Optimum Conditions For Paraffinic Hydrocarbons Separation From Petroleum Products

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Abstract:

This research work involves the determination of the optimum conditions for the separation of n-paraffins from authentic samples and application to kerosene and other petroleum liquid fraction. Study of the variation of temperature indicate that the best temperature for the adduct formation and quantitative separation is 25-30°C. The amount of urea used to the paraffin is found to be (1 paraffin : 3.5 urea) to give almost a complete recovery of the n-paraffin. Activator amount (absolute methanol) is found to be 4.25 gm /1 gm of paraffin. Therefore, the optimum conditions for ideal separation of any paraffin ranging from C₁₅ is; 3.55 urea: 4.25 methanol: 1 paraffin: 25-30°C temperature. In order to test the optimum conditions, the study was extended to the paraffins isolated from kerosene. The study involves using gas chromatography and employing the American standard method UO436 in the Arab company for detergent chemicals. The method was modified to suit the case of the study.

Key words: n-Paraffin, Kerosene, Gas chromatography.

Introduction:

Paraffinic hydrocarbons have relatively simple chemical composition, as they consist almost entirely of n-alkanes. Separation of straight-chain paraffin by means of the formation of urea adduct is employed in this area, as well as for the treatment of wax used for wax cracking and in lubricant production $^{(1,2)}$.

Separation of n-alkanes by means of urea is proceeded through four steps; adduct formation, adduct separation, adduct decomposition, and post- treatment. Feed stocks to be considered for n-alkane separation by adduct formation include atmospheric and vacuum distillates of petroleum in the boiling ranges corresponding to C_6 and higher n-alkanes⁽³⁾.

The discovery of adduct formation with urea is linked with Bergen's name, who, after his first results, systematically studied numerous straight chain alcohols, aldehydes, ketones, acids and esters with respect to their capacity for adduct formation. He found that in addition to hydrocarbons, these compounds also form urea adduct ⁽⁴⁻⁷⁾.

Experimental studies carried out with kerosene in the Hungarian Oil and Gas Research Institute demonstrated that the n-alkanes removed from kerosene by extractive crystallization yield satisfactory grades of n-alkanes as primary materials for chemical industry ^(7,8). The development in the separation of straight chain paraffin was encouraged by the need of such feedstocks to produce biodegradable detergents, now almost mandatory in many parts of the world, as being a necessary means of simplifying the treatment of domestic sewage containing detergents ^(8,9).

Solvent de-waxing process using a mixture of sulfur dioxide and benzene has also been put into practice. Liquid sulfur dioxide is used in the Edeleanu solvent refining process for lubricating oils. In this process, by a mixture of sulfur dioxide and benzene, the de-waxing and oil refining operations are combined. However, the process did not spread, chiefly owing to the corrosive action of sulfur dioxide^(10,11).

Urea adduction has been the most suitable method to separate long, straight chain hydrocarbons, as urea chlethrate, from branched molecules. At the higher molecular weights certain types of terminal substitution are permissible⁽¹²⁾. The complexes formed between the urea and the adductable compounds are solids and may be filtered from the matrix and then washed free from the other oils. n-Paraffin is recovered by destruction of the chlethrate complex. Heating or treatment with water is a common method of decomposing the complex and thus recovering the straight chain hydrocarbons^(13,14). The original observation in which that urea forms solid molecular compounds with a wide variety of linear molecules including hydrocarbons is attributed to Bergen ⁽⁴⁾.

In this research work we aimed to determine the optimum conditions for separation of n-paraffins from authentic sample and kerosene. Also employing gas chromatography to study the components quantitatively and qualitatively.

Experimental:

1-Variation of the ratio of feedstock; authentic paraffin(C_6 - C_{15}) to urea:

2.00 gm of pure urea was dissolved in 8 ml of absolute methanol by shaking for 0.5 hour at room temperature. Add 2gm of the authentic materials exactly weighed to the activated urea and shake the mixture at temperature of 25-30°C for 5 minutes. The presence of normal paraffin is indicated by a gel type crystalline product named urea adduct. The adduct is separated by filtration or decantation and purified by washing with 10ml of cold methanol. 25ml of water was added to the adduct and the resultant mixture is heated between 60-70°C till a clear solution of the adduct is indicated. The mixture was transferred quantitatively to a separating funnel and the aqueous solution discarded. The organic layer was dried used anhydrous sodium sulfate. The weight and percentage of the recovered paraffin was determined.

The experiment was repeated using 2, 4, 5, 6, 7, 8, 9, and 10 gm of urea while other parameters were kept constant (Table 1).

Ľ	constant					
	Authentic	Added	Used	Temp. °C	%Recovered	
	mixture	urea	Methanol		hydrocarbon	
	(gm)	(gm)	(gm)			
	2	2	8		20	
	2	4	8	25-30	42.5	
	2	5	8		32	
	2	6	8		37.85	
	2	7	8		100	
	2	8	8		61	
	2	9	8		81.5	

 Table (1): Variations of the amount of urea in the separation of n-paraffin while other variables are constant

2-Variation of activator amount:

Dissolve 7gm of urea in various amounts of methanol as activator at a temperature of 25-30°C. The amount of methanol varied between 5 and 10 gm. The mixture of urea and added alcohol was mixed thoroughly for 0.5 hr. 2gm of the hydrocarbons under study was added. The mixture was shacked mechanically till the appearance of adduct and 10 minutes afterwards. The recovered paraffin was determined as in step 1.

The weight and percentage of the adducted paraffin was shown in (Table 2).

 Table (2): Variations of methanol amounts while

 keeping other parameters constants in the urea

 adduction

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	Weight of	Weight of	Weight	Temp.	%
	authentic	added	of	°C	Recovered
	hydrocarbon	methanol(gm)	urea		hydrocarbon
	sample (gm)		(gm)		
	2	5	7.0		30
	2	6	7.0	25-30	50
	2	7	7.0		100
	2	8	7.0		110
	2	9	7.0		101
	2	10	7.0		104

3-Effect of temperature on the addution of nparaffin:

One gram of authentic paraffin mixture exactly weighed was added to a solution of 7 gm of urea in 8.5 gm of methanol. The mixture was shacked well at different temperature (25-70°C) till the formation of the adduct. The adduct is allowed to cool to room temperature. Liquid materials with the adduct was decanted and the adduct washed with 10 gm of cold isooctane. The adduct was allowed to stand for 2hrs to insure evaporation of isooctane and finally decomposed with 25 ml of distilled water at 60-70° C till complete dissolution of the adduct. The supernatant liquid discarded and the organic layer dried. The weight and percentage of n-alkane was then determined (Table 3).

 Table (3): Effect of temperature on the adduct formation and quantitative separation of paraffin

and quantitative separation of paratiti					
Weight	Weight	Weight	Temp.	%	
of	of	of	°C	Recovered	
urea		authentic		paraffin	
(gm)	methanol	sample			
	(gm)	(gm)			
7	7	2	25	77	
7	7	2	30	100	
7	7	2	35	72	
7	7	2	40	72	
7	7	2	45	72	
7	7	2	50	70	
7	7	2	70	70	

4-Optimum conditions for separation of liquid paraffinic hydrocarbons as obtained from 1,2, and 3 bove

Dissolve 7 gm of urea in the idealistic amount of absolute methanol. The mixture was shacked for 10-15 minutes at room temperature (25-30°C). One gram of pure authentic hydrocarbons was added alone. The mixture was shacked till formation of the adduct appeared as a white crystalline-gel type materials. The supernatant was decanted and the solid washed with isooctane and kept to dry at room temperature for 1hr. The adduct was decomposed by using 25ml of distilled water at 50-70° C. The experiment also aimed to fit other n-paraffin with higher and lower molecular weights. Hydrocarbons used in the investigation were authentic C_{6^-} C_{14} , in a mixture of them. The conditions were extended to pure dry kerosene.

5- Separation of n-paraffins from kerosene:

5 gm of dried kerosene was added to pre dissolved 7 gm of urea in 8.5 gm of methanol. The mixture was shacked at 25-30°C till a complete formation of the adduct. The solvent was decanted and the adduct was washed with isooctane and kept to dry at room temperature (25° C) for 1-2hr. Decomposition of the adduct was conducted by adding 25ml of distilled water and heating between 50-70°C till clear solution of two layers was appeared. The isolated paraffins were dried and weight (Table 4).

Table (4): Retention times of the separated straight chain paraffins of the standard mixture (%wt) with their theoretical and practical ratios

 corected and practical ratios					
Authentic	Retention time	Theoretical	Amount from		
paraffin	(min)	amount	GLC (% wt)		
		ratio (%wt)			
C7	8.89	12.743	12.722		
C8	10.34	11.765	11.535		
C9	15.45	12.745	12.900		
C10	21.21	8.824	8.791		
C11	27.05	12.745	12.342		
C12	32.33	10.784	10.811		
C13	38.10	10.784	11.522		
C14	42.65	9.804	10.143		
C15	44.85	9.804	10.300		
Total	-	100	101.066		

Results and Discussion:

Separation of n-paraffinic hydrocarbons from other hydrocarbons constituents is a vital task due to the presence of large amount of structural isomers. Paraffins are required in the production of the terminal olefins, halogenated alkyl hydrocarbons, fatty alcohols and finally their application in the production of biodegradable detergents (alkyl benzene sulphonate). Moreover, paraffins are important in the production of single cell proteins and lately their applications in the production of red meat^(8,9).

It is very necessary to fit various parameters, that have a direct relationship to the adduct formation and quantitative separation of paraffins. These parameters include, amount of urea, amount of added activators, amount of n-alkane and finally the temperature. Before adduct formation the feed is usually mixed with the so-called wetting agents (activators) in order to eliminate the effect of impurities interfering with the adduct formation. Since the suspension obtained in the course of adduct formation has a very high viscosity.

In this study, it is aimed to optimize the best conditions for the quantitative separation of n-paraffin from petroleum products. The study included variation of the amounts of used urea while maintaining the amounts of hydrocarbon, methanol and temperature constants. It is found that the best amount of urea used for adducts formation and quantitative separation of paraffin is (1 paraffin: 3.50 urea). The amount of urea used varied between 1:1 and 1:5 (paraffin : urea) as at 25-30°C. The results are given in Table (1) and illustrated in figure (1).

Figure (1): Variation of the recovered hydrocarbons with the used urea and alcohol



Variation of the activator (methanol) in this study was conducted. The amount of methanol lies in between 1:2 and 1:4 (paraffin :methanol) at 25-30°C. The results indicate that the amount of methanol lies between 3.55 and 4 gm as given in Table (2) (see also Figure (1)).

The results in table (2) indicate that, the best amount of methanol to activate the urea to form the adduct in quantitative manner to separate the paraffin is (3.50: 1) (methanol: paraffin). In another part of this study was aimed to investigate the effect of temperature after we found the best amount of urea and activator on the adduct formation and the thermal stability of adduct. The adduct formation was conducted at 25, 30, 40, 45, 50 and 70 °C, the results are given in Table (3).

The results in Table (3) indicate that the best adduction is at 30° C.

Looking back to our results we may say that the best conditions for urea adduct are (1: 3.50:3.5) (feed : urea : methanol).

The application was extended to use a sample of kerosene (b.p. 185-255 °C) gives (21.75)% which is comparable to that obtained from the gas chromatography measured in the Arab Company for Detergent Chemicals using the ASTM for the determination (21.2).

The paraffin isolated by application of the above condition from kerosene were further studied using UOP436 The experimental conditions as given by Arab factory for detergent chemical and modified to suit our cases.

Amount injected	5 microliter
Flow rate of carrier gas (He)	30 ml / min
Injected temperature	350 °C
Detector temperature	300 °C
Column temperature	40-140 °C isothermal
programmable	140-170°C programmed at 2.5 °C / min
	180- 300 °C programmed at 4 °C/min
	300 for 20 min

Figure (2) shows the gas liquid chromatography of standard mixture of straight paraffins and the separated straight paraffins. The results are given in Tables (4 and 5).

Figure (2): Gas chromotography of standard authentic sample and virgin and cracked kerosene



Retention time (min)

Gas chromatography of standard authentic sample and virgin kerosene



Gas chromatography of paraffins from cracked kerosene

cerosene and in the straight parariti part				
	Iraqi	Retention	%Distribution	% of
	keroscene time(min)		in Iraqi	paraffin
			keroscene	from GLC
	C7	8.89	$+ ve^*$	$+ ve^*$
	C8	10.34	0.301	1.640
	C9	15.45	3.106	16.95
	C10	21.21	5.212	28.45
	C11	27.05	5.028	27.45
	C12	32.33	3.763	20.54
	C13	38.10	0.860	4.70
	C14	42.65	0.050	0.27
	C15	47.85	+ ve	+ ve
	Total	_	18 321	_

Table (5): Retention times of the straight paraffin present in the Iraqi keroscene with their ratios in the kerosene and in the straight paraffin part

Applying the above conditions of UOP436 and the data in Table (4) for the analysis of the n-paraffins from kerosene isolated by the developed method is showed in figure (2) and Table (5).

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دراسة الظروف المثلى لفصل الهايدر وكاربونات البارافينية من المنتجات النفطية

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الملخص:

تضمنت الدراسة ايجاد وتقدير الظروف المتلى لفصل البارافينات المستقيمة من نماذج قياسية معروفة والكيروسين النقي في فضلا عن بعض المشتقات النفطية الاخرى كالنفثا مثلا. ان افضل درجة حرارة لتكوين معقد اليوريا مع البارافينات هو ٢٥–٣٠ م. وعند ثبوت درجة الحرارة ثم تغيير كمية اليوريا المستخدمة وجد ان افضل نسبة هي ١ غم بارافين نقي لكل ٣,٥ غم من اليوريا لتعطي استعادة كاملة. اما عند ثبوت كمية اليوريا ودرجة الحرارة وتغير كمية المنشط (والمعتمدة في الادبيات على انها الكحول المثيلي المطلق) وجد انها تتطلب ٤,٢٥ غم من الكحول لكل ١ غم من البارافين

النقي. ومن ناحية اخرى وجد ان الظروف المثلى كانت ٣,٥٥م يوريا الى ٤,٢٥ غم ميثانول الى ١ غم بارافين نقي وفي درجة حرارة ٢٥-٣٠ م. ولغرض معرفة ابعاد الطريقة فقد تم دراسة البارافينات المعزولة بوساطة طيف الرنين النووي المغناطيسي والذي اوضح امتصاصا بارافينيا فقط. في حين تم دراسة البارافينات المعزولة من الكيروسين والاجزاء النفطية الاخرى باستخدام كروماتوغرافيا الغاز واعتمادا على مبدأ الشركة العربية بطريقتها UOP436 المعتمدة في الشركة العربية لكيمياويات المنظفات.