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Full Length Research Paper

Improvement of petroleum of Tawke – Zakho crude oil using local clays

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Evaluation of Tawke crude oil TW4 and TW8 through distillation cuts have been done by analysis chemical constituent (Gas chromatography) and measuring the (density, API, viscosity, pour point, flash point, water content, sulfur content, ash content etc., according both ASTM and IP methods). Improvement of this crude oil TW4 and TW8 have been done using three types of local clay. X-Ray analysis of these clays have been done and the chemical analysis of crude oil performed and compared before and after refluxing this crude oil using gas – chromatography. A series experiments have been done at a different percentage of clay, at different time of reflux and different temperatures and the changes in chemical constituent of this crude oil monitored by gas – chromatography analysis. Also Octane number of the distilled between (34 -200) °C have been measured.

Keywords: Tawke wells Number 4 and 8 (TW4) and TW8, Clay, Specific gravity (SG), Pour Point, Anilin, Crude oil.

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 (James2006).

Crude oil is usually evaluated through various physical and chemical methods of determination density, specific gravity, correlation index…..etc.

The American Petroleum Institute (API) defined the API gravity (degrees API) to quantify the quality of petroleum products and crude oils. The higher the API gravity number, the lighter the crude. For example, light crude oils have high API gravities and low specific gravities. Crude oils with low carbon, high hydrogen, and high API gravity are usually rich in paraffines and tend to yield greater proportions of gasoline and light petroleum products (API 2001).

Refinery Process

Rude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products, liquid petroleum gas LPG, gasoline, kerosene, diesel and a large number of other products that are used as raw material in the petrochemical industry (Hori 2000).

Clays

Clay is a mixture of Al_2O_3,SiO_2,xH_2O and (Mg, Ca, Fe) metals, 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. Clay is a term to describe group of hydrous aluminum silicates minerals, that are typically less than 2 micrometer. These materials are chemically referred to as compounds – Meaning that they are a 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

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bonding of Aluminum and oxygen (Klein 2005). Clays and clay minerals are very important industrial minerals.

The older type of catalysts was acid – treated natural clays (bentonite, kaoline…….etc) with variable amounts of combined silica and alumina.

Synthetic clay were 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 catalyst with high alumina content.

Kaolin

Kaolin is a clay mineral, part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. Rocks that are rich in kaolin are known as china clay, white clay, or kaolin. Kaolin clays have long been used in the ceramic industry, especially in fine porcelains, because they can be easily molded, have a fine texture, and are white when fired (Hweaver et al 2005).

Bentonite

The principle clay mineral composing bentonite is smectite. Commercial value due to its ion exchange ability. Bentonite is a rock or a clay base industrial material. It is therefore a mixture of minerals in general there are two type of bentonite, one is called the swelling type or sodium bentonite, which have single water layer particles containing Na^+ as the exchangeable ion. The other have double water layer particles with Ca^{++}, called calcium or non swelling type (Carlson 2004).

Montmorillonite

The montmorillonite consists of multiple layer structure, each layer consist from three an octahedral sheet surrounded by tow tetrahedral sheet. The montmorillonite is designated by the formula $Si_8O_{20}.(OH_4).nH_2O$. These mineral are characterized by the possibility of displacing number of elements in place of Al in the octal unite (in the octal sheet) and displacing Al in place of Si in the tetrahedral unit or sheets (Enresa 2002).

Zeolite

The word Zeolite was first used by the Swedish scientist (Cronsted) in 1976, and then become familiar term used by researcher in mineralogy and earth sciences. It is consist from tow Greek words Zeo which mean to boil and litho mean stone. Thus Zeolite means the boiling stone, because naturally occurring Zeolites are minerals that absorb water that subsequently boils when heated (Verdujin 2002).

Experiment

The preliminary Distillation of Crude oil have been determined according to the ASTM 89 method, fraction distillation ASTM 286, specific Gravity (S.G) and API Gravity by Pyknometer Methods (IP 190 ASTM D 1217), Anilin point(IP 2ASTM D 611), Pour Point(IP 15 ASTM D 97), Flash Point (IP 36 ASTM D 92), Kinemetic Viscosity (IP 71 ASTM 445), Water in crude oil (IP 74 ASTM D 95), Total Sulphur in Crude Oil ASTM D 129, Ash (IP 4 ASTM 482),Refractive Index measurement ASTM D 2159, Octane number (ON Shatox SX – 100 M). 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 (Xm – 1000, X-Ray instrument). Analysis the research samples by Gas Chromatography (GC), the GC were carried out on an Acme 6000, Young Line instrument.

Results

Physical properties of Raw TW4, TW8 crude oils

The value of some distillation rang and their physical properties for fraction product (SG, API, RI, Anilin, pour point) from TW4, TW8 crude oils are indicated in table 1. According to table (1) the cuts (2-6) have RI values with the range (1.37256 to 1.44631) for TW4 and (1.38325 to 1.44612) for TW8 crude oils. Fractions (7–12) their RI values higher than other fractions and this give the indication of presence of naphthene, olefine and aromatic compounds.

The R.I value increase in order paraffine, naphthene and aromatics (Klein 2005). The aniline point is of considerable value in the characterization of petroleum products for oils of a given type, it increases slightly with molecular weight and it increases rapidly with increasing paraffinic character.

Effect of Crude oils TW4 and TW8 by addition of Clays

Three types of local clay from Kurdistan region have been used in our study, they are in a different colors and chemical composition. Table 2 shows the X-Ray

Table 1. Physical properties for fractional distillation products of TW8, TW4 crude oil

Fr .no.	Cut Temp.	TW8				TW4			
	℃	Aniline point	S.G*	API gravity	R.I	Aniline point	S.G*	AP I gravity	R.I
1	40								
2	60	66.2	0.6531	85.75	1.38325	67.2	0.6587	83.31	1.37256
3	80	65.0	0.6618	82.31	1.40402	66.2	0.6787	76.98	1.38325
4	100	63.6	0.6944	72.27	1.42502	64.4	0.7003	70.55	1.42502
5	120	62.4	0.7219	64.51	1.43552	63.0	0.7196	65.13	1.43552
6	140	61.6	0.7653	53.39	1.44612	62.8	0.7406	59.56	1.44631
7	160	60.0	0.7762	50.70	1.45658	61.0	0.7627	54.02	1.45658
8	180	58.2	0.7781	50.35	1.46703	57.6	0.7842	48.93	1.46703
9	200	56.6	0.8072	43.79	1.47742	55.4	0.8400	36.95	1.47742
10	220	55.0	0.8288	39.22	1.48789	54.2	0.8577	33.47	1.48789
11	240	54.3	0.8486	35.20	1.50102	53.3	0.8746	30.28	1.50124
12	260	53.0	0.8784	29.58	1.50706	52.4	0.8830	28.74	1.50869

Table 2. Metal oxide in local clay (1,2,3) according to X – Ray fluoresces(Oxford UK)

Metal oxide	Clay 1 % W	Clay 2 % W	Clay 3 % W
SiO_2	36.27	35.53	24.19
Al_2O_3	6.71	7.11	9.67
SiO_2 / Al_2O_3	5.405	4.997	2.25

Table 3. Effect of addition clay(1,2,3)on cumulative volume of fraction of TW4 Crude oil

Clay	% W	2h		4h		6h	
		Cum. Vol. of cuts from (32-180)℃	Cum. Vol. of cuts from (200-260)℃	Cum. Vol. of cuts from (32-180)℃	Cum. Vol. of cuts from (200-260)℃	Cum. Vol. of cuts from (32-180)℃	Cum. Vol. of cuts from (200-260)℃
1	0	25.7	26.0	25.7	26.0	25.7	26.0
1	1	38.1	19.2	40.5	18.5	44.4	16.8
1	2	40.1	18.9	43.9	17.6	46.7	16.0
1	3	43.6	17.4	45.0	17.1	48.6	14.8
1	5	47.1	16.6	47.5	16.0	50.1	14.1
1	7	49.2	14.9	49.5	15.3	52.7	13.8
2	1	37.2	19.6	38.3	18.9	41.3	17.9
2	2	38.1	18.3	39.3	17.0	42.9	16.3
2	3	39.2	16.5	40.2	16.4	44.3	15.9
2	5	42.7	15.8	44.5	15.6	46.6	15.4
2	7	44.9	15.3	45.6	15.0	47.2	14.4
3	1	38.9	19.9	40.2	18.2	43.3	17.4
3	2	40.7	18.9	42.8	17.4	45.0	16.4
3	3	43.3	17.1	43.6	16.8	46.3	15.6
3	5	45.4	15.1	46.5	15.9	47.4	15.1
3	7	46.1	14.7	47.8	15.0	48.2	14.1

fluoresces data for the three type of clays.

Effect of different percentage of clay (1,2,3) and different reflex time on the fractions distillation of TW4,TW8 crude oils

Our work aimed to study the effect of types of clay, clay percentage , time of reflex and temperatures on the improvement of TW4,TW8 crude oils .In these studies three type of clay (1,2,3) with different percentage (1,2,3,5,7,) % W and reflexed for (2,4,6) hour reflex time at different average temperatures of boiling crude oils . The results are shown in tables 3 and 4.

According to the tables 3, 4 and figures 1, 2 volume of fractions that have temperatures range (34 – 180) ℃ are increased with increasing the percentage of clay. The 7%, 5% is more suitable for the fraction distillation of cuts from TW4, TW8 Crude oil, compared with 3%, 2%, 1%.

Table 4. Effect of addition clay (1,2,3)on cumulative volume of fraction distillation Cuts TW8 Crude Oil

Clay		2h		4h		6h	
	% W	Cum. Vol. of cuts from (34-180)℃	Cum. Vol. of cuts from (200-260)℃	Cum. Vol. of cuts from (34-180)℃	Cum. Vol. of cuts from (200-260)℃	Cum. Vol. of cuts from (34-180)℃	Cum. Vol. of cuts from (200-260)℃
1	0	24.0	29.4	24.0	29.4	24.0	29.4
1	1	34.7	19.6	38.5	19.0	39.3	17.1
1	2	37.0	18.5	40.0	16.9	42.8	16.6
1	3	38.9	17.5	43.7	16.4	45.9	15.3
1	5	40.7	17.0	45.9	15.7	47.5	14.5
1	7	45.9	14.4	48.1	14.3	49.8	13.8
2	1	34.8	19.2	35.8	19.0	35.4	19.8
2	2	35.5	19.0	36.3	18.3	38.9	18.5
2	3	37.0	18.4	38.0	16.4	42.6	17.1
2	5	39.1	17.7	39.0	16.3	45.1	15.7
2	7	44.1	16.6	44.1	14.3	47.6	14.0
3	1	30.0	21.4	34.5	21.6	34.8	19.4
3	2	34.5	21.1	34.6	20.9	35.8	17.7
3	3	38.3	20.3	38.8	19.7	40.5	16.1
3	5	41.6	18.0	42.1	18.7	43.4	15.3
3	7	42.9	17.3	43.7	18.1	47.3	14.8

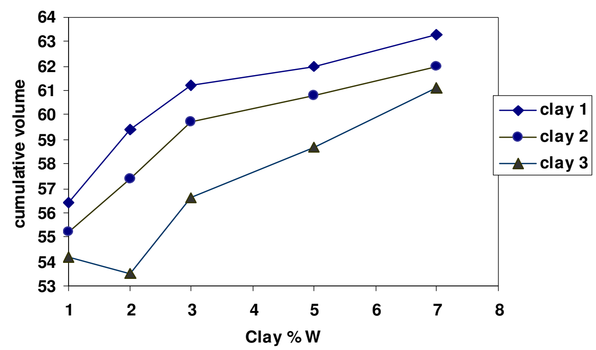

Figure 1. Effect of clay (1,2,3) concentration %W on the TW4 fraction distillation at 6 hour reflex time

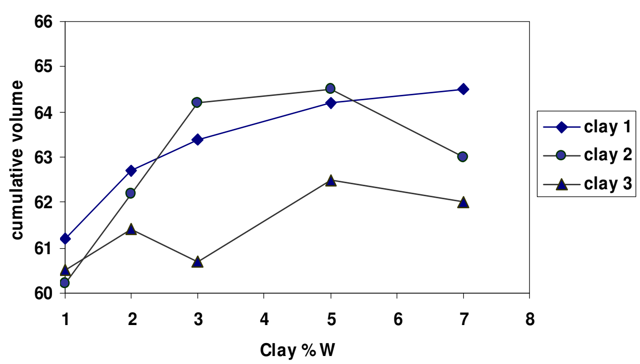

Figure 2. Effect of clay (1,2,3) concentration %W on the TW8 fraction distillation at 6 hour reflex time.

According to figures 3, 4, show that the best time of reflex was 6h for increasing the volume of fraction distillation Cuts of TW4,TW8 crude Oil with using 7% W clay (1,2,3).

In order to study the effect of temperatures on increasing the distillation cuts volume for TW4,TW8 crude oils .The results in tables 3, 4 for TW8,TW4 crude oils shows that the (7% W) of clay (1,2,3) with 6 h

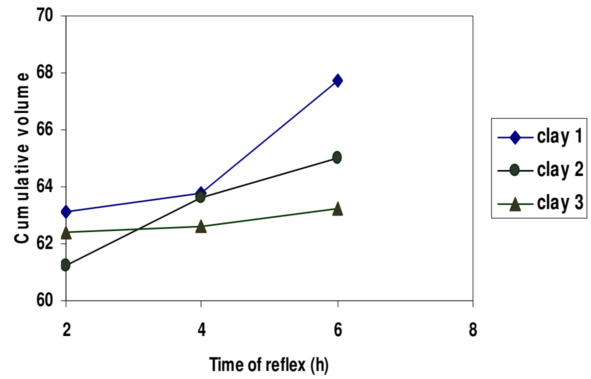

Figure 3. Effect of reflex time on the TW8 fractional distillation with 7% W of clay (1,2,3)

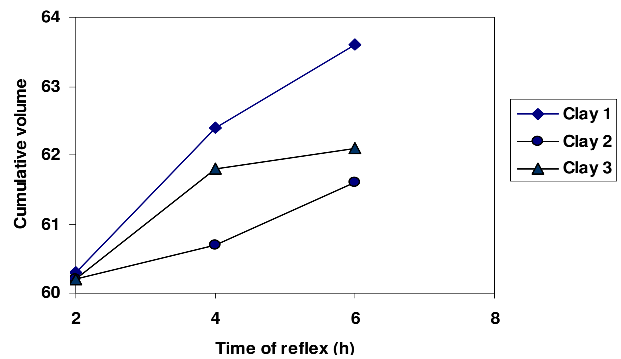

Figure 4. Effect of reflex time on the TW4 fractional distillation with7% W of clay (1,2,3)

Table 5. Retention time and peak area percentage for peaks of heavy part for TW4, TW8 crude oils without clays

Retention Time for TW4 crude oil (min.)	Area %	Retention Time for TW8 crude oil (min.)	Area %
21.5742	30.2783	21.6025	27.3813
30.5767	23.3679	30.6017	31.1253
34.1225	1.2891	34.0983	1.2954
34.7217	1.0391	34.7433	1.5763

time at 350 °C have more effect to change distillation cuts volume.

In order to study effect of clay types on the increasing the percentage of distillation cuts oil of TW8, TW4, table (2) shows that the clay (1,2,3) have SiO_2 W % (36.27, 35.53, 24.19) respectively, as the amount of silica increase, the activity of clay should be increase 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 (5.405, 4.997, 2.25) for clay (1,2,3) respectively and Clay with high Si/Al ratios are more stable.

Effect of clay (1,2,3) on chemical composition of TW8 crude oil by gas chromatography GC

Gas chromatographic method are used for separation of our distillate, these distillate are obtained from both crude oils with using clay 7 %W for 6h time of reflux. The retention time RT of hydrocarbons compound in each sample of TW4 clay 1 products indicated in chromatogram figure 6.

According to table 5 which indicated the retention time (RT) for normal hydrocarbons, the results of GC analysis for fractions that isolated from TW8, TW4 and

Table 6. Retention time and peak area percentage for peaks of heavy cuts for TW**8** crude oil with clays

Retention Time (min.) for TW8 crude oil with clay 1	% Area	Retention Time (min.) for TW8 crude oil with clay 2	% Area	Retention Time(min.) for TW8 crude oil with clay 3	% Area
21.6	6.93	21.0	15.7	19.26	3.6
30.0	13.5	30.0	17.4	30.63	16.57
34.116	1.054	34.125	0.693	-	-
34.757	1.693	34.7725	0.779	-	-

Table 7. Retention time and peak area percentage for peaks of heavy cuts for TW4 crude oil with clays

Retention Time (min.) for TW4 crude oil with clay 1	% Area	Retention Time (min.) for TW4 crude oil with clay 2	% Area	Retention Time (min.) for TW4 crude oil with clay 3	% Area
21.6275	9.646	21.6367	9.252	21.6250	10.176
30.6208	13.367	30.6342	17.578	30.6225	14.755
34.122	1.289	34.133	1.265	34.1242	0.905
34.7658	1.039	34.7683	1.186	34.7658	0.751

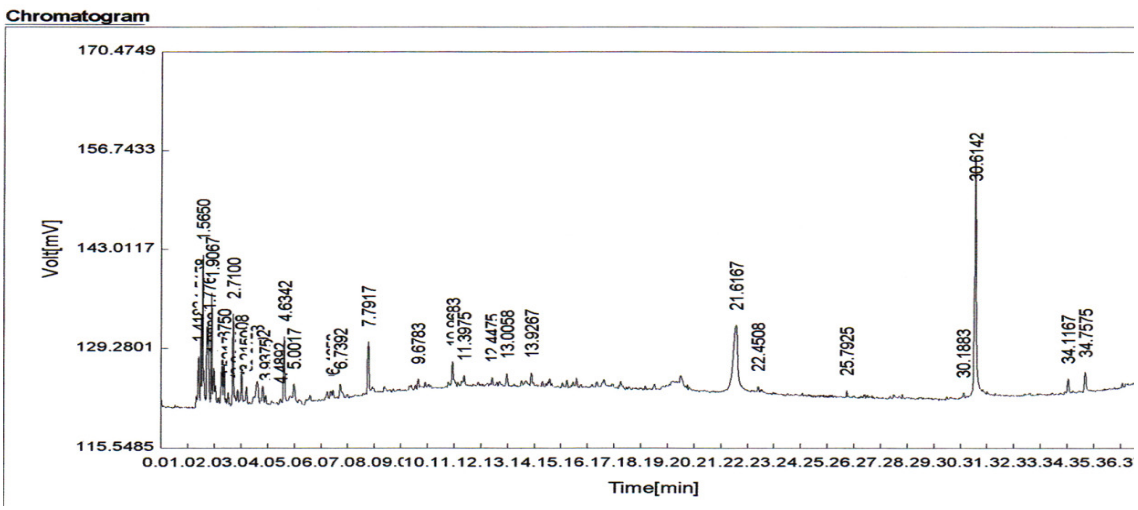

Figure 5. Chromatograph of fraction distillate (3**2** – 260) ℃ which isolated from TW**8** crude oils treated with clay **1**at 7% W concentration and 6 h time of reflex

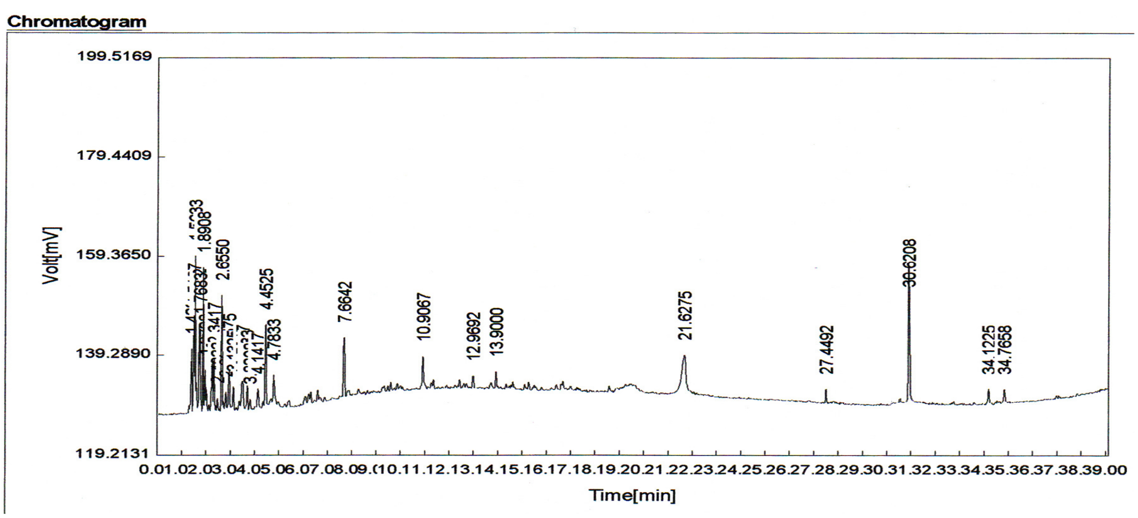

Figure 6. Chromatograph of fraction distillate (34 – 260) ℃ which obtained from TW**4** crude oils treated with clay 1at 7% W concentration and 6 h time of reflex

thus show that the crude oil is heavy type.

Tables 6, 7 and figures 5, 6 show the results of GC analysis for the fractions that are isolated from TW8, TW4 after using clay (1), these results indicated the decreases in the peak area percentage of the hydrocarbons (C19, C>20) and thus causes increase of cracking the large hydrocarbon to increase the light fractions with using clays.

CONCLUSIONS

This research shows that it is possible to improve the quality of these crude oils by refluxing it with clay at certain period of time and certain percentage.

The clay number one is the best for both Tawke wells .that may be due to the X – Ray analysis of it and it contain higher ratio of SiO_2/ Al_2O_3 also it contain lower percentage of MgO. certain local clays act as active catalyst to convert long chain hydrocarbon's to shorter as a nature zealots

Different clay have been used to improve the crude oil long time ago such as Bentonite, Kaoline and Zeolite.

Our results show that the three type of clay are effective to change distillation cuts volume and chemical composition of the cruds at 6 hour and 350℃ when the percentage of clay was 7% W for TW8and TW4 but the clay 1 is more effective than others type of clays.

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