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The Evaluation of Two Local Petroleum Residues

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Abstract *Two vacuum residues were delivered from two different petroleum refineries, one from Suez Petroleum Company and the second from Alexandria Petroleum Company. They were subjected to solvent extraction using n-pentane, n-heptane, and ethyl acetate. The process of solvent extraction aims to separate maltenes and asphaltenes. The maltenes were further subjected to liquid chromatography (column chromatograph) in order to separate them into saturates and aromatics (mono-, di-, and poly-) and resins. The saturates that were separated from the maltenes of the two vacuum residues with different solvents were studied by gas chromatography in order to determine how much n-paraffins and cyclo-paraffins they contained.*

Keywords column chromatography, fractions, gas chromatography, solvent extraction, vacuum residues

1. Introduction

Petroleum heavy distillates and residues are necessary raw materials for the production of valuable light fuel products. The efficient conversion of these resources to useful products requires knowledge about the chemical composition of complex mixtures. A great deal of effort has been invested by petroleum chemists to develop analytical methodologies to obtain detailed structural information on petroleum fractions.

The composition of the crude oils becomes more complicated as the boiling range of the components increases. The structural diversity of the hydrocarbons increases astronomically with molecular weight. Thus, the extreme sample complexity of heavy fractions makes compositional analysis by the isolation of individual compounds a practical impossibility. Therefore, separation and isolation must be accomplished in the structure features of the compounds rather than the individual compounds.

Major work in the compositional and structural analysis of high-boiling petroleum distillates (360°C–525°C) was implemented in the early 1970s under API project 60, to support an upgrading program in the U.S. refinery industry (Coleman et al., 1973; Dooley et al., 1974a, 1974b, 1974c; Hinds, 1969, 1970; Badoni et al., 1992; Al Zaid et al., 1998; Kapur et al., 2000; C. Zhang et al., 2008). An analytical scheme was developed for the separation and identification of major component types in the high-boiling distillates of crude oils. As an extension of this work, Mckay et al. (Mckay et al., 1981a, 1981b, 1981c;

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Luo and Gu, 2007; Lu et al., 2008; Antoaneta, 2009; Yuan et al., 2009), in a series of three papers, described the separation and characterization of petroleum residues. Because we are analysis and evaluation labs, our role is to study the higher petroleum fractions in order to upgrade them in another lab, namely, the refining department. The aim of the present work is to evaluate two local vacuum residues delivered from different areas.

2. Experimental

Two vacuum residues (VRs) were delivered, one from Alexandria Petroleum Company and the second from Suez Petroleum Company. Three solvents, n-pentane, n-heptane, and ethyl acetate, were used for studying the composition of the two residues. The solvents used were analytical grade from Fluka Chemical Company.

2.1. *Determination of Physicochemical Properties of the Residues and Their Constituents*

The physicochemical properties of the residues and their constituents were carried out according to ASTM and/or IP standard test methods as illustrated in Table 1. The results of the analysis are given in Tables 1–3.

2.2. *Fractionation of the Residues into Their Constituents*

The studied residues were fractionated into their asphaltenes; maltenes; resins; aromatics; mono-, di-, and polyaromatics; and saturates (Altgelt and Gauw, 1979; Q. Zhang and Ye, 2009). This is shown in Figure 1.

2.2.1. Separation of the Asphaltenes and Maltenes. Asphaltenes and maltenes were separated from the two vacuum residues according to the standard test method IP-143.

2.2.2. Separation of the Maltenes into Saturates, Aromatics, and Resins by Alumina Column Chromatography. Maltenes resulted from deasphaltening of the residues were further separated into saturates, aromatics, and resins using alumina column chromatography.

Table 1
Elemental distribution of sulfur and nitrogen

	In Alexandria			In Suez	
Element wt%	n-Pentane	n-Heptane	Ethyl acetate	n-Heptane	Ethyl acetate
Sulfur in					
Asphaltenes	3.69 (0.57)[a]	2.83 (0.31)	3.65 (0.61)	3.12 (0.24)	2.99 (0.48)
Maltenes	2.90 (2.46)	2.98 (2.74)	2.95 (2.46)	2.85 (2.63)	2.81 (2.36)
Nitrogen in					
Asphaltenes	2.05 (0.31)	2.37 (0.19)	2.27 (0.38)	0.97 (0.07)	0.92 (0.15)
Maltenes	0.40 (0.34)	0.49 (0.45)	0.31 (0.26)	0.40 (0.37)	0.34 (0.28)

[a] The figures between parentheses are calculated relative to weight of the residue.

Table 2
Physicochemical properties of the studied samples

	Vacuum residues		
Sample properties	From Alexandria	From Suez	Standard method
Density at 60°F, g/gml[a]	1.0050	1.0009	IP 190
Gravity[a]			
Specific, at 60/60°F[a]	1.0060	1.0019	ASTM D 1250
API[a]	9.16	9.74	IP 200-API 2540
Viscosity, cSt at			
50°C[a]	23,466.83	17,072.38	ASTM D 445
80°C	1,658.60	1,369.60	IP 71
100°C	460.50	401.80	
Pour point, °C	+48	+48	ASTM D 97-IP 15
Sulfur content, wt	3.09	2.89	ASTM D 42924
Nitrogen, wt%	0.65	0.44	ASTM D 3228
Carbon residue, wt%	18.19	18.75	ASTM D 524-IP 14
Wax content, wt%	2.89	1.75	UOP 46
Ash, wt%	0.038	0.039	ASTM D482-IP 4

[a] Calculated.

A glass column (150 cm × 4 cm i.d.) was packed with 800 g alumina (neutral; 70–230 mesh, Merck) activated overnight at 300°C in a muffle furnace. The column was wetted with n-hexane, and then 40 g of the maltenes dissolved in the least amount of n-hexane was charged onto the column. The saturates, aromatics, and resins were eluted by n-hexane, toluene, and methanol–methylene chloride mixture (1:1), respectively. The solvents were distilled off and the separated saturates, aromatics, and resins were dried in an oven to constant weight.

2.2.2.1. Gas chromatography. A fraction of saturates, separated from maltene by column chromatography, was analyzed using a Perkin-Elmer 8700 gas chromatograph equipped with a fused silica capillary column (30 m × 0.53 mm i.d.). Oven temperature was programmed from 75°C to 300°C with a fixed rate of 3°C min^{-1}. The temperatures of the injector and detector (FID) were 300°C and 350°C, respectively. The carrier gas was nitrogen at a flow rate of 6 mL min^{-1}.

2.2.3. Separation of the Aromatics into Mono-, Di-, and Polyaromatics by Silica Gel Column Chromatography. Aromatics were further separated into mono-, di-, and polyaromatics using silica gel column chromatography.

A glass column (150 m × 2 cm i.d.) was packed with 200 g silica gel (100–200 mesh, Merck) activated at 180°C in an oven for 4 hr. The column was wetted with

Table 3
Physicochemical characteristics of separated maltenes

Properties*	Alexandria n-Pentane	Alexandria n-Heptane	Alexandria Ethyl acetate	Suez n-Heptane	Suez Ethyl acetate
Density at 60°F, g/mL[a]	0.9815	0.9945	0.9887	0.9876	0.9823
Gravity					
Specific, at 60/60°F	0.9825	0.9955	0.9897	0.9886	0.9833
API[a]	12.53	10.65	11.47	11.63	12.40
Viscosity, cSt at					
50°C[b]	801.25	1230.77	666.87	1,288.07	567.43
80°C	505.84	401.19	220.50	377.17	207.82
100°C	101.91	218.90	122.05	195.94	120.74
Pour point, °C	42	45	42	45	39
Sulfur content, wt	2.90	2.98	2.95	2.85	2.81
Nitrogen, wt%	0.40	0.49	0.31	0.40	0.34
Carbon residue, wt%	11.88	13.28	12.83	14.12	12.15
Wax content, wt%	3.38	3.14	3.47	1.88	2.07

[a] Calculated: API = 141.5/sp.gr-131.5 60/60 F.

n-pentane, and then 10 g of the sample dissolved in the least amount of n-pentane was charged onto the column.

Monoaromatics were eluted from the column by n-pentane–benzene mixture (95:5). After collection of the first 100 mL, 25 mL of each of the eluted fractions was collected in a weighed flask and the solvent was distilled off. The separated fraction was dried in an oven to constant weight. The refractive index of each fraction was measured. Monoaromatics were collected from the fractions having refractive index up to 1.53 at 20°C.

Diaromatics were eluted from the column by n-pentane–benzene mixture (85:15) using the same procedure used for monoaromatics until reaching the refractive index of 1.59 at 20°C. Polyaromatics were finally eluted from the column by benzene.

3. Results and Discussion

Petroleum is a product whose composition varies due to its natural origins and to transportation and storage conditions (Falla et al., 2006). In some origins, petroleum comes from a variety of different oil fields that produce predominantly heavy petroleum.

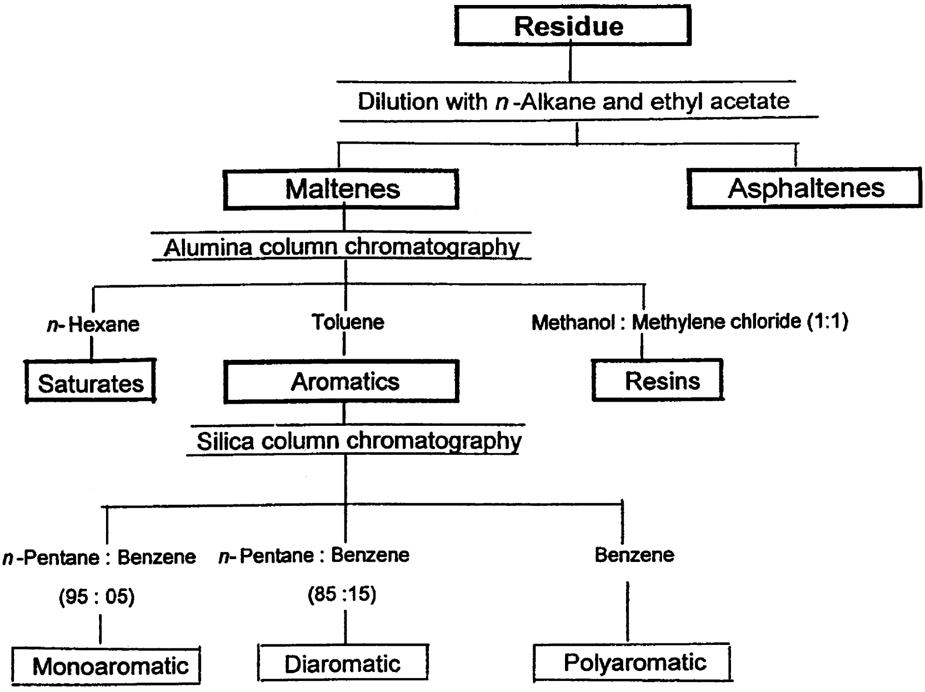

Figure 1. Scheme of separation of the residue into saturates, aromatics, resins, and asphaltenes.

Large proportions of crudes processed in oil refineries are set aside as distillation residue. At present, these residues are of relatively little commercial value. More detailed structural characterizations are necessary before improved process routes to upgrade these materials can even be contemplated.

3.1. Physicochemical Properties of the Residues and Their Constituents

Physicochemical properties of the residues and their maltenes separated by different solvents have been determined using ASTM and/or IP standard methods. The results are given in Tables 1–3. The physicochemical properties of the studied residues (Table 2) show that these residues are high in density, viscosity, and pour point. The results also reveal that these residues have high contents of sulfur and nitrogen. The results of the physicochemical properties of the maltenes (Table 3) show that the density and viscosity of the maltenes are less than that of the corresponding residues. The results also reveal that the sulfur and nitrogen contents in the maltenes are less than that of the corresponding residues. On the other hand, wax content in the matlenes is higher than that in the residues. This indicates that the sulfur and nitrogen elements are more concentrated in the asphaltenes, whereas the paraffinic compounds are concentrated in the maltenes. The results of the physicochemical properties of the maltenes also show that the sulfur and nitrogen contents of the maltenes separated by ethyl acetate solvent are less than that of maltenes separated by n-heptane solvent, whereas the wax content shows the reverse trend.

Table 4
Composition of the two residues using different solvents[a]

	Alexandria			Suez	
Components wt%	n-Pentane	n-Heptane	Ethyl acetate	n-Heptane	Ethyl acetate
Asphaltenes	15.09	8.11	16.67	7.65	16.13
Maltenes	84.91	91.89	83.33	92.35	83.87
Saturates	15.28	14.14	15.94	8.63	8.48
Aromatics	42.29	41.31	45.45	65.24	62.48
Mono-		8.73		17.61	
Di-		16.76		24.02	
Poly-		15.82		23.61	
Resins	27.34	36.44	21.94	18.48	12.91

[a] All the figures in the table are calculated with reference to the residue.

3.2. *Composition of the Studied Vacuum Residues*

The two studied residues were analyzed in order to know how much saturates, aromatic, resins, and asphaltenes they contain. The results are given in Table 4 and illustrated in Figures 2 and 3. From Table 4, one can see the following:

1. The two VRs contain a high percentage of aromatics over both saturates and resins. The order of the percentage of the three components is as follows, whatever the solvent used: aromatics > resins > saturates.
2. The VR from Suez has a high aromatic content than that in the VR from Alexandria. On the other hand, the VR from Alexandria has a higher percentage of both saturates and resins over those in Suez VR.
3. The asphaltenes content of Alexandria VR is higher than that of Suez VR.
4. In the two studied residues the yield of the asphaltenes separated by ethyl acetate solvent is higher than that separated by n-heptane solvent. This indicates that ethyl acetate is more efficient for the separation of the asphaltenes than n-heptane.

The data in Table 4 also show the distribution of hydrocarbons as saturates (n-paraffins and cyclic compounds) and aromatics (mono-, di-, and poly). It is clear that n-heptane is less efficient for the separation of asphaltenes than n-pentane. On the other hand, n-heptane gives better results than ethyl acetate and n-pentane for the separation of maltenes. These data are in full agreement with the data given by Alboudwarej et al. (2002) and Souza and Ferreira (2009), who stated that if higher-carbon-number alkanes are used, less asphaltenes are separated.

3.3. *Gas Chromatographic Analysis of the Separated Saturates*

The saturates separated from maltenes by different solvents were subjected to gas chromatographic analysis, and the data are shown in Table 5. From Table 4 we can see that

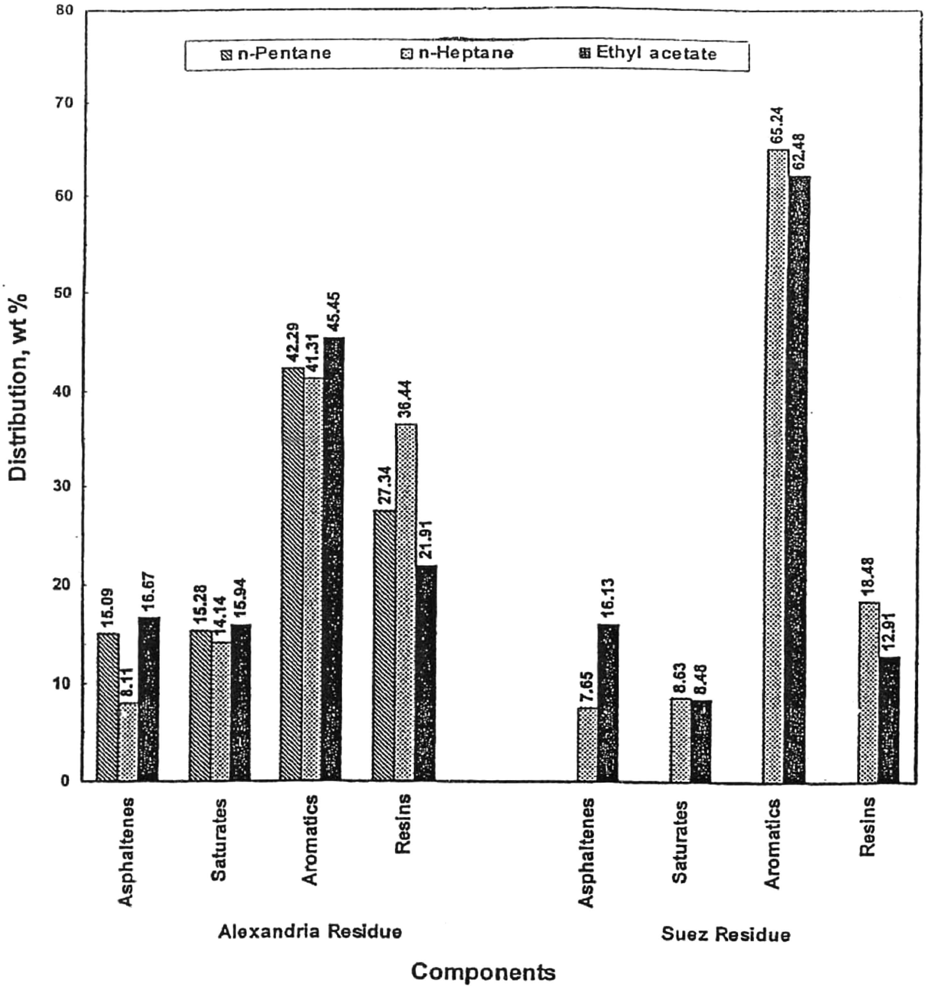

Figure 2. Distribution of the saturates, aromatics, resins, and asphaltenes (SARA) in the studied vacuum residues.

the saturates separated from maltenes of Alexandria VR show a higher percentage than that separated from Suez VR (Figure 2).

Figures 4 and 5 show the gas chromatograms of the saturates separated from both vacuum residues by different solvents. The chromatograms indicate that the saturates are formed from the resolved components (n- and iso-paraffins) and the hump, which is the unresolved complex mixture of naphthenes. The n-paraffin distribution of all the saturates separated ranges from about C_{20} to about C_{40} in addition to some traces lower than C_{20} and higher than C_{40}.

As shown from Table 5, the maximum percentage of n-paraffins was separated using n-heptane (14.14% from Alexandria VR and 8.63% from Suez VR). The table also shows that although ethyl acetate is less efficient for the separation of n-paraffins, it is more efficient than n-pentane, which was used in the case of Alexandria VR only.

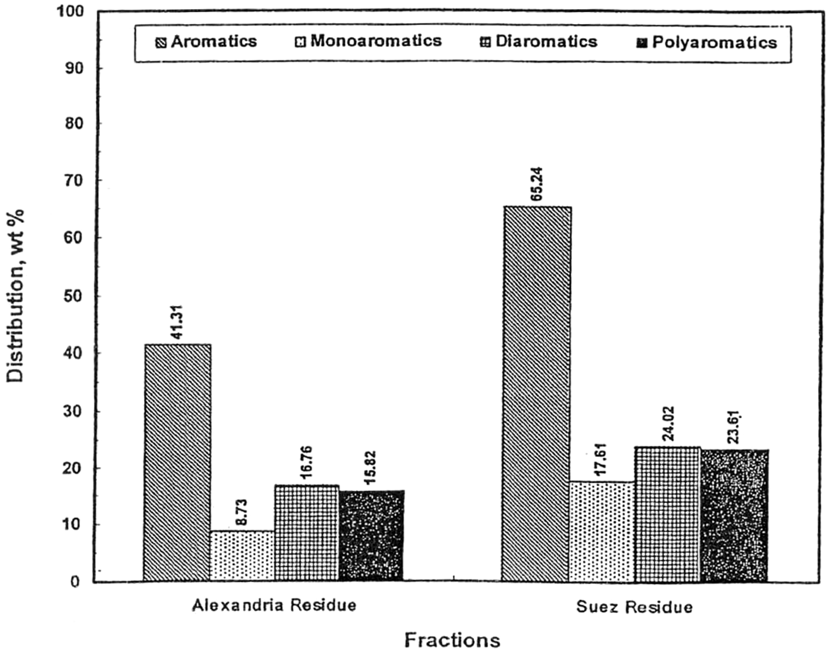

Figure 3. Distribution of the aromatics, mono, di- and polyaromatics in the studied vacuum residues.

Table 5
Gas chromatographic data of the saturates separated from maltenes by liquid (column) chromatography

Fraction	Saturates of Alexandria n-Pentane	Saturates of Alexandria n-Heptane	Saturates of Alexandria Ethyl acetate	Saturates of Suez n-Heptane	Saturates of Suez Ethyl acetate
n-Paraffins	10.98	14.65	13.04	13.70	12.31
Cyclic compounds	89.02	85.35	86.96	86.30	87.69

4. Conclusions

Two different vacuum residues, delivered from Suez Petroleum Company and Alexandria Petroleum Campany, were analyzed to determine their different constituents of aromatics, asphaltenes, resins and saturates. Data analysis showed the following:

1. The saturates separated from maltenes of Alexandria VR show a higher percentage than that separated from Suez VR.
2. The two vacuum residues contain higher aromatic contents over both saturates and resins. The order of the percentage of the three components was aromatics > resins > saturates.
3. The VR from Suez was found to have higher aromatic content than the Alexandria residue.

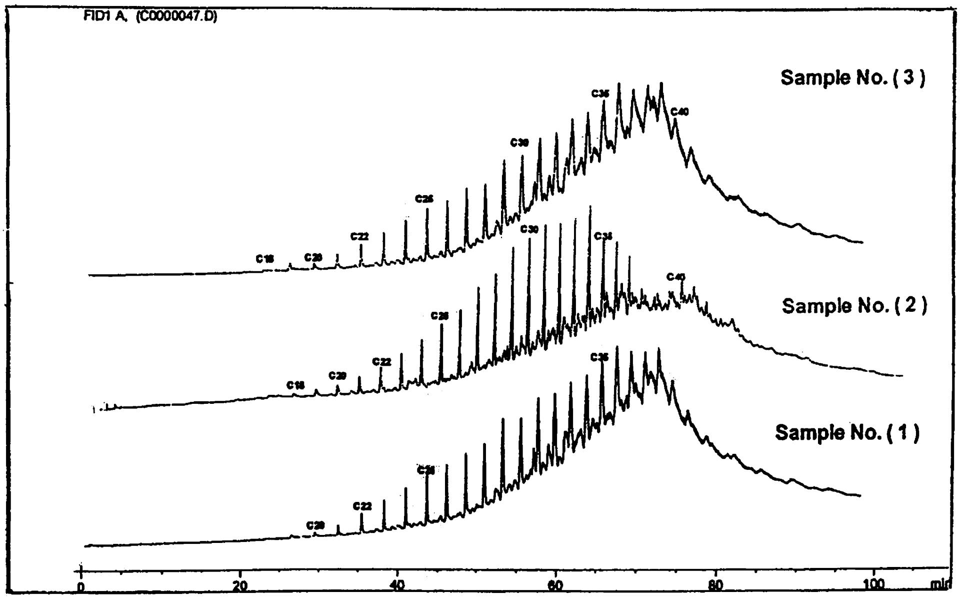

Figure 4. Gas chromatogram of saturates separated from Alexandria residue using n-pentane, n-heptane, and ethyl acetate.

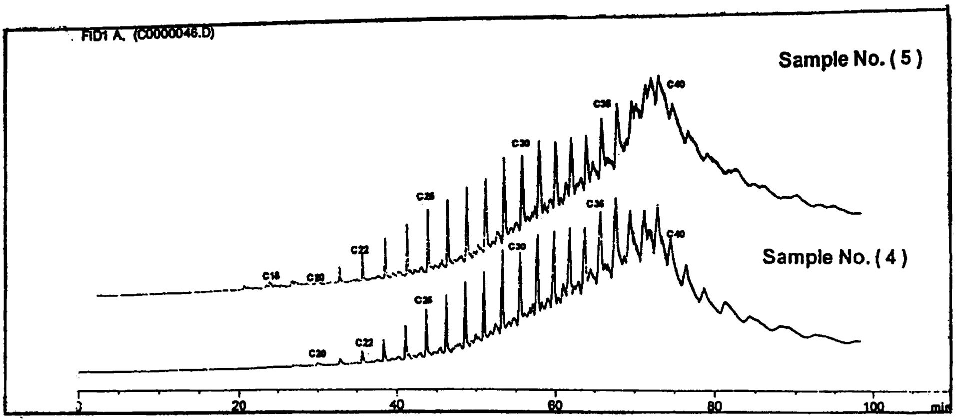

Figure 5. Gas chromatogram of saturates separated from Suez residue using n-heptane and ethyl acetate.

4. The data also show that the VR from Alexandria had a higher asphaltene content than that in Suez vacuum residue.
5. The gas chromatographic analysis for saturates separated from maltenes of Alexandria and Suez VRs shows how much n-paraffins and cycloparaffins are contained in the saturate fractions.

It was stated and concluded that the product yield depends on the constituents of the feedstock. It was found that most of the gasoline yield originates from the saturate constituent of the vacuum residue, whereas the aromatic constituent contributes to gasoline and diesel yield. Therefore, we can conclude that the vacuum residue of Alexandria may be suitable for the production of gasoline when upgraded, whereas the residue of Suez is more suitable for the production of much quantities of diesel fuel over gasoline.

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