

Solvent dewaxing of Kuwait heavy gas oil

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ABSTRACT

Kuwait heavy gas oil has been dewaxed using five different solvents: methyl ethyl ketone, methylene chloride, ethylene chloride, methyl isobutyl ketone and methyl isopropyl ketone. The dewaxing temperatures were in the range of (0°C to -20°C). The most important factors which affected the properties of dewaxed oil were: wax crystallization temperature, dewaxing temperature and the waxy raffinate properties.

Empirical correlations were developed to predict the properties of the dewaxed oil and wax produced in terms of these factors.

NOMENCLATURE

A, B	Dewaxed oil property coefficients
k_1	Dewaxed oil yield correlation factor
k_i	Dewaxed oil property correlation factor
k_m	Wax correlation factor
P_f	Waxy raffinate property
P_i	Dewaxed oil property
t	Dewaxing temperature, °C
t_m	Wax property
t_m^*	Wax property coefficient
t_s	Wax crystallization temperature, °C
x_w	Wax content of dewaxed oil, wt %
x_{wf}	Wax content of waxy raffinate, wt %
Y_D	Dewaxed oil yield, wt %

1. INTRODUCTION

Although dewaxing has been used extensively in industry for the last five decades, no quantitative study has been carried out to predict the properties of the dewaxed oil and wax produced, based on the waxy raffinate properties under known dewaxing conditions.

Recent studies on dewaxing involved work for obtaining amorphous cake with

Table 1. Physical properties of the heavy gas oil.

Characteristics	Values
Boiling point, °C	210–393
Specific gravity, at 15/15.6°C	0.8772
Flash point, °C	104
Cloud point, °C	15
Color (ASTM)	2.5
Refractive index, n_D^{20}	1.4891
Wax content, wt %	9.9
Aromatic content, wt %	30

high filterability and thus increasing the output of the process as reported by Guidelis *et al.* (1973). Deep dewaxing by direct cooling had been used by Passut *et al.* (1977) to obtain very low pour point oils. However, the literature revealed that very little quantitative work has been done to correlate dewaxing parameters.

The purpose of this work is to establish some empirical correlations for dewaxing which might be useful for designing and operating dewaxing processes using Kuwait heavy gas oil.

2. EXPERIMENTAL

Heavy gas oil (b.p. 210–393°C) was obtained from the Kuwait National Petroleum Company as a distillate fraction from crude oil. The physical properties of this feed are summarized in Table 1.

Commercially available reagent grade solvents were used without further purification. Chromatographic grade silica gel (100–200 mesh) was also used. The refractive index was measured using an Abbe refractometer. To determine the number of components in each sample, a Hewlett Packard series 5840A gas chromatograph equipped with a flame ionization detector was used. The column was stainless steel, 0.5 m long and 1/8" diameter with UCW 982 (10%) on Chromosorb WAW/DMSCB₂ as support. Helium was employed as the carrier gas (15 cm³/min). The temperature of the column was programmed at 10°C/min from 100 to 250°C.

2.1. CHARACTERIZATION OF THE HEAVY OIL

The composition of the feedstock (heavy gas oil) was determined by gas chromatography as shown in Fig. 1. The chromatogram revealed the presence of more than 22 peaks. Thirteen components were identified as the major ones for normal paraffinic hydrocarbons.

Determination of aliphatic, aromatic and naphthenic hydrocarbons was carried out by column chromatography on silica gel, with isopropylalcohol as eluent and dyed silica gel as indicator using standard methods (ASTM D1319 and ASTM D1019) with the following modifications: (1) Silica gel (140–230 mesh rather than 100–200 mesh) was activated for 3–5 hr. (2) Isoamyl alcohol was used instead of isopropyl alcohol. (3) The cooling temperature was increased from 2°C to 10°C. The

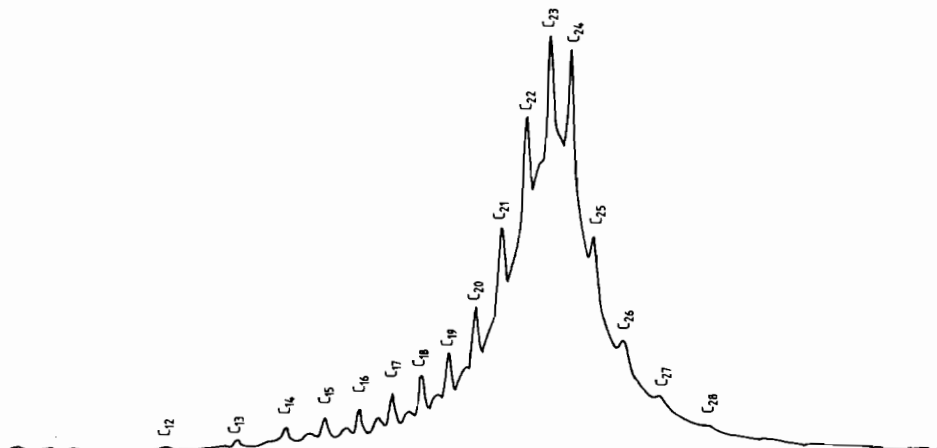


Fig. 1. Chromatogram of heavy gas oil.

fraction representing the aromatic components was confirmed by UV measurement. The aromatic content was determined and found to be 30% by wt, while the normal and isoparaffinic components represented 70% by wt, with a trace amount of naphthenic compounds.

2.2. EXTRACTION OF THE HEAVY GAS OIL

To prepare the raffinate stock for dewaxing, 250 g of the heavy gas oil was extracted with 500 g of N-methyl-2-pyrrolidone (NMP) to produce the waxy raffinate. The extraction run was carried out in a jacketed vessel of 8 cm diameter and 30 cm long. The temperature was controlled by a water bath at $50^{\circ}\text{C} \pm 0.5$. A spiral glass rod was used for mixing oil and solvent at a controlled rate of 100 strokes/min for 1 hr before the extract was separated. The solvent was removed as overhead product by distillation under reduced pressure according to (ASTM D1160). It was found that the raffinate was contaminated with 1–2.5% of NMP. This was removed by shaking the raffinate with twice its volume of distilled water. The aqueous layer was separated and the product dried over anhydrous calcium chloride which was kept as a feedstock for dewaxing.

The same procedure was repeated several times to find the optimum conditions for extraction at different temperatures.

2.3. DEWAXING OF WAXY RAFFINATES

A jacketed vessel with a stirrer was used for dewaxing. The same vessel was fitted with a sintered glass bottom on which filter paper was supported and used in the filtration stage. Thirty g of the raffinate were heated to 80°C for five min; 150 g of the heated methyl ethyl ketone were added and mixed well until the oil was completely dissolved. The mixture was transferred to the dewaxing vessel which was agitated continuously.

The temperature of the mixture was decreased gradually by circulating a cold solution (industrial methylated spirit) through the outer jacket of the vessel down to 0, -5, -10 and -20°C , respectively. The agitation was stopped at the desired

Table 2. Physical properties of the extraction and dewaxing solvents. M.W. = molecular weight, B.P. = boiling point, M.P. = melting point.

Name	Formula	M.W.	B.P. °C	M.P. °C	Density 20°C	Ref. Index n_D^{20}
1-Methyl-2-pyrrolidone	C ₅ H ₉ NO	99.13	209.0	-23.0	1.0320	1.4700
Methyl ethyl ketone	C ₄ H ₈ O	72.12	79.6	-86.4	0.8054	1.3788
Methylene chloride	CH ₂ Cl ₂	84.93	40.0	-95.1	1.3266	1.4242
Ethylene chloride	C ₂ H ₄ Cl ₂	98.96	83.5	-35.4	1.2351	1.4448
Methyl isopropyl ketone	C ₅ H ₁₀ O	86.14	94.5	-92.0	0.8051	1.3880
Methyl isobutyl ketone	C ₆ H ₁₂ O	100.16	116.9	-84.7	0.7978	1.3962

dewaxing temperature, and the wax-oil-solvent mixture was allowed to settle for 15 min. The filtrate was then taken out through a fritted disc to a volumetric receiver by means of a low vacuum pressure, and the wax was washed with 100 g of cold methyl ethyl ketone. The cake was transferred to a small dish by means of hot acetone which was evaporated by hot air to recover a white crystalline wax. The solvent was removed from the filtrate under reduced pressure (2 mmHg) and the dewaxed oil was obtained.

The same procedure was repeated with different solvents to find the optimum conditions for dewaxing. These solvents were methylene chloride, ethylene chloride, methyl-isopropyl ketone and methyl-isobutyl ketone; their physical properties are reported in Table 2.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF EXTRACTION CONDITIONS ON DEWAXING

The first problem in this study was to determine the optimum extraction conditions for preparation of a raffinate for dewaxing. In general, increasing the temperature of extraction will result in removal of more aromatics at the expense of the raffinate yield (Fahim *et al.* 1981). The presence of aromatics in the final lube oil stock is not desirable, since they are oxidized to form resinous materials during engine testing. To resolve this problem, a series of extraction runs were carried out at different temperatures using N-methyl-2-pyrrolidone as the extracting solvent. The results of these runs are presented in Table 3. Above 50°C, substantial loss of raffinate yield occurs

Table 3. Extraction-dewaxing of Kuwait heavy gas oil with N-methyl-2-pyrrolidone (extraction solvent/feed: 2/1) (dewaxing at -20°C with methyl ethyl ketone, solvent/feed: 5/1). DWO = dewaxed oil.

	Extraction temperature, °C				
	40	50	60	70	80
Raffinate yield, wt %	60	62	50	40	30
Viscosity index of DWO	100	90	95	97	96
Pour point of DWO, °C	-22	-21	-20	-19	-19
Wax yield, wt %	7.6	9.9	6.7	5.2	4.1

Table 4. Properties of the waxy raffinate.

Characteristic	Value
Refractive index at 20°C (N_D^{20})	1.4592
Viscosity at 40°C, c St	8.97
Viscosity at 100°C, c St	2.67
Wax content, wt %	20
Aromatic content, wt %	0.5

for a slight gain in the viscosity index (VI). It is seen from these results that some wax was also removed at higher extraction temperatures. However, this did not improve the dewaxed oil pour points. On the contrary, runs carried out at lower temperatures gave lower pour points. It seems also that the aromatic content in the waxy raffinate did not affect dewaxing. For these reasons, an extraction temperature of 50°C was used and maintained for the preparation of raffinates for all dewaxing runs. The properties of the waxy raffinate used in this work are given in Table 4.

3.2. DEWAXING OF WAXY RAFFINATES

Five dewaxing solvents were tested: methyl ethyl ketone, methylene chloride, ethylene chloride, methyl isopropyl ketone and methyl isobutyl ketone. The results of dewaxing with these solvents at different temperatures are given in Table 5. It is difficult to make an evaluation of these solvents directly from such a table.

The factors which might affect the outcome of the dewaxing process include: rate of cooling, dewaxing temperature, type of dewaxing solvent, initial wax content of the feed, and the solvent to feed ratio. In this study, the rate of cooling and the solvent to feed ratio were kept constant. In fact, the most important parameter in this case was the dewaxing temperature (t) and the crystallization temperature for each solvent (t_s). The properties and yields of the dewaxed oil and wax produced can be correlated in terms of Δt , where $\Delta t = (t_s - t)$. Thus, the yield of dewaxed oil was calculated as

$$Y_D = 100 + k_1 x_{wf} \Delta t \quad (1)$$

where x_{wf} is the wax content of the waxy raffinate, and k_1 is the yield correlation factor. On the other hand, the properties of the dewaxed oil can be calculated from the relation

$$P_i = P_f + k_i \Delta t \quad (2)$$

where P_i is a property of the dewaxed oil, e.g. viscosity (μ), refractive index (RI), pour point (PP), wax content of the oil (x_w), and viscosity index (VI).

The correlation factor (k_i) had to be estimated first at different temperatures. It was assumed that it was a linear function of dewaxing temperature (t). This assumption was verified later by the results shown in Table 6.

$$k_i = A + Bt. \quad (6)$$

The least squares method was used to determine the constants A and B as given in Table 7. The viscosity index correlation was not included in this table; however, VI can be calculated by predicting the viscosities of the dewaxed oil at 40°C and 100°C.

Table 5. Experimental data for dewaxing at 5:1 solvent/raffinate at cooling rate of 0.5°C/min. M.P. = melting point, MEK = methyl ethyl ketone, MC = methylene chloride, EC = ethylene chloride, MIPK = methyl isopropyl ketone, MIBK = methyl isobutyl ketone.

	Dewaxing temp., °C	Dewaxed oil				Wax		
		Yield, wt %	Pour P., °C	Viscosity @ 40°C, c St	Viscosity @ 100°C, c St	Refractive index @ 20°C	M.P., °C	Refractive index @ 60°C
MEK								
1 A	0	89.0	0	10.54	2.82	1.47350	48.0	1.4335
2 A	-5	86.0	-6	11.10	2.84	1.47370	47.5	1.4333
3 A	-10	84.3	-12	11.50	2.86	1.47396	47.0	1.4330
4 A	-20	81.0	-21	12.30	2.89	1.47503	46.0	1.4325
MC								
1 B	0	89.7	9	9.25	2.63	1.47044	50.0	1.4355
2 B	-5	85.0	2	9.73	2.68	1.47210	49.5	1.4353
3 B	-10	82.3	-3	10.70	2.77	1.47305	49.0	1.4352
4 B	-20	75.0	-12	10.89	2.78	1.47381	46.0	1.4350
EC								
1 C	0	90.0	0	11.62	2.71	1.47335	49.5	1.4352
2 C	-5	88.0	-5	11.80	2.73	1.47337	49.0	1.4348
3 C	-10	86.0	-6	11.83	2.74	1.47340	48.5	1.4345
4 C	-20	87.0	-18	12.33	2.81	1.47595	47.0	1.4335
MIPK								
1 D	0	91.0	3	11.80	2.89	1.47366	51.5	1.4335
2 D	-5	88.0	-1	11.86	2.85	1.47380	51.0	1.4332
3 D	-10	87.3	-3	11.90	2.87	1.47412	51.0	1.4330
4 D	-20	83.3	-16	11.45	2.93	1.47534	49.0	1.4325
MIBK								
1 E	0	91.7	3	11.20	2.80	1.47228	52.0	1.4345
2 E	-5	90.0	-3	11.60	2.84	1.47309	51.5	1.4341
3 E	-10	89.0	-6	11.70	2.87	1.47381	50.5	1.4335
4 E	-20	85.7	-18	11.80	2.90	1.47458	49.5	1.4330

Table 7. Property coefficients for calculation of coefficient factors (k_i), $k_i = A + Bt$.

Property	Methyl ethyl ketone		Methylene chloride		Ethylene chloride		Methyl isopropyl ketone		Methyl isobutyl ketone	
	A	B	A	B	A	B	A	B	A	B
Dewaxed oil										
1. Yield, wt %	0.031787	0.000254	0.059130	0.000837	0.034450	0.000755	0.031720	-0.000379	0.032130	0.000560
2. Pour point, °C	1.399800	0.008600	1.746360	0.025065	1.553400	0.020730	1.404400	0.008825	1.628300	0.019500
3. Refractive index at 20°C	-0.000888	-0.000020	-0.001266	-0.000040	-0.001054	0.000033	-0.000988	-0.000028	0.001008	0.000029
4. Viscosity at 40°C, c St	-0.092150	0.000088	-0.047388	0.001722	-0.171560	0.004125	-0.152250	0.003017	-0.174590	0.004566
5. Viscosity at 100°C c St	-0.008611	-0.000140	0.002763	0.000428	-0.002523	0.000066	-0.015300	0.000403	-0.010450	-0.000166
Wax	t_m	k_m	t_m^*	k_m	t_m^*	k_m	t_m^*	k_m	t_m^*	k_m
6. Melting point of wax, °C	46.00	0.10	46.30	0.20	47.10	0.13	49.30	0.13	49.40	0.13
7. Refractive index of wax at 60°C	1.432500	0.000050	1.435000	0.000025	1.433600	0.000085	1.433500	0.000050	1.434400	0.000075

The melting point of the wax was estimated using the equation

$$t_m = t_m^* + k_m (t + 20), \quad (4)$$

where t_m^* is the melting point of the wax obtained by dewaxing at a dewaxing temperature of -20°C . Dewaxing the raffinate down to -40°C did not change the melting point of the wax, indicating that most of the wax was removed at -20°C . The wax melting point at -20°C was therefore taken as a reference. However, Equation 4 applies only in the range from 0°C to -20°C . The values of k_m are given also in Table 7. A similar correlation was also used to calculate the RI of the wax.

To test the physical properties obtained by using Equations 1-4, predicted values were compared with experimental values measured at a dewaxing temperature of -20°C . The predicted and measured values given in Table 6, show quite reasonable agreement.

Comparison of the results for different solvents at a certain dewaxing temperature reveals that the oil yield is almost the same for all solvents. However, methylene chloride was the only solvent which had a positive viscosity coefficient indicating a decrease in the dewaxed oil viscosity as contradicted by all other solvents. A solution of low viscosity of oil in methylene chloride would, in fact, assist in the filtration process. On the other hand, this solvent gave the highest viscosity index (VI), indicating good thermal response. Methyl ethyl ketone, gave a quite low pour point, indicating good performance in low temperature weather. Other solvents did not show any special advantage. It seems that a mixture of methyl ethyl ketone and methylene chloride might prove to be of special interest.

4. CONCLUSION

The properties of dewaxed oil were correlated with the properties of the waxy raffinate obtained from solvent extraction of a heavy gas oil. These correlations were carried out for five solvents which were also rated according to their dewaxing performance. Methyl ethyl ketone gave significantly lower pour points than other solvents. On the other hand methylene chloride gave a dewaxed oil of lower viscosity but of high viscosity index. The most important parameters which affected the properties of dewaxed oil were: wax crystallization temperature, dewaxing temperature, and waxy raffinate properties.

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فصل الشمع من الزيت الكويتي الثقيل

موسى عجام وصفاء فائق عارف
قسم الكيمياء بجامعة الكويت

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قسم الهندسة الكيميائية بجامعة الكويت

خلاصة

تمت عملية فصل الشمع من الزيت الكويتي الثقيل بواسطة التبريد المباشر وغير المباشر بدرجات حرارة تراوحت بين درجة الصفر المئوي ودرجة -٢٠م باستخدام خمسة مذيبات مختلفة هي مثيل أثيل كيتون ، مثلين كلورايد ، أثلين كلورايد ، مثيل آيزوبروبيل كيتون ومثيل آيزوبوتيل كيتون . ومن أهم العوامل التي أثرت في عملية الفصل وخواص زيت التزيت الناتج طبيعة المقطر المستخدم ودرجة التبريد ودرجة حرارة بلورة الشمع . كما تم إيجاد صيغة رياضية لحساب صفات النواتج من الشمع وزيت التزيت .