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MEK De-waxing of Sudanese crude oil (Rawat) to enhance their physical and molecular characterization

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Abstract
Waxy crude oil creates difficulties during transportation and refining process. This study investigated the feasibility of Methyl Ethyl Ketone (MEK) as selective solvent to de-wax a Sudanese heavy crude oil (Rawat area) with wax content 26.3 wt% and pour point 54°C and determine the possible optimum conditions. Experiments were conducted on four solvent to feed ratios (10: 1, 8: 1, 6: 1 and 4: 1) at de-waxing temperature -10 °C, mixing temperature 40°C and crystallization time 24 hrs. The crystallized wax which forms in the mixture was then vacuum filtered, dried, and weighed. The results indicated that MEK de-waxing performance improved at higher mixing temperatures. This could be explained by the disruption of dispersion forces which exist between the molecules in the crude oil, allowing new intermolecular bonds to form between MEK and oil molecules in greater preference than with the wax molecules. It was also discovered that the use of a higher solvent to oil ratio resulted in a greater wax yield that is attributed to a greater oil solubility, In contrast, it was found that a lower cooling temperature resulted in a greater extraction of wax from the mixture. Finally, the greatest oil yield (19.75 wt%) was achieved at a solvent to oil ratio of 8:01, a mixing temperature of 40°C and a de-waxing temperature of -10°C with pour point - 4.5°C.

Keywords: waxy crude oil, refining process, Methyl Ethyl Ketone, de-waxing temperature, pour point and wax content

1. Introduction
Petroleum waxes are substance, which are solid at normal temperatures. Paraffin and microcrystalline waxes in their pure form consist only solid saturated hydrocarbons. Petrolatum, in contrast to the other two waxes, contains both solid and liquid hydrocarbons. Petrolatum is semi-solid at normal temperatures and is quite soft as compared to the other two waxes. Paraffin wax is a solid and crystalline mixture of hydrocarbons; it is usually produced in the form of relatively large crystals. It consists mainly of normal paraffin ranging from C_{16} – C_{30} and possibly higher. Varying proportions of slightly branched chain paraffins ranging from C_{18} – C_{36} and naphthenes; especially alkyl-substituted derivatives of cyclopentane and cyclohexane; are also present. Generally aromatics are present only in very low percentage, most of them are of the mono-aromatic type with a long paraffinic side chain (Gottshall and McCue, 1973; Mazee, 1973; Fruend *et al*., 1982; Letcher, 1984 & Concawe, 1999) [1, 2, 4, 5].
The average molecular weight of these paraffin waxes is about 360 – 420 (Gottshall and McCue, 1973 & Nakagawa and Tsuge, 1983) [1, 2]. There is a general arrangement that carbon atoms in n-paraffins are arranged in a zig – zag fashion:
A paraffin wax melting at 53.5ºC showed a space lattice having C – C bond length of 1.52ºA, a C – C – C bond angle of 110ºA, a C – H bond length of 1.17ºA and a H – C – H bond angle of 105ºA (Vainshtein and Pinsker, 1950) [6]
Dewaxing process is the important operation in the production of lubricating oils. Dewaxing is the removal of wax from lube feed stocks fraction to produce lubricants with low pour points suitable for use at low temperature.
Dewaxing 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 (Bushnell and Eagen, 1975; Brenken and Richter, 1979; Klamann *et al*, 1984 & Sequeira, 1994) [7, 8, 9].
The trend in new dewaxing processing is towards solvent away from filter pressing (Ryan and Burke, 1907) [11] and naphtha centrifuge (Lindgren, 1948 & Zurcher, 1951) [12, 13].
The solvent dewaxing 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 (Hoppe, 1964) [14].
The solvent dewaxing 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 dewaxing.
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 dewaxing processes are classified according to the nature of the solvent employed or the type of equipment used to separate the wax (Kalichevsky, 1949 & Li, 1968 and 1969) [15, 16].
Crystal structure of the paraffin wax is of great importance in commercial solvent dewaxing 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 (Rossi, 1990 & Nimer *et al*., 2010) [17, 18].

The manufacture of petroleum waxes is closely related to the manufacture of lubricating oils. The raw paraffin distillates and residual oils contain wax and they are normally solid at ambient temperature. Removal of wax from these fractions is necessary to permit manufacture of lubricating oil with a satisfactory low pour point. Manufacture of petroleum waxes includes the following technological processes:

- Production of slack waxes and petrolatums by de-waxing petroleum products.
- Refining of the wax products:
- Deoiling and fractional crystallization.
- Percolation process.
- Hydrofinishing process.
- Acid treatment.
- Adsorption process.

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 ethyl ketone, 99%, (Riedel-deHaen).
- Methyl Tertiary butyl ether, 99% (Riedel-deHaen).
- Petroleum ether 40-60^{o}C, 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 me thod.

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 -10^{o}C 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 5^{o}C 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 -10^{o}C 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 -10^{o}C 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 (Snyder, 1975) [19].

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 (Mair and Rossini, 1958) [20].

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 *(Tadema, 1951 & ASTM D-3238)* [21] 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, mm^2/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.%	1.80
Total acid number, wt.%	1.282
Water content, wt.%	
Molecular type composition	
Saturates content, wt.%	57.50
n-paraffins content, wt.%	47.14
Iso and cyclo- paraffins content, wt.%	10.36
Aromatics content, wt.%	42.50
Mono-aromatics, wt.%	1.50
Di-aromatics, wt.%	13.30
Poly-aromatics, wt.%	27.70

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). *(Jr and Sequeria 1994, Speight 2007).*

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 MEK at de-waxing temperature of -10 oC 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.%	14.29	19.14	19.75	16.81
Pour point, ºC	- 7	- 5.5	- 4.5	2
Density @ 20ºC	0.8883	0.8959	0.9055	0.9100
Density @ 15.56ºC	0.8892	0.8967	0.9063	0.9108
Specific gravity @ 15.56ºC	0.8901	0.8976	0.9072	0.9117

API gravity @ 15.56ºC	27.47	26.15	24.47	23.70
Refractive index @ 70 ºC	1.4779	1.4784	1.4796	1.4868
Kinematic viscosity @ 40 ºC, mm^2/s	25.00	26.00	27.00	57.00
Kinematic viscosity @ 100 ºC, mm^2/s	5.50	5.75	5.90	8.25
Viscosity index	166	173	172	115
Mean molecular weight	478	495	498	503
Sulfur content, wt.%	0.4666	0.4621	0.4635	0.5128
Wax content, wt.%	0.05	0.10	0.15	0.18
Total acid number, wt.%	1.775	1.692	1.572	1.498
Molecular type composition				
Saturates content, wt.%	57.52	57.03	56.70	56.33
n-paraffins content, wt.%	28.09	25.90	21.96	24.83
Iso and cyclo- paraffins content, wt.%	29.43	31.13	34.74	31.50
Aromatics content, wt.%	42.48	42.97	43.30	43.67
Mono-aromatics, wt.%	11.90	11.31	10.61	11.50
Di-aromatics, wt.%	18.07	18.50	19.35	18.55
Poly-aromatics, wt.%	12.51	13.16	13.34	13.62
Structural group analysis				
Carbon distribution analysis				
% C_A	16.33	13.34	10.47	16.23
% C_N	12.93	21.00	30.52	21.55
% C_R	29.26	34.34	40.99	37.78
% C_P	70.74	65.66	59.01	62.22
Ring content analysis				
R_A	0.97	0.82	0.64	1.02
R_T	2.00	2.53	3.14	2.88
R_N	1.03	1.71	2.50	1.86

MEK tends to precipitate the wax and at the same time has high solubility to low molecular weight oil, so it needs another solvent added to it (co-solvent such toluene) to increase its efficiency of solubility of the oil inherent to the wax crystals. But addition of toluene to MEK causes blocking of the crude sample through de-waxing process (i.e., it is difficult to separate the oil from the wax). This is due to the nature of the composition of crude oil obtained from Sudanese Rawat Company. Also, recovery of mixed solvents is not desirable due to the differentiation in their boiling points range and it's too hard to separate the two solvents upon making distillation and to be recovered for another de-waxing step.

MEK solvent gives the separated de-waxed oil of the lowest pour point and consequently, the lowest wax and n-paraffin contents and the highest iso and cyclo-paraffins content (Fig. 1 and 2).

The rate of filtration of the de-waxed oil increases with dilution. The amount of solvent used in de-waxing technique have an obvious effect upon the yield, quality molecular type composition and structural group analysis of the de-waxed oils isolated from Sudanese crude oil by using MEK solvents at de-waxing temperature of -10^0C (Table 2). Data indicate that, the yield of the separated de-waxed oil increases with increasing of dilution solvent ratio from 4/1 to 8/1 (Fig. 4). But, further increase in dilution solvent ratio to 10/1, the yield of the separated de-waxed oil decreases by using MEK. This may be attributed to that MEK firstly dissolves the oil and precipitates the wax at the same time and with further increase in dilution solvent ratio it starts to precipitate the wax only. Although, the increase of dilution solvent ratio by using MEK is accompanied with the improvement of lubricating oil characteristics in terms of increasing the mean molecular weight, density, refractive index, viscosity and viscosity index (Fig. 5) for the de-waxed oils as a result of their decreased saturated content specially n-paraffin content (Fig. 6) and consequently their increased iso and cyclo-paraffin content (Fig. 7) by using MEK. This may be attributed to the increase of solvent power towards the high molecular weight iso and cyclo-paraffins present in Sudanese crude oil by using MEK. Data of structural group analysis are parallel to the previous results whereas, % C_P decrease and % C_N and R_N increase as the dilution solvent ratio increases from 4/1 to 8/1 by using MEK.

Also, it is obvious that by using MEK, the increase of dilution solvent ratio from 4/1 to 10/1 increases the de-waxing temperature differential (i.e., increases the pour point from -7 to 2ºC by using MEK solvent Fig. 3): the spread between de-waxing temperature and the pour point of the de-waxed oil: by 3 to 12ºC using MEK higher than the de-waxing temperature (-10ºC). Data of wax content are parallel to the previous results whereas, wax content increases from 0.05 to 0.18%.

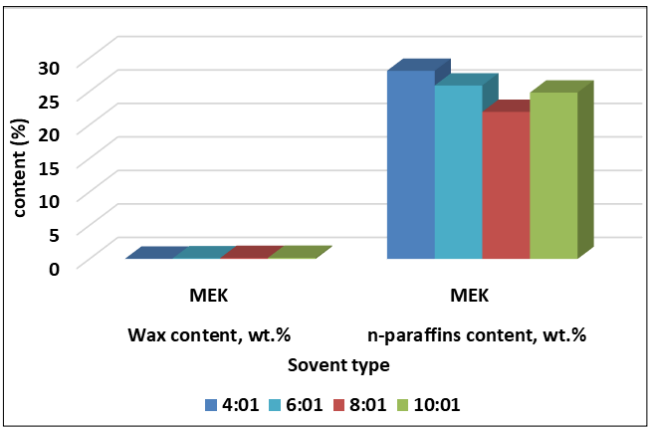

Fig 1: Relationship between solvent type and (wax and normal paraffins content).

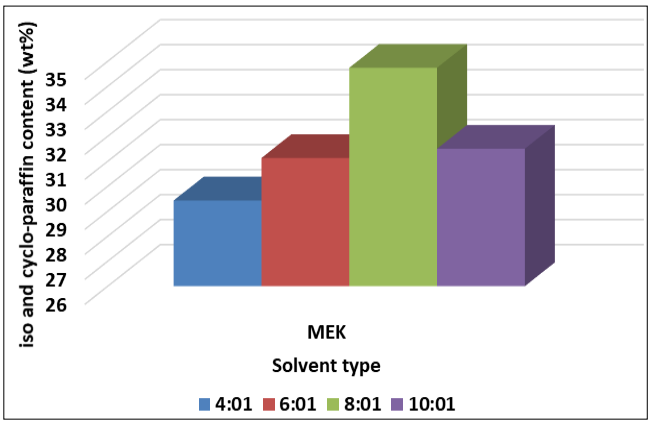

Fig 2: Relationship between solvent type and (iso and cyclo paraffins content).

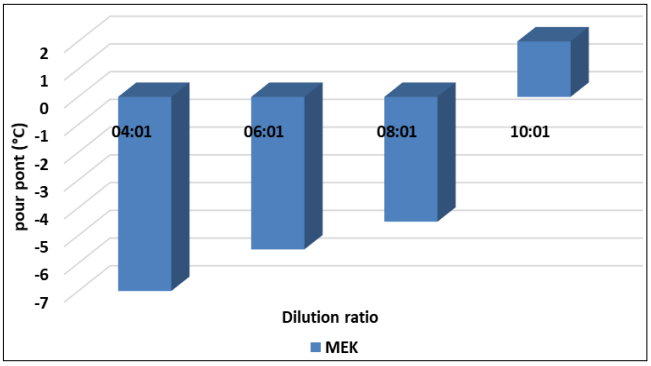

Fig 3: Relationship between dilution ratio and pour point.

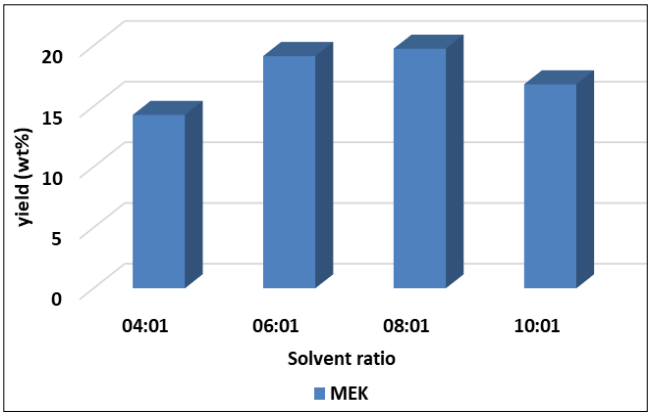

Fig 4: Relationship between solvent ratio and yield.

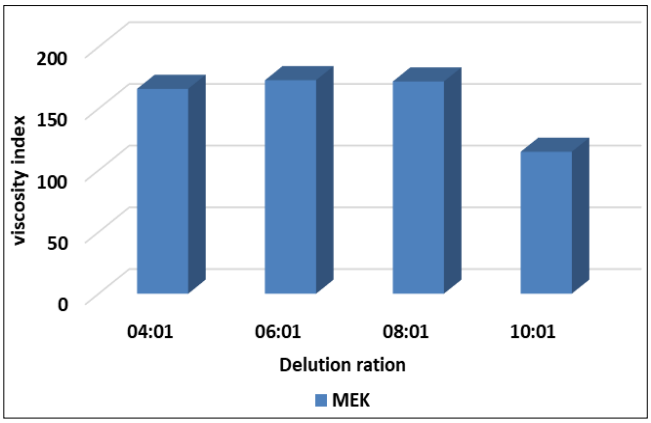

Fig 5: Relationship between dilution ratio and viscosity index.

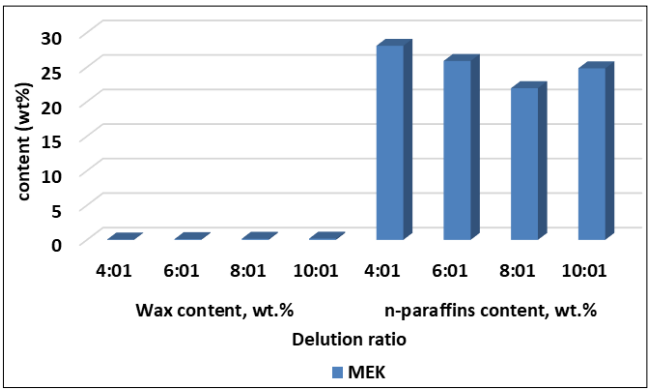

Fig 6: Relationship between dilution ratio and (wax and normal paraffins content).

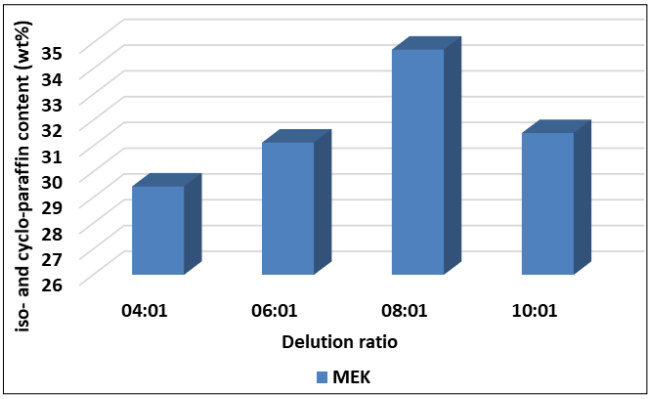

Fig 7: Relationship between dilution ratio and (iso and cyclo paraffins content).

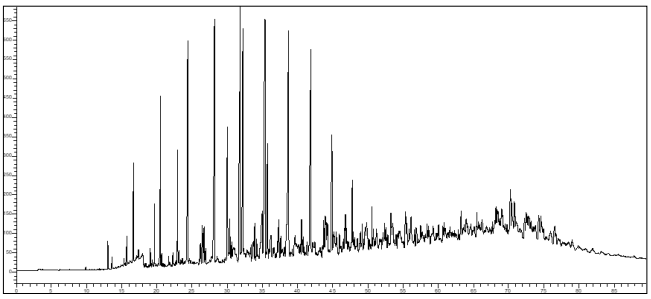

Fig 8: GC (MEK S/F 4:1).

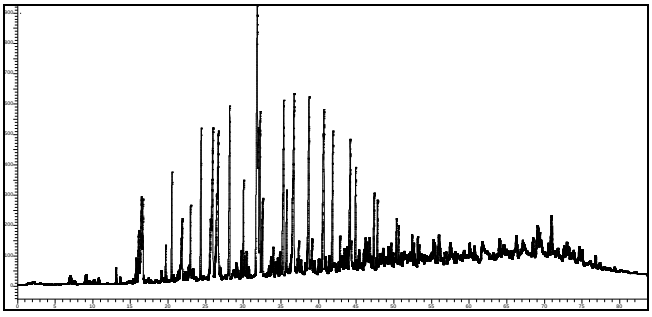

Fig 9: GC (MEK S/F 8:1).

4. Conclusion

Using of MEK as solvent for de-waxing process is good but need high S/F ratio, and this process was enhance the physical and molecular properties of de-waxed oil compared to feed stock like decrease of pour point and sulfur content. the greatest oil yield (19.75 wt%) was achieved at a solvent

to oil ratio of 8:01, a mixing temperature of 40°C and a de-waxing temperature of -10°C with pour point - 4.5°C.

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