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فصل وتشخيص المكونات الاساسية للنفط الخام من حقل الراشدية - شرقي بغداد باستخدام تقنية الكروموتغرافيا

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الملخص:

تم فصل ودراسة المكونات الاساسية لنماذج من النفط الخام من حقل الراشدية الواقع شرقي بغداد، حيث جمعت النماذج وفصلت مكوناتها، الاسفلتين، المالتين والمركبات (المشبعة، الاروماتية والراتنج) باستخدام مذيبات عضوية مثل الهكسان. وقد تم فصل المالتين باستخدام تقنية كروموتغرافيا العمود (سائل - صلب) الى مكوناته من المركبات المشبعة، الاروماتية والراتنج والاسفلتين وهذة الطريقة تدعى اختصارا (SARA). استخدامت ثلاث طبقات امتصاص لغرض الفصل وهي الالومينا (Al_2O_3)، السليكا (SiO_2) ومزيج منهما لغرض فصل المكونات ودراسة نسبها المئوية. تمت كذلك تشخيص التركيب الكيميائي للمكونات المعزولة باستخدام تقنية (^{1}H- NMR, ^{13}C NMR)

كلمات دالة: الكروموتغرافيا؛ النفط الخام؛ المكونات الكيميائية؛ حقل الراشدية

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Fractionation and characterization of Crude Oil Components from Al-Rashidiya Field - Eastern Baghdad using Chromatography Method

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Abstract

Study and separating of crude oil components from Al-Rashidiya field - Eastern Baghdad- Iraq was achieved. Samples were taken and separated into two important parts Asphaltene and Maltin (saturated, aromatic and resin). The separation was done by organic solvent such as n-hexane. Maltin separated by column chromatography technique (liquid – solid) to basic saturated, aromatic and resin components, this technique called (SARA) (saturated, aromatic, resin and asphaltene). Three absorption layers used, alumina layer Al_2O_3, silica SiO_2 and combination layer from Al_2O_3 and SiO_2. All the components were collected dried and weighted. In order to determining the classification types, isolated compounds

were studied spectrally using NMR spectrum (^{13}CNMR, ^{1}HNMR) by identify structures of separated materials.

Keywords: Chromatography, Crude oil, Chemical composition, Al-Rashidiya Field,

1. Introduction

Crude oil is a profoundly complex blend of organic components, extending from little particles in vaporous state to bigger fluid molecules. The partitions of these mixes at refineries are for the most part performed by the boiling point ranges, accordingly creating profitable products. The chemical compounds of a raw petroleum are grouped by its SARA content (saturates, aromatics, asphaltenes and resins). Commonly, a wax makes up around 14%. The cyclic (naphthenic) and branched compounds represent for 16 and 30%, respectively, while the aromatics make up around 30% and asphalting – resins 10% [1]. The asphaltene is available in the heaviest division of crude oil and signify one of the fundamental sources problem for the crude oil business, among them precipitation amid generation and transport, harming amid refining, other than the adjustment of water in oil emulsions. The asphaltenes divisions are the most polar in the unrefined oils and show up as dull solids that don't dissolve and break down at 300 to 400℃. They increase the crude oil density and viscosity, hindering its transport and are also responsible for its color (brown to black). During crude oil refining in a fractionation Colum, the asphaltenes portion are not refined, staying cemented alongside with the resins. This refining deposit is called asphaltic residue [2],[3],[4],[5]. Asphaltene and resin can be isolated by dissolving them in non–polar solvents (paraffinic) such *n*-pentane or *n*-heptane, creating precipitates that liquefy in aromatic solvents such as toluene [6]. The precipitated asphaltene, named as C_{51} and C_{71} when using *n*-pentane and *n*-heptane as a solvent, respectively. A grater yield is acquired when utilizing *n*-pentane this division constitutes particles with a more extensive appropriation of molar masses and polarities. Indeed, asphaltenes C_{15} contains all particles of asphaltenes C_{71} [4], [6], [7]. The profile of the asphaltenes isolated amid refining relies on upon the sort petroleum, its inception and the sort amount of flocculation agent added during the process, in the last case communicated as the flocculants/oil ratio [8], [9]. A structure of asphaltenes are shaped by aromatic poly-condensate nuclei connected to the cyclical and aliphatic chains, containing heteroatoms such as nitrogen, oxygen, and sulfur along with metals including iron, nickel and vanadium. Their correct is obscure because of the multifaceted nature and assortment of their chemical structure. They are a profoundly heterogeneous polydispersity blend in connection to atom size and creation. Different basic models have been proposed and the macromolecular model of asphaltene division remains the concentration of exceptional review. Presently, the principle models recommended are the archipelago continental models [10],[14]. The precipitation of asphaltenes are connected with the flocculation of particles, which stars because of differences in the structures of the petroleum and temperature, pressure and flow regime [15],[16],[17]. The flocculation can be advanced by the expansion of polar solvents to the raw petroleum. At the point when a substantial amount of aromatic solvent is available, molecular aggregates can be shaped in the scattered medium [18],[19],[20]. Aromatics are often classified as mono-, di-, and tri- aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltene fraction. Resins fraction is comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or Sulfur. The resin fraction is operationally defined, and one common definition of resins is as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane [1],[5],[6]. Since the resins are defined as audibility class, overlap both to the aromatic and asphaltene fraction is expected. Despite the fact that the resin fraction is very important with regard to crude oil properties, little work has been reported on the characteristics of the resins, compared, for instance, to the asphaltenes. However, some general characteristics may be identified. Resins have a higher H/C ratio than asphaltenes, 1.2 – 1.7 compared to 0.9 – 1.2 for the asphaltenes [6]. Resins are structural to asphaltenes, but smaller molecular weight (<1000 g/mole). Naphthenic acids are commonly regarded as a part of the resin fraction.

Here, samples from Al-Rashida filed were collected and fractionated to their chemical compositions by using column chromatography through utilizing three solid layers Alumina Al_2O_3, Silica gel SiO_2 and combination layer from Al_2O_3 and SiO_2. The fractions were weighted and the percentage content was calculated. The isolated chemical components were studied structurally by using Nuclear Magnetic Resonance (^{13}C, ^{1}H-NMR).

2. Experimental

Raw Materials: In this study, crude oil samples from AL-Rashidiya field Eastern Baghdad- Iraq were used. The obtained crude stored in sealed glass ampoules in the dark place. The physio-chemical properties of crude oil sample were determined such as: API gravity = 25.32, total acid number mg KOH/g Sample = 0.15 and total base number mg KOH/g Sample $\leq$ 0.06.

Chemicals and reagents: The chemically pure grade *n*-Pentane, *n*-Heptane, Toluene, Methanol, Benzene and *n*-Hexane were used as the solvent for precipitant and fractionation of all samples and were purchased from sigma- Aldrich Co. Alumina and CCl_4 from Fluka Co.

3. Instrumentation and Measurements

3.1. Column chromatography Using Alumina Al_2O_3: [21]

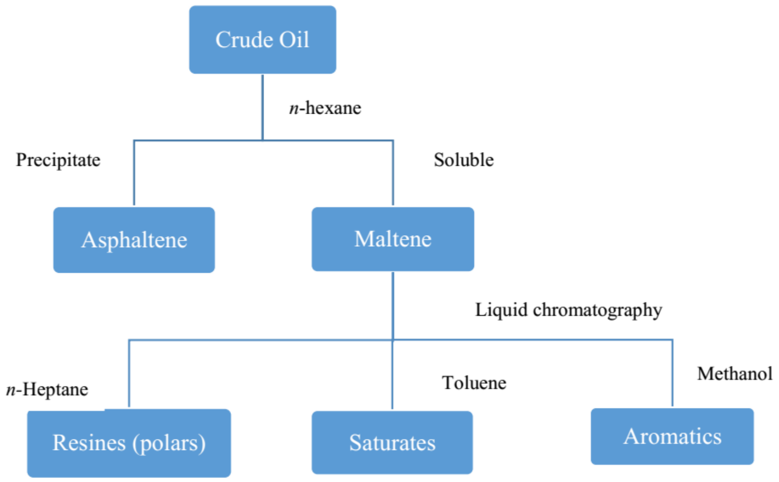
The crude oil's samples were taken and the amount of 5 g dissolved in 250 mL of *n*-Hexane, with the ratio 1:50, W/V, with continuous shaking for one hour to complete dissolving of crude oil components. The solution filtered by using filter paper non-ash No.42. The oil has been separated into two parts, the first undissolved precipitate in the bottom which was dried and weighted accurately to determine their ratio in the crude oil. The second part is Maltines and was taken and distillated simply for casting out of the dissolvers, the column was fixed, which have 50 cm height and 2 cm diameter, on a holder and put a small piece of glass cotton inside it to prevent passing any layers of absorption materials. Alumina Al_2O_3 50 mg was activated in a drying oven at 350 ℃ for two hours, then cooled and transferred into the column and while filling the column we must use a plastic bar for hitting of the column's sides until arranging material's molecules in a right shape and avoid forming any bubbles inside the column. This material or absorption layer treated with the first solvent, *n*-Heptane, then the Maltines was taken after treated it with *n*-Heptane too, the Maltine was added into the column and started collecting descending material from the column, the ration of drop descending must be 5 drop in minute. The first part, saturated Parafines, collected and separated, the filtered was taken and after simple distillation for evaporating the solvent, Parafine was weighted, and their ratio was calculated in the crude oil. The second part, the Aromatic materials was separated and by the same previous method, the filtered was dried, weighted and their ratio was calculated in crude oil. For separating of the last part from Maltines which is the Resin, Methanol was and the collected Resin was weighted and their ratio was calculated in crude oil.

3.2. Column chromatography using Silica gel SiO_2:

By the same steps which discussed previously silica gel SiO_2 was used for separating Maltines into its main components from paraffin's, aromatics and resin in order to take their ratios and comparing them with ratios that obtained by using Alumina Al_2O_3.

3.3. Column chromatography using combination layer of Al_2O_3 +SiO_2

After activating the Silica and Alumina 25 g from each one, the combined layers transferred into the column, one by one and then the same procedures above was repeated to separate the Malitines components. The result obtained was weighted and their ratio was calculated. Finally each ratio obtained from three columns were compared. Scheme.1 showing the SARA method:



Scheme.1: Illustration of SARA method

4. Results and calculation

Column chromatography method, liquid – solid, was used for separation, this method used to separate crude oil components taken from Rashidiya field, these parts are saturated (paraffinic compounds), aromatic and polar compounds such as resin, by using organic solvents such as normal heptane to separate saturated and toluene to separate aromatic and methanol to separate resin, this method called SARA. Adsorption layers such as alumina, silica and combined layers from alumina and silica were used for the separations.

Using Al_2O_3 layer:

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This layer was used to separate materials, the weight and the ratio of the components were calculated as shown in Table 1. The proportion of saturated (paraffin) is higher, so this oil considered paraffinic and the proportion of aromatic is coming next. The small value of resin ranked last. The little value of resin gives oil the preference in kind, because it's increasing is unwanted due to its being resinous material has high molecular weight and increase the viscosity of the crude oil.

Using SiO_2 layer:

Matlins was separated by using silica and Table 2 illustrated the results. The proportion of paraffin was higher than the aromatic, Asphaltene and resin's values and proportions are approximately similar to those obtained by the above method, however the values are different.

Using combination layers of Al_2O_3 and SiO_2:

By this method Maltin can be separated into basic components by same previous steps used in two methods (Alumina and Silica). Table 3 demonstrated the results obtained. These values and proportions were approximate with their similar in two previous methods with little difference in the values.

Table (1): Percentages of separated materials by using Al_2O_3

Isolated compounds	Wt. g	%
Asphaltene	0.6190	12.380
Paraffinic	2.24789	44.9578
Aromatic	1.6285	32.570
Resin	0.3199	6.398
Residue	0.18471	3.6942

Table (2): Percentages of separated materials by using SiO_2

Isolated compounds	Wt. g	%
Asphaltene	0.616	12.320
Paraffinic	2.292	45.589
Aromatic	1.6598	33.496
Resin	0.308	6.160
Residue	0.1242	2.44

Table (3): Percentages of separated materials by using Al_2O_3 and SiO_2

Isolated compounds	Wt. g	%
Asphaltene	0.620	12.400
Paraffinic	2.3081	46.162

Aromatic	1.602	32.040
Resin	0.3294	6.588
Residue	0.1405	2.81

^{1}HNMR Spectrum Analysis:

^{1}H and ^{13}C NMR spectrometry were used to study and identify the structures of the isolated compounds. The study achieved by using the area under the curve by identifying the different absorption of protons which includes aromatic protons (Ha), proton in Alpha site (Hα), Naphtenes protons (Hmy) and methyl paraffinic protons (Hme). Access to the values of the results obtained by H NMR of oil and their parts we observed that the proportion of saturated materials were higher compared to other separated parts, this proved also from the weight ratio which had been obtained from separated parts. Values are distributed on the basis of the area ranged (6.5 – 8.5) belongs to aromatic protons. Protons belonged to alpha site from aromatic circle located within (1.7 – 3.4), protons belong to Naphtenes system found in range (1.4 – 2.2), paraffinic aliphatic methylene groups located within range (0.9 – 1.8), methyl groups located within range (0.5 – 1.4). Figures 1, 2 and 3 showed some NMR spectra for the separated compounds.

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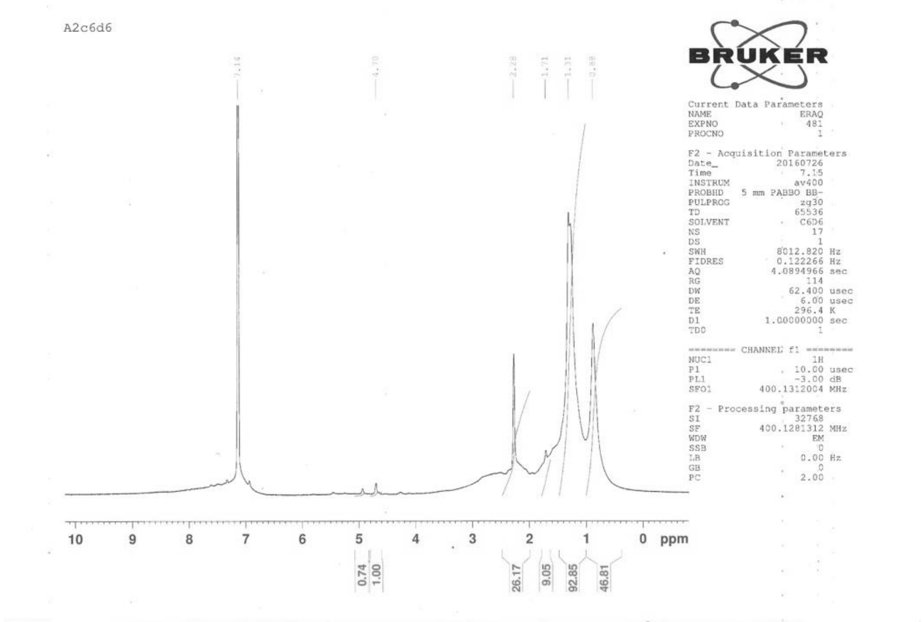

Figure 1: Spectrum Analysis ^{1}HNMR for saturated fraction by using SiO_2

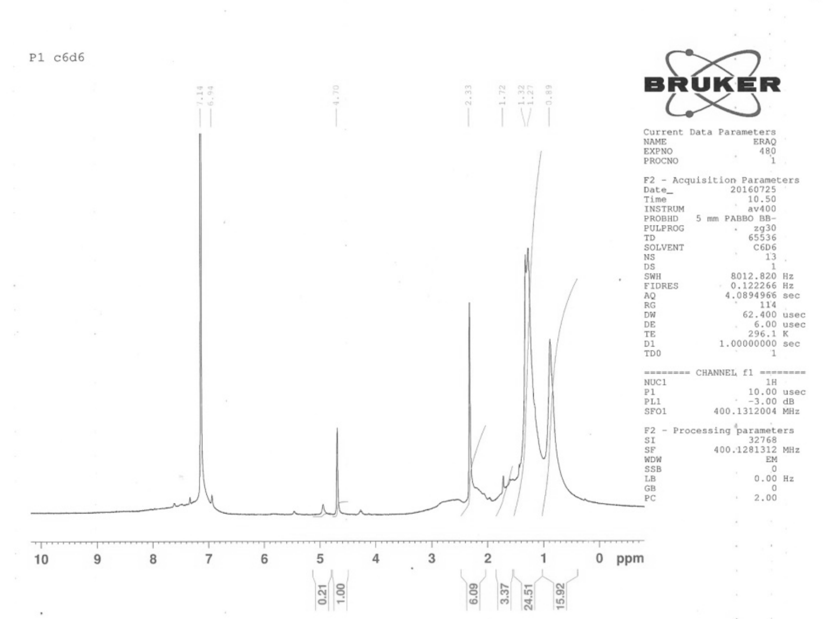

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Figure 2: Spectrum Analysis ^{1}HNMR for saturated by using Al_2O_3

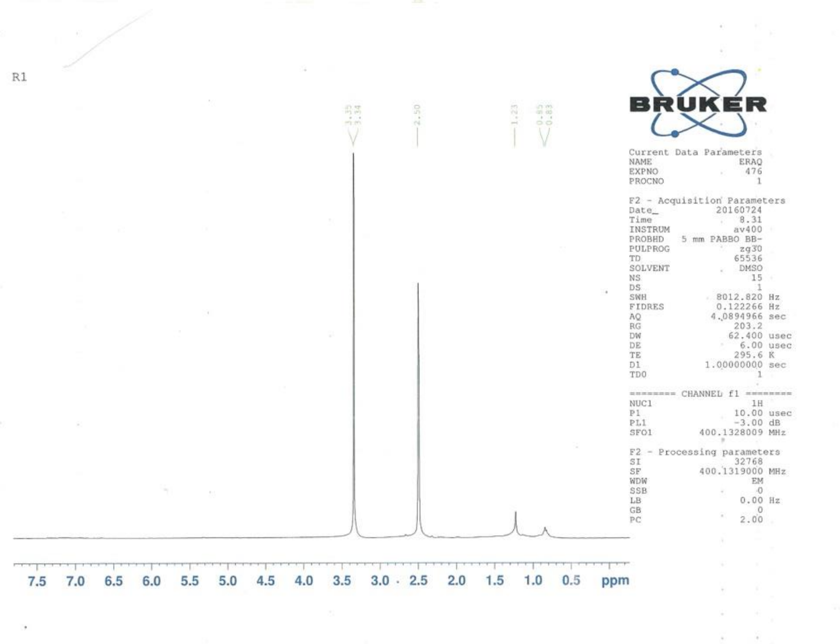

Figure 3: Spectrum Analysis ^{1}HNMR for resin by using Al_2O_3

5. Conclusion

The weight and proportion of separated components obtained from samples from AL-Rashida field was achieved by using column chromatography method. The results showed that the proportion of saturated (paraffin) was higher which means clearly that the oil falls within the classification of paraffin oils, the difference was great if compared to other compounds followed by aromatic proportion which it is not bad because it earns oil acceptable properties, because these materials (aromatic) are desired in oil, as for Asphaltene is ranked third has high molecular weight that earns oil chemical complexity and increases its colloidal. The resin proportion is the less among all separated materials worth approaching 6%, its acceptable proportion in crude oil, because they are materials have high viscosity (Resins) and increase the viscosity of the crude oil.

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