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Refining of Libyan Kerosene for Use as a Solvent for Pesticide

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تنقية الكيروسين الليبي لغرض إستعماله مذيباً في خلطة مبيدات الحشرات

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تعد عمليات خفض محتوى الكربون العطري وإزالة الرائحة الغير مقبولة من المشتقات النفطية ذات أهمية بالغة نظراً لطبيعة إستعمالاتها، حيث تستخدم من بين إستعمالاتها بنسبة 30% في خلطة المواد القاتلة للحشرات إضافة إلى استعمالاتها العادية الأخرى في التدفئة والطبخ... إلخ.

لقد تحقق في هذه الدراسة تقليصاً فعالاً لمحتوى الكربون العطري وإزالة تامة للرائحة من كيروسين خام السرير باستعمال مواد مازة صلبة مثل الكربون المنشط وتحسنت نتائج عمليات التنقية أكثر بمرافقة الكربون المنشط مع مواد مازة صلبة أخرى مثل هلام السليكا والألومينا.

تم خفض محتوى الكربون العطري إلى 1% بمعاملة نسبة وزنية بمقدار 1:1 من كيروسين خام السرير إلى مزيج المواد المازة والتي احتوت على 14% كربون منشط و43% سليكا و43% ألومينا ضمن هذا المزيج.

توضح هذه النتائج تفوق عملية إزالة المواد العطرية بالمواد المازة الصلبة مقارنة بإزالتها بالاستخلاص بالمذيبات الإنتقائية مثل مادة مثيل البيراليدينون (NMP) على إن الاستخلاص بهذا المذيب مكّننا من فصل وتعريف عدة مركبات أحادية وثُنائية الحلقة الأروماتية في مشتق الكيروسين من خام السرير وقد تم تعريف هذه المركبات بواسطة التحليل بتقنية كروموتوغرافيا الغاز وبمطابقة نتائج هذا التحليل مع نتائج قياس مركبات أروماتية معروفة.

Abstract: *Reducing aromatic carbon content and removal of obnoxious odour are operations of prime importance for the purpose of domestic use of petroleum derived materials such as kerosene. This derivative is widely used as a solvent for pesticides and usually represents about 30% of the total formulation.*

Effective reduction of aromatic carbon content and removal of bad odour from Sarir kerosene was achieved by using solid adsorbents, mainly activated carbon (AC). Attainment of improved results was possible by synergism between AC, silica and alumina adsorbents. Thus, removal of bad odour and reduction of aromatic carbon content to 1% was possible by a 1:1, volume to weight ratio of kerosene to combined adsorbents weights; activated carbon (14%), silica (43%)and alumina (43%).

The use of solid adsorbents for dearomatization was superior to solvent extraction by N-methyl pyrrolidinone (NMP). Meanwhile, extraction by NMP enabled the identification of several mono- and di-ring aromatic compounds in Sarir kerosene by capillary gas chromatography. The

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identification was ascertained by matching with authentic aromatic compounds.

INTRODUCTION

Kerosenes represent a class of the most widely used solvents for pesticides. Libya imports several hundred tons per year of expensive, special grade kerosene for the manufacturing of pesticides. Petroleum naphtha in the kerosene range from most libyan crude oils, which are known to be paraffinic in nature and contain low sulfur percentages, are expected to be suitable solvents for pesticides after some mild treatment.

The presence of sulfur in kerosene, and especially in the form of mercaptans, is detrimental to its use as a pesticide solvent because of unacceptable bad odour. Another important aspect is the aromatic carbon content which should be reduced to a minimum permissible limit because of potential health hazards [1]. It is well established that mono - and di- ring systems comprise the aromatic carbon content, which ranges between 10 to 20 % in most kerosenes [2]. It is thus expected that the main obstacles encountered in the use of Llibyan kerosenes as solvents for pesticides are the following:

1. Proper choice of the kerosene source.
2. Reducing aromatic contents to permissible limits.
3. Removal of bad odour.

The specifications of the imported kerosene [3] and relevant characteristics of some Libyan kerosenes [4] and methods of their determinations are given in Table 1.

Perhaps it is imperative to give a few words on the standard methods of aromatic carbon content determination in petroleum fractions. The ASTM-D 1319-77 (IP:156/70) measures volume percent of aromatic carbon content after development and elution according to specified standard steps. This means that aliphatic carbon in olefinic, alkylenic and naphthenic substituents on the aromatic rings are included in the aromatic carbon content. Added to this, and as stated in this particular standard method, all sulfur, nitrogen and oxygen compounds are also included in the aromatic carbon content. This is so, since these compounds have similar adsorption affinities on silica gel when they are desorbed by isopropyl alcohol. Another shortcoming of the method is that the fluorescent dye indicator (Petrol Red AB4) is quite sensitive and should be stored in the dark under nitrogen atmosphere. Even with such precautions, batches stored over six months should be considered suspect. One final important point concerning this method, is that the determination of the PONA (Paraffin, Olefin, Naphthene and Aromatic) layer boundaries is subject to human error since these boundaries are assessed and observed by the analyser's naked eye.

A modification of the ASTM method was registered in 1989 [ASTM-D1319-89;IP156/84]. This modification put further limitations on the applicability of the method. The method will not be precise for aromatic carbon concentration of less than 5%. Since in our work we intend to achieve aromatic carbon concentrations much lower than 5%, thus this standard method is of no use to us. We successfully developed a new spectroscopic method which measures the actual aromatic carbon content with no interference from substituted, olefinic, alkylenic, or naphthenic carbons on the aromatic rings [5]. Also, interference from heteroatoms (S,O,N) is excluded. The new method gives the following relationship for the determination of the percentage of the real aromatic carbon content (CA).

$$\%\ CA = 1.053 \sum_{250}^{290} A + 0.0196$$

CA = Carbon in mono-and di-aromatic ring systems.

$\sum_{250}^{290} A$ = Summation of the Absorbance values of the total aromatic envelope measured at:

λ = 250, 260, 270, 280 and 290 nanometers.

Specialty grade kerosenes can be produced by a special hydro-treating operation (chemical refining) at the refinery. However, and to the best of our knowledge, such a refining line is non-existent at the Libyan refineries. In the present paper, the results of an alternative physical refining scheme are cited.

Table 1. Specifications of imported kerosene and relevant values of some Libyan kerosenes

Specification	Imported kerosene (Typical value)	Libyan kerosenes				Determination method
		Sarir	Brega	Sedra	Hamada	
Density $g.cm^{-3}$ at 15°C	0.793	0.793	0.800	0.809	0.798	ASTM D1298
Total sulfur %	0.0002	0.03	0.06	0.14	0.03	ASTM D1266
Mercaptic sulfur, ppm	-	3	3	89	3	ASTM D3227
Flash point °C	53	66	65	66	65	IP 170
Aromatics, wt %	1.5	9.0	13.6	14.6	10.2	ASTM D1319
Distillation:						ASTM D86
IBP°C	155	192	188	188	188	
50 % vol. °C	203	202	202	202	202	
95 % vol. °C	-	220	221	221	236	
FBP °C	253	233	227	225	236	

Experiments were designed to arrive at solutions for the reduction of the aromatic carbon content to acceptable limits and the removal of bad odour from Sarir kerosene since it possesses the most proper characteristics as inferred from Table 1. Emphasis was on operations that achieve both goals simultaneously. Thus, attention was focused on refining by solid adsorbents. Further justification for this choice will be given later in the discussion section.

EXPERIMENTAL

Refining of Crude Sarir Kerosene (CSK) by Commercial Activated Carbon

10 g of granulated activated carbon (AC) was packed in a 30 x 1.6 cm glass column and 100 ml of crude Sarir kerosene was eluted through the AC bed. Rate of elution was 3 ml per minute and room temperature was 23°C. 10 ml fractions were collected in clean test tubes and aromatic carbon content was determined at certain kerosene: AC, vol. to wt. ratios.

Refining of CSK by Petroleum Research Centre (PRC) - Prepared Activated Carbon

5 g of PRC-AC was packed in the same glass column as above, and 50 ml of crude Sarir kerosene was eluted through it at a flow rate of 3 ml. min^{-1}, at room temp. (25°C). Fractions (5 ml each) were collected and aromatic carbon content was determined.

Refining of CSK by Commercial -AC with Mechanical Mixing at Elevated Temperatures

(a) 15 ml of crude Sarir kerosene was mixed with 5 g of comm.-AC in a 100 ml conical flask. The mixture was agitated for 15 min. in a thermostated box agitator at 60°C. Kerosene was filtered and aromatic carbon content was determined.

(b) In a similar experiment as in (a) above, agitation was carried out at 90°C, followed by filtration and aromatic carbon content determination.

Refining of CSK by Activated Silica - Alumina Adsorbents

5 g silica (thermally activated 1h at 110°C) + 5 g alumina (thermally activated 1h at 200°C, were packed in the same 30 x 1.6 cm glass column. Crude Sarir kerosene (100 ml) was eluted through the chromatographic bed at an uncontrolled rate of 0.5 ml. min^{-1} at room temperature of 25°C. Ten fractions (10 ml each) were collected and aromatic carbon content was determined.

Refining of CSK by Combined Silica - Alumina - AC Bed

Thermally activated Comm. AC, was stationed at the lower part of a 50 x 1.6 cm glass column. Two millimeter glass wool cover was positioned on top of the AC layer followed by activated SiO_2 (15 g) and Al_2O_3 (15 g). Crude Sarir kerosene (100 ml) was eluted through the combined bed and the first five 10 ml fractions were examined for their aromatic carbon content.

Refining of CSK by N-Methyl Pyrrolidinone (NMP)

A series of solvent extraction experiments were carried out by mixing certain volumes of kerosene (K) and NMP as given below:

(a) 40 ml K + 20 ml NMP
(b) 20 ml K + 20 ml NMP
(c) 20 ml K + 40 ml NM
(d) 20 ml K + 80 ml NMP

The mixtures were shaken 30 minutes at 60°C in a thermostated agitating box. The solutions were cooled, kerosene layer was separated and aromatic carbon content was determined.

Spectroscopic Determination of Aromatic Carbon Content (CA) in Kerosene (K)

One milliliter (accurately measured) of the Kerosene sample was dissolved in 500 ml of iso-propyl alchohol (IPA) in a volumetric flask, and the ultra-violet (UV) spectrum of the solution was obtained; against IPA in the reference cell; in the range 400-200 nanometer. The absorbance values at 250, 260, 270, 280 and 290 nm were used to calculate the percentage of carbon in aromatic rings according to an already published mathematical relationship [6].

Determination of Some Aromatic Compounds in Sarir Kerosene by Gas Chromatography

20 ml of crude Sarir kerosene sample were extracted with 60 ml of NMP at room temperature (25°C). NMP extract was directly injected in a capillary GC column operating under the following conditions:

GC column:	CP-Sil 5 CB; 50 m X 0.32 mm, df = 0.12 μm
Conditions:	inj. temp. 300°C, detect temp. 300°C, rate/rise 5°C/min.
Instrument:	Packard GC Mod. 439.

Peak assignment was obtained by running authentic aromatic, mono-and di-ring, compounds under identical conditions.

Removal of Bad Odour from Crude Sarir Kerosene

Complete removal of obnoxious odour affected by stirring 25 ml of crude Sarir kerosene with 1g of activated carbon, followed by filtration of the odourless kerosene. The operation was carried out at room temperature.

RESULTS

The results of refining of crude Sarir kerosene by elution on a chromatographic bed of commercial activated carbon (comm. AC) and PRC prepared activated carbon (PRC-AC) [6] are given in Table 2. This table also gives the results of refining the same kerosene by mechanical mixing with Comm. AC. Aromatic carbon content (CA) was determined by the newly developed spectroscopic method [5].

The results of refining of crude Sarir kerosene with thermally activated silica (Si), alumina (Al)

Table 2. Refining Sarir kerosene by activated carbon

Type of operation	Volume eluted or treated (ml)	K/AC (vol.: wt)	Operation temperature (°C)	% Carbon in aromatic rings (CA)
(a) Chromatographic bed of Comm. AC.	Crude Sarir K		-	3.82
	5	-	Room T.(25°C)	0.60
	10	0.50:1		0.70
	20	1:1		1.75
	30	2:1		1.66
	40	3:1		1.80
	50	4:1		1.96
	60	5:1		2:10
	80	6:1		2.33
	100	8:1		3.21
		10:1		
(b) Chromatographic bed of PRC-AC			Room T.(25°C)	0.82
	5			1.07
	10	1:1		1.15
	15	2:1		3.77
	25	3:1		
		5:1		
(C) Mechanical mixing with Comm. AC	15	3:1	60°C	1.63
	15	3:1	90°C	1.63

and activated carbon (AC) conducted by elution chromatography on mixed adsorbents beds at room temperature, are given in Table 3.

Table 4 presents the results of refining of crude Sarir kerosene by solvent extraction with N-methylpyrrolidinone (NMP) at 60°C.

The results of the determination of some aromatic compounds,

Table 3. Refining of crude Sarir kerosene by elution through mixed adsorbents beds.

Chromatographic system	Volume eluted (ml)	K/Si+Al (vol.:wt.)	K/Si+Al+AC (vol.:wt.)	K/AC (vol.:wt.)	% Carbon in aromatic rings (CA)
(a) Silica (5 g) +Alumina (5 g)	10	1 : 1			0.48
	20	2 : 1			2.67
	30	3 : 1			2.81
	50	5 : 1			2.53
	80	8 : 1			2.41
(b) Silica (15 g) + Alumina (15 g) +AC (5 g)	10	1 : 3	0.29 : 1	2 : 1	0.18
	20	2 : 3	0.57 : 1	4 : 1	0.29
	30	1 : 1	0.86 : 1	6 : 1	0.76
	50	4 : 3	1.14 : 1	8 : 1	1.06
	80	5 : 1	1.43 : 1	10 : 1	1.38

Table 4. Refining crude Sarir kerosene by NMP at 60°C

Kerosene volume (ml)	NMP volume (ml)	K/NMP (vol.:vol.)	% Carbon in aromatic rings
40	20	2 : 1	1.33
20	20	1 : 1	0.80
20	40	1 : 2	0.50

actually present in the kerosene cut of Sarir crude oil, are given in Table 5.

Table 5. Some aromatic compounds identified in NMP extract from Sarir kerosene.

Retention time (min)	Carbon number zone	Aromatic compound	% Concentration
7.448	i^*-C_8	Benzene	0.0082
8.513	i-C_9	Toluene	0.0653
11.030	i-C_{10}	Ethylbenzene	0.0931
11.631	i-C_{10}	(p+m) Xylene	0.1778
11.937	i-C_{10}	o-Xylene	0.1240
13.080	i-C_{10}	Cumene	0.1242
13.978	i-C_{11}	n-propyl benzene	0.1757
14.508	i-C_{11}	Mesitylene	0.2692
21.467	i-C_{13}	Naphthalene	0.3907
25.388	i-C_{14}	1-Methyl naphthalene	0.3710

(*) i- = (iso-) = all forms of carbon except paraffinic straight chain (normal).

DISCUSSION

The results of refining crude Sarir kerosene by Comm. AC and PRC-AC, performed by elution chromatography, and measured by the new spectroscopic method are given in Table 2. The commercially activated carbon was provided by the Arabian Company for the Production of Beverages in Tripoli. It was a granulated type of particle with a diameter around 1-2 millimeters. This carbon was thermally activated in a tubular furnace at 800°C under a stream of nitrogen gas, for 30 minutes prior to use, and in a manner similar to that used in the preparation of activated carbon [6].

The results of examining the efficiency of refining by activated carbon by mechanical mixing at mildly elevated temperature of 60°C and 90°C are also given in Table 2. The concentration of CA is lowered to 1.63 % for the K/AC ratio of 3 : 1 which is almost identical with that obtained by elution chromatography. This indicates that neither agitation nor temperature improved the efficiency when a fixed 3:1 K/AC ratio was examined. Other solid, multi-adsorbent systems (a) a 50%+50% di-combination system of alumina + silica and (b) a 43% +43% +14% tri-combination system of alumina + silica + activated carbon were examined for the reduction of aromatic carbon content .The results are given in Table 3. Very high efficiency was observed for only the 1:1 ratio of K/Si +Al di-combination system. Beyond that, efficiency was lowered drastically. On the other hand, a pronounced improvement in the AC activity in terms of increasing K/AC ratio and decreasing %CA content was obtained by the combined action of Si + Al + AC. It seems that Si + Al treatment removes compounds that adversely affect AC activity by blocking pores which are normally active in removing mono- and di-ring compounds present in the kerosene fraction.

Figure 1 is constructed from data in Tables 2 and 3, and it displays a comparison between the three refining systems. The superiority of the three adsorbents combined action is clearly indicated. This suggests a practical procedure in which a known weight of crude kerosene is stirred with nearly equivalent weight of silica-alumina (50%-

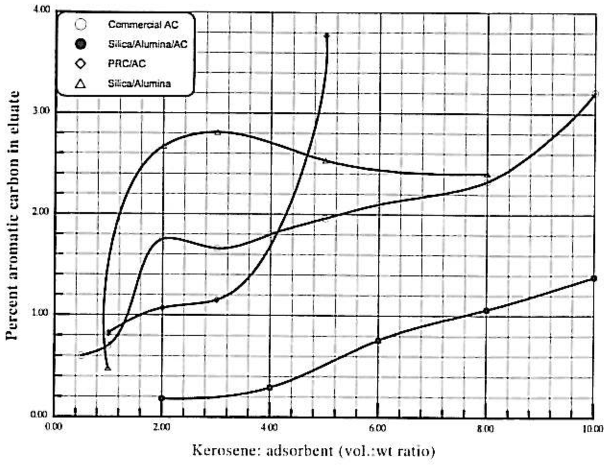

Fig. 1. Efficiency of pure and mixed adsorbents in removing aromatic compounds from kerosene.

50%). The solution is let to settle and the decantate is eluted through AC bed of a weight equivalent to one eighth (1/8) that of the kerosene original weight. The operation, carried out at room temperature, may yield a refined kerosene containing about 1 % carbon in aromatic rings (CA).

It is of significance at this stage to look into the possibility and efficiency of reducing % CA by solvent extraction methods [7].One of the used solvents to extract aromatics from petroleum fractions is N-methyl pyrrolidinone (NMP). We conducted a series of experiments using this solvent and the results are given in Table 4. It is evident that reducing % CA to less than 1% requires a 1:1 volume ratio of K/NMP. This is in a way comparable to the AC results alone (Table 2), but much less efficient compared to the combined Si + Al + AC results (Table 3).

The price and availability of adsorbents or solvents, their ease of regeneration and their ease of application coupled with their efficiency in reducing aromatic carbon content, are prime factors directing the choice of an industrial process. In this particular study, results show that adsorbents are clearly preferable to solvents in reducing aromatic carbon content.

To supplement the last conclusion, in regards with the availability of adsorbents, we refer again to the series of experiments which were carried out on the efficiency of activated carbon prepared at our Petroleum Research Centre (PRC-AC) [6]. The results are re-presented in Table 2. Further to this, a comparison of the activity of PRC-AC with that of the commercial-AC and $SiO_2 + Al_2O_3$ is indicated in Figure-1. It is obvious that PRC-AC is superior to both Comm-AC and $SiO_2 + Al_2O_3$ when applied alone and when K/adsorbent ratio is ≤ 3:1.

Finally, in order to present a proof on the prevalence of mono-and di-aromatic systems in the kerosene under investigation (Sarir kerosene), separation of some of these aromatic compounds by capillary column-GC from the NMP extract was obtained. The assignment of peaks was ascertained by matching with authentic aromatic compounds. The results are given in Table 5.

CONCLUSIONS

Major conclusions from this work are the following:

1 Reducing aromatic carbon content is more effective with solid adsorbents than with solvent extraction using NMP. The adsorption operation also effectively removes the obnoxious bad odour.

2 Solid adsorbent technology is expected to be preferred in comparison with solvent extraction on the basis of ease of operation and control, lower economical requirements, and lower general and place of work environmental impacts.

3 Most important solid adsorbent in this field is activated carbon, which may be prepared locally. We have already presented successful results in this respect [6].

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