International Journal of Multidisciplinary Research and Development
Online ISSN: 2349-4182, Print ISSN: 2349-5979; Impact Factor: RJIF 5.72
Received: 22-06-2019; Accepted: 24-07-2019
www.allsubjectjournal.com
Volume 6; Issue 9; September 2019; Page No. 143-149

Solvent De-waxing of Sudanese crude oil (Rawat) Using MIBK solvent to enhance their physical and molecular characterization

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Abstract

Solvent de-waxing process is a good way to decrease the pour point and enhance the physical and molecular properties of heavy crude oils, in this study methyl iso-butyl ketone (MIBK) was used as solvent to separate wax from Sudanese petroleum crude oil (Rawat) which has high pour point (54°C) and mean molecular weight (628) and low refractive index (1.4745) due to its high saturates content; especially its n- paraffins content (47.14%) and consequently its high wax content (26.3%); and at the same time high aromatics content (42.50%). by using MIBK solvent at de-waxing temperature -10 °C and crystallization time 24hrs the yield of the separated de-waxed oil increases with increasing of dilution solvent ratio from 4/1 to 10/1. decreases the pour point of the de-waxed oil with increasing the solvent ratio from 4/1 to 10/1. it appears that when a high solvent to oil ratio (S/F = 10/1 by weight) is used and a higher yield of oil is achieved due to the increase of the solubility of the solvent.

Keywords: waxy crude oil, crystallization time, Methyl Iso-butyle Ketone, de-waxing temperature, pour point and wax content, main molecular weight

1. Introduction

1.1 De-waxing Processes

De-waxing process is the important operation in the production of lubricating oils. De-waxing is the removal of wax from lube feed stocks fraction to produce lubricants with low pour points suitable for use at low temperature.

De-waxing processes have been developed at an early stage for the reduction of the wax content of oils by crystallization; cooling the waxy oil without addition of a solvent; in order to improve the low temperature properties [1, 2, 3, 4].

1.1.1 Solvent De-waxing Process

The trend in new de-waxing processing is towards solvent away from filter pressing [5] and naphtha centrifuge [6-7]. The solvent de-waxing process is based on the separation of paraffins in the temperature range of the desired pour point. This method is affected by low temperature solvent treatment, and its operation is independent of the structure and distribution of various paraffinic components. It is applicable theoretically and practically over the whole range of distillate fractions and residual stocks [8].

The solvent de-waxing is influenced by many parameters such as type of solvents, cooling rate, and temperature and solvent to oil ratio. Several pure solvents or mixtures of solvents have been in use for solvent de-waxing**.**

The rate of cooling has a strong influence on crystal formation and particle characteristic. A high cooling rate is found to promote the formation of small crystals but they are of the needle type that clogs the filter.

Solvent de-waxing processes are classified according to the nature of the solvent employed or the type of equipment used to separate the wax [9-10]**.**

Crystal structure of the paraffin wax is of great importance in commercial solvent de-waxing processes due to the importance of rapid filtration rate, particularly when rotary filters are used for separating the liquid and solid phases. The crystal size and the consequent filtration rate depend on the boiling range width and paraffin concentration of the distillate fraction, previous treatment of the feedstock, the method of dilution and the cooling rate [11].

1.1.2 Propane De-waxing Process

Propane de-waxing process was developed and firstly used in 1932. It is applicable for bright stock manufacture, the propane de-waxing is usually combined with de-asphalting process. Therefore, the oil containing propane from de-asphalting can be directly de-waxed. Thus removal of propane by distillation after de-asphalting is eliminated.

Propane is the most popular de-waxing solvent due to the cheap of the solvent, non-corrosive and readily available in most refineries [12].

The main disadvantage of propane de-waxing process is due to the relatively high solvent power for paraffin waxes, therefore, it is much more difficult to obtain easily filterable paraffin wax crystals. De-waxing additives have then to be used for distillates and often for residual stocks [13, 14-15]. Also the high solubility of wax in the solvent leads to a large de-waxing temperature differential. The use of ketone solvent as a wax anti-solvent in combination with propane has been proposed for improving the economics of the propane de-waxing process [16]. Research and development studies indicated that a mixture of propylene with acetone was superior to propane in both the ultimate pour point capability and filter rate. In addition, the required amount of filter aid was also less. Exxon Research and Engineering

Co., therefore, developed a commercial process for this solvent [17, 16-18].

1.1.3 Ketone De-waxing Process

The first commercial ketone de-waxing process was put into operation in 1927. The solvent originally used was a mixture of acetone – benzene [19, 20-4].

Methyl ethyl ketone (MEK) has replaced acetone in practically all of the benzene–acetone units because of its higher boiling point which minimize solvent losses. Today, the MEK process is the most widely applied de-waxing process [21-22].

The MEK process is suitable for de-waxing the entire range of lube oils, either prior or subsequent to the solvent extraction [15-23].

Ketone solvents containing no aromatic component, e.g. methyl iso-butyl ketone (MIBK), can be used alone for de-waxing. MIBK shows better performance than MEK-toluene blends as far as filtration, de-waxing temperature and yield of de-waxed oil are concerned [24, 25-26].

The most widely used ketone processes are the Texaco solvent de-waxing process and the Exxon Dilchill process.

A- Texaco Solvent De-waxing Process

This process is commonly called MEK process, normally uses a mixture of MEK and toluene as the de-waxing solvents and sometimes uses a mixture of other ketones and aromatic solvents.

In this process the waxy feedstock is heated to 10–15 ºF above the cloud point of the oil and diluted with solvent while chilling at a controlled rate in double pipe scraped–surface exchangers and chillers. Two to four volumes of solvent using an incremental dilution procedure for low to medium viscosity stocks and a double dilution controlled shock–chilling procedure for high viscosity stocks [27-28].

B- Exxon Dilchill De-waxing Process

This process is a modification of Texaco solvent de-waxing process. In this process a special crystallizer is used in place of the scraped–surface exchangers. Direct chilling of the feedstock in the crystallizer is accomplished using a cold solvent, multiple dilution and shock–chilling technique in a highly sheared environment. This high degree of mixing is used as a means of overcoming the poor filtration obtained with the conventional shock chilling techniques. Eagen *et al*. have reported an increase in filtration rate of 40 to 50% and a decrease in the solvent oil ratios of 10 to 30% have been reported for Dilchill de-waxing as compared to conventional MEK de-waxing [16-29].

De-waxing with selective solvents for lube oil production from paraffin–base crudes requires high investments and operating expenses. For this reason [30], proposed a number of methods of increasing the efficiency have been proposed: proportioned feed of a mixture of selective solvents while cooling the feedstock solution; slow mixing of the cooled solution; feed of inert gas before filtration to enlarge the wax crystals; selection of an effective ketone; use of special modifier additives capable of forming wax crystals of the necessary shape during cooling of the feedstock.

Di / Me De-waxing Process

The Di / Me de-waxing process uses a mixture of dichloroethane and methylene dichloride as the de-waxing solvent. A few refineries in Europe use this process. This process was developed by Edeleanu Gellschaft. The main advantage of the process is that very low oil–content slack waxes (2–6 wt.%) can be obtained in a single filter stage. The process is only slightly sensitive to changes in solvent ratio and maintaining low de-waxing temperature differential value. In general, chlorinated solvents have disadvantage of being hydrolyzed thus becoming corrosive, particularly in the solvent recovery equipment [31].

1.1.4 Urea De-waxing Process

Urea de-waxing relies upon the fact that various straight chain organic compounds and also slightly branched compounds are capable of forming complexes with urea, called adducts, which are crystalline at room temperature. These adduct crystals can be separated.

Urea has been used for de-waxing lower boiling mineral oil fractions; it was used for both the manufacture of low pour point oil and / or pure n-paraffins from paraffinic feedstock [32].

In recent years, the urea de-waxing process has new and greater flexibility to make special products from a wider range by crude oil types [33-34].

The success of urea de-waxing depends on the structure of paraffins to be isolated and on their influence on the pour point. The paraffinic components, which affect the pour point, are not only linear but also branched chain paraffins. The weight ratios of these components depend on the origin and boiling range of the particular fraction. However, urea is not very selective for the removal of long chain branched hydrocarbons; urea will remove hydrocarbons containing branched and rings providing the molecule contains a long unbranched chain [31].

1.2 Refining of petroleum waxes

Petroleum waxes were considered as by-products in the de-waxing of lubricating and gas oil. They were used as components of furnace residual fuel oil. Today they are available petroleum products.

The specifications for finished waxes depend on their end use which determines the degree of refining, required. Refined wax is achieved by de-oiling and hydrogenation or acid treatment and adsorption processes.

1.2.3 De-oiling processes (Wax Fractionation Processes)

Slack waxes and petrolatums separated from lubricating oil and residual feedstocks respectively in de-waxing operation, usually contain from 2 to 45 wt.% oil. Low oil content wax (0.1 to 1.0 wt.%); with a specific melting point and penetration; is produced by selective removal of the oil and low melting waxes. The solidification temperature and the hardness of the wax; which is indicated by the needle penetration value; are important characteristics. This process is called de-oiling or wax fractionation.

The commercial wax de-oiling or fractionation processes are the sweating process, the re-crystallization process, the warm–up de-oiling process, and the spray de-oiling process [16-4].

1.2.4 The Sweating Process

Sweating serves the purpose of de-oiling and fractionating the wax. It is the oldest wax de-oiling process, which has been replaced with the more modern processes. In this process, the molten wax is solidified by chilling in large pans contained in large ovens. The wax is slowly heated in these ovens wherein the oil and lower melting point wax are separated from the higher melting point wax. Sweating is an extremely slow process, one cycle take more than 50 hours.

This process can be used for the de-oiling slack waxes yielding well developed macro-crystalline, preferably needle-shaped paraffin wax crystals. Petrolatums and slack waxes, which contain too large quantities of iso-paraffins, cannot be sweated because their structure is very finely crystalline. This type must be handled by solvent de-oiling process since it is suitable for any type of feedstock [20 & 4].

2. Materials and Method:

2.1 Materials

2.1.2 Chemicals

- Feed stock: Sudanese crude oil obtained from Rawat Petroleum Company in Sudan is used in this study to lower its wax content and improve its properties mainly the pour point of crude oil.
- Color: black.
- Quantity: 50 liters.
- Net weight: 44 kg.
- Gross weight: 48.5 kg.
- Sampling time and date: 18/11/2018, 1:00 pm.
- Sample well: central 10.
- Methyl isobutyl ketone, ACS for analysis, Reagent Ph. Eur-Reag. USP (Carlo Erba).
- Petroleum ether 40-60ºC, for analysis (Carlo Erba).
- N-Heptane, 99% (Carlo Erba).
- Benzene, Pure reagent for analysis (ADWIC)
- Methanol, 99.5% (Piochem. Co.)
- Silica gel 60-200 mesh size (Loba Chemie, India).
- Aluminum oxide, for chromatographic analysis (Riedel-deHaen).

2.1.2 Instruments

- Digital Refractometer; model RFM870 (UK).
- X-ray fluorescence sulfur meter analyzer; model Spectro Phoenix II (USA).
- GC apparatus used was model (Perkin Elmer instrument, Clarus 500, England), equipped with a hydrogen flame ionization detector and fused silica capillary column (30 cm x 0.25 mm i.d.), packed with poly (dimethyl siloxane) HP-1 (non-polar packing) of 0.5 µm film thickness. The apparatus was also equipped with an integrated data handling system for computing the peak area and concentration.
- Density meter, Anton Paar Model: SVM 3001
- SETA Cloud and Pour Point Refrigerator, SETA Model: STANE HOPE SETA
- Total acid number measured according to ASTM D-664 Potentiometric titration method.
- Wax content, Asphaltene content, Water content, Carbon residue and ASTM distillation are measured by glass systems.

2.2 Methods

2.2.1 Sampling

The sample was taken according to standard sampling method.

2.2.2 Solvent De-waxing Technique

Solvent de-waxing technique was used for de-waxing the Sudanese crude oil (Rawat crude oil) by using different de-waxing solvents at different dilution solvent ratios of 4:1, 6:1, 8:1 and 10:1 by weight and under constant washing solvent ratio of 2:1 by weight. In the stage of solvent de-waxing, the high melting components of wax precipitated while the low melting components (low melting point wax and soluble oil) remained in the solution. The process of solvent de-waxing was repeated by using de-waxing temperature -10ºC and at crystallization time 24 hours.

Procedure

A known weight of Sudanese crude oil was dissolved in the corresponding amount of solvent in a beaker and heated till the mixture becomes homogeneous. Then the mixture was cooled gradually at room temperature for half an hour and transferred to a refrigeration unit at 5ºC for 24 hours. The beaker and the Buchner funnel were transferred to a controlled temperature unit and gradually cooled to the desired de-waxing temperature of for 3 hours. The beaker contents were transferred to the funnel and filtered through a Whatman filter paper No.43 by using controlled suction (8.6 Psi). The precipitated wax cake and oil were washed with an additional solvent at the same de-waxing temperature and added at small increments. Solvents were removed from the precipitated wax cake by distillation.

2.2.2.1 Solvent De-waxing Variables

a) Solvent Type

Solvent de-waxing of Sudanese crude oil was carried out using methyl ethyl ketone (MEK) at fixed de-waxing temperature of -10ºC and fixed washing solvent ratio of 2:1 by weight and at different dilution solvent ratios of 4:1, 6:1, 8:1 and 10:1 by weight.

b) Dilution solvent ratios

Solvent de-waxing of Sudanese crude oil was carried out using (MEK) at different dilution solvent ratios of 4:1, 6:1, 8:1 and 10:1 by weight and at fixed de-waxing temperature of -10ºC and fixed washing solvent ratio of 2:1 by weight.

2.2.3 Physical Characteristics

The physical characteristics of the Sudanese crude oil and isolated oil products were carried out according to American Society for Testing and Materials *(ASTM)*, International Petroleum test methods *(IP)* and Universal Oil Products standards *(UOP)*. The standard methods for analysis are as follows:

Congealing point	ASTM D-938
Pour point	ASTM D-97
Density	ASTM D-4052
Specific gravity	ASTM D-4052
API gravity	ASTM D-4052
Refractive index	ASTM D-1747
Kinematic viscosity	ASTM D-445
Mean molecular weight	ASTM D-2502
Wax content	UOP-64
Water content	ASTM E-203
Asphaltene content	IP-143
Carbon residue, wt.%	ASTM D-189
Total acid number	ASTM D-664

Sulfur content, X-ray fluorescence sulfur meter ASTM D-4294

2.2.4 Molecular Type Composition

2.2.4.1 Aromatic Content

The total aromatic content of the Sudanese crude oil and the oil products was determined using liquid-solid column chromatography technique [35].

Procedure

A 1.3 cm diameter column packed with activated alumina for chromatographic purposes (65gm) and activated (60-200 mesh) silica gel (65gm) to a total height of 130 cm was used. The column was then moistened with 100 ml of n-heptane (in case of crude oil) or petroleum ether 40-60ºC (in case of oil products) to dissipate the heat of adsorption. A 10 grams sample of the crude oil or the oil product dissolved in few milliliters of n-heptane or petroleum ether 40-60ºC was transferred to the column. The column was then eluted with 300 ml n-heptane or petroleum ether 40-60ºC followed by 200 ml benzene and finally 100 ml of a 1:1 mixture of absolute methanol and benzene. Fractions of 25 ml were collected from the column, the solvent distilled off and the refractive index at 20ºC of each fraction was determined. According to the refractive indices data, the fractions were combined into saturates, mono-, di- and poly-aromatics. The saturate hydrocarbons have refractive indices not more than 1.48. The mono-cyclic, bi-cyclic and poly-cyclic aromatics have refractive indices from 1.48 to 1.53, 1.53 to 1.59 and higher than 1.59, respectively [36].

2.2.4.2 n-Paraffin Content

N-Paraffin content was determined for the saturates of Sudanese crude oil and the oil products by using gas chromatography technique (GC).

Procedure

In the chromatograph, the injector was heated at 350 ^{0}C. The column temperature was programmed from 80 to 300 ^{0}C at a fixed rate of 3 ^{0}C/min., and nitrogen (oxygen-free) was used as a carrier gas with flow rate of 2 ml/min. The detector was heated at 350 ^{0}C, and the flame operated with air and hydrogen flow rates adjusted to optimize the detector sensitivity. The sample was melted and 0.1µl of it was introduced into the injector. A mixture of pure n-paraffins was used as standards. The peak area of each resolved component (consisting of n- and iso-paraffins) is determined individually. However, the unresolved complex mixture (hump) is presumably composed of non n-paraffins iso- and cyclo-paraffins.

2.2.4.3 Structural Group Analysis

Carbon distribution analysis; the percentage of aromatics carbon (%C_A), paraffinic carbon (%C_P) and naphthenic carbon (%C_N) and ring content analysis; aromatic ring (R_A), naphthenic ring (R_N) and the total ring (R_T); per average molecule were determined by n-d-m method [37-38] for the oil products.

3. Results and discussion

3.1 Characterization of Feed Sample

Table 1: The physical characteristics and molecular type composition of Sudanese crude oil (Rawat)

Physical characteristics	Value
Pour point ºC	54
Density @ 15.56 ºC	0.8794
Specific gravity @ 15.56 ºC	0.8802
API gravity @ 15.56 ºC	29.25
Refractive Index at 70 ºC	1.4745
Kinematic viscosity at 100 ºC, mm²/s	9.23
Mean molecular weight	628
Wax content, wt.%	26.3
Asphaltene content, wt.%	0.28
Carbon residue, wt.%	4.29
Sulfur content, wt.%	1.8
Total acid number, wt.%	1.282
Water content, wt.%	
Molecular type composition	
Saturates content, wt.%	57.5
n-paraffins content, wt.%	47.14
Iso and cyclo- paraffins content, wt.%	10.36
Aromatics content, wt.%	42.5
Mono-aromatics, wt.%	1.5
Di-aromatics, wt.%	13.3
Poly-aromatics, wt.%	27.7

The physical characteristics and the molecular type composition for the Sudanese crude oil are presented in Table 1. Data indicates that the Sudanese crude oil has high pour point (54ºC) and mean molecular weight (628) and low refractive index (1.4745) due to its high saturates content; especially its n- Paraffins content (47.14%) and consequently its high wax content (26.3%); and at the same time high aromatics content (42.50%). Thus, in order to produce lubricating oils (having good fluidity characteristics at low temperatures) from the Sudanese crude oil, the pour point must be reduced by subjecting to solvent de-waxing process (a crystallization–filtration process) [39, 40].

3.2 Characterization of De-waxed Oils

Table 2: Effect of solvent dilution ratio on the physical characteristics, molecular type composition and structural group analysis of the de-waxed oils obtained by using MIBK at de-waxing temperature of -10 °C and S/F for washing 2:1

Physical characteristics	**S/F for dilution solvents**			
	4:1	6:1	8:1	10:1
Yield on Sudanese crude oil, wt.%	12.09	27.30	29.17	29.14
Pour point, °C	7	7	6	5
Density @ 20°C	0.9300	0.9134	08956	0.8918
Density @ 15.56°C	0.9308	0.9142	0.8964	0.8926
Specific gravity @ 15.56°C	0.9317	0.9150	0.8973	0.8935
API gravity @ 15.56°C	20.37	23.14	26.20	26.87
Refractive index @ 70 °C	1.4934	1.4853	1.4801	1.4739
Kinematic viscosity @ 40 °C, mm^2/s	100	61.54	39.67	26.79
Kinematic viscosity @ 100 °C, mm^2/s	12.00	8.70	6.60	5.15
Viscosity index	110	115	120	124
Mean molecular weight	576	507	468	430
Sulfur content, wt.%	0.5506	0.5068	0.4635	0.4256
Wax content, wt.%	0.4	0.35	0.27	0.15
Total acid number, wt.%	0.931	1.20	2.27	3.36
Molecular type composition				
Saturates content, wt.%	50.11	50.83	51.82	56.90
n-paraffins content, wt.%	28.22	30.10	37.90	35.20
Iso and cyclo- paraffins content wt.%	21.89	20.73	13.92	21.70
Aromatics content, wt.%	49.89	49.17	48.18	43.10
Mono-aromatics, wt.%	14.20	13.94	11.06	9.53
Di-aromatics, wt.%	23.99	22.69	21.92	14.82
Poly-aromatics, wt.%	11.70	12.54	15.20	18.75
Structural group analysis				
Carbon distribution analysis				
% C_A	13.83	13.09	15.73	11.37
% C_N	31.71	28.70	17.97	26.86
% C_R	45.54	41.79	33.70	38.23
% C_P	54.46	58.21	66.30	61.77
Ring content analysis				
R_A	0.99	0.82	0.91	0.60
R_T	4.16	3.27	2.31	2.44
R_N	3.17	2.45	1.40	1.84

Data indicates that the yield of the de-waxed oils (Fig. 1) separated at all solvent to feed ratios increases in the following order:

10:1 ≥ 8:1 > 6:1 > 4:1

- MIBK solvent is very expensive and tends to precipitate the wax and has mean solubility to oil, (i.e., it does the two operations at the same time), thus it gives mean yield of oil. Also, recovery of solvent is desirable because it is a single solvent.

Also, data indicate that the pour point of the de-waxed oils (Fig. 2) separated at all solvent to feed ratios decreases in the following order:

10:1 = 8:1 > 6:1 > 4:1

- MIBK give the separated de-waxed oil of mean pour points and consequently, the mean wax and n-paraffin contents and the mean iso and cyclo-paraffins content (Fig. 3 & 4).

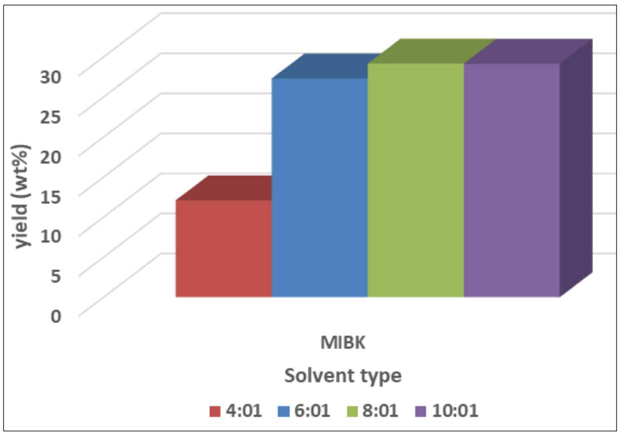

Fig 1: relationship between solvent type and yield%

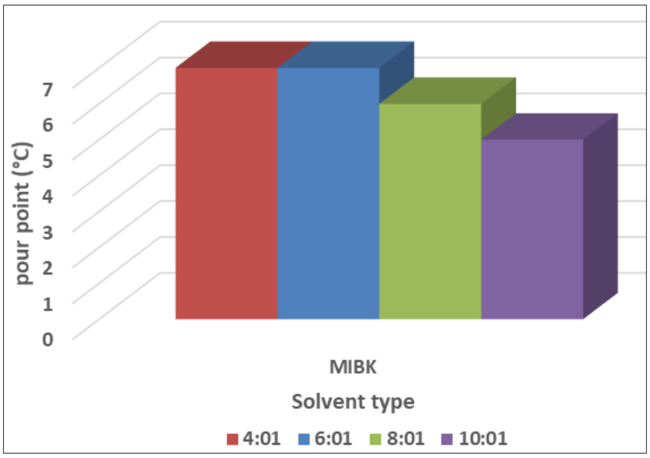

Fig 2: Relationship between solvent type and pour point (°C)

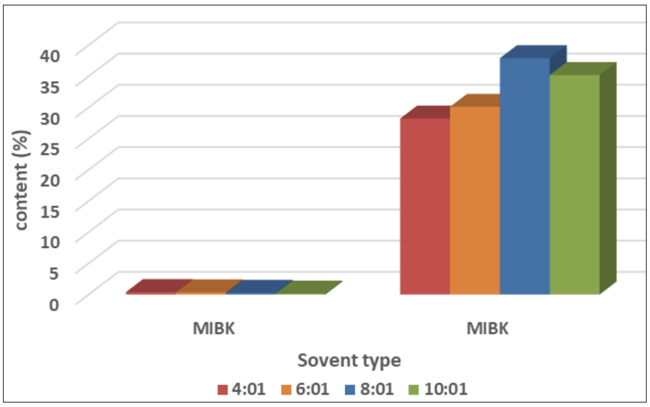

Fig 3: Relationship solvent type and (Wax and n-Paraffins content%)

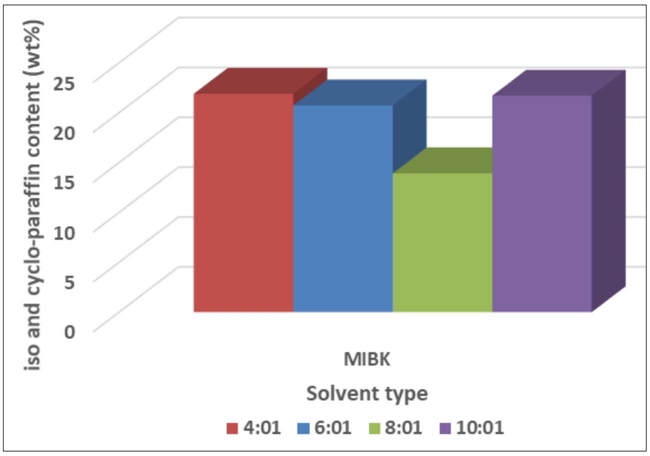

Fig 4: relationship solvent type and (iso and cyclo-paraffin content wt%)

Using MIBK, the yield of the separated de-waxed oil increases with increasing of dilution solvent ratio from 4/1 to 10/1. The results can be justified by the fact that the high solvent ratio result in a greater reduction of the mixture's viscosity and the solvent itself enhances the formation and growth of wax crystals, which in turn, resulted in an improved filtration performance. More so, the greater ratio of solvent to oil molecules which have a greater solubility preference for the oil than the wax serves to improve the de-waxing performance, i.e., decreases the pour point of the de-waxed oil with increasing the solvent ratio from 4/1 to 10/1. Data of wax content are parallel to the previous results whereas, the wax content decreases as the solvent ratio increases. Although, the increase of dilution solvent ratio is accompanied with the improvement of lubricating oil quality in terms of decreasing the mean molecular weight, density, refractive index, viscosity, and increasing viscosity index for the de-waxed oils as a result of their increased saturated content specially n-paraffin content and consequently their decreased iso- and cyclo-paraffin content by using MIBK. This may be attributed to the increase of solvent power towards the low molecular weight n-paraffins present in Sudanese crude oil by using MIBK. Data of structural group analysis are parallel to the previous results whereas,% C_P increases and% C_N and R_N decrease as the dilution solvent ratio increases from 4/1 to 10/1.

More specifically, it appears that when a high solvent to oil ratio (S/F = 10/1 by weight) is used and a higher yield of oil is achieved due to the increase of the solubility of the solvent. Thus, it can be concluded that the process of de-waxing at de-waxing temperature of −10°C would be economical. It can be concluded that the process of de-waxing at crystallization time of 24h would be suitable and is selected for de-waxing of Sudanese crude oil using MIBK at dilution solvent ratio of 10:1 and at de-waxing temperature of −10°C.

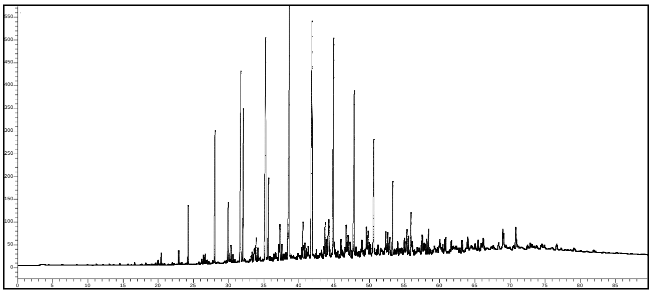

Fig 5: GC graph for de-waxed oil using MIBK (-10^{o}C, S/F 6:1)

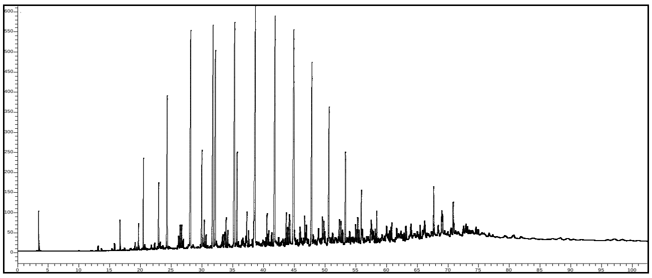

Fig 6: GC graph for de-waxed oil using MIBK (-10^{o}C, S/F 10:1)

3.3 Conclusion

MIBK solvent is very expensive and tends to precipitate the wax and has mean solubility to oil, but recovery of solvent is desirable because it is a single solvent, the pour point of de-waxed oils at the rang 5 to 7 ^{o}C an wax content 0.15 to 0.4 wt%.

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