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THERMOGRAVIMETRIC STUDY OF KEROSENE-DOPED GASOLINE

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Motor gasoline must present characteristics that guarantee its quality and the good performance of internal combustion engines without harming the environment. The contamination of gasoline by solvents can seriously adulterate its physical-chemical properties and affect its volatility and detonation capacity. To investigate organic solvent adulteration in gasoline samples, thermal analysis technique (TG/DTG) can be used as an auxiliary tool in the study of the thermal behavior of liquid fuels, as demonstrated by the present work involving a comparative analysis of kerosene-free and doped gasoline.

Keywords: *gasoline, kerosene, thermogravimetry*

Introduction

Gasoline is a petroleum-derived fuel constituted mainly by a complex mixture of paraffinic, naphtenic, olefinic and aromatic hydrocarbons (C4–C12), and to a lesser extent, by oxygenated products. Hydrocarbons are formed by small carbon chain molecules, normally from 4 to 12 carbons. In addition to hydrocarbons and oxygenated compounds, gasoline also contains sulfur, nitrogen, and metallic compounds, all in low concentration. The distillation temperature ranges from 30 to 220°C, varying with the production process [1].

Basic gasoline (free of oxygenated compounds) has a complex composition. Its formulation may demand the use of several noble streams derived from petroleum processing such as light naphtha (product obtained from the direct distillation of petroleum), cracked naphtha, which is obtained by cracking heavier hydrocarbon molecules (gas oil), reformed naphtha (obtained from a process that increases the quantity of aromatic substances), alkylated naphtha (obtained from a process that produces high octane paraffins from *iso*-butanes and olefins), etc., defined to attend product quality requirements [1, 2]. The increase in gasoline production driven by the growth of the car industry was possible through the refining and catalytic cracking processes, which afforded cracking of large molecules into smaller ones with increased production yield.

Gasoline is used in vehicles propelled by internal combustion engines – automobiles, buses, planes, boats, etc., the former ones presenting the largest demand. Motor gasoline is the appropriate fuel for spark ignition internal combustion engines which use the Otto cycle [3]. Motor gasoline is produced according to specific quality, engines and environment protection requirements. Qualities that aim meeting specific operational and conservation requirements. For such, gasoline must result in clean burning without knocking, and evaporate completely in the carburetor when the engine is at work. Excessive vaporization produces carburetor inlet tube clogging due to the formation of vapor bubbles, which interferes with product flow. The presence of low volatility fractions in the fuel, in addition to more difficulty vaporization, also leads to incomplete product burning and the ensuing dilution of lubricant oil, which leaks through the walls of the piston/cylinder assembly.

Gasoline quality control is based on ASTM methods [4], being distillation (D-86) the most appropriate one to verify its volatility characteristics. It allows anticipating engine work conditions based on data relative to the initial point, 10, 50 and 90% evaporation, and final boiling point. These points allow controlling volatilization of light, intermediate, and heavy gasoline fractions, and the formation of residues (gums) during the gasoline combustion process inside the engine.

In Brazil, gasoline is added with a mixture of either anhydrous alcohol (ethyl alcohol obtained from sugar cane) to produce type C gasoline (22 to 25%) or methyl-tert-butylic ether (MTBE) to produce type B gasoline (12% MTBE until April 1999 only in the State of Rio Grande do Sul). The regulations for quality control of fuels are ruled by a governmental agency, ANP (Agência Nacional do Petróleo) [2, 5]. But, in Brazil, the addition of other organic solvents (like kerosene, toluene and other heavy aliphatic, light aliphatic and aromatics) in gasoline is very frequent, although illegal, and this practice does not guarantee gasoline

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quality. Contamination of gasoline by solvents during and after its production leads to variations of its physical-chemical characteristics, which affects fuel stability and volatility, damages engines, and results in low engine performance. Many a time criminal contamination by dealers seeking to maximize profits occurs. This practice is a crime against consumers and the national treasure, and therefore it must be repressed. In view of this, it is imperative the analysis of the thermal stability and the volatility conditions of gasoline to assure its quality control.

Several studies were made about additives in gasoline and fuels, using different techniques, as RMN, gas chromatography, distillation curves, high-resolution TG, to detect contamination or solvent addition [6–9]. Statistical analysis and thermodynamic model were developed to study Brazilian gasoline [10, 11].

Thermogravimetry (TG) can contribute to the study of the thermal behavior of gasoline, either with or without adulterant (solvents) [12, 13]. With pure compounds, this technique affords experimental records typical of the material under study, being frequently so characteristic that they allow the identification of simple mixtures.

This work evaluated the thermal behavior of gasoline doped with kerosene by thermogravimetry. This solvent is the fraction after gasoline and before diesel in the distillation of petroleum and it predominately contains paraffinic compounds distilled in the 150–300°C range.

This work by TG/DTG is an innovation in the analysis of liquid fuels, which requires technique improvement. Analysis conditions used to evaluate the analytical interferences of sample mass variation were flow and draft gas type, and the heating rate [14–17].

Experimental

Samples were prepared in our laboratories using type A gasoline supplied by PETROBRAS – Refinaria Gabriel Passos, REGAP/Betim. Type C gasoline (GC0%) was prepared by adding 240 mL anhydrous ethyl alcohol p.a., from Merck to 760 mL type A gasoline. Samples of gasoline type A, gasoline type C, and gasoline type C doped with kerosene had their physical-chemical properties determined using specific ASTM standards. Mixtures of gasoline and commercially available kerosene were prepared from the sample of type C gasoline. Aliquots of kerosene were added with the aid of burette so as to obtain concentrations equivalent to 2, 4, 6, 10 and 20% volume. The samples were identified as GC2%, GC4%, GC6%, GC10%, and GC20%, respectively.

The experiments were carried out in the thermobalance TGA50H from Shimadzu. Alumina crucibles of 70 μL with perforated lid were used as sample support. The heating rate used was 50°C min^{-1} under dynamic nitrogen atmosphere with a flow rate of 100 mL min^{-1}. The mass used was approximately 19 mg.

Results and discussion

Table 1 shows the physical-chemical characteristics of gasoline type C, and gasoline type C doped with kerosene. Tests of distillation method ASTM D-86, density 20/4 ASTM D 1298, and alcohol content were carried out.

It was observed that the addition of kerosene to gasoline sample does not affect the distillation temperature corresponding to distillates 10, 50, 90%, density and FBP – final boiling point – significantly. There is a small variation in temperature for 90% distillate and FBP only for the sample doped with 20% kerosene, which would compromise volatilization of heavy fractions and result in the formation of soot and residues as combustion products.

Figure 1 shows the TG curve of solvent-free gasoline (gasoline type A). It is observed that the mass loss is gentle and continuous, characterized by overlapping of four rather discrete events. DTG curve allows the observation of the overlapping events.

Figure 2 shows the TG/DTG curve of anhydrous alcohol. Its volatilization occurs in a single, smooth, and continuous stage. Mass loss occurs in the interval 59–193°C. The DTG peak indicates a maximum mass loss around 160°C.

Table 1 Analysis of gasoline type C and gasoline type C doped with kerosene

Distillated fraction/°C	Specification values	GC0%	GC2%	GC4%	GC6%	GC10%	GC20%
10%	60 max.	60.6	58.0	57.9	60.0	58.9	62.2
50%	80 max.	70.6	72.6	73.5	73.7	73.6	114.0
90%	145–190	166.0	172.4	179.1	182.2	187.8	199.9
FBP	220 max.	212.0	215.9	220.4	222.6	223.4	228.8
$d_{20/4}$ g mL^{-1}	–	0.7585	0.7599	0.7585	0.7608	0.7406	0.7541
Alcohol/V%	24±1	24.1	24.1	24.0	24.0	24.3	24.2

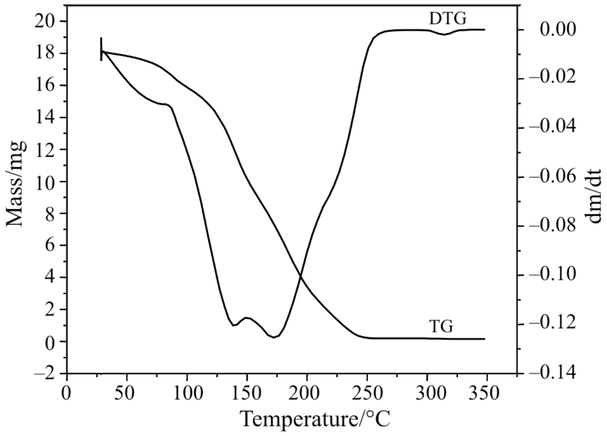

Fig. 1 TG and DTG curves of gasoline type A

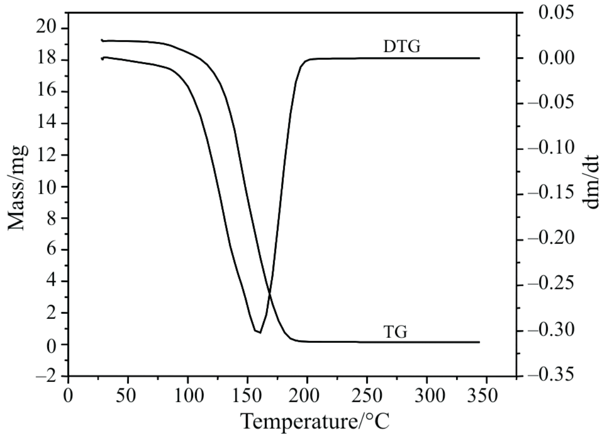

Fig. 2 TG and DTG curves of ethyl alcohol

Figure 3 shows the overlapping of the TG curves of alcohol, gasoline type A and gasoline type C. It is observed that the addition of alcohol to gasoline produces a differentiated separation of some fractions of gasoline, which occurs in three distinct stages. It can be seen that the addition of alcohol, as allowed by law, affects the volatility characteristic of some gasoline fractions, making the mass loss more pronounced in comparison to the mass loss given by the TG curve of type A gasoline. Figure 4 shows the overlapping of the DTG curves, which allows a better observation of this event.

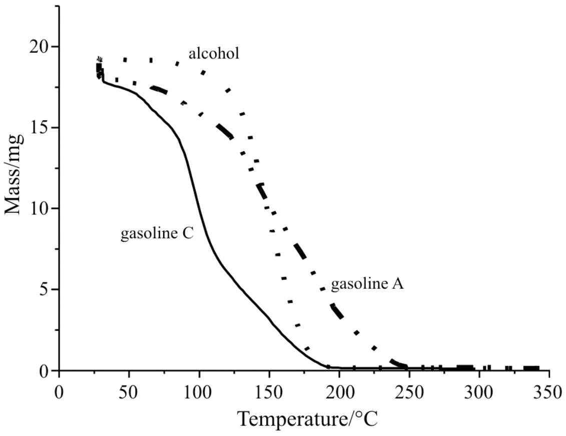

Fig. 3 TG curves of gasoline type A, gasoline type C and ethyl alcohol

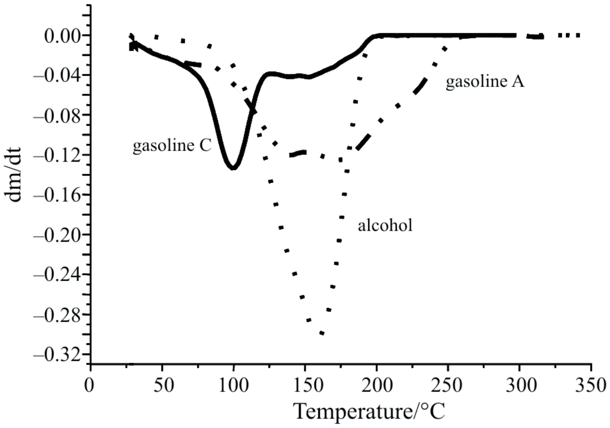

Fig. 4 DTG curves of gasoline type A, gasoline type C, and ethyl alcohol

From TG and DTG curves, it can be anticipated that the mass loss of type C gasoline occurs in three stages, which corresponds to the volatilization of the light fractions (first event), intermediate fractions (second event), and heavy fractions (third event). The first event overlaps the second one, which makes its observation difficult. Table 2 presents the transition temperature ranges obtained from TG/DTG curves of gasoline type C.

Figure 5 displays the overlapping of the TG curves of samples of gasoline type C doped with kero-

Table 2 Events observed on TG and DTG curves of gasoline type C

TG	Temperature/°C	Event
1st mass loss	32.8–74.1	Vaporization of light fractions
2nd mass loss	74.1–134.5	Vaporization of intermediate fractions
3rd mass loss	134.5–221.3	Vaporization of heavy fractions
DTG	**Temperature/°C**	**Event**
1st peak	100.5	Vaporization of light and intermediate fractions
2nd peak	164.7	Vaporization of heavy fractions

Table 3 Mass loss (%) observed in TG curves of the gasoline type C doped with kerosene

	Mass loss/%					
	GC0%	GC2%	GC4%	GC6%	GC10%	GC20%
1st step	10.3	13.3	11.4	11.4	9.9	13.4
2nd step	55.8	45.4	44.0	42.9	40.3	32.8
3rd step	28.3	33.3	38.8	39.9	42.1	46.9

sene. The curves of gasoline type C and kerosene are also shown. According to the TG curves, the addition of kerosene to gasoline does not provoke significant changes in its thermal behavior. DTG curves (Fig. 6) allows the observation of these changes.

The addition of kerosene to gasoline type C affects the volatility of heavy fractions of the fuel, which is evidenced by the broadening of the third event recorded in DTG curves.

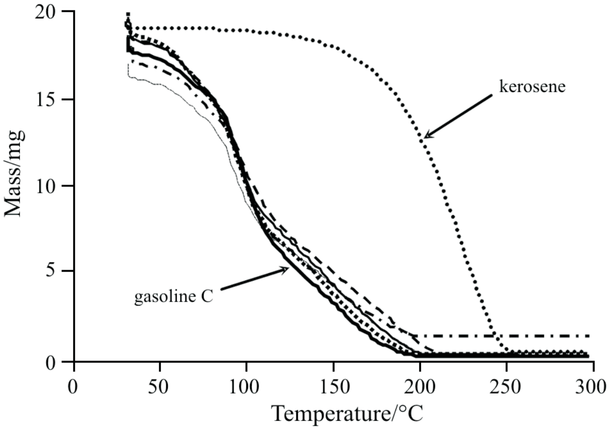

Fig. 5 TG curves of gasoline type C doped with kerosene, gasoline type C and kerosene

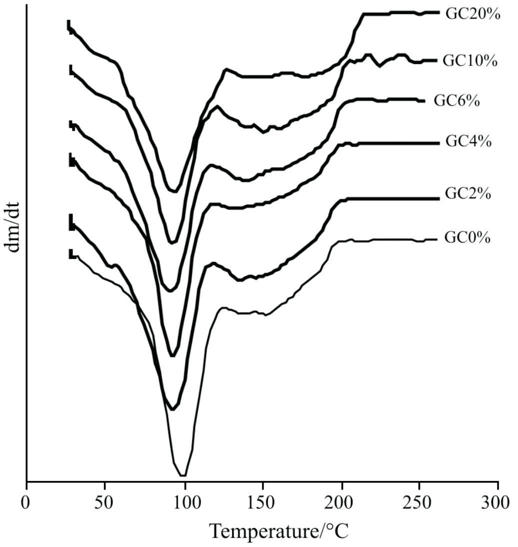

Fig. 6 DTG curves of gasoline type C doped with kerosene

Table 3 presents the mass losses (in %) obtained in TG curves of the samples of the gasoline doped with kerosene where is observed the decreasing mass losses in the 2nd stage and increasing mass losses in the 3rd stage in relation to the gasoline type C. These observations are explained by the components of the kerosene; the heavy fractions have difficulties to volatilize and tend to stay in the crucibles making the mass loss more slowly.

Although the maximum degradation temperature of kerosene is approximately 240°C, it is not observed the degradation of the gasoline samples doped with kerosene at this temperature, even with 20% content.

Conclusions

In internal combustion engines, the changes in fuel properties may provoke problems related to fuel detonation as the heavier fractions tend to build up in the cylinders and promote the formation of residues and the incomplete burning of hydrocarbons. As a result, the vehicle will present power loss and harm the environment. The addition of kerosene to gasoline provokes modifications in the thermal behavior of the gasoline causing variations in the volatility of the components of the heavy fractions. This alteration may cause problems related to the detonation of the combustible in combustion engines because the heavier fractions tend to accumulate in the cylinders of the cars.

The thermogravimetric (TG) curves of the samples of type C gasoline doped with kerosene display reduced mass loss in the second stage, relative to the volatilization of light and intermediate fractions, and increased mass loss in the third stage. This change is explained by the composition of kerosene, which is a mixture of hydrocarbons of high molar mass. Its constituents tend to concentrate in the heavier fractions, building up in the pan and making volatilization difficult and slowing down mass loss. Even with 20% kerosene, there was no significant change of onset temperatures of gasoline adulterated with kerosene. The DTG curves are more suitable than the TG curves for this comparative study.

TG/DTG can be used as an auxiliary tool in the study of the thermal behavior of gasoline, presenting fast comparative answers of easy interpretation.

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References

1 Petróleo Brasileiro S/A., Manual de Produtos de Petróleo, Petrobrás, Centro de Pesquisas e Desenvolvimento Leopoldo Miguel de Mello (CENPES), Rio de Janeiro 1990.
2 ANP (Agência Nacional do Petróleo), avaiable at: http://www.anp.gov.br, accessed at June 13, 2004.
3 G. W. Castellan, Physical Chemistry, 2nd Ed., Addison-Wesley, Reading 1972.
4 ASTM D86-99a, Standard Method for Distillation of Petroleum Products at Atmospheric Pressure; ASTM International, 1987.
5 M. S. Rocha and J. R. Simões-Moreira, Fuel, 84 (2005) 447.
6 A. Zanier, J. Therm. Anal. Cal., 64 (2001) 377.
7 F. S. Oliveira, L. S. G. Teixeira, M. C. U. Araujo and M. Kom, Fuel, 83 (2004) 917.
8 N. Kosal, A. Bhairi and M. A. Ali, Fuel, 68 (1990) 1012.
9 J. Burri, R. Crockett, R. Hany and D. Rentsch, Fuel, 83 (2004) 187.
10 L. S. M. Wiedemann, L. A. d'Avila and D. A. Azevedo, Fuel, 84 (2005) 467.
11 T. Lanzer, O . F. Meien and C. I. Yamamoto, Fuel, 84 (2005) 1099.
12 M. L. Felsner and J. R. Matos Jr., Anais da ABQ, 47 (1988) 308.
13 G. D. Christian and J. E. O'Reilly, Instrumental Analysis, Allyn and Bacon Inc., Boston 1986.
14 R. F. Speyer, Thermal Analysis of Materials, Marcel Dekker Inc., New York 1994.
15 R. F. Schwenker and P. D. Garn, Thermal Analysis-Proceedings of Second International Conference on Thermal Analysis, Vol. 1 and 2, Academic Press, New York 1972.
16 W. W. Wendlandt, Thermal Analysis, 3rd Ed., John Wiley & Sons, New York 1986.
17 T. Hatakeyama and Z. Liu, Handbook of Thermal Analysis, John Wiley & Sons, Chichester 1998.

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