

## Separation and identification of *n*-paraffins from Kuwait kerosene cuts

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### ABSTRACT

Normal paraffins and denormal (deparaffinised) products separated from Kuwait petroleum fractions were identified and characterised. Straight-run kerosene (b.p. 204–285°C) and naphtha-kerosene blend (b.p. 164–215°C) were selected as feedstocks because of their relatively high *n*-paraffin content. The separation was accomplished by urea adduction and the efficiency of the separation was determined in terms of product yield and purity. The percent recovery of *n*-alkanes ranged between 79–87% and the purity ranged between 85–91% depending on the nature of the original feed. Large improvements were achieved in the pour points of the deparaffinised feedstocks which would extend their application, as hydrocarbon fuels, to low temperatures encountered in cold climates.

### INTRODUCTION

Normal paraffins are important raw materials for the manufacture of biodegradable detergents, synthetic fatty acids, secondary alcohols, chloroparaffins, single cell protein, various pharmaceutical products and many other industrial items. Industrial applications of *n*-paraffins depend on the number of carbon atoms in the *n*-alkane chain. Normal paraffins containing C<sub>6</sub>–C<sub>13</sub> can be used for the production of special solvents. Normal paraffins isolated from kerosene petroleum cuts and containing C<sub>8</sub>–C<sub>20</sub> are used in the manufacture of surfactants and single cell protein. C<sub>12</sub>–C<sub>13</sub> paraffins are used as antidetonation additives, C<sub>10</sub>–C<sub>17</sub> are used as plasticisers and C<sub>20</sub> and higher can be used as additives for lubricating oils.

Petroleum fraction distillates contain varying amounts of *n*-paraffins in addition to other constituents such as olefines, isoparaffins, aromatics, cycloparaffins, naphthenes, thionaphthenes, etc. Severity of catalytic reforming conditions are considerably reduced when *n*-paraffins are removed from reformer feeds resulting in a larger reformat yield. The separation of *n*-alkanes from naphtha is most valuable for improving the octane rating of products from isomerisation processes leading to reduction in the amount of lead alkyl required. Also removal of *n*-paraffins from various hydrocarbon fuels results in a decrease in the pour point of the non-linear

(denormal) products. This improvement should be evaluated against the decrease in diesel index, but it is generally attractive for cold-climate applications.

The two most commonly used techniques for the separation of *n*-paraffins from petroleum distillates are selective adsorption on molecular sieves and urea adduction. The normal or straight chain molecules of paraffins have smaller radii than other hydrocarbons and can enter the openings in the urea adduct or zeolite crystals and become occluded in their cavities. Yata *et al.* (1966) studied the urea adduction method for several years and reported that this method was competitive with the adsorption on molecular sieves. Ijam & Al-Zaid (1979) investigated the *n*-paraffin content and distribution in straight-run kerosene obtained from Kuwait crude oil and reported that it contained 25–30% *n*-paraffins. Recovery of these *n*-paraffins from various refineries provides a boost to the local paraffin-based industries which depend heavily on imported raw materials.

In this paper, the urea adduction technique will be applied to separate *n*-paraffins from two different Kuwait petroleum fractions. The yield and the physico-chemical properties of the resulting products will be determined.

## EXPERIMENTAL

Straight-run kerosene and naphtha–kerosene blend obtained from Kuwait National Petroleum Company (KNPC) were selected as feedstocks for urea adduction because of their relatively high *n*-paraffin content. The physico-chemical properties of these feedstocks are presented in Table 1. The urea used was obtained from Petrochemical Industries Company of Kuwait (PIC) with a density of 0.73 g/cc and a moisture content of 0.2% by weight.

A schematic diagram of the experimental set up is shown in Fig. 1. Equal weights (100 g) of each of hydrocarbon feed, iso-propanol and crushed urea were used. Urea

Table 1. Physico-chemical properties of feedstocks

Property	Straight-run kerosene	Naphtha–kerosene blend
Aniline point, °C	68.3	60.0
Flash point, °C	78	51
Freezing point, °C	–26	–53
Smoke point, mm	23	27
Specific gravity @ 60/60 °F	0.8216	0.7850
Refractive index @ 20°C	1.4578	1.4380
Hydrogen content, % wt	13.63	14.06
Naphthalenes, % vol.	4.39	0.30
Olefins, % vol.	0.0	0.0
Sulphur, % wt	0.67	0.14
<i>Distillation</i>		
Initial b.p., °C	204	164
10% Recovery	228	175
50% Recovery	249	187
90% Recovery	274	201
End point	285	215

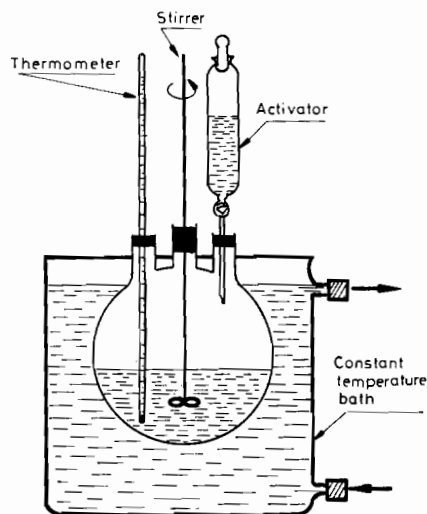


Fig. 1. Experimental apparatus.

was added gradually with continuous stirring to the hydrocarbon feed iso-propanol mixture in a one litre glass flask immersed in a water bath maintained at 25°C. An amount of distilled water which worked as an activator, equivalent to 10% of the mixture total volume, was added dropwise directly into the mixture. The glass container was then left in the water bath for one hour with continuous stirring. The complex formed in the glass container was filtered under vacuum. Iso-propanol solvent was added to the complex during filtration in order to wash the filter cake. The filtrate was then removed and washed with hot water several times until all the kerosene was separated from the iso-propanol layer.

Samples of the kerosene cuts, the separated paraffins (in the liquid state, hitherto called paraffins) and the denormal products were analyzed by gas liquid chromatography (GLC), ultra violet (UV) and fluorescent indicator adsorption (FIA) spectroscopic techniques. The distribution of *n*-alkanes and the aromatic content were determined for each sample.

## RESULTS AND DISCUSSION

Fig. 2 shows the UV spectra for straight-run kerosene (a) and naphtha-kerosene blend (b). Both spectra exhibit three distinct peaks corresponding to monoaromatics, diaromatics and triaromatics in the order of increasing wavelength in the range from 190–270 nm. Using the method suggested by Siryuk *et al.* (1975), Fig. 2 was analyzed to determine the amounts of these aromatics. The results are presented in Table 2. It is seen from this table that while straight-run kerosene contains slightly lower benzene hydrocarbons (16.42% wt) than naphtha-kerosene blend (18.61% wt), the amounts of naphthalene hydrocarbons are 4.90% and 0.075% respectively. This is clearly reflected in the relative sizes of the second peaks of spectra (a) and (b) in Fig. 2. The amount of phenanthrene and anthracene hydrocarbons in the straight-run kerosene (0.59%) is higher than that in the naphtha-kerosene blend (0.026%).

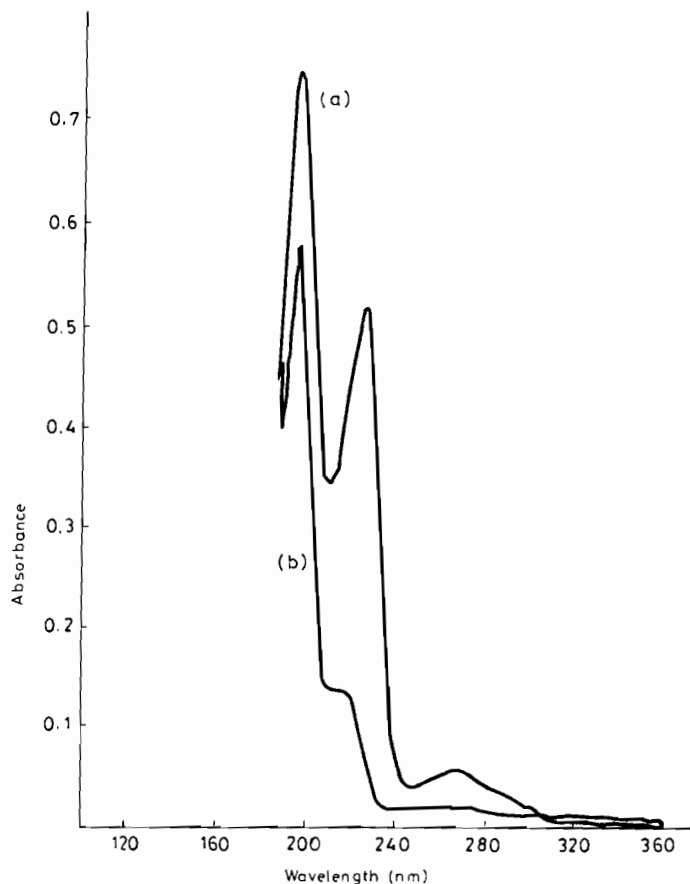


Fig. 2. UV spectra for: (a) straight-run kerosene; (b) naphtha-kerosene blend.

Figs 3a and 3b show the GLC chromatograms for the straight-run kerosene feed and the isolated paraffins obtained from it. Comparing Fig. 3a with Fig. 3b, it is clear that most of the indistinct peaks, corresponding to iso-alkanes, cycloalkanes, sulphur and aromatic hydrocarbons, which were present in Fig. 3a disappeared in Fig. 3b.

The distribution of *n*-alkanes, as determined by GLC, in the isolated paraffins, straight-run kerosene and denormal kerosene are illustrated in Fig. 4. The purity of the isolated paraffins was 85.0%. Freund *et al.* (1982) reported that X-ray studies

Table 2. Aromatics in straight-run kerosene and naphtha-kerosene blend as determined by UV analysis

Feedstock	Monoaromatics % wt	Diaromatics % wt	Triaromatics % wt	Total % wt
Straight-run kerosene	16.416	4.896	0.588	21.90
Naphtha-kerosene blend	18.610	0.075	0.026	17.81

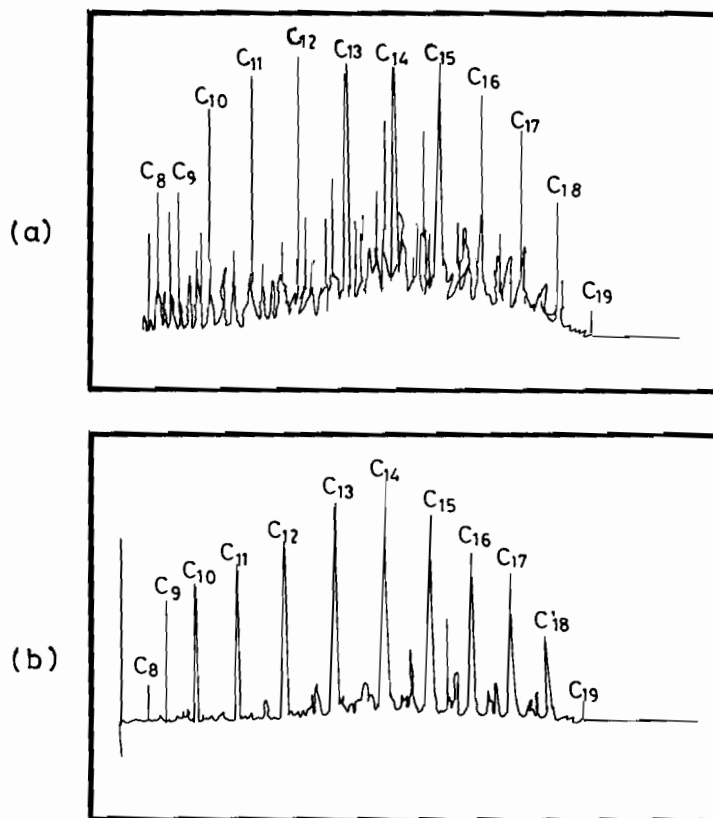


Fig. 3. GLC Chromatograms for: (a) straight-run kerosene; (b) isolated *n*-paraffins.

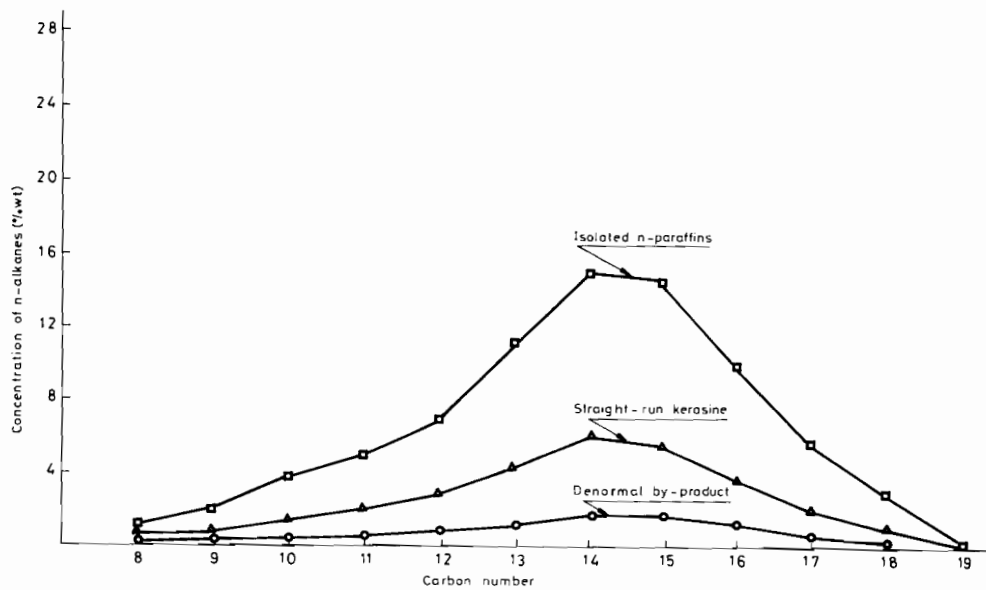


Fig. 4. Distribution of *n*-alkanes as determined by GLC.

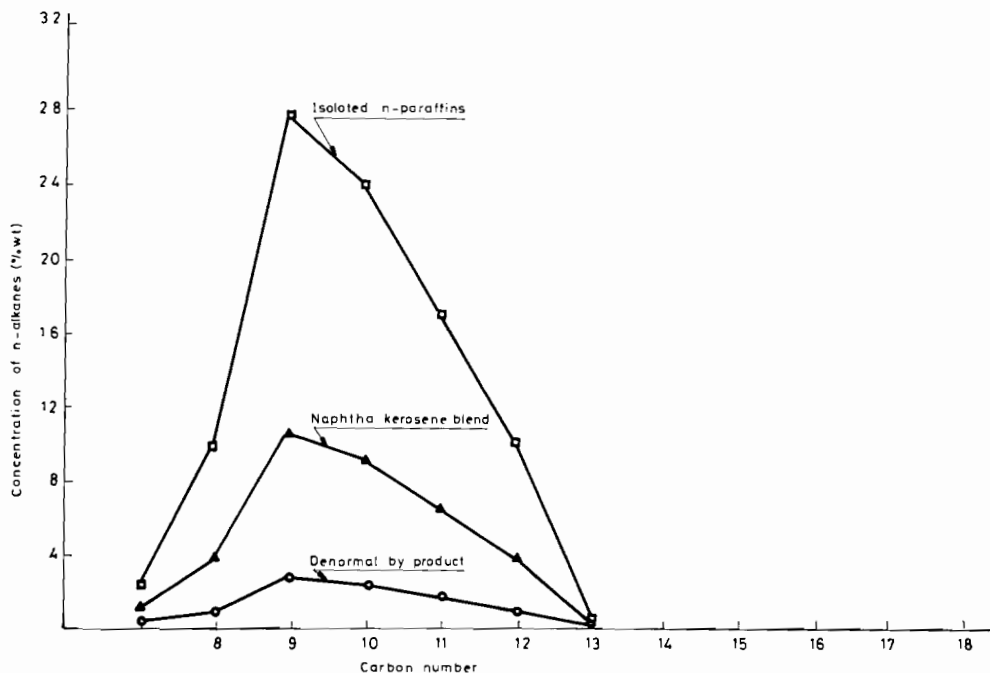


Fig. 5. Distribution of *n*-alkanes as determined by GLC.

showed that the long chains of *n*-alkanes as well as long chains of iso- and cycloalkanes were enclosed in the tubular channels of the urea adduct resulting in a hexagonal urea lattice. In our study, in the case of straight-run kerosene feed, the iso- and cycloalkanes and other impurities which were separated along with the *n*-alkanes amounted to approximately 15% by weight. It is observed from Fig. 4 that the distribution of *n*-alkanes in the straight-run kerosene feed is close to being a normal distribution. The data for the isolated paraffins and the denormal kerosene also retain nearly normal distribution trends as in the original feed.

Fig. 5 presents the distribution of *n*-alkanes, as determined by GLC, for the second case in which naphtha-kerosene blend was used as the feed. It is also observed here that the distribution of *n*-alkanes in the paraffins and the denormal product is similar to that in the original feed from which they were separated. However, the distribution in these cases is far from being normal. The purity of the separated paraffins (91.4%) was better than that obtained in the case of straight-run kerosene (85.0%). In general, it is noticed that as the molecular weight of *n*-alkanes increases, the degree of their recovery increases. This is to be expected since adduct formation is an equilibrium exothermic reaction whose heat of reaction increases as the alkane chain becomes longer. Hence the longer the adduct-forming molecular chain, the greater the stability of the adduct (i.e., the greater the degree of its recovery).

The extent of adduct formation reaction also depends on the concentration of urea, the nature of solvent and the reaction temperature. Experimental work conducted by Dorodnova *et al.* (1982) showed that the temperature required for maximum yield of individual *n*-alkanes depends on the molecular weight. For example a maximum yield of 62% wt. was reported for C<sub>10</sub> at 0°C, 83% for C<sub>13</sub> at 10°C and 94%

**Table 3.** Material balance for the separation of paraffins by urea adduct

Material	Straight-run kerosene	Naphtha-kerosene blend
<i>Input, g:</i>		
Total feed	100	100
<i>n</i> -alkanes in feed	31.87	34.71
<i>Output, g:</i>		
Paraffins	32.67	30.03
<i>n</i> -alkanes in paraffins (recovered)	27.77	27.45
Denormal product	65.93	68.60
<i>n</i> -alkanes in denormal product (lost)	4.10	7.26
Percent recovery of <i>n</i> -alkanes	87.1	79.1

for C<sub>16</sub> at 15°C. Thus the longer the hydrocarbon chain, the higher the yield and the higher the temperature required.

Table 3 summarizes the material balance results for the two different feeds used in this study. The data given in Table 3 represent the average of the results of three different runs carried out for each case. The percent recovery of *n*-alkanes from straight-run kerosene and naphtha-kerosene blend were 87.1% and 79.1% respectively. The lower percent recovery in the second case was due to the absence of high molecular weight *n*-paraffins (C<sub>15+</sub>) in the naphtha-kerosene blend. The straight-run kerosene contained approximately 13.5% C<sub>15+</sub> which formed stable adducts and thus were easier to separate than lower molecular weight *n*-alkanes which formed unstable adducts.

In this study, urea adducting was performed at a fixed temperature of 25°C. The recovery of *n*-alkanes, which is strongly dependent on the composition of *n*-alkanes present in the original feed, can be maximised by selecting the optimal adducting temperature which is of practical interest. At temperatures higher than the optimal, the recovery is lower because of the shift of equilibrium in the direction of adduct breakage. At lower temperatures, the yield is lower because of low diffusivities of *n*-alkane molecules in the liquid phase (Usachev 1967). The relatively high yield obtained in the case of straight-run kerosene indicated that the operating temperature was not far from the optimal. It is expected however, that better yields can be achieved in the case of naphtha-kerosene blend if adduction is performed at temperatures lower than 25°C.

The original feeds, the isolated paraffins and the denormal products were analyzed by UV and FIA methods. Table 4 presents a summary of the analytical results. The amounts of mono-, di- and triaromatics in each sample were determined by UV and the total aromatic content was determined by UV and FIA. The total aromatic content as determined by UV, for most of the samples, is consistent with that determined by FIA indicating that the two methods are comparable in accuracy. Monoaromatics constitute the major portion of aromatics present in the feed and the products. The total aromatic content in the paraffins isolated from straight-run kerosene was 10% while in the case of naphtha-kerosene blend it was lower (8.6%). This was expected since the total aromatics in the original feed was lower in the second case (18.7% compared to 21.9% in the straight-run kerosene). It is observed from the data presented in Table 4 that the relative amounts of mono-, di- and triaromatics in

**Table 4.** Aromatic content of original feed and products as determined by UV and FIA

Sample	Aromatic content by U.V. (wt %)				Total aromatics by FIA (wt %)
	Mono-aromatics	Di-aromatics	Tri-aromatics	Total aromatics	
Straight-run kerosene	16.416	4.896	0.588	21.900	22.08
Isolated paraffins	7.430	2.323	0.266	10.019	9.79
Denormal kerosene	17.099	5.727	0.663	23.489	25.82
Naphtha-kerosene blend	18.610	0.075	0.026	18.711	17.81
Isolated paraffins	8.390	0.066	0.109	8.565	7.74
Denormal kerosene	25.238	0.095	0.849	26.182	22.76

**Table 5.** Physico-chemical properties of straight-run kerosene, denormal product and isolated paraffins

Property	Straight-run kerosene	Denormal kerosene	Isolated paraffins
Density (@ 15°C), g/cc	0.8216	0.8999	0.7993
Pour point, °C	-26	-45	-6
Smoke point, mm	23	17	-
Total <i>n</i> -alkanes, % wt	31.87	6.22	85.00
<i>Distillation</i>			
Initial b.p., °C	204	181	-
10% Recovery	228	236	-
50% Recovery	249	260	-
90% Recovery	274	285	-
End point	285	289	-

-- = not tested.

**Table 6.** Physico-chemical properties of naphtha-kerosene blend, denormal product and isolated paraffins

Property	Denormal		Isolated paraffin
	Naphtha-kerosene blend	naphtha-kerosene blend	
Density (@ 15°C), g/cc	0.7815	0.8001	0.7666
Pour point, °C	-53	-68	-39
Smoke point, mm	27	23	-
Total <i>n</i> -alkanes, % wt	34.71	10.58	91.41
<i>Distillation</i>			
Initial b.p., °C	164	165	-
10% Recovery	175	176	-
50% Recovery	187	191	-
90% Recovery	201	218	-
End point	215	228	-

-- = not tested.



the isolated paraffins and the denormal products remained almost the same as those in the original feeds from which they were separated. This indicates that the urea adduct has no special selectivity for any type of aromatics.

Tables 5 and 6 show a comparison between the physico-chemical properties of the original feeds and those of the recovered paraffins and the denormal products. It is observed from these tables that a large drop in the pour point of the hydrocarbon feedstocks is achieved upon deparaffinisation. In the case of straight-run kerosene the pour point dropped from  $-26$  to  $-45^{\circ}\text{C}$  compared to a drop from  $-53$  to  $-68^{\circ}\text{C}$  in the case of naphtha-kerosene blend. This improvement in pour point is obviously attractive for cold-climate applications.

The smoke point, which is an important factor in determining the quality of kerosene, should be in the range of 20–25 mm. In practice, certain amounts of paraffins (particularly cycloparaffins) are intentionally left in the denormal product to improve its smoke point. The relatively low smoke point (17 mm) of denormal kerosene, caused by removal of a large amount of paraffins, can be improved by maintaining the paraffins in it at the desired level.

## CONCLUSIONS

Separation of *n*-paraffins from two different petroleum fractions was accomplished using urea adduct method. The degree of recovery of *n*-paraffins depended strongly on the average molecular weight of *n*-alkanes present in the original feed. It was found that the higher the average molecular weight of *n*-alkanes, the larger the percent recovery, which was in agreement with the literature. The purity of the isolated *n*-paraffins ranged between 85.0 and 91.4% depending on the nature of the original feed. The ratios of mono-, di- and triaromatics in the isolated paraffins and the denormal products remained almost the same as in the original feed which indicated that urea adduct had no special selectivity for any type of aromatics. The large improvement in the pour point of the feed, upon separating *n*-paraffins from it, makes it more suitable for application in cold climates.

## ACKNOWLEDGEMENTS

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## دراسة خواص البرافينات الاعتيادية المستخلصة من كيروسين الكويت

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بمعهد الكويت للابحاث العلمية

### خلاصة

تم فصل البرافينات الاعتيادية من مشتقات نפט الكويت ودراسة خواصها ، كما تمت دراسة خواص المشتقات الاخرى (الخالية من البرافينات) والناجمة عن عملية الفصل . وقد اختير كل من الكيروسين المعتاد (درجة غليان ٢٠٤-٢٨٥م) وخليط من النافثا والكيروسين (درجة غليان ١٦٤-٢١٥م) كمواد خام نتيجة لاحتوائهما على نسبة عالية من البرافينات الاعتيادية . وقد استخدمت اليوريا في عملية الفصل والتي قيست كفاءتها بتحديد كمية المنتجات ودرجة نقاوتها . وتراوحت نسبة البرافينات المستخلصة بين ٧٩ و ٨٧% من تلك الموجودة في المادة الخام ، وتراوحت درجة نقاوتها بين ٨٥ و ٩١% . وقد أدى فصل البرافينات الى تحسن في درجات حرارة سكب المواد الخام مما يجعلها مناسبة للاستخدام كوقود في المناطق الباردة .