Extraction from Oily Sludge of Paraffinic Hydrocarbons with Gasoline as Solvent

P. Ze Bilo'o and M. B. Ngassoum

Abstract — From hazardous wastes produced in Petroleum Refineries, the most generated in large quantities is oily sludge. The use of gasoline for the extraction and characterization of paraffinic hydrocarbons from oily sludge was realized. The experimental design was applied to realize the extraction while the gas chromatographic method helped in the characterization of the paraffinic hydrocarbons. The results of extraction and characterization showed that the Ratio Solvent/Sludge has positive effect while Temperature and Contact time have negative effects on the effectiveness of the extraction process. 14825 ppm is the highest concentration obtained through experimental conditions of Contact time = 30 min, Temperature = 40°C, and Ratio = 6:1. 2,6,10,14-Tetramethylpentadecane (Pristane) is the compound having the highest concentration (2373 ppm) followed by 2-Methylhexadecane with a concentration of 848 ppm.

Index Terms — Paraffinic Hydrocarbons, Experimental design, Hazardous waste, Oily sludge, Paraffins.

I. INTRODUCTION

The remains found at the base of tank and other storage facilities are generally referred as sludge [1] which is constituted of considerable amounts of hydrocarbons, water and solid particles [2]-[4] and of mutagenic, carcinogenic, or poisonous compounds [4]-[7]. As the composition of crude oil varies, that is also how the one of the oily sludge varies as well as the one of the hydrocarbon fraction. Great amount of high molecular weight paraffinic hydrocarbons were found in Cameroonian oily sludge [8], [9]. The crude oil production companies' usually face pipeline transport issues of the desirable lighter paraffins due to heavy paraffins that often drop on the inner parts of production equipment and on the walls of tubing [10].

Knowing that products like petrolatum are manufactured heavy paraffins, our study is orientated toward the recovery of paraffinic hydrocarbons in oily sludge from Cameroon Petroleum Refining Company. This work have as objectives to bring out the effect of some physical parameters on the recovery of paraffinic hydrocarbons from oily sludge with a fraction of commercialized gasoline used as solvent and to characterize the extracts by identifying and quantifying the compounds that were extracted from the Cameroonian oily sludge.

II. MATERIAL AND METHODS

A. Material

Studied oily sludge were sampled and prepared as described by Ndjeumi et al. [11]. Its average constitution was as follows: 25.36 % of hydrocarbons, 2.20 % of fine particles, and 72.45 % of water [9].

B. Methods

1) Solvent Preparation

For the recovery of aliphatic hydrocarbons from Cameroonian oily sludge, the commercialized gasoline, cut into three (03) fractions were used as solvent. Obtained from a fuel station, the sample of gasoline went through a fractional distillation. The ranges of temperatures used were $T_1 < 70^\circ\text{C}$, $T_2 = 70-110^\circ\text{C}$ and $T_3 > 110^\circ\text{C}$. The gas chromatography as described by Ze and Ngassoum [8] were used to analyze the various obtained fractions. T_2 was chosen after the analysis of the fractions to be used as solvent for the paraffinic hydrocarbons recovery based on an experimental design.

2) Paraffinic hydrocarbons extraction

The composite factorial plan with centered faces experimental design was used to conduct the extraction of paraffins. The influence of three different parameters studied (contact time, temperature, and solvent/sludge ratio) on the aliphatic hydrocarbon recovery were the purpose of the research. Upper and lower limits of the three parameters of the experimental design could be fixed based on the literature, and are as presented in the below Table 1.

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

The way the experimental design was made up brought out a total of 16 manipulations among which two analyses at the center. The calculation was done following the Equation 1 below:

$$N = 2^k + 2k + 2 = 2^3 + 2 \cdot 3 + 2 = 16 \quad (1)$$

Each of the 16 obtained extracts went through the experiments as described by Ze Bilo'o and Ngassoum [8]. In

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order to acquire the spectra, and to be able to identify and quantify the hydrocarbon compounds in each extracts, the software Peak sample 432-64bit was used. The percentages of groups of recovered compounds and the mass of the extract (mg) are the two responses observed from the experimental design.

III. RESULTS AND DISCUSSION

A. Solvent Preparation

The spectra obtained by chromatographic analysis brought out a list of compounds that were classified into families (aromatic compounds, linear, cyclic, and ramified paraffins) and the fraction containing heptane and its various isomers was selected. Heptane was chosen as selection parameter since it has been used as solvent by Zubaidy and Abouelnasr [12] for hydrocarbon recovery. The Figure 1 illustrates the graphic representation of the amounts of ramified paraffins and aromatic compounds that keeps increasing with the temperature range. Comparatively to Kerosene [11], aromatic compounds are abundantly present in Gasoline while linear and cyclic paraffins are reduced. It has been noted that the amounts of linear and cyclic paraffins reached their highest amount in the temperature range of 70-110°C. In the other hand, it is in the range 70-10°C that heptane and its isomers are highly present. Paraffinic hydrocarbons molecules in this fraction are in the range of 6 carbons (Methylcyclopentane) to 11 carbons (2-Methyldecane).

Fig. 1. Amount of families of compounds present in each fraction of Gasoline.

B. Aliphatic Hydrocarbons Recovery

1) Study parameters effect of on the recovery

The assessment the effect of the three studied parameters (A: Solvent/Sludge ratio, B: Temperature, and C: Contact time) on the recovery of aliphatics based to the experimental design was done and the various extracted masses were recorded. The standardized Pareto graphic (Fig. 2) could be plotted after the analysis of values obtained. It is noted that only the Solvent/Sludge ratio and its interaction with Temperature has a significant positive effect on paraffin extraction with an important weight. Temperature, contact time and interaction ratio-contact time have negative effect with an important weight on the mass of recovered paraffins. This graphic shows that, practically, the more the ratio and its

interaction with temperature increase the extracted mass, the more contact time and the temperature should be reduced gradually. The equation model (2) below is confirming the previous statement with the coefficient of each factor representing their weight. By contrary with the results of Ndjeumi *et al.* [11] who had positive significant effect while working with Kerosene, the temperature and the interaction between Ratio and Contact time have significant negative effect on the extraction effectiveness.

Fig. 2. Paraffins recovery standardized Pareto graphic.

$$Y = 1.455 + 0.776A - 0.989B - 0.575C + 0.644AB - 1.449AC - 0.051BC + 0.130A^2 - 0.198B^2 - 1.004C^2 \quad (2)$$

Fig. 3. Spectra of recovered paraffinic hydrocarbons under experimental conditions of Ratio = 6:1, Temperature = 40 °C, Contact time = 30 min.

2) Composition of recovered hydrocarbon fraction

The software Peak sample 432-64bit associated to GC-FID were used to acquire the spectra of all analyzed extracts, and to characterize each extract by identifying and quantifying the hydrocarbon content. A similarity of shape of spectra were noticed even though only the intensity and number of peaks were different. The Figure 3 above shows the chromatogram obtained at experimental conditions of Ratio=6:1, Temperature = 40 °C, Contact time = 30 min.

The spectra illustrated that, mixed with some unidentified hydrocarbon compounds, the paraffinic hydrocarbons recovered and identified have the number of carbons atoms ranged from eleven (11) to twenty-six (26). By contrary, it was observed that [11] the number of carbons of extracted aliphatic hydrocarbons ranged from eight (8) to twenty eight (28). Based on their structure, the extracted aliphatic hydrocarbons were identified, quantified, and classified. The classification is linear aliphatics, aliphatics with one, two, three, and more than three ramifications, cyclic aliphatics and non-identified aliphatics.

The highest total concentration of extracted paraffins was 14825 ppm, obtained under experimental conditions of Contact time = 30 min, Ratio = 6:1, Temperature = 40 °C, while the least concentration was obtained at Contact time = 30 min, Ratio = 2:1, Temperature = 60 °C. The 2,6,10,14-Tetramethylpentadecane (Pristane) which is a homologous of heptadecane is the compound having the highest concentration (2373 ppm) followed by 2-Methylhexadecane with a concentration of 848 ppm. The Table 2 below illustrates the proportions of the various groups in each extract. With Gasoline, it was observed that [11] 2,6-Dimethyldecane followed by 2,6-Dimethylundecane were the most extracted paraffins.

The concentrations of families in all extracts were determined. The highest extraction obtained with the fraction of Gasoline for each give concentrations of 3005 ppm (linear aliphatics), 4622 ppm (aliphatics with one ramification), and 1345 ppm (aliphatics with two ramifications) under experimental conditions of Contact time = 30 min, Ratio = 6:1, and Temperature = 40 °C. Aliphatics with three ramifications (551 ppm) and above (2923 ppm), led to the highest concentrations under Ratio = 6:1, Temperature = 50 °C, Contact time = 60 min. These last results could be justified by the fact that the molecular structure of these

compounds with heavy molecular weight need higher temperature and contact time for their dissolution and diffusion to take place. With the fraction of Kerosene [11] used as solvent, the amounts extracted for each group of paraffins are far away grater. Based on recovery conditions, the corresponding compound family that is the most recovered is presented in Table 3. It came out that the amount of recovered solid paraffinic hydrocarbons having more than 16 atoms of carbon was higher in each extract compare to liquid paraffinic hydrocarbons.

Standardized Pareto graphic illustrated that the Temperature has a negative influence on the effectiveness of the recovery. The increase of Temperature from 40 °C to 60 °C at constant Ratio (6:1) and Contact time (30 min) decreases the concentrations of the various families of paraffins to 2497 ppm, 3747 ppm, 1273 ppm, 102 ppm, and 2757 ppm respectively for linear aliphatics, aliphatics with one ramification, aliphatics with two ramifications, aliphatics with three ramifications and aliphatics with more than three ramifications. The quality and the quantity of aliphatics recovered are also strongly associated to the constitution of the solvent since the one used is a mixture of compounds which some have been used as solvent when pure.

TABLE II: RATIO OF RESPECTIVE ALIPHATIC GROUPS IN EACH EXTRACT

Designation (Ratio – Temperature – Contact time)	N°1 (2-40- 30)	N°2 (6-40- 30)	N°3 (2-60- 30)	N°4 (6-60- 30)	N°5 (2-40- 90)	N°6 (6-40- 90)	N°7 (2-60- 90)	N°8 (6-60- 90)	N°9 (2-50- 60)	N°10 (4- 40-60)	N°11 (4- 50-30)	N°12 (6- 50-60)	N°13 (4- 60-60)	N°14 (4- 50-90)	N°15 (4- 50-60)	N°16 (4- 50-60)
TPS (ppm)	311	14825	92	13203	4997	9290	1695	1820	386	447	1832	11994	9118	8671	7633	7579
LP (%)	41.48	20.27	27.17	18.91	13.77	12.41	7.14	11.15	21.50	22.82	16.81	18.62	21.33	17.91	21.52	21.59
P1R (%)	20.26	31.18	29.35	28.38	32.68	28.16	22.54	22.75	29.53	27.52	32.53	32.08	32.07	30.15	32.57	32.48
P2R (%)	6.75	9.07	0.00	9.64	5.26	5.89	5.07	12.80	6.99	6.04	4.53	6.45	6.72	6.77	5.86	5.94
P3R (%)	4.18	0.63	7.61	0.77	3.44	3.60	6.13	5.16	6.22	4.70	1.91	4.59	3.55	5.18	5.03	5.04
P+3R (%)	27.33	19.27	35.87	20.88	20.47	18.62	15.52	14.18	29.02	24.38	24.24	24.37	18.81	23.23	19.34	19.45
CP (%)	0.00	0.32	0.00	0.58	0.25	0.42	0.00	0.00	0.00	0.00	0.00	0.24	0.50	0.46	0.10	0.08
UP (%)	0.00	19.26	0.00	20.84	24.13	30.90	43.60	33.96	6.74	14.54	19.98	13.65	17.02	16.30	15.58	15.42

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.

TABLE III: MAXIMUM CONCENTRATION RECOVERED, AND OPTIMAL EXPERIMENTAL CONDITIONS FOR EACH GROUP OF ALIPHATICS

N°	Groups of paraffins	Maximum concentration extracted (ppm)	Optimal ratio (%)	Optimal temperature (°C)	Optimal contact time (min)
1	Linear Paraffins	3005	6	40	30
2	Paraffins with 1 ramification	4622	6	40	30
3	Paraffins with 2 ramifications	1345	6	40	30
4	Paraffins with 3 ramifications	551	6	50	60
5	Paraffins with more than 3 ramifications	2923	6	50	60
6	Cyclic Paraffins	77	6	60	30

IV. CONCLUSION

The assessment on the effect of three parameters on the aliphatics hydrocarbons recovery from Cameroonian oily sludge with a fraction of commercialized gasoline showed that all of them have a significant influence, on the effectiveness of the recovery, may it be positive (Ratio Solvent/Sludge) or negative (Temperature and Contact time). The qualitative and quantitative analysis of compounds that can be recovered from the Cameroonian oily sludge were achieved. It appeared that the aliphatics with one ramification are highly recovered (4622 ppm) at a Contact time of 30 min, Ratio of 6:1, and Temperature of 40 °C. The observed differences with results obtained when Kerosene is used as

solvent can primarily be attributed to the constitution of the fraction used as solvent. In fact, the constituents in each fraction of solvent (Gasoline and Kerosene) have specific affinity with compounds of hydrocarbons present in the oily sludge.

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