Aliphatic Hydrocarbons Extraction from Oily Sludge using Kerosene

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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 extraction, identification and quantification of aliphatic hydrocarbons that can be recovered from oily sludge were assessed. The extraction was conducted following an experimental design and the distribution of the aliphatic hydrocarbons of the sludge was realized by using a simple gas chromatographic method. The extraction results showed that all the factors have positive effect on the extraction. It was also found that the highest concentration of 127992 ppm was obtained under experimental conditions of Ratio = 6:1, Temperature = 40°C, Contact time = 90 min.

Index Terms —Oily Sludge; Aliphatic Hydrocarbons; Experimental Design; GC-FID; Paraffins.

I. INTRODUCTION

The oily sludge is made up of considerable quantities of solid particles, water and hydrocarbons [1,2,3] and of poisonous, carcinogenic or mutagenic compounds [3,4,5,6]. The composition of hydrocarbon fraction 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. Previous analysis made on oily sludge of the National Petroleum Refinery of Cameroon [7,8] showed the high content of aliphatic hydrocarbons with high molecular weight. These aliphatic hydrocarbons are also called paraffins in the petroleum vocabulary and are hydrocarbons having the formula CnH2n+2 (e.g., methane, CH4; ethane, C2H6). Heavier paraffin hydrocarbons (i.e., CnH2n+3) form a wax-like substance that is called paraffin. These heavier paraffins often accumulate on the walls of tubing and other production equipment, restricting or stopping the flow of the desirable lighter paraffins [9].

Knowing that paraffins are used in the manufacturing of products like petroleum jelly, our survey is oriented toward the recovery of paraffins in oily sludge of the National Petroleum Refinery of Cameroon. The objectives of this work were to study the effect of some parameters on the paraffinic hydrocarbons extraction from oily sludge using a fraction of commercialized kerosene and to identify and quantify the various compounds that can be extracted from the oily sludge.

II. MATERIAL AND METHODS

A. 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. The withdrawals were mixed prior to analysis in order to ensure a representative sample of the oily sludge. The studied oily sludge had an average constitution of 72.45 % of water, 2.20 % of fine particles and 25.36 % of hydrocarbons [8].

B. Methods

1) Solvent Preparation

The liquid used as solvent for the extraction of paraffinic hydrocarbons from oily sludge is a fraction of commercialized kerosene. The sample of kerosene was obtained from a petrol station and a fractional distillation was done on it. The ranges of temperatures used were T1 < 130 °C, T2 = 130 – 180 °C and T3 > 180 °C. The various fractions obtained were analyzed by gas chromatography as described by Ze Bilo’o and Ngassoum., (2012) in order to identify and quantify the aliphatic hydrocarbons present in each. After the analysis, the fraction T2 was chosen to be used as solvent in the aliphatic hydrocarbons extraction following an experimental design.

2) Aliphatic hydrocarbons extraction

The extraction of paraffins was conducted following the experimental design composite factorial plan with centered faces. The purpose of the work was to study the influence of three different parameters which are temperature, contact time and solvent/sludge ratio on the paraffinic hydrocarbon extraction. Based on the literature, upper and lower limits could be fixed for these three parameters as shown in the Table 1 below.

| TABLE I: FACTORS AND EXPERIMENTAL DOMAINS |
|-------------------------------------------|
| Factors | Units | Designations | Experimental domains |
| Solvent/Sludge ratio | / | A | 2:1 – 6:1 |
| Temperature | °C | B | 40 – 60 |
| Contact time | Minutes | C | 30 – 90 |

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With two analyses at the center, the experimental design with two levels and three parameters gave a total of 16 manipulations calculated as follows:

\[ N = 2^k + 2k + 2 = 2^3 + 2*3 + 2 = 16 \]  

(1)

Each of the 16 extracts obtained went through the cleanup and the chromatographic analysis of paraffins (identification and quantification) as described by Ze Bilo’o and Ngassoum, (2012). The software Peak sample 432-64bit was used to acquire the spectra, to identify and quantify the compounds of the extracts. Two responses from the experimental design were expected: the mass of the extract (mg) and the percentages of groups of compounds extracted.

**III. Results and Discussions**

**A. Solvent preparation**

The chromatographic analysis came out with a list of compounds that were regrouped into families as follows: linear, cyclic, and ramified paraffins. As illustrated in Figure 1 below, the amounts of ramified paraffins and cyclic paraffins reached their highest amount in the temperature fraction of 130 – 180°C. The fraction of 130 – 180°C was retained for the extraction of aliphatic hydrocarbons. The aliphatic hydrocarbons molecules in this fraction are in the range of 8 carbons (Octane) to 14 carbons (2,6,10-Trimethylundecane).

![Fig. 1: Groups of compounds found in each fraction of Kerosene](image)

**B. Paraffinic hydrocarbons extraction**

1) **Effect of parameters on the extraction**

The effects of three factors (A: Solvent/Sludge ratio, B: Temperature, and C: Contact time) on the extraction of paraffins were assessed according to the experimental design and the various masses of extracts recorded. The analysis of the values allowed the plotting of the standardized Pareto graphic shown on Figure 2. It has been observed that the Solvent/Sludge ratio and Temperature has positive effect with an important weight on the extracted mass of paraffins. Only the quadratic effect of Contact time has a negative effect with an important weight on the extracted mass of paraffins. It means that, if the contact time is very high, the mass extracted will reduce. This graphic shows that, practically, the more the ratio and its interaction with contact time and the temperature tend to increase the extracted mass. This is confirmed by the modelization equation below with the coefficient of each factor representing their weight.

\[ Y = 7.893 + 0.739A + 0.466B + 0.168C – 0.113AB + 0.283AC + 0.293A^2 + 0.813B^2 – 0.896C^2 \]  

(2)
2) Composition of extracts

All the extracts were analyzed with GC-FID from which the software Peak sample 432-64bit was used to acquire the spectra, to identify and quantify the compounds of each extract. All the spectrum obtained were similar with differences on the number and intensity of peaks. The Figure 3 below shows as sample, the spectra obtained at Ratio = 2:1, Temperature = 50°C, Contact time = 60 min as extraction conditions.

It appears from the spectra that the aliphatic hydrocarbons extracted have the number of carbons from eight (8) to twenty eight (28) mixed with some unidentified hydrocarbon compounds. The identification and quantification of the extracted aliphatic hydrocarbons permit the grouping of compounds based on their structure. The considered groups or families are linear paraffins, paraffins with one, two, three, and more than three ramifications, cyclic paraffins and non-identified paraffins.

The highest total concentration of paraffins extracted of 127992 ppm was obtained under experimental conditions of Ratio = 6:1, Temperature = 40°C, Contact time = 90 min while the lowest concentration of 6031 ppm was given by a Ratio = 2:1, Temperature = 40°C, Contact time = 90 min. The compound having the highest concentration (14912 ppm) is the 2,6-Dimethyldeca nine followed by 2,6-Dimethylundecane with a concentration of 12640 ppm. The proportions of the various groups in each extract are presented in the Table 2 below.

The concentrations of groups in each extract were determined. It appears that, the highest concentrations of linear paraffins (13498 ppm), paraffins with one ramification (28849 ppm), paraffins with two ramifications (7827 ppm), paraffins with three ramifications (2975 ppm) and paraffins with more than three ramifications (27736 ppm) were obtained under different experimental conditions. These last responses are justified by the molecular structure of these compounds with light molecular weight and the constitution of the solvent that facilitated their dissolution and diffusion. Table 3 presents the highest concentrations of each group and the corresponding experimental conditions they were obtained. It was also noticed that the amount of extracted liquid aliphatic hydrocarbons with the number of carbon less than 17 was higher in each extract compare to solid aliphatic hydrocarbons.

As illustrated by the Pareto graphic all the factors have a positive effect on the effectiveness on the extraction, the simultaneous increase of factors is leading to the increase of the amount of extract and even the increase of the concentration of various groups of compounds. The amount and the quality of paraffins extracted are also strongly associated to the composition of the solvent since what was used is a mixture of compounds.
| Designation (Ratio – Temperature – Contact time) | N1 (2-40-30) | N2 (4-40-30) | N3 (4-40-30) | N4 (4-40-90) | N5 (2-40-90) | N6 (6-40-30) | N7 (6-40-90) | N8 (6-40-90) | N9 (4-40-60) | N10 (4-40-60) | N11 (4-40-60) | N12 (4-50-60) | N13 (4-50-60) | N14 (4-50-60) | N15 (4-50-60) | N16 (4-50-60) |
|-----------------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| TPS (ppm)                                     | 22463        | 104979       | 22689        | 95262        | 6031         | 127992       | 8396         | 102416       | 11608        | 41433        | 45548        | 43652        | 58463        | 40446        | 78984        | 85460        |
| LP (%)                                        | 11.98        | 11.57        | 16.43        | 2.41         | 28.78        | 5.77         | 33.80        | 13.18        | 36.83        | 8.98         | 10.31        | 22.86        | 6.62         | 10.97        | 9.16         | 8.04         |
| P1R (%)                                       | 19.71        | 21.46        | 20.56        | 22.29        | 34.16        | 22.54        | 20.50        | 21.75        | 22.92        | 20.26        | 20.12        | 22.24        | 19.93        | 19.06        | 22.17        | 25.57        |
| P2R (%)                                       | 25.16        | 31.21        | 22.24        | 35.01        | 9.12         | 23.18        | 3.97         | 22.45        | 6.77         | 13.43        | 16.53        | 6.70         | 16.38        | 17.66        | 29.96        | 33.15        |
| P3R (%)                                       | 1.54         | 0.17         | 1.83         | 0.21         | 2.54         | 2.80         | 8.31         | 0.51         | 7.13         | 15.67        | 0.98         | 17.93        | 0.51         | 0.51         | 0.50         | 0.25         |
| P+3R (%)                                      | 3.12         | 1.14         | 1.96         | 1.29         | 11.89        | 1.32         | 6.06         | 0.81         | 9.51         | 7.18         | 2.09         | 3.13         | 1.24         | 2.02         | 1.23         | 1.36         |
| CP (%)                                        | 10.19        | 14.13        | 10.94        | 12.29        | 3.13         | 21.67        | 1.73         | 19.50        | 2.15         | 2.58         | 12.98        | 3.38         | 12.13        | 10.31        | 14.90        | 13.30        |
| UP (%)                                        | 28.31        | 20.32        | 26.04        | 26.50        | 10.38        | 22.72        | 25.63        | 21.80        | 14.69        | 31.90        | 36.99        | 23.76        | 43.19        | 39.47        | 22.08        | 18.33        |

TPS = Total Paraffins in the Sample  
LP = Linear Paraffins  
P1R = Paraffins with 1 ramification  
P2R = Paraffins with 2 ramifications  
P3R = Paraffins with 3 ramifications  
P+3R = Paraffins with more than 3 ramifications  
CP = Cyclic Paraffins  
UP = Unidentified Paraffins

| N° | Groups of paraffins | Maximum concentration extracted (ppm) | Optimal ratio (%) | Optimal temperature (°C) | Optimal contact time (min) |
|----|---------------------|---------------------------------------|-------------------|--------------------------|---------------------------|
| 1  | Linear Paraffins    | 13498                                 | 6                 | 60                       | 90                        |
| 2  | Paraffins with 1 ramification | 28849                              | 6                 | 40                       | 90                        |
| 3  | Paraffins with 2 ramifications | 33351                              | 6                 | 60                       | 30                        |
| 4  | Paraffins with 3 ramifications | 7827                               | 6                 | 50                       | 60                        |
| 5  | Paraffins with more than 3 ramifications | 2975                               | 4                 | 40                       | 60                        |
| 6  | Cyclic Paraffins    | 27236                                 | 6                 | 40                       | 90                        |
IV. CONCLUSION
Investigations on effect of some parameters on paraffinic hydrocarbons extraction from oily sludge using a fraction of commercialized kerosene showed that all of them have an important positive influence on the extraction. The identification and quantification of various compounds that can be extracted from the oily sludge were realized. It came out that the paraffins with two ramifications are the most extracted (33351 ppm) at a Ratio of 6:1, Temperature of 40°C and a Contact time of 90 min.

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