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A comparative study of Iraqi crude oil taken from the Nasiriyah refinery with various local and global crude oils.

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Abstract

In the present work, was evaluated and compared some physicochemical properties of crude oil which is obtained from Nasiriyah refinery in south of Iraq with some physicochemical properties of various local and global of crude oils. Many methods were used in this study to evaluate some chemical content as sodium ,potassium ,calcium, magnesium, vanadium,Iron, copper, lead and nickel in samples of Iraqi Oil in Nasiriya Refinery , as well as some physical properties included color , density, Ash content wt%, carbon residue wt% , water, salt , Sulfur content % wt, Heat of combustion Kcal/Kg , Thermal conductivity, Specific heat and Latent heat of vaporization were determinate . Also in this study viscosity were measured with different temperatures to observe the effect of temperature on oil viscosity. Range concentration of metals can be cleared by the series Ca > Na > Mg> V > Ni > K > Fe> Pb > Cu.

The present study has shown that high levels of metals ions in oil refinery whereas the physical properties were closed to previous findings conducted on a crude oil in Iraq and other countries. The study recommended to possible using of high levels of heavy metals in oil in scientific and industrial purposes as well as removal these metals contribute in reducing of contaminations problems.

Key words: crude oil, Nasiriyah refinery, heavy metals

دراسة مقارنة للنفط الخام العراقي المأخوذ من مصفاة الناصرية مع مختلف الخامات المحلية والعالمية

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قسم الكيمياء قسم الجيولوجيا التطبيقية

كلية العلوم – جامعة ذي قار

الخلاصة

تم تقييم ومقارنة بعض الخصائص الفيزيائية والكيميائية للنفط الخام المأخوذ من مصفاة الناصرية في جنوب العراق مع بعض الخصائص الفيزيائية والكيميائية لأنواع مختلفة من النفط الخام المحلية والعالمية. استخدمت في الدراسة الحالية طرق عديدة لتقييم المحتوى الكيميائي مثل الصوديوم ،البوتاسيوم ،الكالسيوم ،المغنيسيوم ،الفناديوم ،الحديد, النحاس ,الرصاص والنيكل بالإضافة الى بعض الخصائص الفيزيائية مثل اللون,الكثافة , محتوى ألاش , محتوى الكاربون المتبقي, النسبة المئوية للمحتوى المائي والملحي والكبريتي , حرارة الاحتراق واللزوجة عند درجات حرارية مختلفة. المعدل العام لتراكيز الفلزات المدروسة اتبع السلسلة الآتية Ca > Na > Mg> V > Ni> K > Fe> Pb > Cu. , الدراسة الحالية بينت أن هناك مستويات عالية من الايونات

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المعدنية في النفط الخام بينما كانت الخصائص الفيزيائية قريبة الى دراسات سابقة أجريت على النفط الخام في العراق وفي بلدان أخرى . ألدراسة أوصت الى أمكانية الاستفادة من المستويات العالية لتلك العناصر واستخدامها للأغراض العلمية والصناعية فضلا عن كون الإزالة تساهم في تقليص مشاكل التلوث .

الكلمات البديلة: النفط الخام, مصفى الناصرية ,العناصر الثقيلة.

Introduction

Crude oil represents a complex mixture containing essential organic materials such as alkanes, cycloalkanes and different aromatic hydrocarbons as well as inorganic chemical types. Organic compounds contain sulfur, nitrogen, oxygen, and trace amount of metals as copper, iron, vanadium, and nickel. Metals are one group the inorganic components present in this type of matrix(Dedhk, et al. 2002).The definition of metals in crude and its products is significant for exploration, production and refining aims(Elrich, et al., 1985).

The exact molecular composition varies widely from formation to another but the proportion of chemical elements vary over fairly narrow limits as Carbon 85% to 90%, Sulfur 0. 2% to 3%, Nitrogen < 0.1–2%, oxygen (1%–1.5%), and other organo-metallic compounds like Ni, V, Pb,… in traces. Therefore, the traditional use of the expensive and unstable organometallic standards is avoided. Trace metals existing in the crude oil precocious vary in its arrangement from source rocks, mostly as organometallic edifices, particularly metalloporphyrins, which are extremely steady.

The nature of occurrence of metals, their distribution patterns and concentration in crude oils can give information on the origin, migration, environment of deposition, maturation of petroleum and the geochemical characterization of source rocks and also to allow corrective actions during crude oil processing. The ratio of their concentration and toxicity in crude oil determine the pollution of the environment (Heinemann, 2011; Oluwole, et al. 1993). As instance, V is a poison and causes corrosion in furnaces and boilers during oil processing. Knowing about the concentration ratio between V and Ni in crude oil provides powerful geological information allowing oil-oil and oil-rock correlation evaluation of the environmental conditions of sedimentation (Aereo, et al. 2007).

Other metals, such as Na, Ca and Mg, may also present in significant amounts. Chemical species of these metals can be partially transferred to fractions (fuels for instance), decreasing their quality and performance.

The aim of the present study is to define Ca, Na, Mg, K, Pb, V, Ni, Cu and Fe and some physical properties of crude oil in the Nasiriyah refinery of Iraq, and compare their results with some of the local and global studies.

Materials and methods

The American Society for Testing Materials (ASTM)(Annual book of ASTM standards,1991) and the Institute of Petroleum (IP) indicate standard procedures to prepare crude oil derivatives previously to spectrometric metal determinations (Standard Methods for Analysis and testing of petroleum and related products, 1990).

Oil samples can be examined directly or after ashing of the sample. The direct determination is usually avoided due to the incompatibility of the sample with the instrumental apparatus employed for the analysis. In addition, the complexity of the matrix may affect the accuracy of the measurements. Procedures that require sample ashing are time consuming and the complete recovery of the analytes is often affected by vapor-phase loss due to the high volatility of some of the analyte chemical species. Extraction methods involve intricate steps and are time consuming (Standard Methods for Analysis and testing of petroleum and related products,1993). Flame photometry and AAS are a mature and robust multi element analytical techniques suitable to trace determination of many elements, in special in the refractory ones. The cost of instrumentation also makes it an attractive technique when compared to ICP-MS,NAA,XRF and AAS. Because of the high viscosity, the analysis of crude oil using AAS generally requires some degree of sample preparation previous to the aspiration into the flame. Therefore Atomic Absorption Spectrometry (AAS) and flame photometer were using in most Iraqi studies (Sayer, 2010; Khwedim, 2016;

Barbooti, 2015; Jadoon, et al. 2016) and global studies(Ger, 2009; Christiane,2008; Azubuike, et al. 2016; Yasin, et al. 2013).

Instrumentation

1- Flame photometer U.K M410.Determination method: calibration curves using to determine Na and K.
2- Atomic Absorbance Spectrometry AAS PG-990 Optic System (Figure 1). Wavelength Range: 190nm - 900nm, Monochromator: Czerny-Turner configuration, Spectral Bandwidth: 0.1nm, 0.2nm, 0.4nm, 1.0nm, 2.0nm, Wavelength Accuracy: 0.25nm. Wavelength Repeatability: 0.15nm .Baseline Stability: 0.005A/30 min. Data processing .Analytical method: flame, graphite furnace and hydride .Determination method: calibration curves using to determine V, Ca, Mg, Pb, Fe, Cu and Ni.

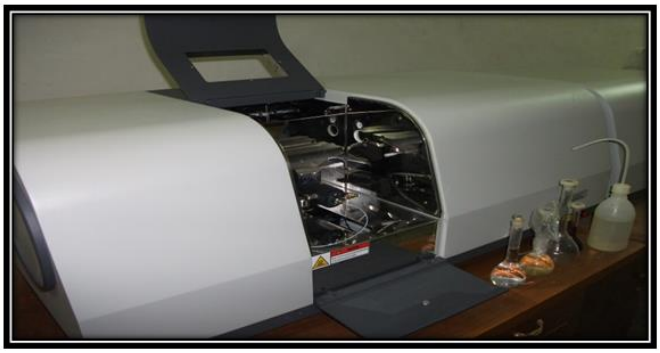

Figure 1. AAS Instrumental which used in determination heavy elements.

3- Heat of combustion were measured in lab and calculated by using empirical equation for compression that At a constant volume the heat of combustion of a petroleum product can be approximated as follows:

$$Q_v = 12{,}400 - 2{,}100d^2$$

where Q_v is measured in cal/gram and d is the specific gravity at 60 °F (16 °C).(Aucvbio, et al. 2006)
4- The viscosity was measured at different temperatures by using DV-I PRIME from digital viscometer from Brookfield company (USA).

Reagents and solutions

All reagents employed were of analytical grade. Analyte (Ca , Na , Mg, Pb, Cu, Fe, V , Ni and K) standards solutions were prepared from a 1000 mg L^{-1} stock solution from Merck. Five crude oil samples were also used (Randomly Sampling). These samples were collected from local Nasiriya oil refinery and they were identified as "sample 1" , "sample 2", "sample 3", "sample 4" and "sample 5".

Results and discussion

1- physical properties:

The physical properties and exact chemical composition of crude oil varies from one locality to another. Table (1) shows the measured physical properties of crude oil in this study.

Color: Raw oil varies extremely in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish, reddish, or even greenish)(Charles, et al. 2013).

Density : The quality of raw oil can be known by the density. There are two types of density light and heavy if it has low and high density respectively. heavy crude oil is less desirable than light oil since it produces a lower yield of oil. The density range of crude oils in North region of Punjab -Pakistan is (0.7910–0.8500) and in the south of it is (0.8088-0.9320)(Yasin, et al. 2013), Eocene crude oil (Mckene,1981) 0.92-0.98, Ratawi-Burgan crude oil(Yen, 1975) 0.91-0.95. Density of this study was closed at Kuwait crude oil(Hussain, et al. 2008) 0.82-0.91 gm/cm^3 at 15°c.

Sulfur content : There are two types of heavy raw oil depending on Sulfur content:

1- Heavy raw oil has over 1% sulfur (high sulfur raw oils), as this study with asphaltenes and aromatics, and these are especially found in North America United States (California, Mexico), Canada (Alberta, Saskatchewan), South America (Colombia, Venezuela and Ecuador) and the Middle East (Kuwait, Saudi Arabia).

2- Heavy raw oil less than 1% sulfur (low sulfur crude oils), with naphthenes aromatics, and resins, and these are especially found in Western Africa Central Africa (Angola), Chad, and East Africa (Madagascar)(Vanloon, 1980).

Carbon residue Wt.%: The microscopic plankton organism is broadly responsible for the relatively high carbon content of fine-grained sediments like the Chattanooga shale which are the principle source rocks

for petroleum. Raw oils contain more carbon in relation to hydrogen, thus releasing more carbon dioxide (a greenhouse gas) per amount of usable energy when burned (Gondal , 2007). Carbon residue wt% lower than Eocene crude oil 9.0-13% Ratawi-Burgan crude oil 9.0-12.0 % and Kuwait crude oil contains 4.5-6.0%.

Water content %vol: In this study higher than Eocene crude oil 0.01-0.12 % Ratawi-Burgan crude oil 0.02-0.15 % and Kuwait crude oil contains 0.002-0.01% that attributed to pumps process to deducing of oil . that attributed to pumps process to deducing of oil . This percent mean to avoid the problems of water content the oil should be treated to decrease water percent by setting process or by another ways.

Heat of combustion: This property has been measured in lab by using traditional method and also by empirical equation from previous studies.

Viscosity: lighter grades of heavy crudes include higher viscosity and heavier molecular composition. Extra heavy crude from the Orinoco region(Al- Shahristany, et al. 1972) has a viscosity of over 10,000 centipoise (10 Pa·s) Generally, a diluent is added at regular distances in a pipeline carrying heavy crude to facilitate its flow **.**

For example, the viscosity of Venezuela's Orinoco extra-heavy crude oil lies in the range 1000–5000 cP (1–5 Pa·s), while Canadian extra-heavy crude has a viscosity in the range 5000–10,000 cP (5–10 Pa·s), about the same as molasses, and higher (up to 100,000 cP or 100 Pa·s for the most viscous commercially exploitable deposits)(Gondal , 2007). Data of measured viscosity at different temperatures were listed in table (2). As is clear in the table, the viscosity was measured at a higher temperature and cannot continue with heating because the oil start to boil at 55ºC also if oil was pumped, there are some problems because instead of one phase flow there are two phase liquid and vapor. The data of viscosity useful for how to deals with this fuel and to choose the best pump for pumping and suitable temperature for this process.

Table (1): Physical properties of crude oil

Test name	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average
Color	dark brown	dark brown	dark brown	dark brown	dark brown	dark brown
Density gm/cm^3 at 15°c	0.851	0.896	0.905	0.882	0.871	0.881
Sulfur content %wt	7.6	7.2	7	7.3	7.4	7.3
Carbon residue wt%	4	3.4	2.7	3.5	3.5	3.42
Ash content wt%	7.2	5.3	4	6	6.3	5.76
Water content %vol	0.8	0.7	0.6	0.8	0.8	0.74
Heat of combustion Kcal/Kg	10879	10714	10680	10850	10867	10798

Table 2: Viscosity at different Temperatures.

Viscosity (at different T °C)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average
Viscosity at 25°c(mm^2/sec)	23	24	31	24	25	25.4
Viscosity at 38°c(mm^2/sec)	22	23	24	22.5	23	22.9
Viscosity at 40°c(mm^2/sec)	20	20	20	21	20	20.2
Viscosity at 44°c(mm^2/sec)	16	16	19	16	16	16.6
Viscosity at 50°c(mm^2/sec)	16	16	16	15.5	16	15.9
Viscosity at 55°c(mm^2/sec)	15	14	16	14	15	14.8

2- Metals of Ca , Na , Mg, V , Ni, K, Pb, Fe and Cu:

The concentrations obtained for metals in crude oil are shown in table (3). Raw oil is a combination of many various compounds, commonly combinations of carbon and hydrogen, all with their own certain single properties. Crude oil as such is just not corrosive. Nevertheless, it involves corrosive impurities, like inorganic salts(Bagdasarian et al, 1996).

Inorganic salts are existent in the brine produced with the raw oil or raised as a contaminant. Magnesium chloride ($MgCl_2$), sodium chloride (NaCl), and calcium chloride ($CaCl_2$) represent the bulk of the salts. When the raw oil is preheated, most of the $CaCl_2$ and $MgCl_2$ begin to hydrolyze at about 120 ^oC and form hydrogen chloride vapor. At 370 ^oC, neerly 15% of the $CaCl_2$ and 95% of the $MgCl_2$ have hydrolyzed. The chemical reaction for $MgCl_2$ is:

$MgCl_2 + H_2O \rightarrow 2HCl + MgO$

An identical reaction occurs for the $CaCl_2$. The sodium chloride, being more temperature stable, does not hydrolyze to any appreciable range. The refiner oftentimes washes the oil with water and uses a desalting vessel to eliminate the added water and most of the inorganic contaminants from the raw oil prior to distillation in the crude unit to minimize the influences

of inorganic salts (Bagdasarian et al,1996; Kane et al, 1999).

Iraqi crude contains high salt content. This might explain the presence of calcite as part of the scale (Al-Shahristany, 1972). Ca and Na concentrations of the present study in table (3) were higher than oil of Basin 37.6 ppm and 30 ppm (Christiane Duyck, 2008) respectively. Mg levels followed Na levels were higher than oil of Basin 35 ppm(Christiane Duyck, 2008) , USA crude oil 16.2ppm (Annual Book of ASTM standards. 1991) and Concentrations of Some elements that measured (Sommervill M.,1999) in table (4).

Also K was followed Mg and Na were higher than concentration of USA crude oil 13.2 ppm (Annual Book of ASTM standards. 1991) and Concentrations of Some elements that measured (Sommervill M.,1999) in table (4). The Iraqi crude oil are contain a high concentrations of Ni and V , they ranged between 0.7 – 25 ppm and 1.6 – 100 ppm respectively (Al-Shahristany et al;1972). V value in this study was closed to some Iraqi studies like study of (Sayer, 2010) in table (5) and securing Kuwait crude oil limits, but higher than oil of Basin 8.9 ppm(Christiane Duyck 2008) , lower than Eocene crude oil 40-60 ppm, Ratawi-Burgan crude oil 50-70 ppm and lower than Concentrations of Some elements that measured(Sommervill,1999) table (4).

Ni values of this study were higher than Iraqi studies table (5) (Sayer, 2010; Barbooti, 2015;Jadoon et al, 2016; Al- Shahristany et al;1972; Abdulsalam et al,2015) and also higher than oil of Basin19.3 ppm(Christiane Duyck, 2008) and closed to Kuwait crude oil 5-18 ppm but were securing Eocene crude oil 15-30 ppm (Mckene T.N.1981), Ratawi-Burgan crude oil 20-30 ppm limits (Yen ,1975) and ranged at Concentrations of Some elements that measured (Sommervill,1999) table (4) .

It can be significantly assumed that the nature of the raw oil was the catalytic factor for the occurrence of high temperature sulfidation and its localized nature.

In this case, samples show than previous findings executed on a crude oil in Iraq(Sayer, 2010; Barbooti, 2015;Jadoon et al, 2016; Al- Shahristany et al,1972; Abdulsalam et al,2015) and other countries. Whereas ranged insure limits some elements that proposed by (Sommervill,1999) and (Al- Shahristany et al,1972).

As shown in table (5), concentration values of V was higher in samples of Eastern Baghdad area(Barbooti, 2015) and some values of AL-Shahristany studies than this study, but can be noted that conc. values of V is lower in Kurdistan region Swara- tuka (Abdulsalam et al, 2015) than this study and some studies(Barbooti, 2015; Al- Shahristany et al,1972).

Concentration values of Ni was higher than previous studies conducted on a crude oil in Iraq and other countries. The elevation of Ni levels in comparison with other samples in relation to rise of aqua content percent Table 1render to dissolving of Nickel salt solution as NiO in aqua (Al- Shahristany et al,1972) . Nickel, has observed to be correlated positively with the absolute amount of heavy n-alkanes in the petroleums, because this element is approximately more abundant in parafinic petroleum (Muhammad et al, 2013). The coexisting of V levels in crude oil that is found as $Na_{12}V_{24}O_{64}$ (Al- Shahristany et al,1972) is the main reason of observing the vanadium concentration.

According to the researches(Lewan et al, 1982; Lewan, 1984),the depositional environment and source rock type effect on the predicted levels of Ni and V in the petroleum.

The Iraqi crude oil are contain a high concentrations of Ni and V , they ranged between 0.7 – 25 ppm and 1.6 – 100 ppm respectively (Al-Shahristany et al,1972).

Also concentration of metals in crude oils can be used to classify oils into families. Low V/Ni ratios (<0.5) are expected for petroleum derived from marine organic matter, with high to moderate sulphur content, while V/Ni ratios (1–10) (our study) are expected for petroleum derived from lacustrine and terrestrial organic matter (Muhammad, 2013). Oils from marine organic matter have high concentrations of metals (particularly Ni and V), this is expected since for marine source rocks, there is an abundant input of porphyrin-precursor chlorophylls to the organic matter derived from algae and bacteria (Muhammad, 2013).

Moderate quantities of metals are found in oils derived from lacustrine source rocks while little nickel and vanadium is found in land-plant derived oils.

Iron values are closed to crude oil in other countries and ranged at minimum limit to levels elements that proposed by (Sommervill,1999) and most of Fe in crude oil as Fe_3O_4(Al- Shahristany et al,1972).

In the current case, the samples have showed that Pb concentration is higher than the prior lucubration executed on a crude oil in Iraq as shown in (Table 5) (Abdulsalam et al, 2015), but lower than the values of

the researcher(Jadoon et al, 2016). Cu concentration was lower in this study and in studies (Barbooti, 2015, Jadoon et al, 2016) than the research(Sommervill,1999) and was higher than study (Christiane Duyck 2008). The value of the Cu can be attributed to the associated water and/or particles of the sediment from producing wells or the one which is picked up during he transportation. It has noticed that the level of Cu has escalated in different studies accompanying with the increment in the content of sulfur percent as shown in table 1, that agreeableness can be attributed to the existence of Cu ion as $CuSO_4$ salt form.

It is obvious that the collected samples (table 3) of crude oil from the refinery is highest in the level of heavy metals. Where, there is inverse proportional relation between the density and the total transition metal contents.The real cause of the different in the level of the heavy metals can be attributed to the petroleum geochemistry, and these can be decided with the porphyrin structures. For instance, like the deoxo phyllo erythroetio porphyrin (DPEP) and etioporphyrins, that have scrutinized in similar studies (Christiane Duyck, 2008; Carnell, 1989). The oils would contain trace metals, but in the form of porphyrin complexes (species) in petroleum source rocks, in addition, that could contain direct combining from the biomass and formation during sedimentation. Moreover, that would comprise diagenesis from organic molecules beside to the metals derived from different biogenic (biomass) and abiogenic (weathering of minerals) sources. Source rock, type of organic matter and depositional environment have substantial effect on the concentration of trace elements in source rocks (Akinlua, 2015). It should be mentioned that there would be some difficulty of using trace element contents in order to correlate the oils and/or source rocks. However, the proven association of metals with organic compounds could be used as save correlation tools. Cu, Ni and V (usually referred to as biophile elements) are such examples (Onojake, 2016).

Range concentration of heavy metal can be cleared by the series:

Ca > Na > Mg> V > Ni > K > Fe> Pb > Cu.

Table 3:Concentrations of Some metals ions oil of Nasiriya Refinery in Iraqi crude.

Test name PPM	Sample 1	Sample2	Sample 3	Sample 4	Sample 5	Average
Magnesium	93	60	75	80	69	75.4
Sodium	88	80	76	78	74	79.2
Potassium	30	18	26	21	23	23.6
Calcium	130	110	109	113	120	116.4
Nickel	32	22	27	23	21	25
Vanadium	27	47	39	34	34	36.2
V\Ni	0.84	0.46	0.69	0.67	0.61	0,69
Lead	4	2	2	3	2	2.6
Copper	0.8	0.3	0.7	0.2	0.4	0.48
Iron	11	9	12	12	6	10

Table 4 :Concentrations of standard Some heavy elements that proposed by Sommervill,1999.

heavy metals	concentrations ppm
Ba, Mn, Zr, Sr, Pb, Li	1- 0.1
Al, Mg, K, Sn	10 – 1
Ni, Fe, Cu, Na	100 – 10
V	>100

Table 5: Concentrations of Some elements in Iraqi crude oil compared with the present study

Elements	Samples of Eastern Baghdad area(Barbooti, 2015)	Swara- tuka (Abdulsalam et al,2015)	Tawki (Abdulsalam et al,2015)	Taqtaq (Jadoon,2016)	Khurmala (Jadoon, 2016)	AL_Shahristany et al, 1972	Sayer,2010	Present study
K								23.6
Mg								75.4
Ni	17.28	Nil	5			0.7- 25	20	25
Na								79.2
Pb	-	0.01	0.04	10.89	75.34			0.48
Ca								116.4
V	81.78	0.22	10			1.6-100	37	36.2
Fe	25.06	0.4	9	0.367	0.803			10
Cu	4.12	Nil	Nil					2.6
V/Ni	4.73	0.22	2			4- 2.28	1.85	1.44

Conclusion :

The present study showed that the crude oil of the refinery expressed high content of metals levels this could be explained by the geochemical effect on the elemental distribution in a case study and to salt ,aqua, sulfur content % of the crude oil.

The study recommended to treat crude oil before entering the industrial units especially when this crude oil use as a fuel in boilers and furnaces to avoid or decrease the problems of hot and cold corrosion ,if this crude used as a fuel the waste can be a source of some metals like vanadium , nickle, sodium, potassium and others and extracts its by reusing this waste.

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