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The Use of Gas Chromatography for Albanian Crude Oil Characterization

Xhaklina Cani[1], Ismet Beqiraj[2] & Ilirjan Malollari[3]
[1,2&3] Group of Chemical Engineering, Departament of Industrial Chemistry, Faculty of Natural Science, University of Tirana, Albania

Abstract: *Crude oil is a very complex mixture of organic compounds including aliphatic, aromatic and heterocyclic compounds. In order to predict the phase behavior of crude oil mixtures accurately, some description of the oil composition is required. One common laboratory procedure for describing an crude oil is the use of Gas Chromatography to estimate the carbon number distribution of an crude oil. Characterization of crude oils mainly involves characterization of hydrocarbon plus fractions generally expressed in terms of C_7+ fractions. Crude oil is produced by separating light gases from a reservoir fluid and bringing its condition to surface atmospheric pressure and temperature. Therefore, crude oils are generally free from methane and contain little ethane. In this study are determined the constituent components of two important oilfield crude oil in Albania, Kuçova and Ballshi. Determination of the components is done with Varian 450 Gas Chromatography. The study conclude that the oil obtained in the analysis consist mainly of light compounds, and they have a high content of aromatics and naphtenes.*

Keywords*: crude oil, Gas Chromatography (GC), characterization, distillation.*

1. Introduction

Albania consists of seven major oilfileds, which are part of the south-west in our country. Oilfields in Albania divided into sand and limestone. A major part of our country's oilfields are privatized by foreign companies.
Crude oil is naturally occurring oil, bituminous liquid composed predominantly of various organic chemicals. It is found in large quantities below the surface of the earth and the products are used as fuels and as raw material in the chemical industries [1,2]. Crude oil is also known to contain mixture of hydrocarbons including alkanes, naphtenes and aromatics and heteroatom compounds of sulphur, nitrogen and oxygen as well as trace metals [3,4]. Under surface pressure and temperature conditions, lighter hydrocarbons such as CH_4, C_2H_6, and inorganic compounds such as N_2, CO_2 and H_2S occur as gases, while pentane and heavier ones are in the form of liquids or solids.

The crude oil is composed of a large amount of alkanes with different carbon numbers giving rise to a broad range of boiling point. The understanding of the carbon number distribution of crude oil can help to precisely evaluate the factors affecting the properties of crude oil and oil products. It is also important for the designing of the distillation processing equipment and the quality control of the products [5].

Gas Chromatography has the advantages of high column efficiency, high sensitivity, fast analysis speed and ease to be combined with other analytical methods (e.g. Mass Spectrometry) [5]. Thus, it is widely used to analyze crude oil and its products. For this purpose is used Gas Chromatography, to determine the composed components of two samples taken in the study. Gas Chromatography (GC) is a powerful method for both qualitative and quantitative analysis of volatile compounds. Quantitative analysis can be accomplished through the use of a flame ionization. Identification of the components in a mixture is carried out by comparing the retention times of the components in the mixture with the retention times of pure, known samples (standards). Oilfield samples analyzed are Ballshi and Kuçova. Samples are taken in the inlet of decantation plant, before passing through the desalination and dewatering process.

2. Materials and Methods

Samples analyzed in the study include Ballshi and Kuçova crude oil. Data are produced from analysis of the fluid by gas chromatography columns. Samples are initially distilled by ASTM D86 standart. During the distillation process are taken three fractions (0-200°C, 200-300°C and 300-360°C). Then to determine the constituent components, the fractions obtained from the distillation were analyzed by Gas Chromatography [6]. A Varian 450 Gas Chromatography is used for these analyses (Figure 1). The GC is equipped with a PTV injector with flame ionization detector (FID). The separation of hydrocarbon compounds is realized in VF-1ms capillary column. Injector temperature and detector respectively settled at 280◦C and 300◦C . The injection method was chosen

split (1:100). As a carrier gas and auxiliary gas is used nitrogen with a total flow 1 ml/min and 24 ml/min. The initial furnace temperature is maintained at 50◦C for 2 min then is increased to 150◦C for 60◦C/min. Each sample is maintained at 300◦C for 2 minutes and injected on a volume of 2 µl. Quantitative data analyzed compounds are given in % amount. Relative amounts of each component in crude oil is obtained by measuring the peak area to the peak areas of an unknown mixture.

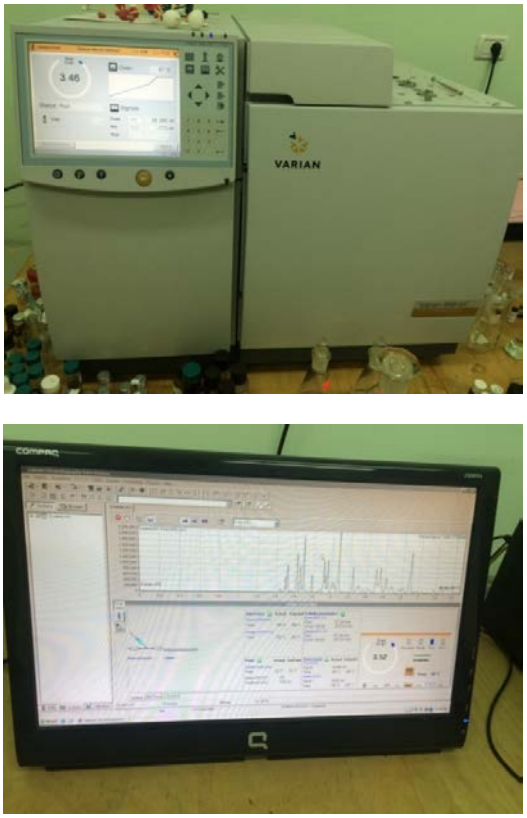

Figure 1. Varian 450 Gas Chromatography with flame ionization detector (FID).

3. Results and Discussion

Analysis of crude oil samples (Kuçova and Ballshi) resulted in the gas chromatography (450 Varian GC) are shown in figure 2.

Compounds component for second fractional in Kuçova and Ballshi crude oil samples are shown in figure 3 and 4.

Figure 5 presents component in third fraction for Kuçova and Ballshi crude oil.

Kuçova oilfiled samples have a small content of heavy compounds compared with Ballshi crude oil (Figure 2).

The second fractions of the samples analyzed mainly consist of C_{12} up to C_{18}, for the both sample (Figure 3).

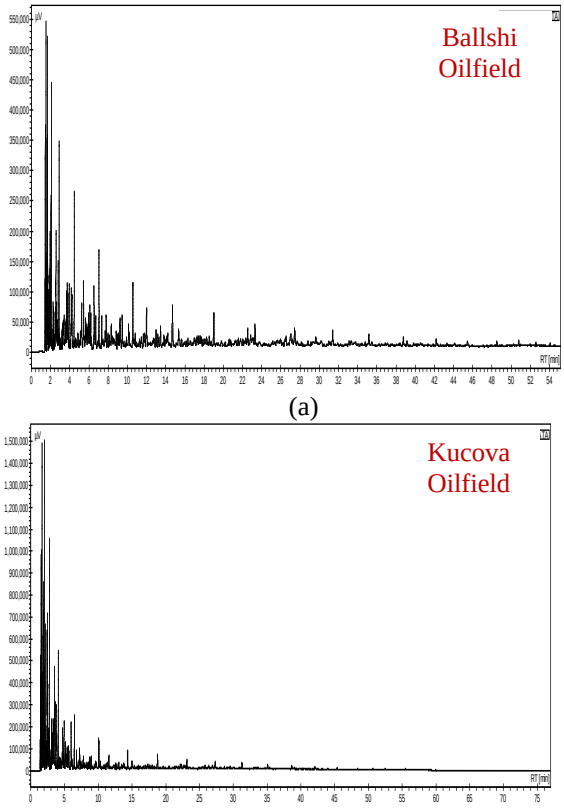

Figure 2. Gas Chromatogrphy for; (a) Ballshi and (b) Kuçova crude oil sample.

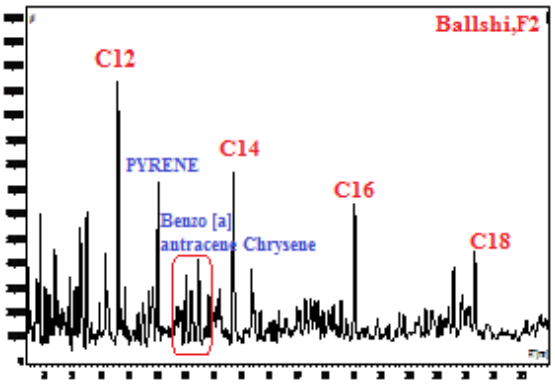

Figure 3. The second Ballshi crude oil fractional , Gas Chromatography.

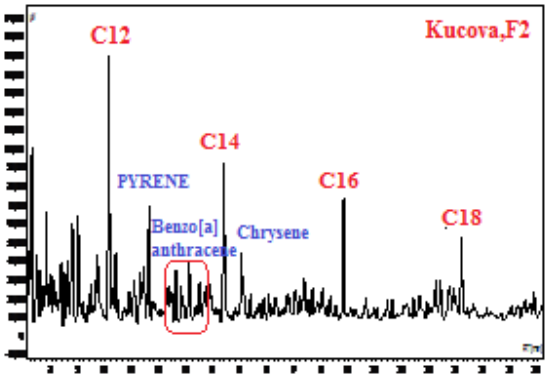

Figure 4. The second Kuçova crude oil fractional , Gas Chromatography.

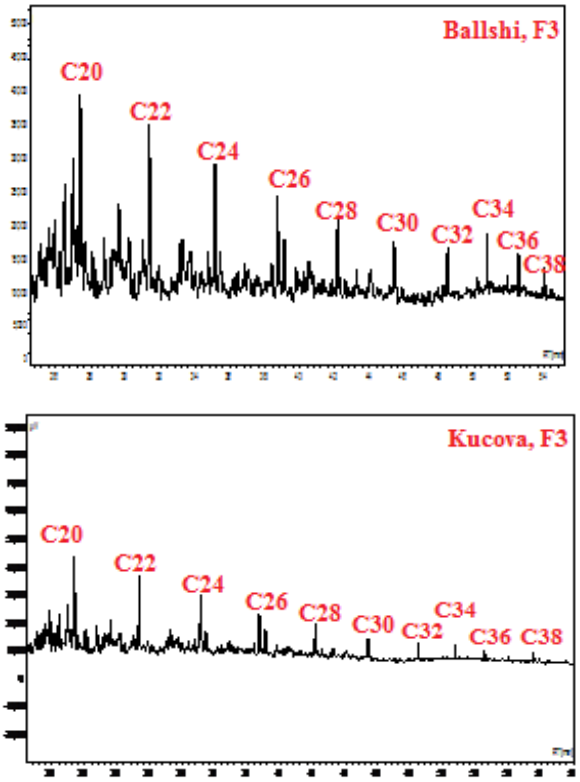

Figure 5. The third Ballshi and Kuçova crude oil fractional, Gas Chromatography

The third Kuçova fraction crude oil has a lower content of compounds from C_{20} up to C_{38} compared with Ballshi crude oil, shown in figure 5.

Table 1. Quantity component (% area) for Ballshi crude oil .

Ballsh , F1 (First fraction)	
Component	**Quantity [% Area]**
C_4	9.382
C_5	10.215
Benzene	3.978
C_7	6.965
Toluene	4.148
p-xylene	2.227
m-xylene	2.036
o-xylene	1.849
C_8	4.24
Ethylbenzene	4.157
C_9	13.351
Naphthalene	4.824
Ballsh, F2 (Second fraction)	
Component	**Quantity [% Area]**
C_{10}	1.883
Acenaphthylene	1.465
Fluorene	1.646
Phenantherene	2.887
Anthracene	2.239
C_{12}	3.615
Pyrene	4.387
Benzo[a] anthracene	4.441
C_{14}	3.316
Chrysene	1.39
C_{16}	2.391
C_{18}	1.809
Ballsh,F3 (Third fraction)	
Component	**Quantity [% Area]**
C_{20}	15.849
Perylene	1.728
C_{22}	3.712
Benzo[b]fluoranthene	2.108
Benzo[k]fluoranthene	2.193
C_{24}	2.396
Indeo [1,2,3 cd] pyrene	1.349
Dibenzo [ab] anthracene	1.617
Benzo [ghi] perylene	1.848
C_{26}	1.407
C_{28}	1.342
C_{30}	1.101
C_{32}	0.949
C_{34}	1.373
C_{36}	1.01
C_{38}	0.344

Ballshi crude oil oilfileds has a high content of light compounds (from C_4 up to naphthalene), shown in table 1. C_4, C_5, C_7, C_8 dhe C_9 include the total isomers of these compounds. The first crude oil Ballshi fraction has a high content of C_5 (10.215%) and C_9 (13.351%) compounds, while the lowest percentage is the o-xylene component (1.849%). The second crude oil Ballshi fraction consists primarily by the pyrenes and benzo [a] anthracene, 4.385% and 4.441% respectively. The third fraction consists mainly by C_{20} compounds, while in the lower percentage are the heavy compounds.

Table 2. Quantity component (% area) for Ballshi crude oil .

Kucove , F1 (First fraction)	
Component	**Quantity [% Area]**
C_4	22.297
C_5	10.875

Benzene	2.248
C_7	6.425
Toluene	5.026
p-xylene	3.287
m-xylene	1.94
o-xylene	2.025
C_8	3.703
Ethylbenzene	3.472
C_9	12.195
Naphthalene	2.68
Kucove, F2 (Second fraction)	
Component	**Quantity [% Area]**
C_{10}	3.668
Acenaphthylene	3.091
Fluorene	4.271
Phenantherene	2.572
Anthracene	1.501
C_{12}	4.609
Pyrene	4.399
Benzo[a] anthracene	4.012
C_{14}	3.641
Chrysene	2.295
C_{16}	2.707
C_{18}	1.896
Kucove,F3 (Third fraction)	
Component	**Quantity [% Area]**
C_{20}	15.96
Perylene	1.557
C_{22}	4.377
Benzo[b]fluoranthene	2.798
Benzo[k]fluoranthene	2.202
C_{24}	2.559
Indeo [1,2,3 cd] pyrene	1.741
Dibenzo [ab] anthracene	1.795
Benzo [ghi] perylene	2.076
C_{26}	1.711
C_{28}	1.344
C_{30}	1.073
C_{32}	0.764
C_{34}	1.103
C_{36}	1.254
C_{38}	0.195

Kuçova crude oil samples (Table 2) also have a high percentage of light components, but compared with the Ballshi sample the percentage of these components is higher. Compared with the first crude oil Ballshi fraction , Kuçova crude oil has a high content of C_4 (22.297%) and C_5 (10.875%), while the lowest percentage constitutes in m-xylene component (1.94%). The second crude oil fraction consists primarily of fluorene, pyrenes, C_{12} and benzo [a] anthracene, 4.271%, 4.399%, 4.609% and 4.012% respectively (Table 2). The third fraction consists primarily of C_{20} compounds, while the heavy compounds are in the lower percentage amount.

C_5, C_9, toluene, pyrenes, benzo [a] anthracene and C_{20} component are in large quantities in Ballshi crude oil. While Kuçova crude oil has a higher content of C_4 component (22.297%) and toluene (5.5026%) compared with Ballshi crude oil 9.382% and 4.148%. Pyrenes, benzo [a] anthracene and C_{12} component for both sample are almost in the same amount. Components amount of C_{10}, acenaphthylene and flourene make up the difference, these components are in greater amount in Kuçova crude oil, 3.668%, 3.091% and 4.271% respectively. The third fraction in the both oilfiled has a high content of C_{20} and low content from Indeo [123 cd] pirene up to C_{38} component.

4. Conclusions

This study demonstrates the utility of determining the chemical composition of crude oil samples with Gas Chromatography (450 Varian with Flame ionization detector), by distilled crude oil at the beginning. Saturated, aromatic, and heterocyclic compounds were identified using this method.

The study conclude that the oil obtained in the analysis consist mainly of light compounds. Compared with the first crude oil Ballshi fraction , Kuçova crude oil has a high content of C_4 (22.297%), while the lowest percentage constitutes in m-xylene component (1.94%).

Components amount of C_{10}, Acenaphthylene and flourene make up the difference, these components are in greater amount in Kucova crude oil, 3.668%, 3.091% and 4.271% respectively. The third fraction in the both oilfiled has a high content of C_{20} and low content from Indeo [123 cd] pirene up to C_{38} component.

C_5, C_9, toluene, Pyrenes, benzo [a] anthracene and C_{20} component are in large quantities in Ballshi crude oil. While Kuçova crude oil has a higher content of C_4 component (22.297%) and toluene (5.5026%) compared with Ballshi crude oil (9.382%). Pyrenes, benzo [a] anthracene and C_{12} component for both sample are almost in the same

amount. The crude oil Ballshi and Kuçova sample have a high content of aromatics and naptenes.

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