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Oil Recovery from Petroleum Sludge by Solvent Extraction Method

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Abstract
Industries developed during the last decades and the importance of oil is increasing. Petroleum is one of the most valuable non-renewable sources and it also, has the biggest effects on the environments after coal. Crude oil became the goal of many countries in order to increase their economies income, despite the outcome that has towards the environment. The crude oil that passes through the refinery process produces a large amount of waste, which is call petroleum sludge. The sludge has countless disadvantage that cause environmental hazards due to its remediation effects. In addition, it is very valuable energy and it can be recovered. So the companies used several methods in order to use this source and get benefit from it. One of the methods is the solvent extraction method and overall, this method can decrease the effect of the petroleum sludge on the environment but not that much. However, it can recover the waste and turn it to useful energy. The recovery can be done by different steps. The first step is making chemical compositions before using the instruments. Second step is to use the centrifuge machine which will separate the sludge and recover it into oil, sludge sediment and water. The third part is to use the residual carbon machine which will measure the solidcontent inside the sludge and it will help us to find the violate and non-violate hydrocarbons. Finally using the GC which is gas chromatography that checks the quality of the petrol and also the composition substance.

Introduction
Petroleum in the last decades became a very significant nonrenewable source. Oil products are very important in our daily life, and in industry work. The process of producing all the petroleum products like gasoline, diesel fuel, and other important product.The preliminary process start from pumping the crude oil from the wells then to the refinery that extracts the crude oil products by either heating and separating the crude oil until it gets to the market. The crude oil is defined as unrefined oil, which is a mixture of hydrocarbons that exist in a liquid phase which remains liquid when at the atmospheric pressure and when it passes through the separation processes to make up different petroleum products[1]. The production of oil is increasing since it was discovered it first in China in 347 AD and produced in USA in 1815 [2]. And because of its importance and the expense of producing one barrel as declared in the Figure 1.1 and Table 1.1 now day, the price of the oil barrel is not stable. In the petroleum industry, the wells might produce a large amount of sludge waste, which is economically not useful [3].Sludge is defined as a solid content of sewage which is produced during treatment or production and removed for subsequent purifictaion[4].Overall, about 3-5% of crude oil is not usable or needed in industrial or daily use. Throughout all these processes, the oil company wanted to decrease the loss of petroleum sludge by cleaning it or recovering it, so they used different methods in order to reach that goal. After refining the crude oil the petroleum sludge forms. Petroleum sludge is a complex mixture containing different quantities of waste oil, wastewater, sand, and mineral matter [5]. The industries need to manage the petroleum sludge and clear the different useless mixtures that can affect the quality of the oil products. So to recover and clear the petroleum sludge the companies used different methods so as to achieve the quality of the oil and the cleaning proccess varies from method to another. One of the most important approaches of treatment is recycling. Recycling is the most acceptable way to decreases the effect of oil on the environment,also protect it from the oil pollution and recover the oil in an perfect way to use it. However, crude oil refineries include three distinct phases primary, secondary and tertiary. There are three primary methods to recover the oil which are gas injection, thermal injection and chemical injection [6] . One of the methods that will be discussed in this project is the solvent extraction method. In addition, there are a couple of solvent techniques like Batchwise single stage extractions,Multistage countercurrent continuous processes, Mixer-settlers and more[7]. The maximum amount that can be recovered from petrol sludge varies from 80%-97% depending upon the composition of the sludge, the amount of oil in the petroluem sludge and the efficiency of the solvent. Solvent extraction is a method used to separate substances from each other Sometimes it is considered as the most widely acceptable method. It is also called liquid-liquid extraction as shown in the Figure 1.2 It shows how one of the solvent extraction methods works. The idea behind this project is to determine the oil chemical and physical properties of Kurdistan petrol from oil sludge. Furthermore, different values and composition used for different types of oil sludge that distinguish it from one location to another, host rocks and more and enhance the oil sludge by using the solvent method. By using the centrfuge method we can extract water and the sediemtent from the petroleum slduge. Then we can measure the solid content by burning the sample using the residual carbon machine.The

recovery quality will be measured by gas chromatography (GC), which is an analytic instrument use to separate substances and to check the quality and percentage of the component in the sample[8]. The component is dissolved in a solvent and vaporized in order to separate it. The system uses two phases so it can be started which arethe stationary phase and the mobile phase. The mobile phase is a chemically inert gas that serves to carry the molecules of the analyzed sampled through the heated column, which consists of gases such as helium and argon [9].The stationary phase consists of pieces of solid or liquid high boiled polymer [10]. The compositionpercentage is determined by a column and an electronic detector that showed in a chart later.

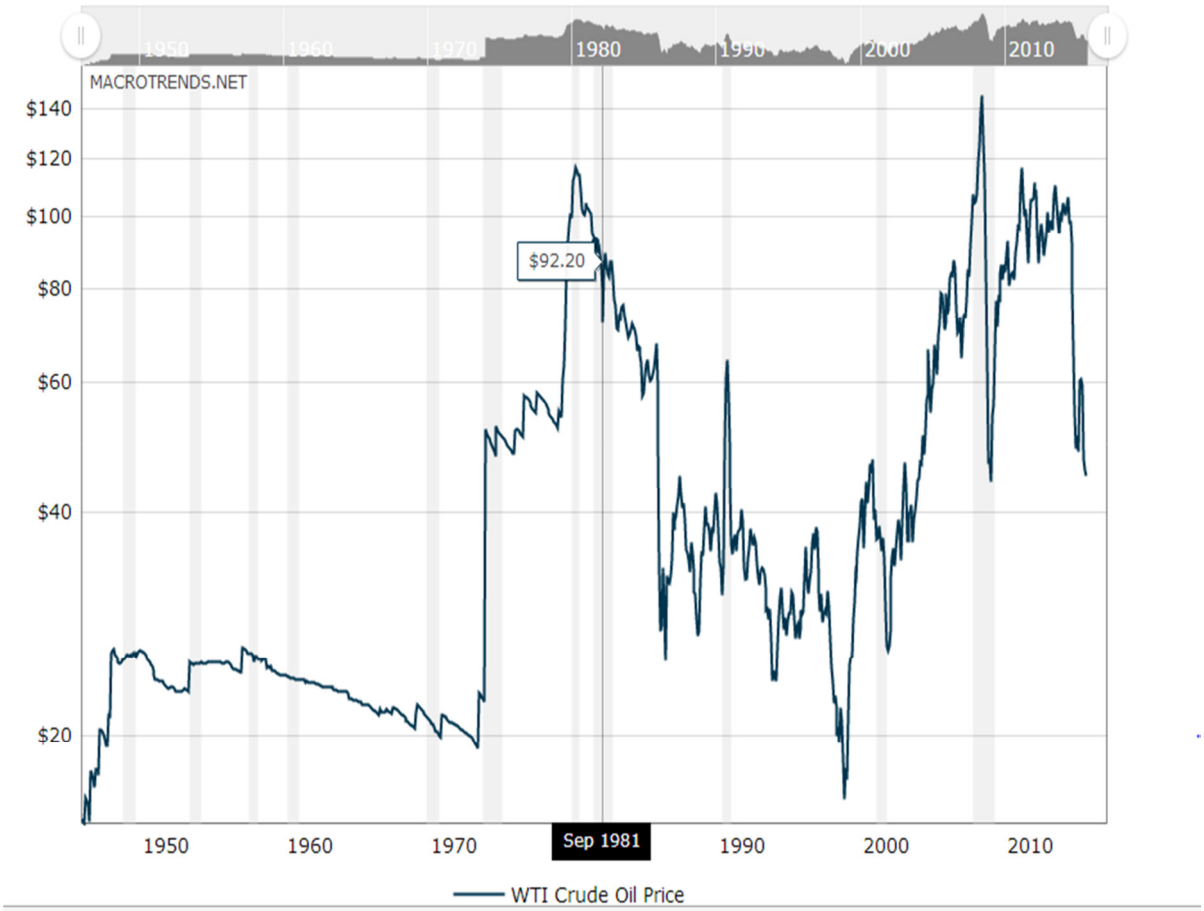

Figure 1.1 the price of WTI crude oil for the last 50 years[11].

Total Oil Supply (Thousand Barrels Per Day)					
Middle East	26,242.0	27,689.1	27,899.2	27,491.7	27,856.1
Bahrain	47.2	48.2	55.2	61.2	63.7
Iran	4,243.1	4,214.0	3,517.8	3,192.4	3,374.7
Iraq	2,402.9	2,629.0	2,986.6	3,057.7	3,371.3
Israel	6.1	5.8	5.7	5.8	5.8
Jordan	0.2	0.2	0.2	0.2	0.2
Kuwait	2,460.3	2,691.8	2,796.8	2,811.8	2,780.4
Lebanon	0	0	0	0	0
Oman	869.9	890.9	923.8	945.1	950.9
Palestinian Territories	0	0	0	0	0
Qatar	1,787.9	1,936.4	2,032.6	2,067.3	2,054.7
Saudi Arabia	10,908.4	11,466.7	11,840.7	11,701.5	11,623.7

Units Conversion Download Excel

Table 1.1 Oil Production supply to the Market in Middle East thousand Barrel Per Day from 2010-2014[12].

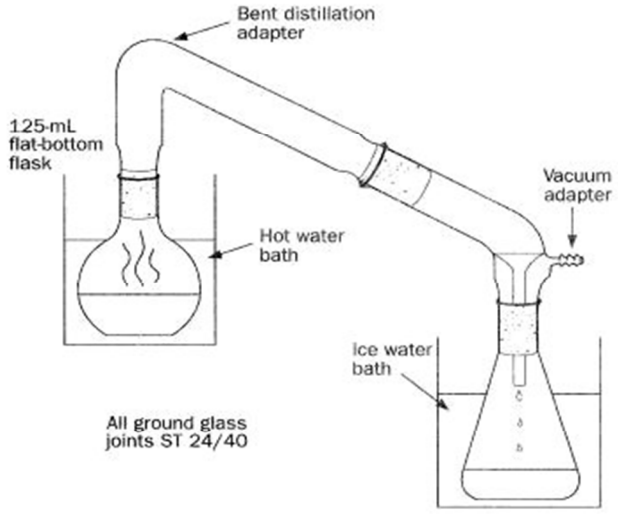

Figure 5520:1. Distillate recovery apparatus.

Figure 1.2 Distillate Recover Apparatus Solvent method [13].

Methodology and Instrumentation

In order to recover the valuable fuel oil. There are some specific requirements to increase the energy efficiency by sustainable growth, which is easy and economically acceptable technologies. [14]. There are certain instruments to use in this experiment, which are the Centrifuge machine, Residual carbon and GC, acids and oil samples. We can also use D95 method in this project.

Procedure

The procedure starts with bowling 50 ml of water until 180c to indirectly heat the oil sludge and settle the content before it is separated by centrifuge method. First, we shake the sample by hand for 10-15 minute. Then we separate the sample into two-centrifuge tubes each containing 25ml of the petroleum sludge. After that, we add toluenes,which is methyl-benzene into both tubes with 25ml of toluenes. Then we add two small drop of demulsifiers. Demulsifiers is used to cling the sample to the walls of the centrifuge tube by promoting the separation of water from the sample. The researcher must be careful using toluenes because it is toxic. Then put the mixture into the bowled water for 15-minute +-3 at 60 C. By the specific gravity tube you can measure the spatial gravity and API for both samples. This will be discussed in the results section. After that the tubes are inserted into the centrifuge machine (Figure 7.1). The centrifuge machine set at 1800 turn per minute for 20 minutes[15]. Then we use the following eqution to find the light hydrocarbon:

$$\text{Light Hydrocarbon} = \frac{Reduced\ Mass, G}{Mass\ Of\ Tested\ sampl, g}\ X\ 100\% - Water\ content.\%$$

Next method is to find the solid content in the oil sludge by using residual carbon machine (Figure7.2) by burning the sludge. First, we prepare two bulbs that are heated alone inside the machine for 10 minutes in order to get rid of the old content. Then we measure the weight of the bulb without the sample. After that, we add the mixture inside the bulb one used for the oil sludge and the other for the separated oil sludge. Last part is adding the two-failed bulb into the residual machine that is set at 550C for 30 minutes. The bulbs inserted in the insulator for 5 minute in order to cool down and the resultswere as the following Table 3.1 we can note that samples from the Makhmore area contain more asphalt and more solid carbonate materials.

Table3.1Weight of the samples before and after separation

Sample All in Gram	Bulb A	Bulb B	Bulb A + Petroleum sludge	Bulb B + Separated oil	Bulb A + Petroleum sludge after the experiment	Bulb B + Oil after the experiment	Petroleum sludge oil content %	Separated oil content %
Khurmala	11.2722	10.5439	12.0552	11.7345	11.3040	10.5611	4.06131	1.445
Guwayer	11.2428	10.5493	12.7327	12.58342	11.2907	10.9310	3.208	18.766

The weight percent can be calculating by this equation

Mass tasted of the sample = the sample weighed inside the bulb -the bulb weight.

$$\text{Solid Content} = \frac{\text{Mass of residue remaining after burning, g}}{\text{mass of tested sample, g}} \text{ X } 100\%$$

After measuring the water content, light hydrocarbon content, and solid content, the nonvolatile hydrocarbon content will be measured by this equation

NVH= 100% - VH + SC + WC

Finally, from this process you can recover the sludge and find their properties and you can also check the recovery and the percentage of the component in the sludge by gas chromatography. First we add the sludge into the instrument by using a Syringe. After that the machine starts to work and heated the sample until it vaporized. Then a neutral gas is added (eluate) like hydrogen or helium. That helps the gases to go through the column easily [16]. The column maybe made of glass or metal which fills with boiling liquid or gas. After that the mixture go through the column and it absorb by the separator to find the compounds composition. So far each substance passes through a column and an electron detector find the percentage, which is placed into a chart.

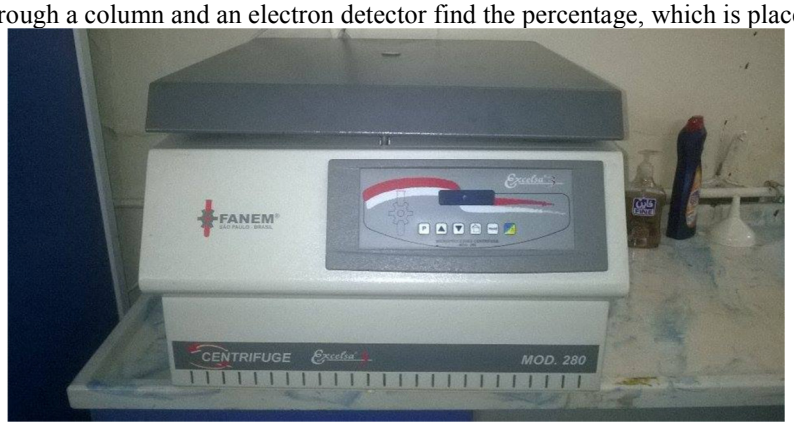

Figure 3.1 centrifuge machine FANEM MOD 280

Figure 3.2Carbon Residual

Figure 3.3 Simple gas chromatography

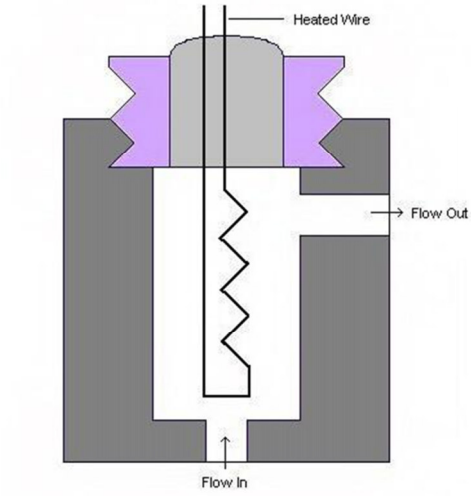

Figure 4.4Schematic of the thermal conductivity detection cell[17].

Results

First we measure the light hydrocarbons in the sample by using this equation. After it tested in the centrifuge machine

$$Light\ Hydrocarbon = \frac{Reduced\ Mass, G}{Mass\ Of\ Tested\ sampl, g}\ X\ 100\% - Water\ content.\%$$

For the first sample and second sample the content percentage was as below

Table 3.6.1 *sample content percentage in the crude*

Sample number	Sample Weight	Sediment %	Water %	Sludge content %	Oil% reduced mass (recovered)	Oil content in gram	Light hydrocarbon %
Khurmala sample 1	50 ML	0.1	0.75	3.23	95.92	47.96	95.17
Guwayer sample 2	50ML	0.5	11	5.25	83.25	41.625	72.25

First change ML into Gram. Each 1Ml=1 g

For sample 1:

$$\text{Light Hydrocarbon} = \frac{Reduced\ Mass, G}{Mass\ Of\ Tested\ sampl, g}\ X\ 100\% - Water\ content.\%$$

$$\text{Light Hydrocarbon} = \frac{47.96\ g}{50\ g}\ X\ 100\% - 0.75.\% = 95.17\ \%$$

Sample 2:

$$\text{Light Hydrocarbon} = \frac{Reduced\ Mass, G}{Mass\ Of\ Tested\ sampl, g}\ X\ 100\% - Water\ content.\%$$

$$\text{Light Hydrocarbon} = \frac{41.625\ g}{50\ g}\ X\ 100\% - 11.\% = 72.25\ \%$$

After that we found the solid content by using the carbon residual we can calculate it by using these equations
Mass tested of the sample = the sample weighed inside the bulb -the bulb weight.

$$\text{Solid Content} = \frac{\text{Mass of residue remaining after burning, in gram}}{\text{mass of tested sample, in gram}}\ \text{X100\%}$$

The result calculated as below.

Table3.6.2*Weight of the samples before and after separation*

Sample All in Gram	Bulb A	Bulb B	Bulb A + Petroleum sludge	Bulb B + Separated oil	Bulb A + Petroleum sludge after the experiment	Bulb B + Oil after the experiment	Petroleum sludge oil content %	Separated oil content %
Khurmala	11.2722	10.5439	12.0552	11.7345	11.3040	10.5611	4.06131	1.445
Guwayer	11.2428	10.5493	12.7327	12.58342	11.2907	10.9310	3.208	18.766

Finally, we find the non-violated hydrocarbon for each sample by this equation.
NVH= 100% - VH + SC + WC
WC= water content
VH= volatilehydrocarbon
SC=Solid content
NVH= Nonvolatilehydrocarbon
For sample One
NVH=100%-95.17%+0.75%+1.445%=2.6354%
Sample Two
NVH=100%-72.25%+11%+3.208=41.958
can also measure spatial gravity by gravity tube, the Sulphur content by manual application in the MNR and API so the final results as in below table.

Table3.6.3Different Properties and content in the crude oil sample

No	Sample area	Sp.gr Room T D1289	Sp.gr at 15.56 C	API ASTM D1298	Sulphur WT% ASTM D4294	Water content v/v% D4007	Sediment V/V% D4007	Sludge V/V % ASTM D4007	Rams bottom Carbon Residue Mass% D524
1	Waste crude oil of Khurmala	0.898 At 18C	0.899	25.80	1.7584	1.5	0.1	6.46	4.061
	After Separation	0.871 At 19C	0.8732	30.54	1.0751	------	------	------	1.445
2	Waste crude oil of Guwayer	1.051 At 25C	1.0568	2.40	0.6961	8.4	1.6	12.4	18.766
	After Separation	0.883 At 20c	0.8859	28.23	0.1982	--------	--------	--------	3.208

Finally, from the GC found that the 75% of the oil is recovered from Khurmala sample. And about 68.5 in Guwayer. Also found that both of the samples are aromatic because the API value is less than 33 [18].

Discussion

From the GC we found that the samples are aromatic and the aromatic percentage is as below

Table 3.7.1 Sludge Aromatic and Aliphatic Property

Sample area	**Aromatc %**	**Aliphatic %**	**Hydrocarbon content %**	**Aromatic-aliphatic ratio**
Guawyer	**64.3**	**35.7**	72.25	**1.8011**
Khurmala	**71.5**	**28.5**	95.17	**2.5088**

From this result we found that Khurmala has a good performance in machine due to extracting useful hydrocarbons as shown in the table above, which is largely depend on the number of extracted (recovered)

hydrocarbons. Also there is a relationship between the specific gravity and the API gravity shows in the equation $\textbf{API Gravity} = \frac{\textbf{141.5}}{\textbf{specific gracity(g)}} - \textbf{131.5}$which will help to find the sulphur content by using this equation $y = 11.903 \times e^{-0.102x}$ [19] where y=sulphur content % x=API ,which it can be plotted in a figure as shows in the below figure picture.

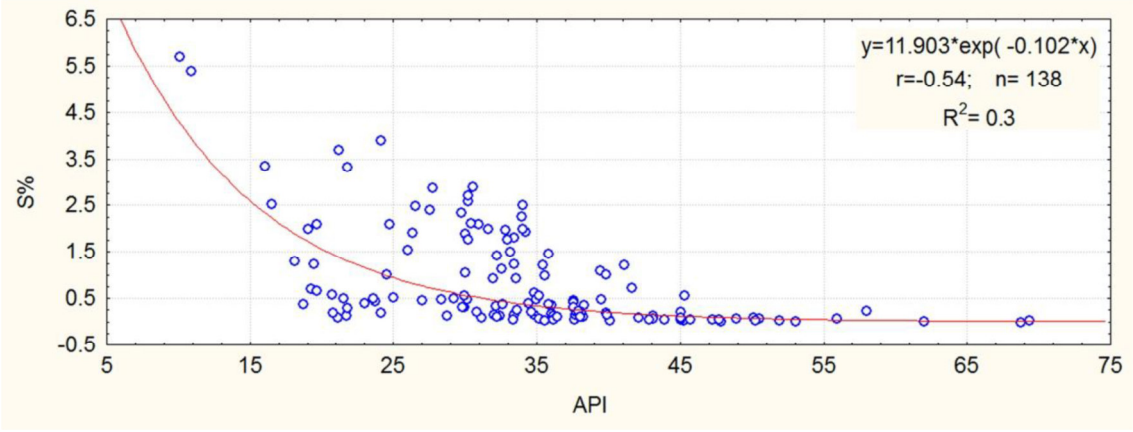

Figure3.7.1: Statistical analysis displays the S% content effect of the API [19].

Also there is a relationship between the Paraffinic, naphthenic and Aromatic with the specific gravity and the molecule weight of the oil which can be found by this equation $\boldsymbol{Kw = 4.5579 M^{0.15178} g^{-0.84573}}$[20].

Where Kw is Watson characterization factor, °R1/3, M is the oil molecular weight, m, lbm/lbm mol

If the result is less than 33 its aromatic and if its more than 33 is aphanitic.So lower values of this factor indicates hydrocarbons with more naphthenic or aromatic components [21]. Soas shows in the experiment Kurdistan oil can be recovered and used as an additive resource by the solvent method which can be done in the MNRE laboratory. From the experiment the project discovered different properties in the two oil fields, which include chemical and physical aspects and differences between the two samples.

Recommendation

This project paper recommendsspread use of the solvent method due to the following reasons like, cheapness, easy to use, fast accurate and economically efficient compared to other methods.

Conclusion

Recovering sludge is a very important process that can affect the environment and also be economically helpful. In order to decrease the effect of the stored sludge and the sludge that has been disposed in the environment that disturbed the soil and water supply which lead to environmental hazards in the future. So the solvent extraction method might be one of the method that can help to decrease the future causes of the sludge. So far it can be economically valuable if the process of recovery was benefit for the company. Different companies can get a huge income from the process and they can also supply the market with more oil.

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