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The characterization by chromatographic methods of petroleum fractions from thermocatalytical processes

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Abstract. Following a previous study about the characterization of crude oils and fractions by combining the chromatographic methods, the working method was extended to petroleum fractions from thermocatalytical processes. The present study is limited to fractions with final boiling point up to 300°C from the Coke unit and the Fluid Catalytic Cracking processes. The composition of the gasolines was found by GC – PIONA method; then, the list of compounds found in gasolines and middle distillates was obtained by GC-MS. The PAHs content in distillates was analyzed by HPLC method. Conclusions appeared concerning the PAHs distribution depending on the process parameters. Also, the optimum parameters for the GC-MS method were found in order to study the occurrence of aromatic compounds in petroleum fractions.

Keywords: oil fractions, GC-PIONA, GC-MS, HPLC

1. Introduction

In a previous study about the characterization of crude oil and crude fractions by combining chromatographic methods, it was demonstrated the possibility to find more about the chemical composition by applying the separation scheme described there [1].

Here, the work continued, by applying the method to petroleum fractions obtained in thermocatalytical processes [2].

The practical goal of the work was to find regularities about the distribution of some hydrocarbon classes, especially the polycyclic aromatic hydrocarbons (PAHs), which can be used as markers for finding the pollution source with spill oil [3,4].

2. Experimental

The following products of the main thermocataytical cracking processes in an oil refinery the Coke Unit and the Fluid Catalytic Cracking, were analyzed: the gasolines and the middle distillates (with final boiling point up to 300°C). The petroleum products were obtained by processing a naphthenic crude oil (crude oil C, in [1]).

Narrow fractions were obtained through distillation in order to have a reduced number of compounds to identify and separate, for more accurate results.

The gasolines were analyzed by the GC method PIANO, ASTM D 5443-04, with a HP 6890 apparatus, with the following columns: OV275, Eth/Alc, Olefin, Molecular sieves 5A, HP1, Porapack, Molecular sieve 13 X, Precolumn. The operating conditions are shown in **Table 1.** The chromatograph separates the hydrocarbon classes as following: i-Parafins, n-Parafins, Naphthenes, Olefins, Aromatics, hydrocarbon with boiling point >200°C and poly-Naphthenes. This method quantifies the hydrocarbon classes on fractions: C_3 , C_4 , …$C_{11.}$

The following fractions were analyzed by PIANO method: the whole FCC gasoline and the light cut of Coke gasoline (boiling points up to 100°C); the whole Coke gasoline or its heavy cut were not proper for the PIONA analysis because of the high sulfur content and coke suspensions.

Table 1. Operating parameters of the GC (model HP 6890), method PIANO for gasolines, ASTM D 5443-04

Injection temperature	130°C
Detector A	190 °C
Detector B	140 °C
Temp. Heater1	330°C
Temp. Heater2	180°C
Temp. Heater3	150°C
Temp. Heater4	150°C
Temp. Heater5	150°C
Flow rate	30 mL/min

Then, the FCC gasoline cut into narrower fractions (cut at 100°C) and the middle distillate fractions (boiling points up to 300°C) were analyzed by GC-MS method for obtaining a comprehensive list of hydrocarbons. The gas chromatograph - mass spectrometer with thermodesorption was GC 6890 and MS 5973 Agilent. For fluid samples the "Gerstel Twister stir bar sorbtive extraction" technique (Gerstel, Mulheim an der Ruhr) combined with the thermal desorption [4,5,6]. The twister adsorbs and concentrates the organic compounds on the surface of the polydimethylsiloxan film (PDMS). The thermal desorption unit (TDS2) has as a main performance the quantitative recovery of high molecular weight compounds. The Cold Injection System (CIS) focuses, concentrates and transfers the compounds in the capillary column. The pneumatic devices of the CIS are controlled by Agilent Chemstation software. All the other TDS or CIS parameters are controlled by Gerstel 505 and are accessed by the Gerstel MASter software. The column is 30 m long, with the inner diameter of 0.25 mm. It is packed with a non-polar substance: 5%-(phenyl)-methylpolysiloxane, very selective for hydrocarbons.

The apparatus worked in the conditions described in **Table 2.**

The GC-MS was also used for the analysis of middle distillates (Coke gas oil and FCC light gas oil, fractions170-270°C), in order to obtain a comprehensive list of aromatic hydrocarbons.

Table 2. Operating parameters of the GC-MS for the identification of hydrocarbon, sulfur compounds and oxygenated compounds in petroleum fractions

Sample concentration	1-2µL/100 mL in water or in methanol/water solvent (15% vol. metanol)
TDS mode	Splitless; from 20°C to 300 °C, heating rate 20 °C/min (10 minutes)
CIS mode	- 45 °C (1.5 minutes), up to 300 °C , heating by 12 °C/sec (10 minutes)
Splitting rate at the column	10/1
Initial pressure	7.04 psi
Column	Agilent HP-5MS
Flow (constant)	1 mL/min
Velocity	36 cm/sec
Oven	40 °C (2 minutes) up to 150 °C, heating rate:10 °C/minut ; 6°C/min up to 300°C (1 minute)

Then, the HPLC method SR EN ISO 17993 was applied to quantify the polycyclic aromatic hydrocarbons in the middle distillates.

The standard substances were supplied by Supelco (PAHs mix 10µg/mL), Sigma Aldrich (2,6-Dimethyl naphthalene) and Merck (1-Methyl naphthalene). The sample preparation consisted on making up dilutions of petroleum fractions (previously cleaned by adsorption on alumina), in ACN solvent (2-4 µg/ 10 mL ACN).

The HPLC analyze was performed on a Varian apparatus model ProStar with fluorescence detector and a column ChromSep HPLC SS100x4,6 mm Pursuit 3 PAH.

The method and the operating conditions were those in the **Table 3.**

Table 3. The operating conditions for the determination of PAHs by HPLC, method SR EN ISO 17993

Flow rate: 0.70 mL/min, initial to the min.5 (50%water+50%ACN), gradient from min.5 to 35 up to 100% ACN, from min.35 to 45- isocratic.

Lamp:

Time(min)	Excitation (nm)	Emission (nm)
0	275	350
17.5	260	420
19.5	270	440
22.5	260	420
28.0	290	430
37.0	250	500

3. Results and discussions

The composition of the gasolines given by the GC- PIANO method is presented in the **Table 4.**

Table 4. The comparative composition of FCC gasoline and Coke gasoline, by GC-PIANO, %wt

Hydrocarbon class	FCC gasoline	Light coke gasoline
Naphthenes C5-C9	7.69	12.97
Parafins C4-C9	31.37	39.34
Cy Olefins C5-C10	2.84	9.75
Olefins C3-C11	19.99	32.77
Aromatics C6-C9	34.15	5.17
High boiling aromatics	2.22	-
High boiling saturates	1.25	-
Polynaphthenes	0.49	-

These results confirm other sources on the composition of these types of gasoline [8,9], but some new compounds can be separated in the conditions of the optimized method (polynaphthenes, high boiling point saturates, high boiling point aromatics). It was also observed the distribution of aromatics in thermocatalytical product gasoline (B:T:X= 1:4.7:8.7), very likely with the distribution in gasoline distillated from crude oil (1: 4.4: 7.4). It is due to the fact that benzene, Toluene and Xylene proceed from the crude oil and they are not formed during the Fluid Catalytic Cracking or in the Delayed Cocking processes.

The GC-MS method applied on the FCC gasoline, light cut heavy cut and large fraction, in the conditions described in the Table 2, gave very interesting results since the short list of 50 compounds (the most abundant 50 compounds in the chromatogram) contains almost exclusively aromatic hydrocarbons. Only in the larger list of 150 compounds appeared the parafins, the naphthenes and the olefins, at low abundance. This is the proof that the sorptive bar technique is very selective for the aromatic compounds. For example, in the Figure 1, the chromatogram for the heavy fraction of FCC gasoline shows the following main peaks:

-Etilbenzene: 6.12;
-*m*+*p*-Xylene: 6.26, 6.59;
-Propylbenzene:7.49;
-trimethyl-Benzene isomers and ethyl-methyl-Benzene:7.68, 7.78, 7.94, 8.14, 8,63;
-tetramethyl-Benzene and ethyl-dimethyl-Benzene: 9.04, 9.20, 9.31,9.50, 9.65, 9.84, 9.91, 10.06
-1-methyl-Indan: 9.68;
-Naphthalene: 11.20;
-pentamethyl-Benzene, ethyl-trimethyl- Benzene: 11.27, 11.32, 11.35, 11.45, 11.56, 11.89;
-dimethyl 1H- Indene: 12.04, 12.09, 12.22
-2-methyl- Naphthalene: 12.67

Other major peaks (retention time 5.52 and 12.93) belong to derivatives of siloxane, produced during the degradation of the polysiloxane film.

In the chromatogram for the light FCC gasoline, appeared the same list of compounds until the Naphthalene and additionally lighter hydrocarbons: Benzene at 4.03 min and Toluene at 4.94 min. Also, some other hydrocarbon than aromatics were identified:

-2-methyl 2-Butene: 3.44
-2 methyl- Pentane: 3.69
-2-methyl- Hexane: 3.95
-1-3 dimethyl- Cyclopentane: 4.08
-methyl- Cyclohexane:4.41
-2,4 dimethyl- Hexane:4.49;
-2-methyl Heptane:4.84
-Octane:5.27

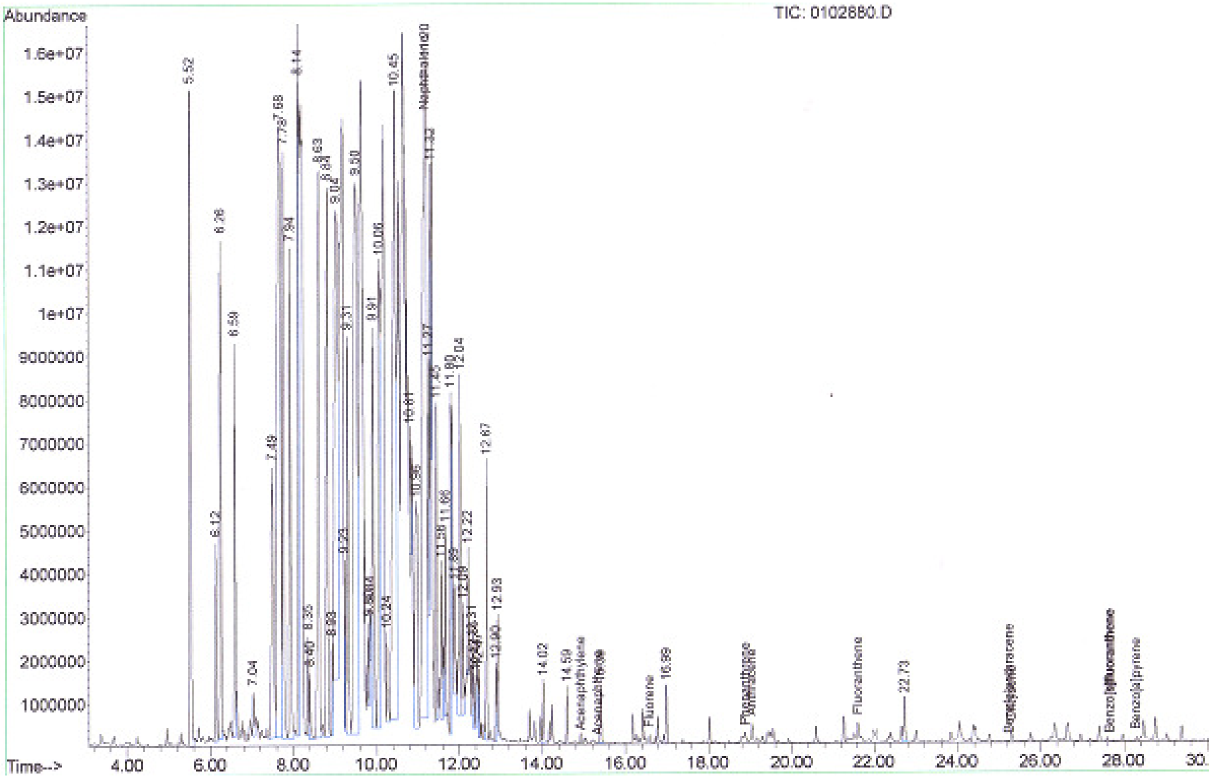

Fig.1. GC-MS chromatogram for the heavy cut of FCC gasoline

After 6.13 min. (Ethylbenzene), all the identified compounds were aromatics, this being due to the selectivity of the stir bar technique for aromatics.

The GC chromatograms for middle distillates are different, not only by the compounds identified but also by the aspect of peaks, indicating a poorer separation of the compounds comparing with gasoline.

In Figure 2, the chromatogram for the Coke gas oil is shown. The bulk of peaks is settled between retention times 7.61-13.10 min, comparable with the FCC gasoline (Figure 1), but other aromatics are specific for gas oil. Ex:

- 2-methylpropyl Benzene-9.08 min
- 1-methyl Indan- 9.58
- 2-butenyl Benzene-10.57
- 1,2,3,4 tetrahydronaphthalene-11.27, 13.10
- pentamethyl Benzene – 11.41, 11.54
- 3-Phenyl -2- Pentene- 11.79

Heavier aromatics are:

- dimethyl Naphthalene- 14.35 , 14.54
- trimethyl Naphthalene-16.51
- Anthracene-20.09

Unlike the lighter alkanes, heavier alkanes were also adsorbed on the twister: Decane (8.16), Undecane (9.70), Tetradecane (14.12), Pentadecane (15.65), Heptadecane (18.75), Octadecane (20.18).

Some olefins are identified (3-Phenyl-2-Pentene-11.79 and 1-Hexadecene-21.45). The great peak between 17.16-17.58 is identified with 40-50% probability as a sulfur compound: (thio) S-decyl ester of Butyric acid.

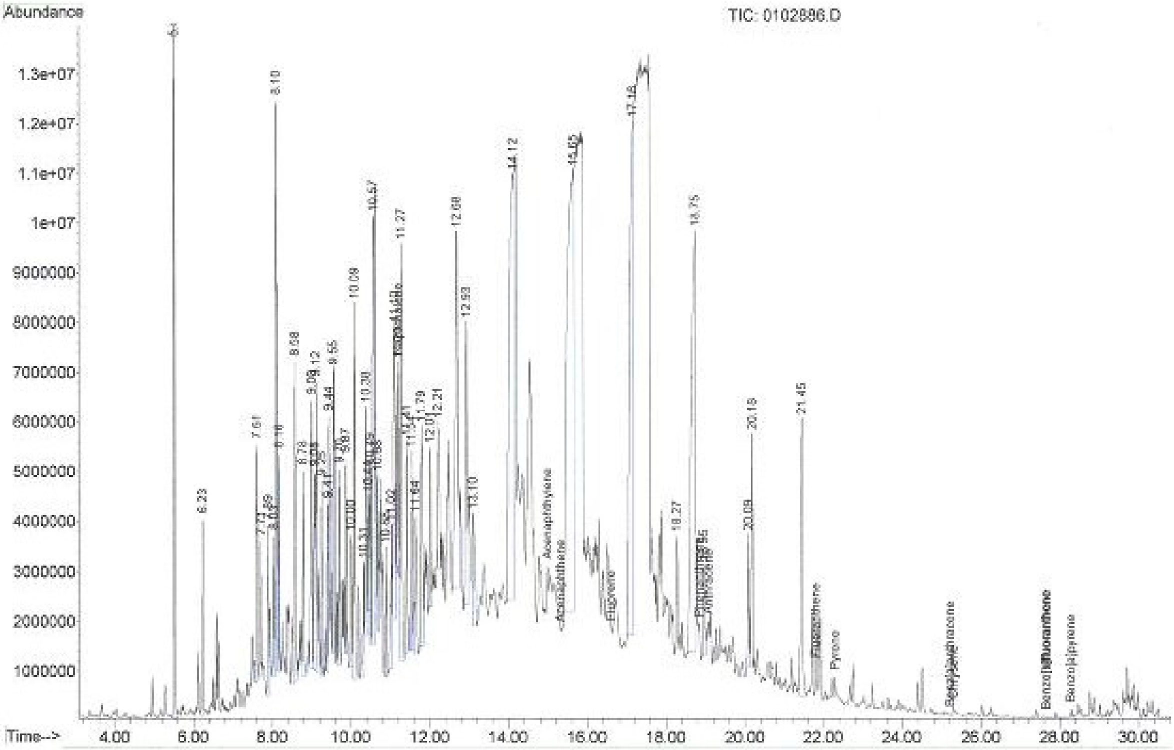

Fig.2. GC-MS chromatogram for the Coke gas oil

The chromatogram for the FCC gas oil 170-270°C contains heavier aromatics, including PAHs:

- 1-(2 butenyl)-2,3 dimethyl Benzene -12.36
- 1-methyl Naphthalene +2-methyl Naphthalene- 12.79, 13.08, 13.10, 13.13
- Biphenyl-13.86
- Ethyl- Naphthalene- 14.11, 14.16, 14.20
- Dimethyl- Naphthalene- 14.35, 14.39, 14.67, 14.73, 14.91, 14.95, 15.11 (all isomers)
- Methyl-1,1'-Biphenyl- 15.45,17.22
- 1-propyl- Naphthalene- 15.51
- Trimethyl- Naphthalene- 15.86, 15.9516.03, 16.13, 16.22, 16.43, 16.50, 16.69, 16.73, 17.04
- Fluorene- 16.98
- 9-methyl-9H-Fluorene- 18.87

The HPLC analysis of the middle distillates served to quantify some of the polycyclic aromatic hydrocarbons, for the standard substances available.

As expected, the FCC gas oil contained more PAHs than the Coke gas oil, as seen in Table 5.

Table 5. The comparative PAHs content in FCC gas oil and Coke gas oil (HPLC analysis)

Compound	FCC gas oil	Coke gas oil
Naphthalene	7.2%	1.3%
α-methyl Napthalene	5.05%	1.1%
Fluorene	0.5%	-
Phenantrene	3.5%	0.5%
Acenaphthene	traces	-
Benzo [a]anthracene	traces	-
Crysene	traces	-
Indeno [1,2,3-c,d] pyrene	ND	1.25%

4.Conclusions

The hydrocarbon composition of light and middle distillates from thermocatalytical processes can be found by chromatographic methods.

The composition of the gasolines is given as hydrocarbon classes and separate for the number of carbon atoms in the molecule. The PIANO method can also measure high boiling aromatics (C10+), high boiling saturates (C10+) and polynaphthenes (C11+). The method can be applied for low sulfur gasolines (up to 2% sulfur) and no suspensions; this is why, in the present study, the Coke gasoline had to be split into 2 fractions and only the lighter was analysed.

The GC-MS method, adsorption on stir bar technique, permits to identify all the aromatic compounds and heavier alkanes, rarely some sulfur or oxygene compounds, at the work parameters described in this paper. This is due to the selectivity of the polysiloxane film for some of the compounds.

The HPLC method permitted the study of the PAHs occurrence in the petroleum fractions. It was observed a big difference between the Coke gas oil and FCC gas oil, the last one containing more compounds and in greater concentration. For both fractions, the Naphthalene was the main PAH.

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6. References

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