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EVALUATION AND IMPROVEMENT OF DIESEL CUT FROM TAWKE CRUDE OIL WELLS, ZAKHO

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ABSTRACT:
The straight run diesel cuts of crude oil from T-8 and T-16 Tawke well-Zakho have been examined (qualitative and quantitative). Physical properties such as (density, API, viscosity, cloud point, flash point, water content, sulfur content…. etc.) of this crude oil and diesel product have been measured according to the ASTM method. To improve chemical constituents of these crude oils and increasing the diesel distillation volume cuts by using three types of local clays, X-Ray fluorescence spectroscopy analysis of these clays have been done, a series experiments have been done at a different percentage of local clays and different time of reflux for Tawke wells T-8 and T-16 crude oil. These experiments were performed, in order to optimize the best clay and percentage, as well as finding the suitable reflux time to enhance the volume of fraction at (200-320) °C. The figures have been plotted to find the optimum percentage weight for each clay, time of reflux, and temperatures. The change in chemical constitutes of these crude oils have been monitored by gas chromatography and tabulated in tables.

KEYWORDS: Tawke wells Number 8 and 16 (T-8) and T-16, Clay, Diesel cut, Crude oil.

1. INTRODUCTION

Crude oil is a mixture of gaseous, liquid, and solid hydrocarbon compounds and also contains small quantities of nitrogen, oxygen, and sulfur-containing compounds as well as trace amounts of metallic constituents(G.S.James, 2006). Crude oil is usually evaluated through various physical and chemical methods of determination: density, specific gravity, correlation index…..etc.(Petroleum, 2000). Crude oil is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation. The terminology of these fractions has been bounded by utility and often bears little relationship to composition (Favennec & Baker, 2001).

1.1 Diesel fuel

Diesel fuels originally were straight-run products obtained from the distillation of crude oil. Diesel fuel may also contain varying amounts of selected cracked distillates to increase the volume available. Since straight-run diesel fraction for a given crude oil is fixed varying amounts of selected cracked distillates from conversion processes such as fluid catalytic cracking, hydrocracking, cocking are used to increase the volume available for meeting the growing demand of diesel fuels (Prasad, 2000).
Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon number between 9 and 23. Most of these compounds are members of the paraffinic, naphthenic, or the aromatic class of hydrocarbons. These three classes of hydrocarbons have different chemical and physical properties. A different relative proportion of the three classes are one of the factors that make one diesel fuel different from another. The important properties of diesel fuels are volatility, heating value, ignition quality/cetane number, viscosity, low-temperature flow, lubricity, storage stability, component compatibility, and sulfur content.

1.2 Clay catalyst

Clay is a mixture of Al2O3, SiO2, xH2O and (Mg, Ca, Fe) a metal, clay is a rock term and is also used as a particle size term. The term clay has no genetic significance because it is used for residual weathering products(Antos & Aitani, 2004). Clay is a term to describe group of hydrous aluminum silicates minerals that are typically less than 2 micrometers, clay consists of a variety of phyllosilicate mineral rich in silicon and aluminum oxides and hydroxides which include variable amount of structural water. These materials are chemically referred to as compounds meaning that they are made of two or more elements that are chemically bonded together. In nature, very few materials exist as pure elements; most have formed chemical bonds with other elements usually oxygen. Silica, for instance is the mineral (or compound) name for the element Silicon that has combined with the element oxygen. Alumina is the mineral name for the material that results from the bonding of aluminum and oxygen (C., 2005).
Clays and clay minerals are very important industrial minerals. The clays used as catalysts in cracking are solid with large surface area and high porosity, with acidic properties (R.W.Mc. Cab, 1992). The older type of

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catalysts was acid – treated natural clays (Bentonite, Kaoline……. etc.) with variable amounts of combined silica and alumina.

Synthetic clay was later developed which, together with a more specific composition and purity gave higher selectivity in the catalytic reaction and increased mechanical thermal resistance, particularly those catalysts with high alumina content (Bhaduri & Mukesh, 2014).

1.3 Experiment

The preliminary Distillation of Crude oil have been determined according to the ASTM 89 method, fraction distillation ASTM 286, Clays have been prepared after break it with motor, grinding and sieving by using sieve type (mesh number 200), reflex at different time and in different Temperatures. Clays analyzed to determine the metal oxides using (X-Ray Fluorescence, PW-1600 Spectrophotometer Philips). Analysis the research samples by Gas Chromatography (GC), the GC were carried out on (Gas-Chromatography Instrument: Varian CP-3800).

2. RESULTS AND DISCUSSION

2.1 Treatment of the crude oil t -8 and t -16 by addition of clay (1, 2, 3)

Clays are natural compounds of silica and alumina, containing the major amount of the oxides of sodium, potassium, magnesium, calcium, iron and other metals. Clays contain water between the layers (S.A. Naman, 2012). Three types of local clay from Kurdistan region have been selected and used in this study; they are in different colors and chemical compositions. Effect clay on the crude oil indicated when the volume of fraction of some cuts is increased by using clays and these due to the breaking of large hydrocarbon molecules into smaller. The yield of the fractional distillation depends on the type of clay, the percentage of clay, reflux time and the temperature. Table (1) shows the X-Ray fluorescence spectroscopy data for the three types of clay.

Table 1. Metal oxide in local clay (1, 2, 3) according to x – ray fluorescence spectroscopy:

Metal Oxide	Clay 1 %W	Clay 2 %W	Clay 3 %W
SiO_2	38.30	41.50	44.60
Al_2O_3	9.62	7.29	7.42
SiO_2/ Al_2O_3	3.98	5.69	6.01
Fe_2O_3	8.98	9.20	5.23
CaO	6.57	10.38	13.26
MgO	11.27	9.82	6.96
K_2O	0.42	0.65	1.72
Na_2O	0.26	0.47	1.77

2.2 Effect of different percentage of clay (1, 2, 3) and different reflux time on the fractional distillation of t-8 and t-16 crude oil

The clays (1, 2) which are used in this study are grinded and then sieved by using scientific sieve type (ASTM Mesh number 200) to produce the same molecular size. The catalytic activity increasing surface area or those are decreasing the crystallite size [9]. In this study, three types of clay (1, 2, 3) with different percentage (1, 3, 5, 6, 8) % W and in (3, 6, 7) hours' reflux time at (240, 350, 375) °C (the temperatures of boiling crude oil) were used. According to the tables 2, 3 and figures 1, 2 volumes of fractions that have temperatures range (200 – 320) ℃ are increased with increasing the percentage of clay. The 8%, 6%, 5% are more suitable for the fractional distillation of cuts from T-8 and T-16 Crude oil, compared with 3%, and 1%.

Table (2): Effect of Addition Clay (1, 2, 3) on Cumulative volume of Fraction Distillation Cuts of T-8 Crude Oil:

Clay	% W	3 hour		6 hour		7 hour	
		Cum. Vol. of cuts from (39-180) ℃	Cum. Vol. of cuts from (200-320) ℃	Cum. Vol. of cuts from (39-180) ℃	Cum. Vol. of cuts from (200-320) ℃	Cum. Vol. of cuts from (39-180) ℃	Cum. Vol. of cuts from (200-320) ℃
1	0	23.9	52.9	23.9	52.9	23.9	52.9
1	1	23.1	54.6	22.8	54.0	22.5	54.0
1	3	22.2	56.8	21.7	56.7	21.8	56.3
1	5	21.4	59.6	21.5	59.7	21.0	59.5
1	6	20.0	62.2	20.2	64.6	20.8	64.6
1	8	19.8	61.8	20.2	64.4	20.9	64.1
2	1	23.1	54.7	23.2	54.9	23.0	54.7
2	3	22.5	56.6	22.3	57.0	22.6	56.7
2	5	21.4	58.4	21.8	61.0	21.8	60.4
2	6	20.8	61.0	21.2	66.0	21.2	65.5
2	8	20.9	57.7	21.2	65.6	21.1	65.1
3	1	23.5	53.6	23.5	54.7	23.3	54.9
3	3	22.7	55.1	22.8	57.4	22.9	57.2
3	5	22.0	56.8	21.9	61.6	22.2	61.8
3	6	21.5	60.7	21.6	66.6	21.9	66.9
3	8	21.2	58.7	21.6	66.3	21.6	66.2

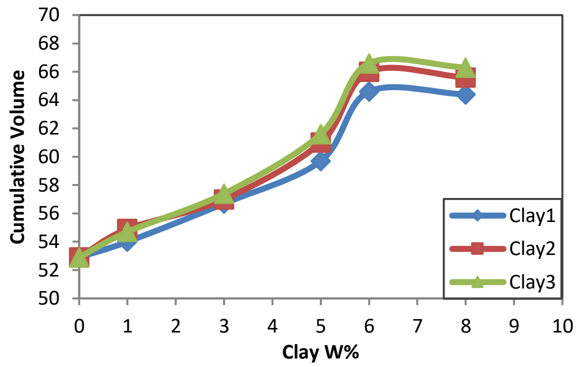


Figure 1. Effect of clay (1, 2, 3) concentration %w on the T-8 fraction distillation at 6 hour reflux time

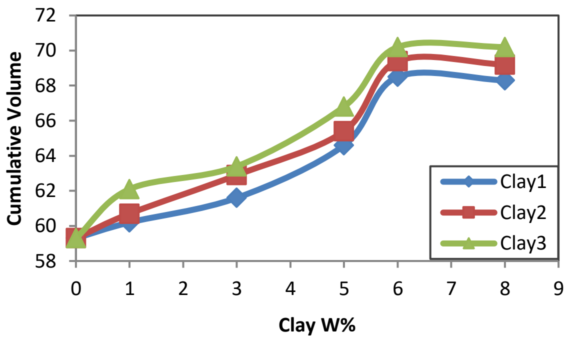


Figure 2. Effect of clay (1, 2, 3) concentration %w on the T-16 fraction distillation at 6 hour reflux time

Table (3): Effect of addition clay (1, 2, 3) on cumulative volume of fraction distillation cuts of T-16 crude oil:

Clay	% W	3 hour		6 hour		7 hour	
		Cum. Vol. of cuts from (37-180) °C	Cum. Vol. of cuts from (200-320) °C	Cum. Vol. of cuts from (37-180) °C	Cum. Vol. of cuts from (200-320) °C	Cum. Vol. of cuts from (37-180) °C	Cum. Vol. of cuts from (200-320) °C
1	0	24.0	59.3	24.0	59.3	24.0	59.3
1	1	23.6	59.8	23.5	60.2	23.4	59.9
1	3	23.1	61.0	23.0	61.6	23.4	61.5
1	5	22.1	62.3	22.5	64.6	22.6	64.4
1	6	21.5	64.2	21.7	68.5	22.2	68.4
1	8	21.4	63.9	21.7	68.3	22.1	67.6
2	1	23.7	60.9	23.0	60.7	23.2	61.0
2	3	23.1	61.2	22.9	62.9	23.2	63.0
2	5	22.6	64.1	21.7	65.4	22.2	64.9
2	6	21.9	65.5	22.0	69.4	22.5	69.2
2	8	21.8	65.3	21.9	69.2	22.3	68.7
3	1	23.4	60.9	23.3	62.1	23.7	60.0
3	3	22.6	61.9	22.1	63.4	21.8	63.3
3	5	22.4	64.6	21.7	66.8	21.8	66.3
3	6	21.3	66.3	20.3	70.2	20.6	69.9
3	8	21.2	66.3	20.6	70.2	19.8	69.9

According to Figures 3, 4 show that the best time of the reflux for increasing the volume of fraction distillation cuts of T-8, T-16 crude oil by using 6% W clay (1, 2, 3). In order to study the effect of temperatures on increasing the distillation cuts volume for T-8,T-16 crude oils .The results in tables 3, 4 for T-8,T-16 crude oils shows that the (6% W) of clay (1,2,3) with 6 h time at 350 °C have more effect to change distillation cuts volume.

In order to study the effect of clays on the T-8 and T-16 crude oils, X-Ray fluorescence spectroscopy analysis clays has been done as shown in table 1 in order to know the percentage of metal oxide in each local clay, while the activity of this clay depended on the chemical composition of clays. Table 1 shows that the clays (1, 2, 3) have SiO2 Wt. % (38.3, 41.5, 44.6) respectively, as the amount of silica increase, the activity of clay increased because high-silica-content clay showed a higher equilibrium activity level and surface area and the clay properties are dependent on the Si/Al ratio which are (3.98, 5.69, 6.01) for clay (1, 2, 3) respectively and clay with high Si/Al ratios are more stable.

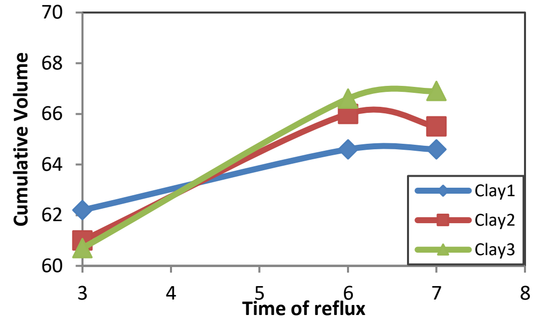


Figure 3. Effect of reflux time on the T-8 fractional distillation with 6% w of clay (1, 2, 3)

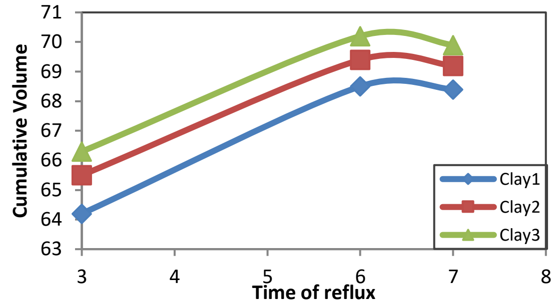


Figure 4. Effect of reflux time on the T-16 fractional distillation with 6% w of clay (1, 2, 3).

Table 4: Weight percentage of carbon number of diesel fraction from T-8 and T-16 crude oil with clay (1, 2, 3).

Analysis	Results Diesel Fuel W%							
Composition	T-8 diesel	Clay 1	Clay 2	Clay 3	T-16 diesel	Clay 1	Clay 2	Clay 3
n-Hexane nC6	0.42	0.23	0.24	0.27	0.03	0.04	0.76	0.34
n-Heptane nC7	0.85	0.81	1.05	1.33	0.26	1.33	2.15	1.17
n-Octane nC8	1.73	1.90	2.72	4.09	0.76	3.01	4.20	2.65
n-Nonane nC9	3.26	2.83	4.20	7.68	1.89	4.31	5.92	3.83
n-Decane nC10	3.53	2.51	3.88	7.54	1.97	4.27	6.18	3.89
n- Un Decane nC11	5.04	3.71	4.76	10.03	3.98	5.03	7.54	5.16
n- Do Decane nC12	5.61	6.18	5.42	10.15	6.08	6.83	7.74	6.96
n- Tri Decane nC13	8.09	11.39	8.46	10.26	10.88	12.07	8.29	13.46
n-Tetra Decane nC14	12.41	15.16	12.76	9.59	16.66	16.76	9.99	17.99
n-Penta Decane nC15	15.54	16.11	13.60	8.43	17.70	15.78	11.13	15.41
n-Hexa Decane nC16	15.50	13.19	14.40	8.26	14.37	12.00	11.10	11.51
n-Hepta Decane nC17	11.85	10.16	11.41	7.40	10.55	8.86	9.96	8.00
n-Octa Decane nC18	7.64	6.70	7.61	5.85	6.88	2.52	7.07	4.59
n-Nona Decane nC19	4.40	4.78	5.25	4.74	4.61	4.20	4.79	2.99
n- Icosane nC20	2.50	2.37	2.31	2.42	1.99	1.90	1.88	1.19
n-Hene Icosane nC21	1.10	1.27	1.20	1.20	0.98	0.76	0.91	0.62
n-Do Icosane nC22	0.53	0.70	0.73	0.76	0.41	0.33	0.39	0.24

2.3 The carbon distribution of diesel fraction from t-8 and t-16 crude oils

Gas chromatography analysis was determined by the carbon number distribution of diesel fraction of both crude oil T-8 and T-16 before and after the treatment with clay (1, 2, 3). Table 4 illustrated the carbon number distribution of diesel fraction from T-8 and T-16 crude oil before and after treatment with clay (1, 2, 3), which shows the number of carbons in hydrocarbon molecules of fractions. The data for GC of diesel cut show in figures (7, 8, 9, 10, 11, 12, 13, 14) respectively.

Figures 5 shows the ability of clay (1, 2, 3) to crack the heavy hydrocarbon in T-8 crude oil with increasing carbon number of hydrocarbon, before the treatment diesel of fraction from T-8 crude oil is shafting C15, and after the treatment from C7 to C15 for Clay 1 and from C7 to C16 for Clay 2, as well as Clay 3 but with shafting to C13. Figures 6 shows the ability of clay (1, 2, 3) to crack the heavy hydrocarbon in T-16 crude oil with increasing carbon number of hydrocarbon, before the treatment of diesel fraction from T-16 crude oil is shafting C15, and after the treatment from C7 to C14 for Clay 1 and from C7 to C15 for Clay 2, as well as Clay 3 but with shafting to C14.

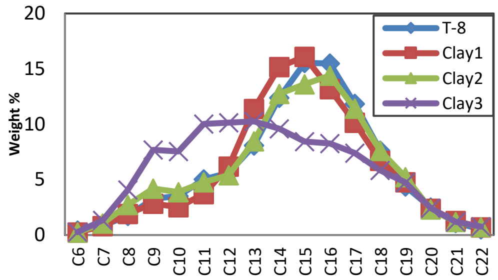


Figure 5. Carbon distribution of diesel fraction at (200-320) °C before and after treatment T-8 crude oil with clay (1, 2, 3)

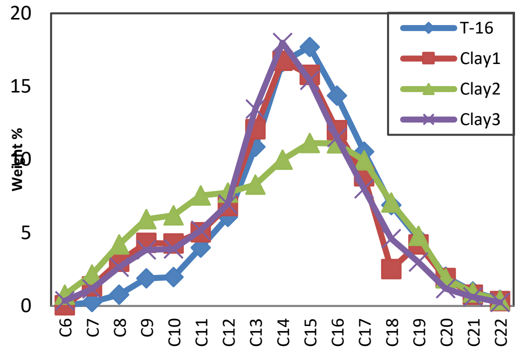


Figure 6. Carbon distribution of diesel fraction at (200-320) °C before and after treatment T-16 crude oil with clay (1, 2, 3)

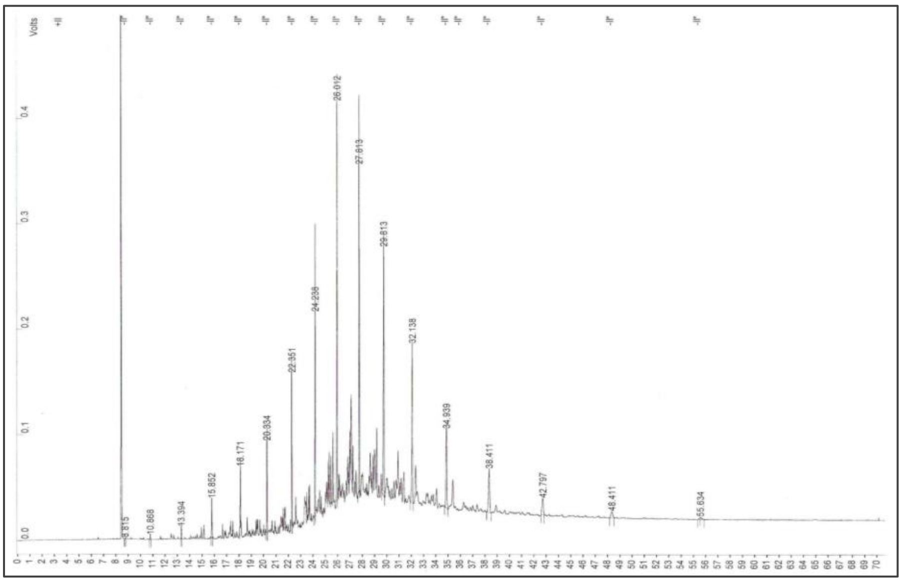
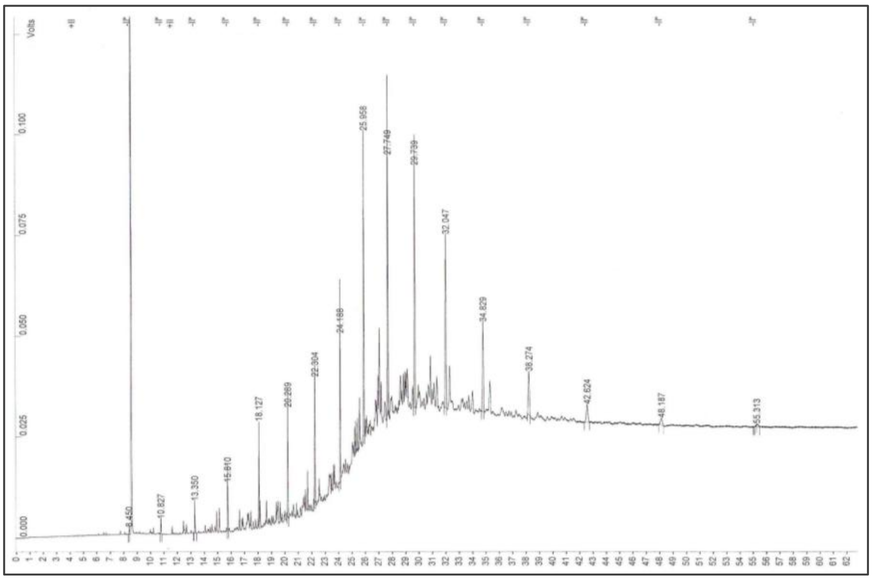
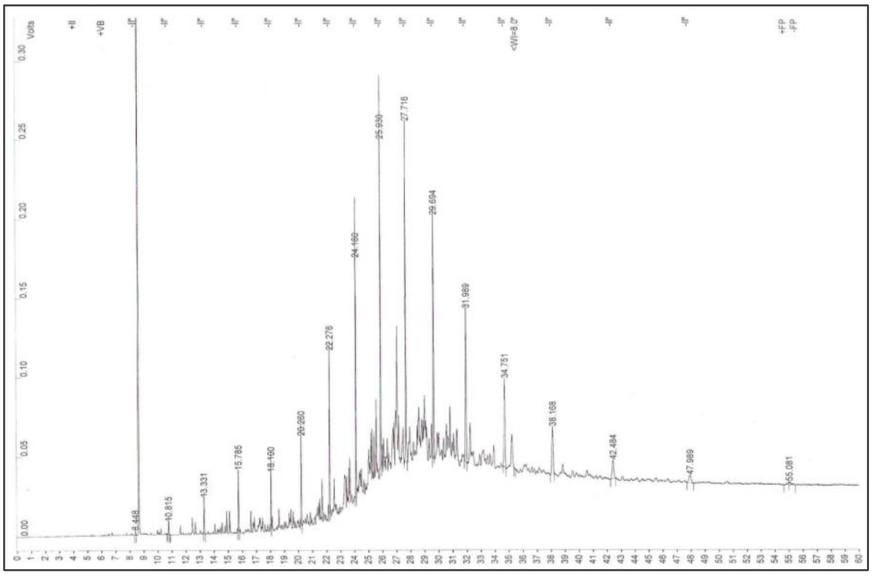


Figure (7): GC Chromatography of Diesel from T-8 Crude oil



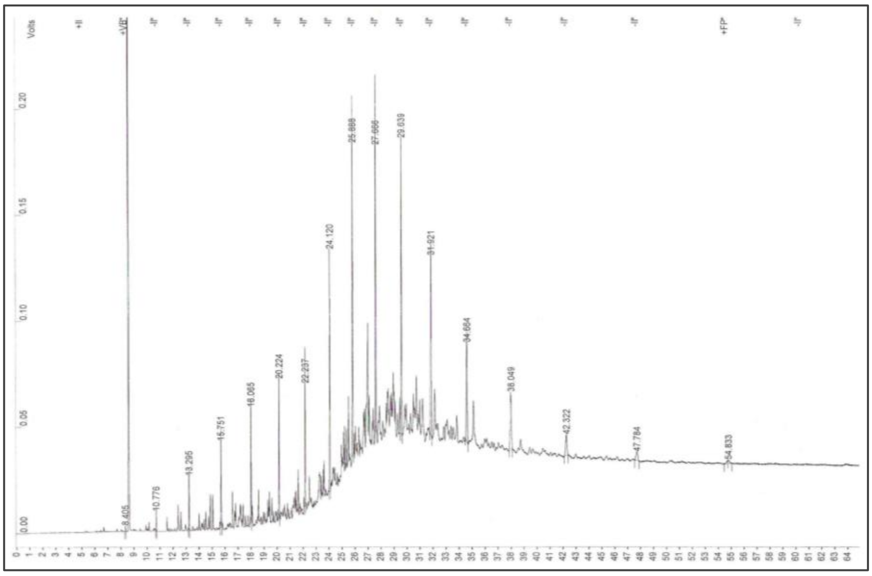
Time (min)

Figure 8. GC Chromatography of Diesel from T-16 Crude oil



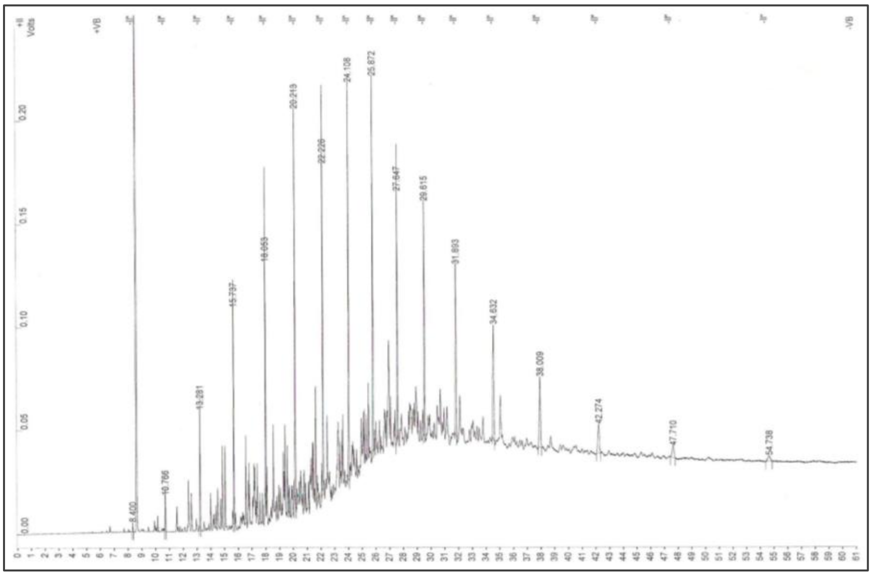
Time (min)

Figure 9. GC Chromatography of T-8 Crude oil with Clay 1



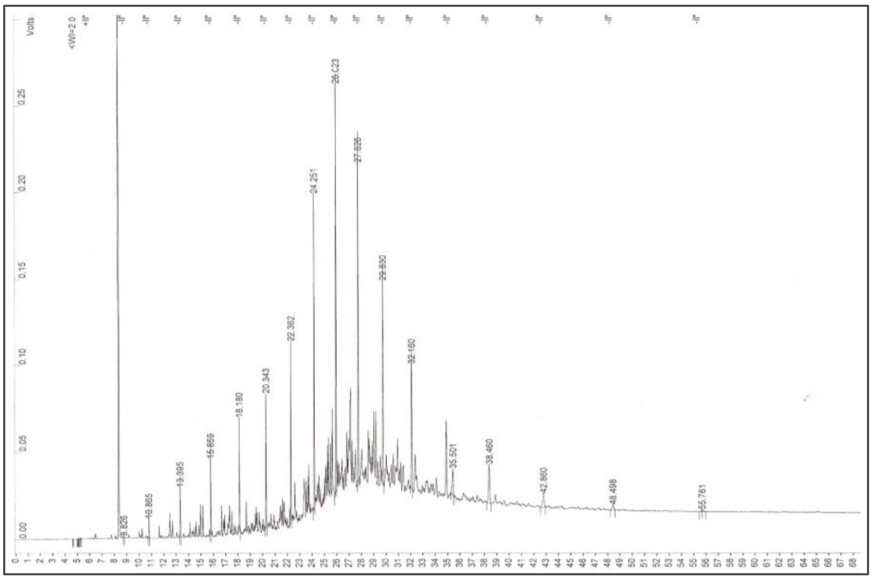
Time (min)

Figure 10. GC Chromatography of T-8 Crude oil with Clay 2



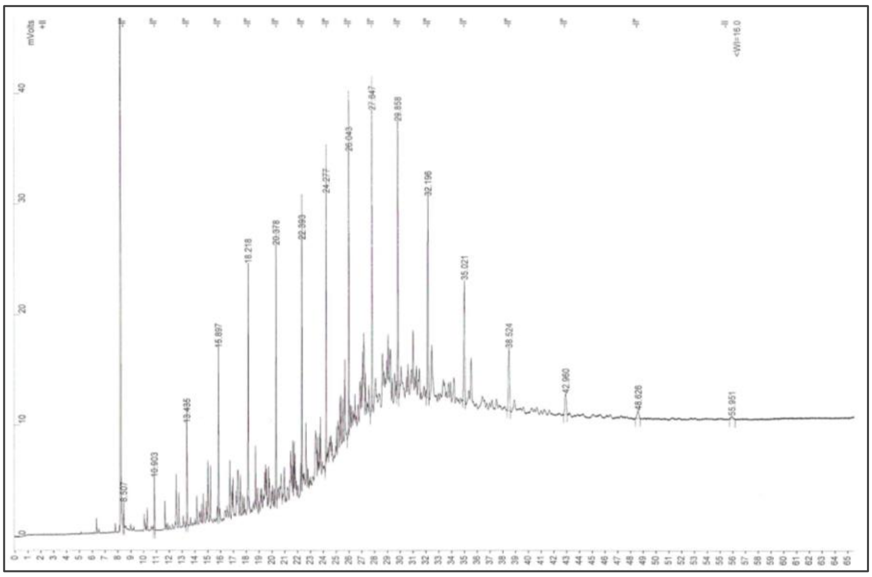
Time (min)

Figure 11. GC Chromatography of T-8 Crude oil with Clay 3



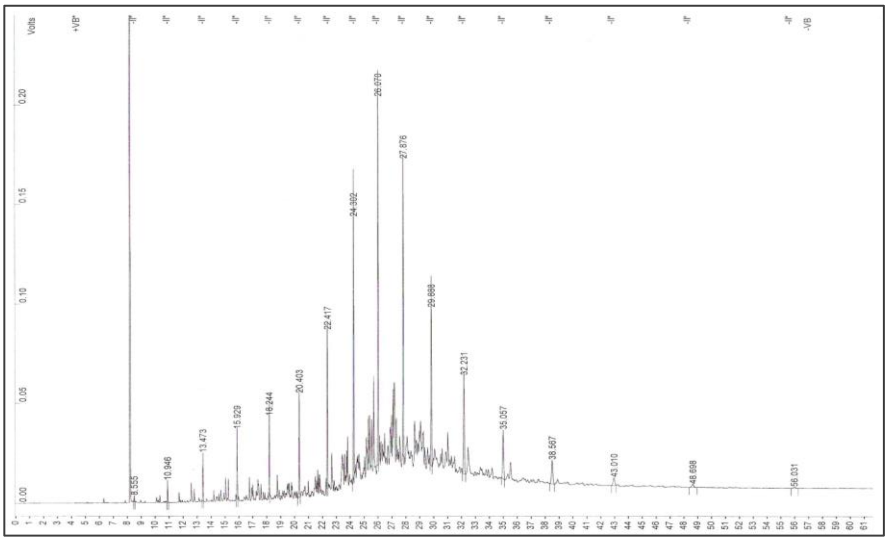
Time (min)

Figure 12. GC Chromatography of T-16 Crude oil with Clay 1



Time (min)

Figure 13. GC Chromatography of T-16 Crude oil with Clay 2



Time (min)

Figure 14. GC Chromatography of T-16 Crude oil with Clay 3

3. CONCLUSTIONS

This research shows that it is possible to improve the quality of these crude oils from T-8 and T-16 by refluxing it with clay at certain period of time and certain clay percentage. The clay number three is best for both Tawke wells that may be due to the higher ratio of SiO2/ Al2O3 also it contains a lower percentage of MgO. In this research to find such as clay that may have a higher ratio of SiO2/ Al2O3 and is similar to Bentonite, Kaoline and Zeolite types of clay. Our results show that the three types of clay are effective to change distillation cuts volume and chemical composition of the crudes at 6 hours and 350 °C when the percentage of clay was 6% W for T-8 and T-16, however the clay 3 is more effective than others types of clay.

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كورتيا لێكولينێ:

پارچا ديزلى هاتە تاقيكرن ژ هەردوو بيرێن تاوكێ 8 - T - 16, T(جور و قەبارە),ساخلەتێن فيزياوى يێن گازوايلا هەردوو بيرا هاتنە پيڤان ولديف رێكێن ASTM بو باشتر كرنا ئاوێتێت كيميايى بوپێكهاتێن ڤان جۆرێن پترولێ وزێدەكرنا قەبارێ پشكا ديزلێ ب كارئينانا سێ جورێن تەقنێن خوجهى, ب رێكا ئاميرێ X- r a y ئەف هەرسێ تەقنە هاتينە شلوفەكرن, زنجيرەكا تاقيكرنا هاتە جێبە جێكرن ل سەر رێژێين جودا ژ تەقنێن خو جهى د دەمێن جياواز بو پترولا بيرێت تاوكێ .8 - T - 16, T ئو پەيداكرنا دەمێ گونجايى ئەوێ بيتە ئە گەرێ زێدە كرنا قەبارێ دلوپكرى ژ ديزلى ژ پلا (200-320) س .° ديسان ديفجونا گهورينێن ئاوێتێن كيميايى بۆ پارچا ديزلا دلوپكرى ژ هەردوو بيرێت تاوكێ ئەوا كارلێكرى دگەل هەرسێ جورێت تەقنا دەست نيشانكرى ب رێكا گازكروماتوگرافى. پارچا دووێ ژ كارێ مە ژڤێ ڤەكولينێ ئەوە كۆ زێدەهيا ژمارەيا سيتانى بو ديزلا بەرهم هاتو دهێتە كرن برێكا زنجيرەكا زێدەكرنێن سيتانى(نترات,پيروكسايد) وزێدەكرنێن ئورگانێن كانزا كو ئوكسيجين تيدايە. (organometallic) زێدەهيا ژمارا سيتانى ئەوا بدەست مە فە هاتى ژ پلا45 بوو هەتا پلا 56 بوو وئەف زێدەهيە لسەر ئەساسێ گازا خام بۆ.

خلاصة البحث:

تم فحص مقطع الديزل المنتج من النفط الخام T - 16, T8 من بئري طاوكي-زاخو (النوعية والكمية) .وقد تم قياس بعض الخصائص الفيزيائية مثل (الكثافة، API، اللزوجة، نقطة سحابة، نقطة الوميض، ومحتوى المياه، محتوى الكبريت.... الخ) للنفط الخام والديزل المنتج وفقا إلى طريقةASTM. في محاولة لتحسين التراكيب الكيميائية المكونة لهذه الأنواع من النفط الخام وزيادة حجم جزء الديزل تم استخدام ثلاثة أنواع من الأطيان المحلية, بعد معرفة محتواها من اكاسيد المعادن بأستعمال جهاز الأ شعة السينية X- Ray. سلسلة من التجارب اجريت لتحديد النسبة مئوية للمختلفة من لأطيان المحلية وزمن لمعالجة ، لبئري طاوكي النفط الخام T - 8 و T - 16. هذه التجارب أجريت لإيجاد أفضل طين محلي و نسبة مئوية، بالإضافة لإجاد الزمن المناسب الذي يؤدي لزيادة حجم المتقطر من الديزل عند درجة (200-320) مْ. وقد تم رسم الشكل الأمثل لايجاد (نسبة الوزن لكل الطين، وقت التصعيد، ودرجات الحرارة). أيضآ تم متابعة التغيرات في التراكيب الكيميائية لمقطع الديزل من نفطي طاوكي بعد معاملتها الاطيان (1,2,3) بواسطة تقنية كروماتوكرافيا بالغاز. الجزء الثاني من هذا العمل هو تحسين نوعية وقود الديزل باستخدام مقياس العدد السيتاني. نوعان من النترات المضافة مثل (نترات -2إيثيل هكسيل، نترات الآيزوبروبيل)، نوع واحد من بيروكسيد المضافة (ثنائي ثالثي بوتيل بيروكسيد)، وثلاثة أنواع من العضوية الفلزية المعقدة المحتوية على الأوكسجين تم استخدامها لزيادة عدد السيتاني، يظهر نتائج زيادة نوعية هذه الديزل بين (10.7-0.5 units) اعتمادا على المكونات الكيميائية للنفط الخام وتكوين المضافة.