, non-significant variation in the content of the carbonaceous residue was observed at different heating rates.

The sample mass was also altered between 10 and 100 mg. The TG curves, using 10, 15, 20, 30, 50 and 100 mg initial sample masses at 20 K min⁻¹ and 50 mL min⁻¹ of N₂ flow, indicated that the volatile content and the formed residual material are practically identical (Table 3).

In case of larger sample masses due to their expansion thermal cracking takes place and gaseous products leave from the sample during the thermal run.

Table 3 Data taken from the TG curve of VR sample: (at $\beta=20$ K min⁻¹ and 50 mL min⁻¹ flow rate) at different masses

Sample mass/mg	Volatile material/%	Carbonaceous residue at 600°C/%
10	83.9	16.2
15	83.9	16.2
20	83.9	16.1
30	84.4	15.5
50	85.5	14.3
	84.0	16.0
100	83.4	16.6
	86.0	14.0

This is one possible reason of the poor reproducibility when 50 and 100 mg initial samples were weighed.

The inert gas flow rates were 50, 100 and 180 mL min⁻¹ to observe differences related to the dispersion of the gaseous pyrolysis products. The TG curves of VR sample obtained applying 20 mg initial mass and 20 K min⁻¹ heating rate, did not present differences with regard to the volatile material and the carbonaceous residue formation (Fig. 2). Table 4 describes the percentage of the formed products at different N₂ flows, indicating that the variation of the gas flow rate does not change the amount of the formed products during the pyrolysis.

None of the variables presented caused any significant difference in the amount of carbonaceous residue or in the volatile products evolved during the thermal degradation of the sample. As a consequence, we can conclude that the pyrolysis occurs by an unequivocal

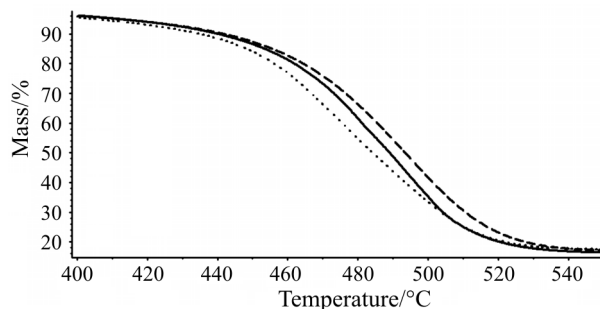


Fig. 2 TG curves of VR (20 mg initial sample, $\beta=20$ K min⁻¹) flow rates: — 50, --- 100 and ··· 180 mL min⁻¹

Table 4 Data taken from the TG curve of VR (20 mg initial sample, $\beta=20$ K min⁻¹) at different flow rates

N ₂ flow/ mL min ⁻¹	Volatile material/%	Carbonaceous residue at 600°C/%
50	84.3	15.3
100	83.0	16.2
180	83.1	16.3

cal mechanism, and that the final product is independent of the reaction behavior, on the condition where there is sufficient time to permit the pyrolysis of all the components that are able to react in this process.

After studying the effect of the different experimental conditions on the TG analysis of refinery residues and concluded that the formation of pyrolysis products does not depend on them, some different petroleum fractions (ASFR, DO and HGO) were analyzed to make complete the understanding of the phenomena involved. All of them (20 mg) are analyzed at 2.5 K min^{-1} and 50 mL min^{-1} N_2 gas flow. TG and DTG curves are presented in Figs 3 and 4.

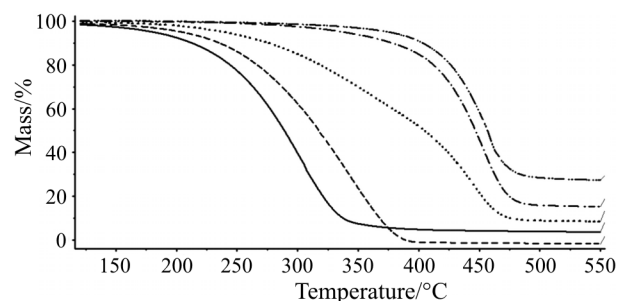


Fig. 3 TG curves of — DO, --- HGO, ... ATR12, - - - VR and - · - · ASFR samples (sample mass=20 mg, $\beta=2.5 \text{ K min}^{-1}$, flow rate= 50 mL min^{-1})

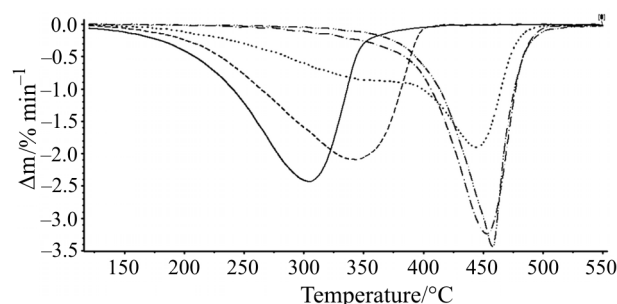


Fig. 4 DTG curves of — DO, --- HGO, ... ATR12, - - - VR and - · - · ASFR samples (sample mass=20 mg, $\beta=2.5 \text{ K min}^{-1}$, flow rate= 50 mL min^{-1})

TG and DTG results are summarized in Table 5. Besides the carbonaceous residue content – coke – formed during the thermal decomposition of each sample, the TG curves give the initial and final temperatures (T_{onset} and T_{end}) of the lost mass; the content of volatile materials formed during the analysis and the temperature of the DTG peak represents the maximum reaction rate (T_{max}).

The DTG curves show increasing T_{max} from DO to ASFR, as expected, since VR and ASFR are residues consequently heavier than DO and HGO (Table 1). The amount of the lost substance in that case is due to rather cracking than to the evaporation of the sample, which is negligible [6].

The content of residual carbonaceous material – coke – produced in the analyzed pyrolysis fractions were also in accordance with the carbonaceous residue determined by the Ramsbottom method (RCR) [17]. Table 6 presents the data obtained by the two techniques and Fig. 5 indicates a good correlation between the two methodologies.

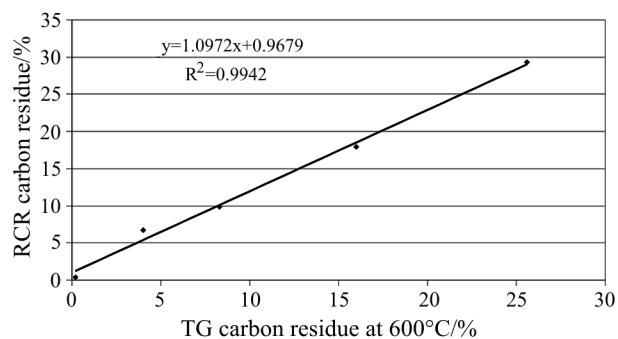


Fig. 5 Correlation between carbon residues obtained from TG at 600°C and RCR methods

Table 7 summarizes data obtained by TG analysis and by the standard distillation methodology, ASTM 2887 [2] for DO and HT750 [4] for HGO, ATR, VR and ASFR samples.

The initial boiling temperature (T_{initial}) determined by standard distillation of each sample is corre-

Table 5 Data taken from the TG and DTG curves of refinery residues and middle fractions: (sample mass: 20 mg, $\beta=10 \text{ K min}^{-1}$ and gas flow rate= 50 mL min^{-1})

Sample	TG				DTG
	$T_{\text{onset}}/^\circ\text{C}$	$T_{\text{end}}/^\circ\text{C}$	volatile/%	residue/%	$T_{\text{max}}/^\circ\text{C}$
DO	222	355	96.0	4.0	304
HGO	257	382	99.8	0.2	341
ATR	282	494	91.0	8.3	444
VR	424	495	83.9	16.1	453
ASFR	429	499	73.9	26.1	458

Table 6 Carbonaceous material by TG and RCR methods

Sample	TG/%	RCR/%
DO	4.0	6.7
HGO	0.2	0.4
ATR	8.3	9.9
VR	16.0	17.9
ASFR	25.6	29.3

lated with the T_{onset} obtained in the TG curve presenting a 0.99 correlation factor (Fig. 6a).

The temperatures at 5 and 10% of the volatile material given off in the same distillation curve also present a good correlation (0.95) with the temperatures at 5 and 10% of mass loss in the TG curve (Figs 6b and c). Nevertheless, a good correlation was not observed be-

tween the final temperatures obtained in the two methods (Fig. 6d). A possible explanation could be that in pyrolysis reactions, when temperature is increased to higher values, some chemical reactions complete [9] and, as TG method is a real thermal method, cracking is observed which is not present in simulated distillation by chromatography, an adsorption method that correlates elution time with known boiling point compounds [4].

Conclusions

None of the variables in TG analysis of refinement residue put in evidence any significant difference in the amount of carbonaceous residue produced or in the volatile products given off during the pyrolysis of

Table 7 Results obtained in the TG curves and standard distillation

Sample	TG temperature/°C				Distillation temperature/°C			
	T_{onset}	T_{end}	* $T_{5\%}$	** $T_{10\%}$	T_{initial}	T_{end}	* $T_{5\%}$	** $T_{10\%}$
DO	222	336	194	217	200	595	279	314
HGO	257	382	218	242	239	591	322	351
ATR	282	465	265	295	242	715	340	377
VR	424	474	356	390	385	569	418	502
ASFR	429	473	388	418	387	536	412	480

* $T_{5\%}$ =temperature at 5% of mass loss, ** $T_{10\%}$ =temperature at 10% of mass loss

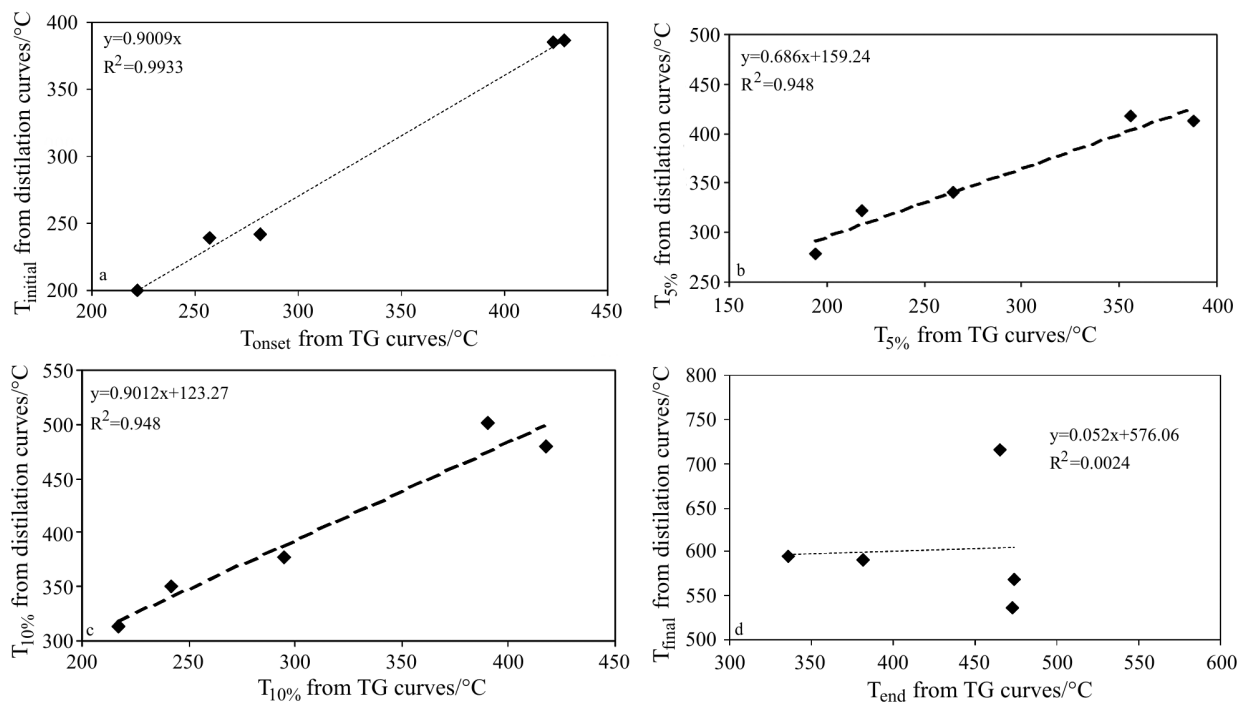


Fig. 6 Correlation curves of TG and standard distillation data: a – T_{onset} ·initial boiling temperature, b – $T_{5\%}$ mass loss· $T_{5\%}$ distilled, c – $T_{10\%}$ mass loss· $T_{10\%}$ distilled, d – T_{end} · T_{final} of distillation

the sample. The final products are independent of the reaction behavior.

In this preliminary investigation the results indicated that TG is a versatile technique to obtain rapid information about the thermal behavior of the residues produced in the petroleum distillation and the behavior of the middle fractions. The method presents a good correlation with distillation initial temperatures and temperatures of 5 and 10% of volatile material given off.

The amount of carbonaceous residue (coke) formed after the pyrolysis was also correlated to the methodology standardized for this determination. Nevertheless, the pyrolysis final temperature did not present a good correlation with the temperatures obtained in the simulated distillation.

Acknowledgments

The financial support of Plano Nacional de Ciência e Tecnologia do Setor Petróleo e Gás Natural and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CT-PETRO/CNPq) and the samples provided by Petrobras are acknowledged.

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