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Characterization of Oily Sludge from Cameroon Petroleum Refinery

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ABSTRACT

The National Petroleum Refinery of Cameroon is a crude oil refining company that generates large quantity of oily sludge. The identification and quantification of standard hydrocarbons that can be recovered from oily sludge, the assessment of the distribution of the Aliphatic Hydrocarbons of the sludge was realized by using a simple gas chromatographic method, and the minerals analysis was realized by using X-ray Fluorescence. The results show that the samples have an average composition of 72.45 % water, 2.20 % fine particles and 25.36 % hydrocarbons. It was also found that the 13 identified aliphatic hydrocarbons had a total concentration of 10,181 ppm where the major hydrocarbon is n-C17 (7,279 ± 62 ppm). The elemental analysis identified 14 elements where the silicon is the most important with 95.70 %.

Keywords: Oily sludge, Hydrocarbons, X-ray fluorescence, GC-FID, Paraffins.

INTRODUCTION

Crude oil is an important source of energy but a common source of environmental pollution [1]. One of the consequences of crude oil exploitation and processing activities is the generation of vast amounts of oily sludge [2]. The oily sludge, which is part of the most important garbage in oil refineries, is generated by the coalescence of hydrocarbons on solid particles.

The processing activities of one kilogram of crude oil can generate 10-20 grams of oily sludge [3]. In the oil refineries, the oily sludge is collected at several points such as oil/water separator, dissolved air flotation units, heat exchanger cleanings, tank bottom cleaning, desalter and API decanters [3,4,5,6,7].

The oily sludge is made up of considerable quantities of solid particles, water and hydrocarbons [2,6,8] and of poisonous, carcinogenic or mutagenic compounds [2,9,10,11]. The composition of oily sludge varies from one refinery to another, and also from one oily sludge to another depending on the type of refined crude oil.

Our survey is orientated toward the oily sludge of the National Petroleum Refinery of Cameroon. The objective of this work is to carry out advanced analysis in order to identify and quantify standard aliphatic hydrocarbons and metals that can be valorized.

MATERIAL AND METHODS

Material

The sample used was provided by the National Petroleum Refinery of Cameroon. Ten (10) withdrawals of 100 mL each were made at different points of the storage tank located at the wastewater treatment plant. The withdrawals were mixed prior to analysis in order to ensure a representative sample of the oily sludge.

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Methods

Water Content

The water content was determined by distillation using a trainer fluid [8] which in this case is a mixture of toluene/xylene in the proportions of 80/20 (v:v). The analysis was realized in triplicate and the mean of the results was expressed as mass percentage of humid oily sludge.

Hydrocarbons Content

The hydrocarbons content was deducted from the results of previous analysis.

Cleanup and Analysis for Identification and Quantification of Aliphatic Hydrocarbons

The extraction of hydrocarbons was made following the method described by [12]. Three grams of oily sludge sample was refluxed with 100 mL of a mixture of MeOH and hexane in the proportion of 50:50 for 4 h. After the addition of 30 mL MeOH into the reflux distilled mixture, the hexane phase was transferred to glass tubes and concentrated to 1 mL under the rotary evaporator Turbo-vap (Varian) at a temperature around 60°C.

Cleanup of the sample took place in a 20-cm chromatographic column with an internal diameter of 0.9 cm. The column was packed with 4 g of silica gel and 4 g of alumina. The filled column was then eluted by 10 mL of hexane and 1 mL concentrated sample was placed on the top of the column. The aliphatic hydrocarbons were obtained in the first separation with 10 mL of n-hexane.

Only analysis of the aliphatic hydrocarbons were performed by gas chromatography (GC) with a SHIMADZU GC-14B equipped with an FID detector and a Peack Simple Chromatography Data System interface linked to a computer. The separation was carried out on a capillary column (HP-5MS) which has 30-m length of polydiphenyldimethylsiloxane, a film thickness of 0.25-mm and with an internal diameter of 0.25-µm (J&W Scientific). The column was held at 40°C, and then heated to 320 °C at a rate of 6°Cmin-1. The carrier gas was nitrogen at a pressure of 2 bars. The injector and detector were maintained at 300 and 330°C respectively. A micro-syringe was used to inject 1 µL samples into the chromatograph. Aliphatic hydrocarbons resolved peaks of the chromatographic sample were quantified by reference to the response factor of the standards (SUPELCO).

Compounds were identified using the Kovats Index or retention index as described elsewhere [13].

Elemental analysis

The X-ray fluorescence was used to conduct the mineral analysis by using the S4 Pioneer Burker XRF. The sample was previously incinerated, shaped in disc that was introduced in a polypropylene bowl. The analysis was done in 12 min.

RESULTS AND DISCUSSION

Sludge Constitution

The results of solid, water and hydrocarbons content of the oily sludge varied slightly from one test to another but the standard deviation showed that the values were close to the mean. The result of water content (72.45 ± 2.10 %) agreed with that observed by other authors [6,8,10,12,13] who reported that the water content of oily sludge ranges between 30% and 90%. The same authors had said that hydrocarbons and solid contents are evaluated in the ranges of 15 – 50% and 1 – 10%, respectively. The values measured for our sample are 25.36 ± 2.31 % for hydrocarbons content and 2.20 ± 0.59 % for solid content. Those compositional values indicate that the oily sludge under study is not out of the interval that obtained for other oily sludges.

Aliphatic Hydrocarbons

The Figure 1 below represents one of the chromatogram obtained from the first fraction containing aliphatic hydrocarbons using the GC-FID. All spectra were slightly similar except for a quantitative difference in concentration levels as presented in Table 1. As shown in Figure 1, thirteen (13) n-alkanes were identified in the sample with n-C13 as the lightest and n-C25 the heaviest, hydrocarbon. The alkane n-C17 was found to be the major constituent, with a concentration range of 7,279 ± 62 ppm which represents 71.5 % of identified aliphatic hydrocarbons. The important amount of paraffins in the oily sludge shows that it can be valorized in the sector of paraffins production.

There was also unresolved complex mixture (UCM) which is typical of spills with petroliferous derivatives [14]. This UCM which represents 68.76 % of Total Aliphatic Hydrocarbons with a concentration of 22,413 ppm can be constituted of naphthenic and ramified hydrocarbons compounds with the same number of carbons. These observations are justified by the fact that the sample studied is a petroleum refining residue.

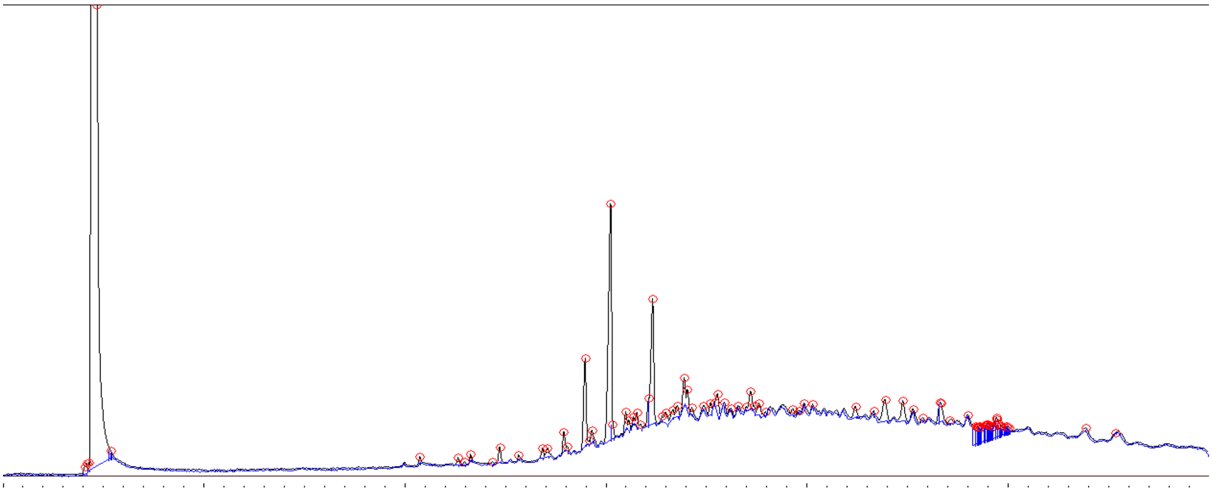

Figure1. *Chromatogram of aliphatic hydrocarbons in oily sludge*

TableI. *Distribution of Aliphatic Hydrocarbons*

N°	RT (min)	Calculated IK	Compounds	Peack surface	Concentration (µg/g)
1	20.686	1294	Tridecane C13	2464	453
2	23.216	1394	Tetradecane C14	2253	169
3	25.6	1494	Pentadecane C15	1427	120
4	28.02	1601	Hexadecane C16	1232	109
5	30.19	1704	Heptadecane C17	122902	7279
6	32.09	1798	Octodecane C18	10950	681
7	33.996	1901	Nanodecane C19	6363	411
8	35.833	1999	Eicosane C20	890	89
9	37.883	2094	Heneicosane C21	882	88
10	40.236	2203	Docosane C22	1544	127
11	42.356	2301	Tricosane C23	5725	374
12	45.236	2405	Tetracosane C24	2412	178
13	47.933	2501	Pentacosane C25	1132	103
Total of peacks of identified alkanes				**160176**	**10181**
Total of peacks of non-identified alkanes				**346583**	**22413**

Elemental Analysis

The X-ray Fluorescence analysis identified and quantified fourteen (14) elements which are presented in Table 2 below. The compounds identified are members of metalloids, alkali metals, earth-alkali metals, transition metals and Lanthanides. It have been noticed that metalloids are the most abundant with 95.70 % while the transition metals are representing only 2.06 %.

The high presence of silicon (95.7 %) in the solid particles fraction is letting to understand that this oily sludge can be valorized in the cement production since silicon is an important element in the manufacturing of the clinker.

The presence of toxic heavy metals such as Chromium, Zinc, Nickel, Copper and Manganese has been noticed. Their respective concentrations are above the restriction from the national environmental law on liquid waste rejection in the environment.

Table2. *Content of minerals in ashes and Oily Sludge*

N°	Elements	Content in ashes (%)	Content in oily sludge (ppm)
1	Silicon (Si)	95.700	21054.00
2	Potassium (K)	1.640	360.80
3	Zinc (Zn)	0.891	196.02
4	Titanium (Ti)	0.839	184.58
5	Barium (Ba)	0.473	104.06
6	Manganese (Mn)	0.138	30.36
7	Terbium (Tb)	0.131	28.82
8	Copper (Cu)	0.122	26.84
9	Chromium (Cr)	0.040	8.80
10	Strontium (Sr)	0.026	5.72
11	Nickel (Ni)	0.016	3.52
12	Lutetium (Lu)	0.014	3.08
13	Zirconium (Zr)	0.011	2.42
14	Rubidium (Rb)	0.001	0.22

CONCLUSION

Investigations of the constitution of the oily sludge sample revealed 72.45 ± 2.10 % of water content, 25.36 ± 2.31 % of hydrocarbons content and 2.20 ± 0.59 % of solids content. The results mainly show that aliphatic hydrocarbons have a concentration of 10,181 ppm. The higher concentration of aliphatic hydrocarbon was found for the n-C_{17} (7,279 ± 62 ppm). The most abundant mineral found in the samples was the silicon for 75.70 %. All this is showing that this oily sludge has the capability to be valorized in paraffins and in cement production.

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