

# **ASSESSMENT OF SLUDGES AND TANK BOTTOMS TREATMENT PROCESSES**

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## **ABSTRACT**

The oil production and petroleum refining industries generate considerable amounts of sludges and tank bottoms as waste. Since the landfilling option has gradually been narrowed, the disposal of these hazardous materials becomes a major problem because of the ever-tightened environmental regulations and expectation of ever-increased company profits margins. To maximize the waste oil recovery from sludges and tank bottoms and to minimize the volume of the hazardous waste, a number of waste recovery and treatment processes are introduced to the local industries. The process designs and unit operations of each process are different and each has its own merits, in terms of the technical complexity, operation friendliness, and costs and economics. A pilot study on each of these technologies and the subsequent tie-up to the existing unit operations is conducted, and the associated technical and economic comparisons are made. Some of these findings will be reviewed.

# INTRODUCTION

The petroleum refining industry generates relatively large amounts of waste from various sources, including wastewater, tank bottoms, slop oil emulsion solids and various sludges from oil/water/solids separation. However, the accumulation of crude storage tank bottoms is a comparatively serious problem experienced by most refineries worldwide. The settling out of the sand, rust and heavy fractions in the crude oil results in a loss of ullage in refinery crude storage tanks, and can ultimately cause refinery problems when slugs of this material are introduced into the plant. Most refineries have managed the problem by accumulating these sludges in a few of their crude tanks. Disposal of these wastes prior to the aggressive environmental regulation was relatively easy, simply by landfilling of solid wastes into a refinery's own landfarm or to commercial landfills. However, since 1990's, the options available for the disposal of this material have been limited and economically prohibitive.

Traditionally, the aims of the waste processing were limited to two functions – to reduce waste volume to minimize the amount of solid waste and thus the disposal cost, and to recover usable oil from the waste to the extent practical enhanced the economics of waste disposal. Nevertheless, the environmental regulatory concerns, economic viability and operational benefits have influenced development or treatment and disposal options. Methodologies range from simple single step in-situ chemical treatment for oil recovery to multistep physical, chemical, biological and thermal treatment to meet treatment standards for land disposal. The local refineries have been exploring better methods to implement the waste minimization and oil recovery from oily sludge to achieve the environmental-friendly objectives. Many refinery waste management techniques have been introduced from various process licensors from different countries. In order to assist the viability and effectiveness of applying any one of these systems under Kuwaiti conditions, pilot tests are carried out to validate or disprove its claims. After validation, further process evaluation will be commenced to select the most cost-effective and appropriate technology.

## THE WASTE PROCESSING TECHNOLOGIES

Many technologies are available to treat the tank bottoms sludges. These are based on a combination of one or more of the following:

- Physical methods such as centrifuging
- Addition of chemicals to aid in extraction
- Thermal treatment such as desorption
- Biological methods

The biomediation methods have been extensively studied previously for the remediation of oil contaminated soils (1) caused by the Iraqi scorch earth policy at the end of the Gulf War. In this contribution, some of the findings on the effectiveness of the physio-chemical separation, solvent extraction and thermal desorption processes, operating in batch mode to recover the petroleum hydrocarbons from the tank bottoms sludges, will be reviewed.

## **Thermal Desorption**

The thermal desorption process is an indirect-fired rotary desorber employing an oil-fired external heat source to volatilise and to recover the petroleum hydrocarbons from the tank bottoms sludges. Nitrogen gas is introduced counter-currently into the desorber to eliminate the constraint of the lower explosion limit or combustion. Typical processing time around 60 minutes and at temperature ranging between 350 to 500°C. A schematic diagram of the process is shown in Figure 1.

The vapourised hydrocarbons and water are condensed and collected for analysis. The solid waste is conveyed out for collect and to be analysed.

## **Solvent Extraction**

The solvent employed in the test is an organic material, which is compatible to the hydrocarbons. There is only a trace of aqueous solution involved and hence the operating temperature can be raised more than 100°C. The solvent does not destroy the wastes but to separate the oil from the solid components.

The process diagram is depicted in Figure 2. A small amount of solvent is added to the selected hydrocarbon fluids as a carrier. The mixture is preheated to the predetermined temperature in a heater before being pumped to the sludges holding tank. The carrier fluid is circulated in the system continuously for certain time depending on the type of fluid. No additional solvent is added to the re-circulating fluid. Liquid and solid samples are collected and analysed.

## **Physio-Chemical Separation**

It is based on the "cavitations" (2, 3) and "hot spot" (4) sonochemistry that creates a dramatic molecular change in organic fluids and gases. Suslick (5) estimated that temperature and pressures of imploding cavities were on the order of 5500°C and 500bars.

An aqueous liquid with a small amount of proprietary chemical is pressured and then pass through the sonochemical generator for a fixed period. The process fluid is then mixed with the tanks bottoms sludges under agitation for a certain time. The mixture is then left for phase separation under gravity. Analysis is performed on the liquid and solid samples. Figure 3 shows the simplified process diagram.

## **Sample Analysis**

From the above selected processes for the tank bottoms sludges treatment, both liquid and solid products are produced. The analyses performed for the process evaluation cover some physical and chemical properties of the materials, total volume analysis, total petroleum hydrocarbons test up to C33 (6, 7) and a mass balance on solid samples. In here, only the TPH, total volume analysis, and mass balance on solids are reported.

The TPH test is relatively inexpensive and quick method, which is based on the ASTM D2887-93, EPA 418.1 or similar. Although it has been recognized that the TPH is not adequate to identify the oil source, it is found to be very effective in the current comparative investigation. The boiling range distribution can provide useful information to the refiners. Since there is only one feed source, i.e., the tank bottoms sludges, the recoverable petroleum hydrocarbons can be analysed both quantitatively and qualitatively.

The mass balance on the solid samples will be carried out on the wet and dry basis. Together with the total volume analysis, the overall effectiveness of each of the treatment process can be evaluated. The methodology for the process evaluation is summarised in Figure 4.

## RESULTS AND DISCUSSIONS

In the following discussions, the concerned processes will be known as Processes 1, 2 and 3; and the order designated is not necessary the same in the previous session.

### Oil Recovery Performance

Before evaluating the three sludges treatment processes, samples from the untreated tank bottoms sludges are analysed to establish a baseline for comparison. Some properties of the crude oils, which have been held in the tank where the sludges are obtained, are shown in Table 1. Since one sample is obtained from each of the three (oil/aqueous/solid) phases after treatment from one of the three processes, and together with the raw sludges, the total number of samples is 12. Coding of all the samples is listed in Table 2.

From the total volume analysis of all samples, apart from those samples that collected from the treatment using light hydrocarbons as the circulation medium, the others are comparable with the baseline values.

The results from the TPH analysis of the samples from the oil-phase are shown in Figure 5 as a cumulative bar chart. OIL0 shows the aliphatic hydrocarbons distribution, in terms of the percentage and carbon number of the untreated sludges. About 80% of the aliphatic hydrocarbons with the carbon number less than 23 is determined. After treatment in Process 1, a slight increase in the aliphatic hydrocarbons with the carbon number higher than 23 is found. Similar observation is also found in the sample treated in Process 2, but with lesser extend than Process 1. However, a reverse trend is observed from the sample treated in Process 3. An increase in the aliphatic hydrocarbons at lower carbon numbers is found.

The results of the TPH analysis on the aqueous samples treated in Processes 1, 2 and 3 are depicted in Figures 6, 7 and 8, respectively. The characteristics of the chromatograms of AQU1 and AQU2 are very similar. However, the peak heights of AQU2 (Figure 7) are generally higher than those of AQU1 (Figure 6). The aliphatic hydrocarbons distribution in AQU3 follows a typical normal distribution curve where the highest peak is at the carbon

number of 18 (Figure 8). Nevertheless, the height of all the peaks is generally higher than that of AQU2 and AQU1.

To determine the remaining hydrocarbons in the solid phase of the product, a known quantity of the solid waste is used. Toluene extraction is applied to strip the remaining residue. After removing the solvent, the extract is weighted and then undergone the gas chromatograph (GC) analysis. The chromatograms of SOL1 and SOL2 are shown in Figures 9 and 10. The characteristics of the aliphatic hydrocarbons from the extracts are very similar but the peak heights in the SOL2 are generally higher than SOL1. Figure 11 shows the GC analysis of SOL3, the characteristics of the aliphatic hydrocarbons distribution is slightly different than the previous two, and the peak heights are generally higher.

Table 3 shows a comparison of the total oil content in the sediments on both wet and dry basis. Process 2 provides a better oil recovery on the wet basis. It is followed by Process 3 and then Process 1. However, when comparing under the dry basis, Process 3 has 83.23% recovery, which is better than Processes 2 (83.07%) and 1 (81.03%). The increase in the water content in all the treated samples is due to the processing media used in the treatment.

### **Process Economics**

The capital cost of each process cannot not be estimated because insufficient process and kinetic data are available for sizing and scaling-up the unit. Moreover, the mode of equipment acquisition, either to own or to lease, has not been determined. Hence, the operation cost is based on running the current pilot plant scale units, and accounted only for the utilities consumption and labour cost. A summary of the estimated cost per ton of sludges is shown in Table 4. Since the processing time and the number and form of utility requirement are differed from process to process, the cost variation is apparent.

## **CONCLUDING REMARKS**

Three sludges treatment processes are evaluated. The preliminary results reported here show that there is not much difference in the process performance between them. Although one of the processes has a slight edge over the others in the oil recovery and volume reduction, the delta is not significant. In terms of the process economics, the operation cost varies quite substantially. Since a number of factors have not been considered in the estimation, this is not conclusive.

One of the processes is comparatively easy to operate and the tie-in to the refinery will be relatively simple. However, in-depth study on the other analytical results must be made before selecting the process for further process evaluation.

**Table 1.** Some properties of the crudes.

<b>Property</b>	<b>Engineering Unit</b>	<b>Value</b>
API	°API	23
Sulphur	Wt. %	4.5
Water	Wt. %	0.2
Boiling Point - IBP	°C	50
FBP	°C	335
Metal - Ni	µg/g	15
V	µg/g	30

**Table 2.** Sample codes.

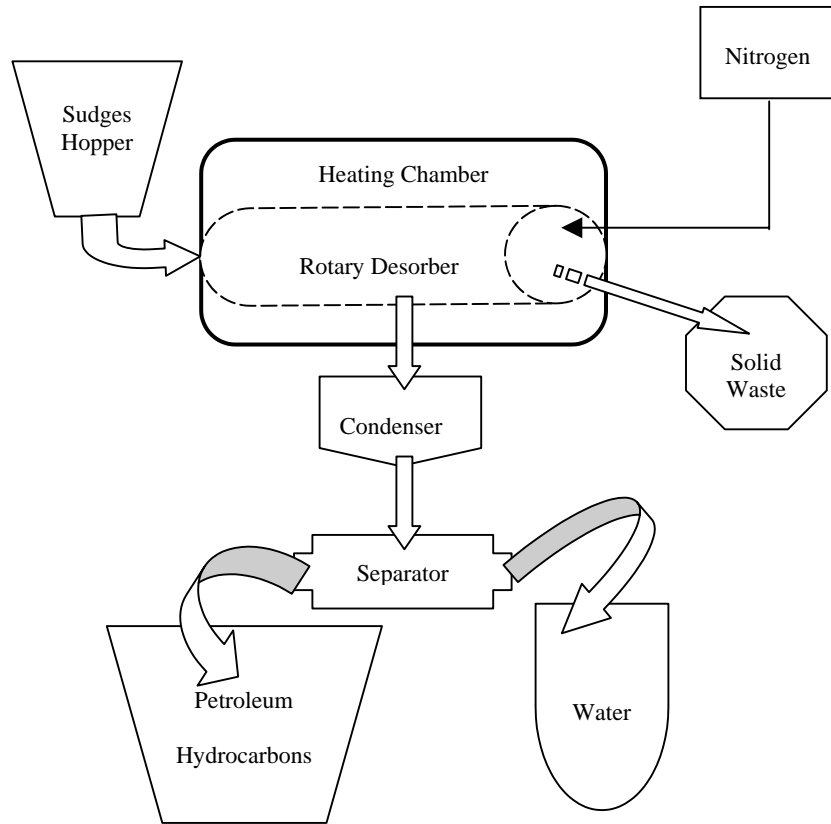
<b>Treatment</b>	<b>Sample Code</b>		
	<b>Oil phase</b>	<b>Aqueous phase</b>	<b>Solid phase</b>
Blank	OIL0	AQU0	SOL0
Process 1	OIL1	AQU1	SOL1
Process 2	OIL2	AQU2	SOL2
Process 3	OIL3	AQU3	SOL3

**Table 3.** A comparison of the sediment contents.

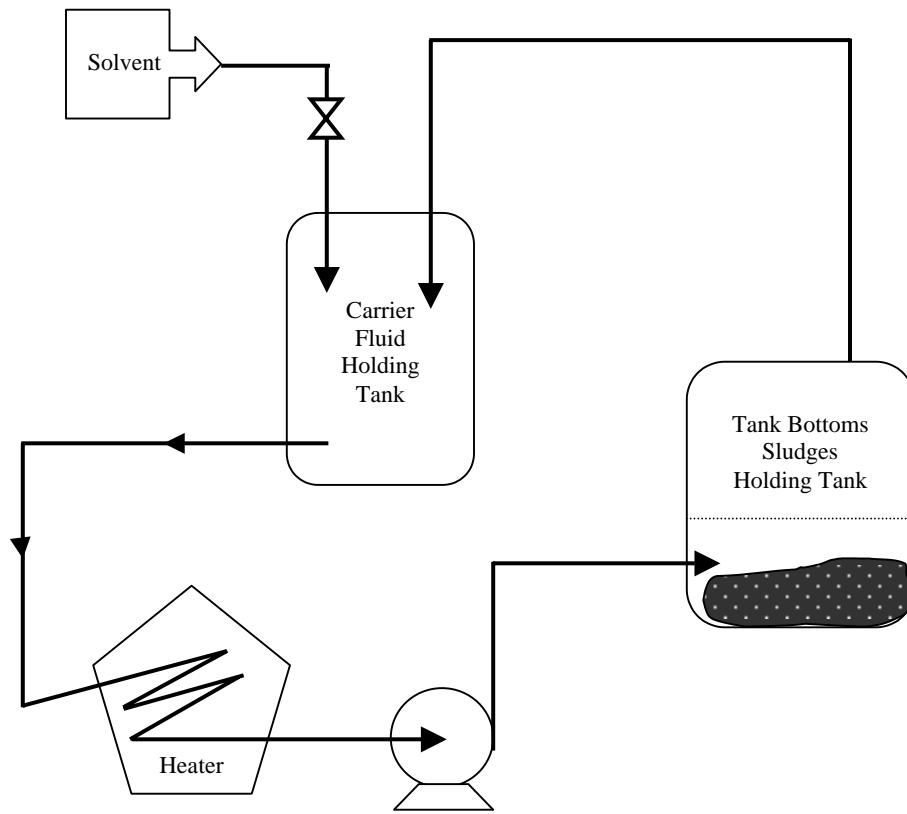
<b>Code</b>	<b>Content on Wet Basis (wt%)</b>				<b>Content on Dry Basis (wt%)</b>		
	<b>Oil</b>	<b>Solid</b>	<b>Water</b>	<b>Loss</b>	<b>Oil</b>	<b>Solid</b>	<b>Loss</b>
SOL0	16.90	73.90	6.50	2.70	18.07	79.04	2.89
SOL1	3.10	85.00	9.50	2.40	3.43	93.92	2.65
SOL2	2.60	81.70	15.00	0.70	3.06	96.12	0.82
SOL3	2.80	88.10	7.70	1.40	3.03	95.46	1.51

**Table 4.** Operation Cost

<b>Process</b>	<b>Cost (\$/ton)</b>
1	310
2	155
3	205

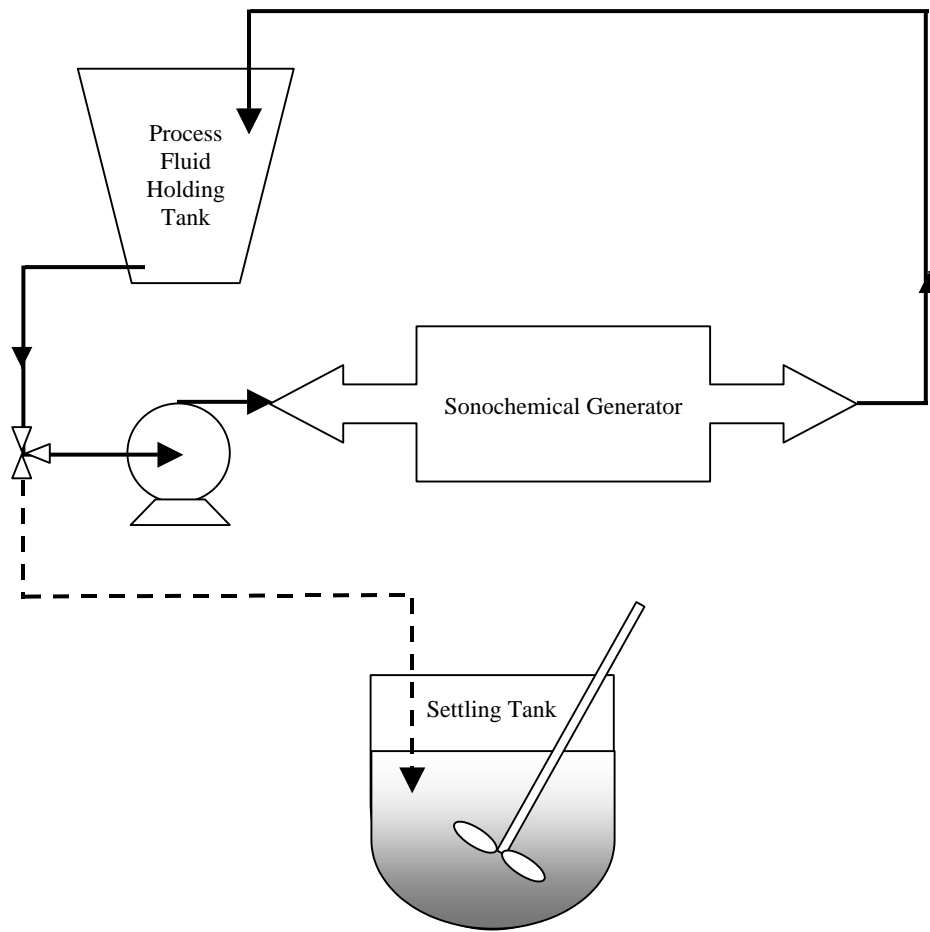


**Figure 1.** A schematic diagram of the thermal desorber process.

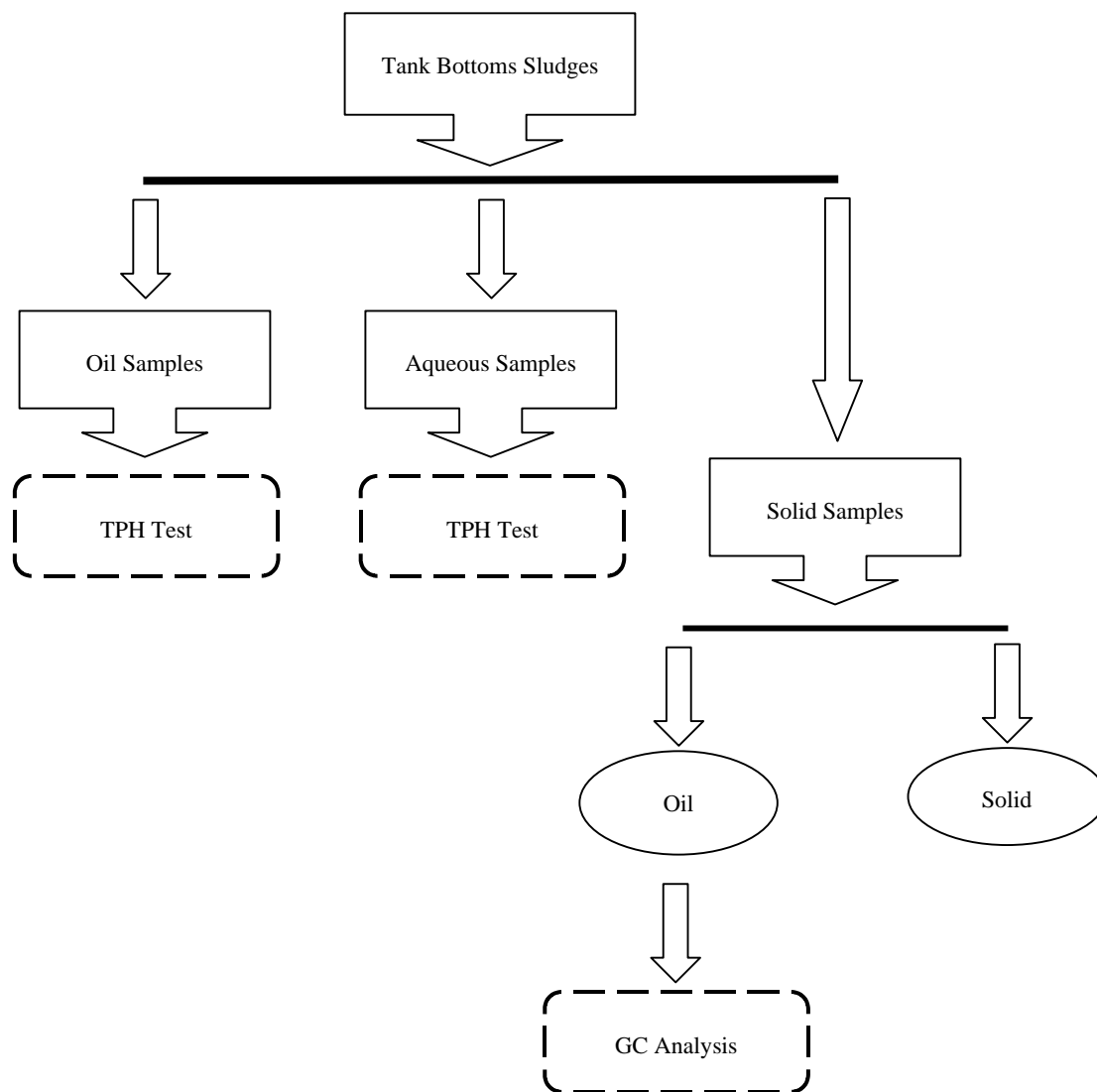


**Figure 2.** A simplified solvent extraction process diagram.

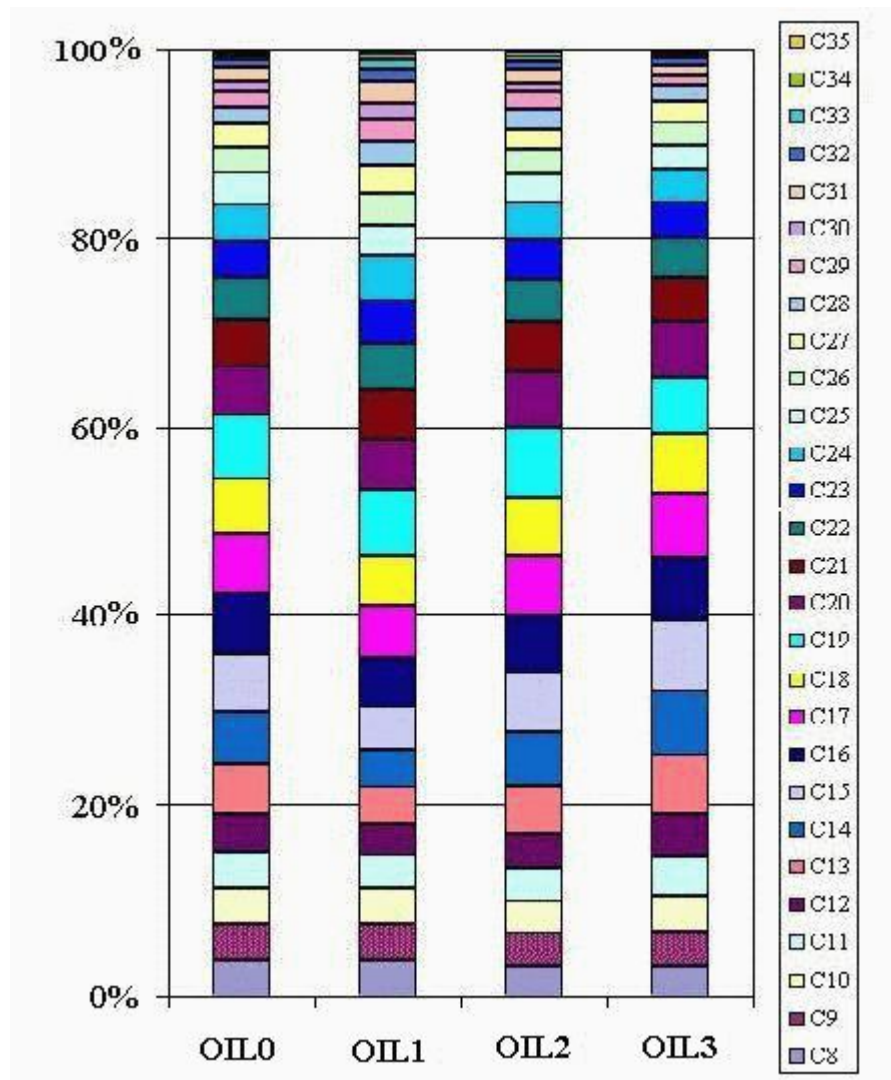




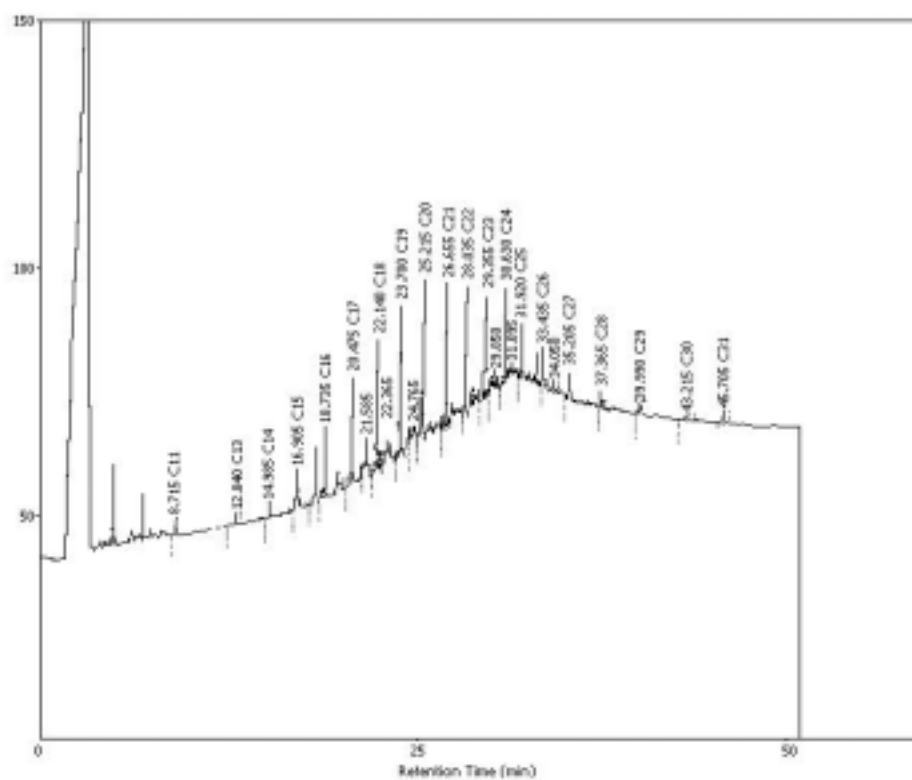
**Figure 3.** A simplified physio-chemical separation process diagram.



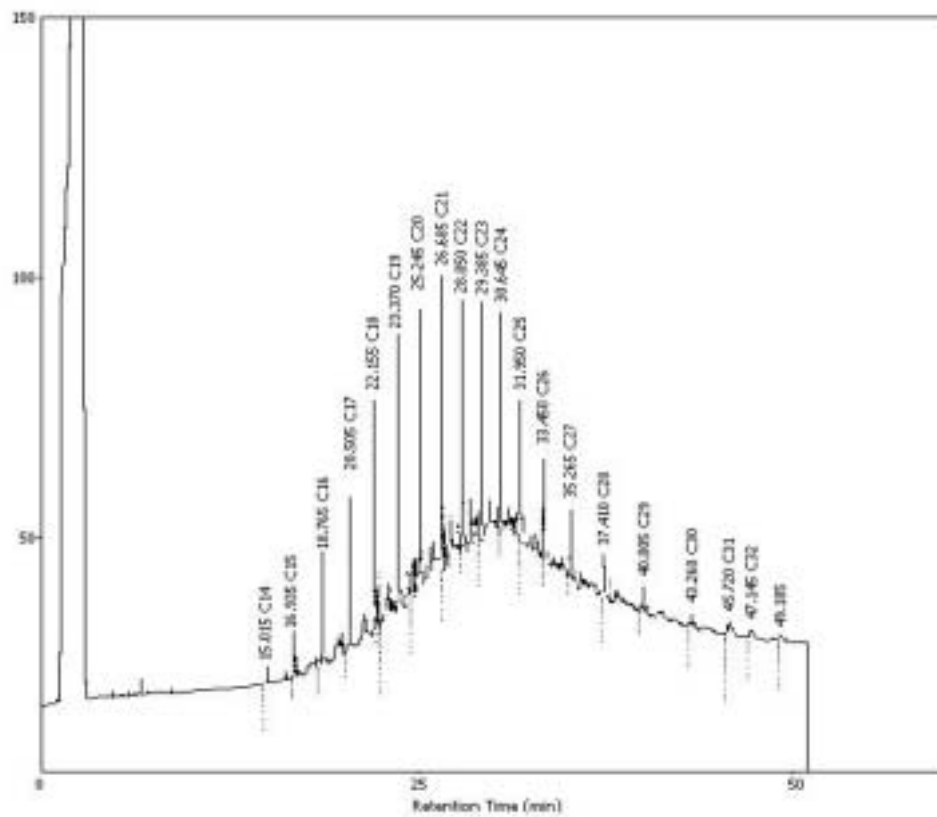
**Figure 4.** A methodology for process evaluation.



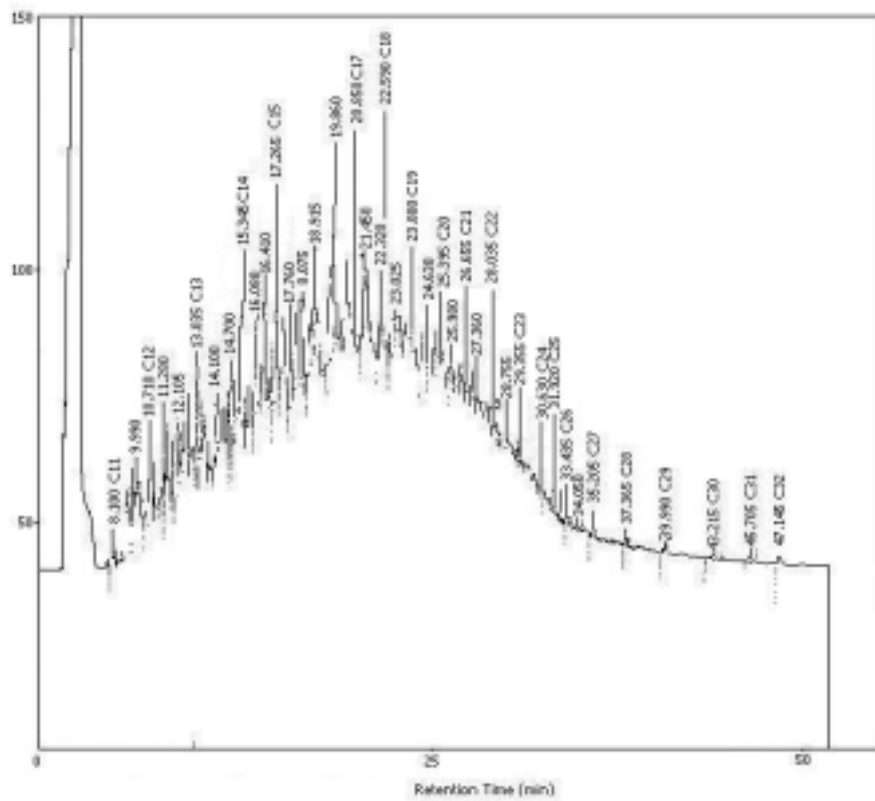
**Figure 5.** A cumulative bar chart comparing oil-phase samples



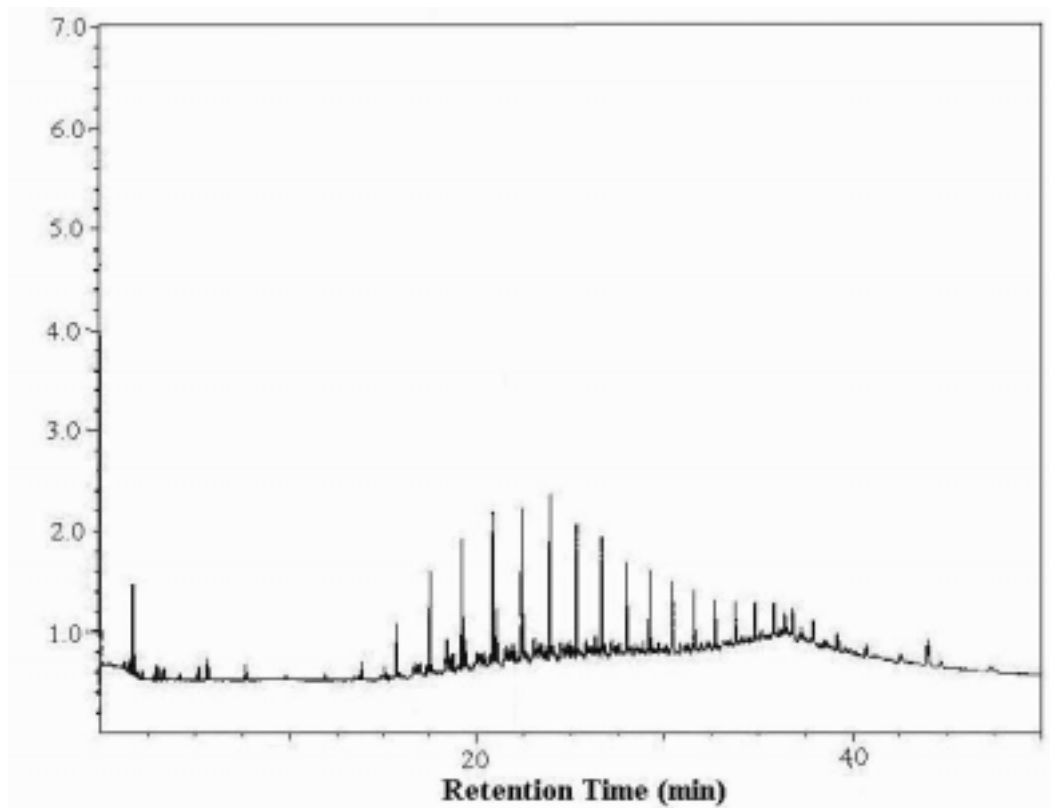
**Figure 6.** The chromatogram of AQU1.



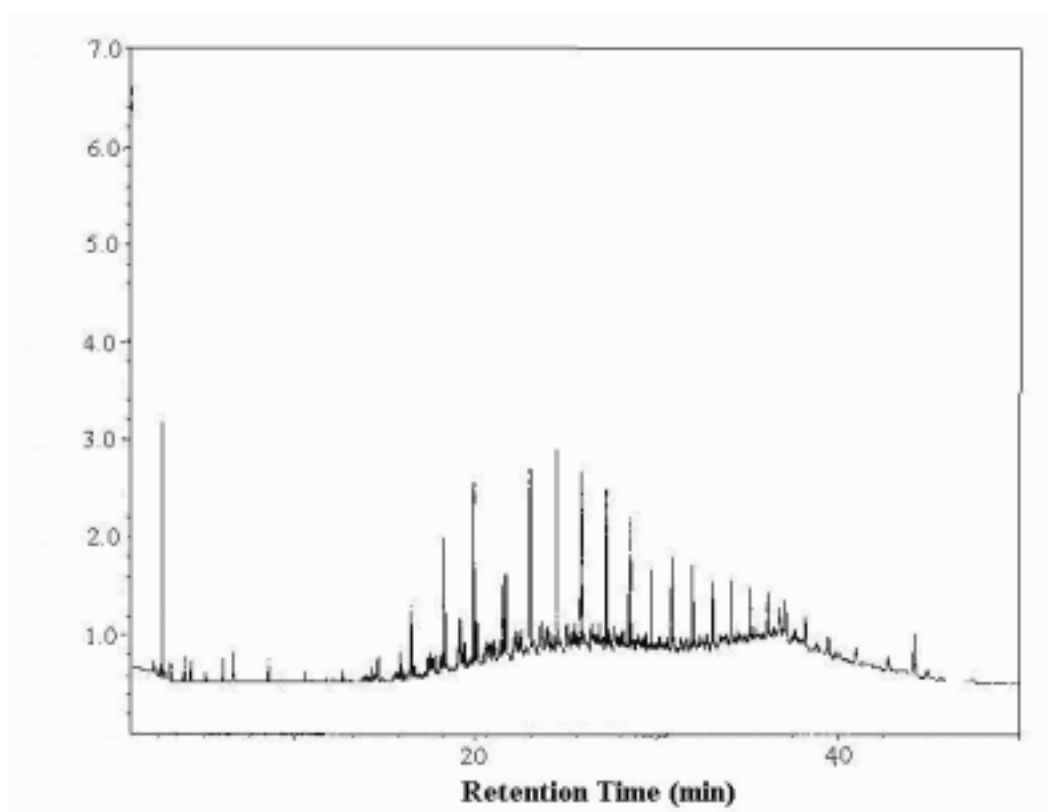
**Figure 7.** The chromatogram of AQU2.



**Figure 8.** The chromatograph of AQU3.

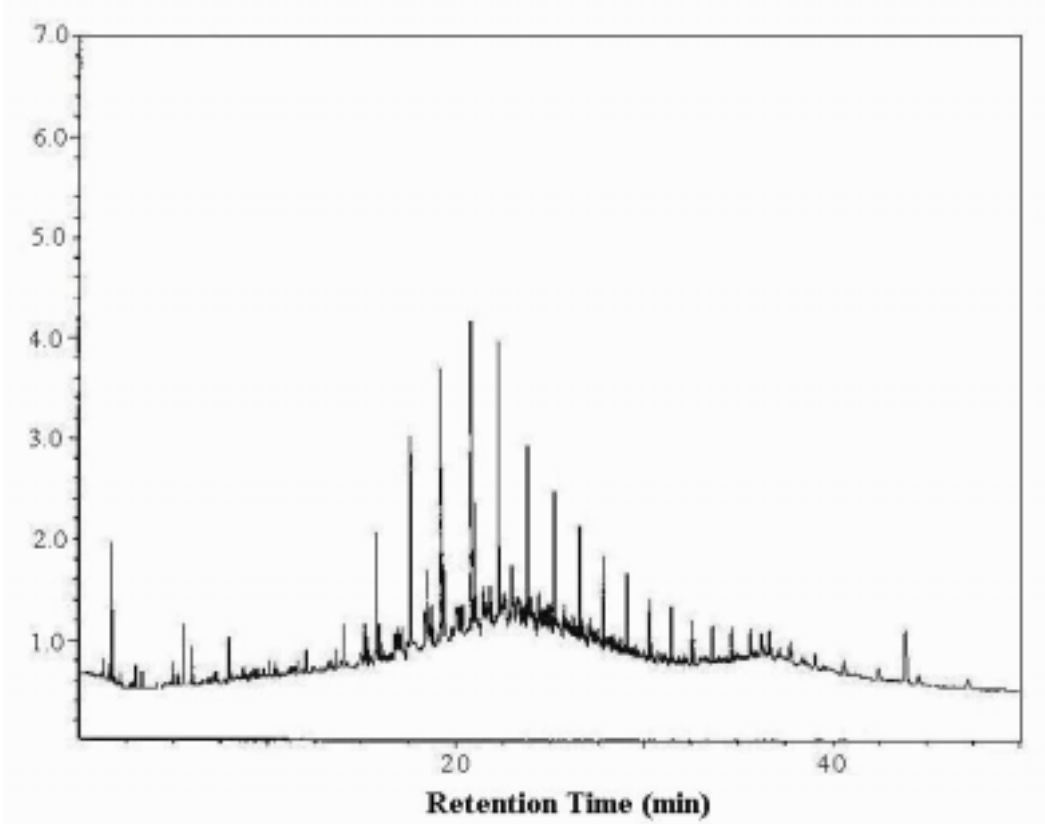


**Figure 9.** The chromatograph of SOL1



**Figure 10.** The chromatograph of SOL2.





**Figure 11.** The chromatograph of SOL3.

## REFERENCES CITED

1. Bella, M.T., Al-Awadi, N, Al-Daher, R., Chino, H. and Tsuji, H. "Remediation and rehabilitation of oil-lake beds in Kuwait: I. Bioremediation of oil-contaminated soil", in proceedings of the Symposium on Restoration and Rehabilitation of the Derset Environment, Amsterdam, Elsevier (1996).
2. Suslick, K.S., Mcleleni, M.M. and Ries, J.T. "Chemistry induced by Hydrodynamic Cavitation", *Advances in Sonochemistry*, **8**, 870-71 (1997).
3. Crum, L.A. and Matula, T.J. "Shocking Revelations", *Science*, **276**, 1348-49 (1997).
4. Suslick, K.S., Gawienowski, J.J., Schbert, P.F. and Wang, H.H. "Alkane Sonochemistry", *The Journal of Physical Chemistry*, **87**, 2299-2301 (1983).
5. Suslick, K.S. "Sonochemistry", *Science*, **247**, 1439-45 (1990).
6. ASTM Method D2887 - 93. "Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography", in Annual Book of ASTM Standards, **Vol. 5.01**, Philadelphia, American Society for Testing Materials (1996).
7. UOP Method 915 - 92. "Normal Paraffins by Capillary Gas Chromatography", UOP (1992).

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