Commun. Fac. Sci. Univ. Ank. Serie B
V. 35. pp. 41-52 (1988)

SEPARATION OF n-ALKANES FROM KEROSENE BY UREA ADDUCTION

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ABSTRACT

n-Alkanes mixture with 99.8 % purity was separated from Kerosene by successive urea adduction. It was not possible to separate branched chain alkanes from n-alkanes of kerosene by successive urea adduction by excess urea because when the total n-alkanes weight percent was decreased to 14.4 in branched chain alkanes, no urea adduct was precipitated.

INTRODUCTION

The aim of this work is to separate n-alkanes and branched chain alkanes from kerosene with a high purity. It is not possible to isolate the above components by distillation methods. In the literature two different routes are given, one is using molecular sieves and based on selective adsorption on the solid surface which is inherently with a low efficiency, latter is chemical method, formation of solid urea aduct of n-alkanes. In the latter method efficiency is high but purity percent is low. (Breck 1974) (Covini, et.al.1975), (Liedholm, et.al.1961), (Mitrofanox, et.al.1973).

Separation of branched chain and straight chain paraffins from petroleum products has a great importance in chemical industry, formers are used as a light lubricant in industry and latters are used mainly in alkylation process especially in detergent industry.

The accidental discovery by Bengen in 1939 that urea forms crystalline complexes with straight chain organic compounds, has led to intense investigations of the complex-forming properties of urea in laboratories throughout the world. (Angla, 1949) (Fetterly, 1951) urea does not crystallize in its usual tetragonal modification. The unit cell is hexagonal, six urea molecules per unit cell. The urea molecules form spirals with the hydrocarbon molecules situated at the center.

Spirals of hydrogen bonds between the 0 and NH_2 groups of adjacent urea molecules account largely for the stability of the structure (Smith, 1950). Urea and reactant straight chain molecule are not united in whole numbered ratios except by chance. The principal requirement for adduction with urea is a long, unbranched chain. The urea complexes form excellent needle-type crystals. They exhibit definite vapor pressure-temperature relationships but the complexes do not exhibit definite melting points. At 25 °C the minimum chain length for alkanes is six carbons. In the lower molecular weight range, dissociation sets in before a fixed melting point can be attained. Complexes which do not dissociate below 132.7° finally dissociate at that point, which is the melting point of urea. The pure complex containing approximately 24 percent n-alkane, has a density of around 1.20 (1.33 for the tetragonal solid urea) (Fetterly, April 1955). This low bulk density together with an apparent tendency of the hydrocarbon to wet the ends of the crystals preferentially, causes considerable occlusion of unreacted hydrocarbon within the mass.

Chemical equilibrium is established in the formation of urea adducts just as in the usual chemical reactions. The equilibrium constant K may be defined, conveniently in terms of the dissociation reaction for one molecule of adduct.

$$\text{Complex (s)} \rightleftarrows \text{Reactant} + \text{m Urea} \tag{1}$$

The dissociation constant for this reaction is defined in terms of the activities (a).

$$K = \frac{(a_r)\ (a_u)^m}{(a_c)} \tag{2}$$

Where, a_r, a_u, a_c activities of reactant, urea and complex respectively. By this definition as the value of K decreases, the stability of the complex increases.

In the case of n-alkanes the value of K decreases as the chain length increases, indicating the greater stability of complexes that contain longer chains. The increase in stability with chain length is much more rapid at lower than at higher temperatures. Best purit of n-alkanes was achieved by Naoki Yata et.al.(1966) the purity of total C_9–C_{16} n-alkanes was 96.2 %. Georgescu. (1974) analyzed urea adducted n-alkanes of kerosene by gas chromatography. Also in Germany a plant was installed to produce low pour oils, using urea adduction, (Hoppe, et al., 1957).

EXPERIMENTAL

Unless otherwise stated all chemicals and solvents were general laboratory or analytical grade. Kerosene was obtained from Orta Anadolu Rafinerisi (Kırıkkale-Ankara-Turkey) which was distilled from Kirkuk origin crude. Specifications were B.P. range 152°–242° in which 20 % distilles in the range 152°–167°, $D_{15} = 0.7826$.

For gas chromatographic analysis a Perkin Elmer Model F11 chromatograph with temperature programmer and flame ionization detector connected to a Spectra Phyciss Autolab Minigrator in series with a 1 mv input sensitivity Perkin Elmer Model 56 Linear Recorder was used. Gas chromatography operating parameters were: $N_2 = 30$ ml min^{-1}, $H_2 = 30$ ml min^{-1}, Air $= 300$ ml min^{-1} Temp. programming from 60° to 120° at 4°C min^{-1}. Amplifier range 50×10^{-2} which was equivalent to 2.5×10^{-12} Amp sensitivity. Injected amount of sample 0.5 μl.

To separate aromatic and unsaturated components of kerosene 40 % (w/w) con. sulfuric acid was added and heated by effective stirring for 2 h at 60°. Organic phase was separated and washed with water, sodium bicarbonate solution and water successively.

To find out the effective separation of n-alkanes different ratios of kerosene and saturated urea solution in methanol were mixed for precipitation of urea adduct. Solid adduct was separated from the mother liquor by filtration and washed several times with mother liquor, to filter off all unadducted kerosene part from the urea complex. Solid complex was decomposed by adding water and heating to 60–80° liquid organic phase was separated and dried over silicagel and analyzed.

In successive purification of urea adduct to find out the best separation, different ratios of urea solution in methanol and previous urea adducted mixture were mixed and urea adduct was precipitated.

To obtain branched chain alkanes free of n-alkanes, successive urea adduct formation was carried under the excess urea until no adduct precipitation was occurred.

A general procedure for urea adduction: 400 g urea (6.67 mol) was dissolved by heating in 1.5 l methanol and 90 g water was added. 640

g kerosene (kerosene/urea 1.6) was placed in a 4 1 beaker equiped with a stirrer and mixed with the urea solution and stirred aobut 30 min let it stand 15 min upper unadducted kerosene layer was decanted to a 1 1 separation funnel. Urea adduct precipitate in methanol phase is filtered in vacuum. Precipitate was washed several times with mother liquor and dried. Precipitate was weighted and equal amount of water was added and heated to decompose the complex. Upper n-. alkanes layer was separated and dried over silicagel.

RESULTS AND DICUSSION

A plot of logK as a function of urea/n-alkanes molal ratio m gives essentially a straight line from this, for n-alkanes equation;

$$m = 0.6848n + 1.496 \qquad (3)$$

where n is the number of carbon atoms (Redlich, et.al.1950) is written Applications usually involve mixtures containing several complex forming substances. Two different cases may be taken into consideration: (a) each complex represents a separate solid phase. (b) A single solid phase, i.e. a solid solution of all reacting substances in urea exists. According to the results of crystal structure analysis (Smith, 1950) case (b) rather than (a) is to be expected.

The two cases can be distinquished by an examination of a mixture of two n-alkanes and another hydrocarbon (n-heptane, n-octane, decalin) and solid urea. In case (a) the mole fractions x_7 and x_8 in the mother liquor can not fall below the values K_7 and K_8 of the respective equilibrium constants. Actually it had been found that they approached much lower values, which satisfied the relation,

$$x_7/K_7 + x_8/K_8 = 1 \qquad (4)$$

The precipitate therefore is a single solid. Solution activity of any reactant in the solid solution is equal to its mole fraction y_i calculated on an urea free basis. The equilibrium constants for mixtures are therefore,

$$K_i = a_i \, a_u^{m_i} \; / \; y_i \qquad (5)$$

where, a_i indicates the acitivity of i component in the mother liquor and m_i its molal ratio, a_u activity of urea.

Since this equation is applicable for each reactant in the mixture, it is apparent that the concentrations of individual reactants in the mother liquor can differ from the equilibrium concentrations for pure reactants. Thus in a mixture, a component whose complex is unstable by itself (That is $K_i > 1$) can be precipitated in the solid solution. As a consequence, sharp separations in mixture can not always be obtained, but a considerable degree of enrichment can usully be achieved, the relative values of K_i controls the degree of separation. Acording to equation (5) the value of a_u may be controlled by the urea concentration in liquid phase to provide the most suitable degree of separation. Unfortunately there is no much data for the urea activity in different solvent. From above discussion best separations can be achieved by mixing dissolved urea in a solvent and n-alkanes mixture. Changing the activity of urea by adding water also influence the degree of separation. Sulfuric acid treated kerosene contains n-alkanes C_7 to C_{16} with the total weight percent 47.04. The gas chromatogram is given in Figure 1. and the weight percent composition in Table 1. As it is seen from Figure 2. Total amount of n-alkanes separated by urea adduction from kerosene do not increase after kerosene urea weight ratio 1.4. So we achived first urea adduct formation from kerosene in the weight ratio of 1.6 (kerosene/urea) where gas chromatogram is given in Figure 3. n-alkanes composition in Table 1. We achieved a total of n-alkanes 90.2 % purity. For the second successive urea adduction we investigated also best reactant urea ratio. Taking inconsideration of percent yield-n-alkanes purity in the adduct: it was found that 1.1 ratio was the best. This correlation is given in Figure 2. At the third and fourth successive urea adduction reactant/urea ratio was 0.6. At fourth adduction we have reached a purity of n-alkanes 99.8 Figure 4. But the overall efficiency is 28.2 %, gas chromatogram of final n-alkanes mixture is given in Figure 5. As it is shown by successive adduct formation pure n-alkanes can be isolated forom kerosene by using different reactant urea ratios. n-Alkanes K_i decreases as the carbon number increases as a consequence in the successive urea adduction higher n-alkanes mole ratio increases while lower decreases in the urea adduct. It is shown in Figure 6.

Kerosene, adducted with excess urea in the separation of branched chain alkanes from n-alkanes in kerosene. Kerosene urea ratio was 0.6 and total n-alkanes left in unadducted kerosene was 23.87 %. This is seen in Figure 7. By succesive urea adduction n-alkanes ratio decreases

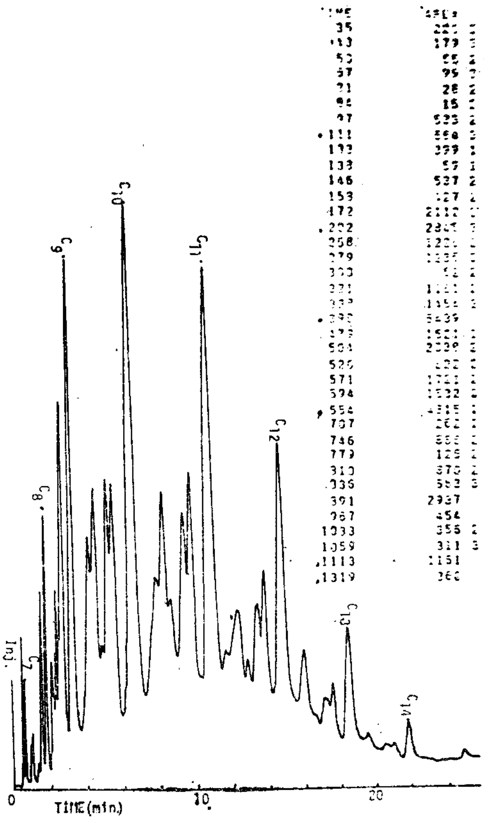


Figure 1. Gas Chromatogram of Sulfuric acid treated Kerosene. Temperature program 60°–120° at 4°C min^{-1}. with nitrogen carrier gas flow rate 30 ml.min^{-1}.

in the unadducted liquid phase, but after seventh adduction no adduct was formed. So it was the minimum amount of n-alkanes in the brach -chain alkanes of kerosene that could be attained; that was 14.48 %, n-alkanes remained in the mixture. It was not possible to separate n-alkanes from branched chain alkanes of kerosene better than this value.

Table 1. n-Alkanes wt% in Kerosene and Successive Urea Adducts.

wt. % of n-Alkanes in	Kerosene	1 st. urea adduct	2nd. urea adduct	3rd. urea adduct	4th.urea adduct
n-C_7	0.190				
n-C_8	1.948	0.706	0.522	0.166	0.048
n-C_9	7.248	6.672	5.819	3.603	2.429
n-C_{10}	13.797	20.700	19.622	17.509	16.666
n-C_{11}	12.761	26.632	29.446	29.864	30.989
n-C_{12}	7.325	20.632	25.986	28.831	28.931
n-C_{13}	2.978	11.195	12.170	14.062	14.851
n-C_{14}	0.794	3.485	3.329	4.172	4.537
n-C_{15}		0.566	0.937	0.985	1.076
n-C_{16}				0.344	0.360
Σ n-C %	47.041	90.205	97.828	99.536	99.887

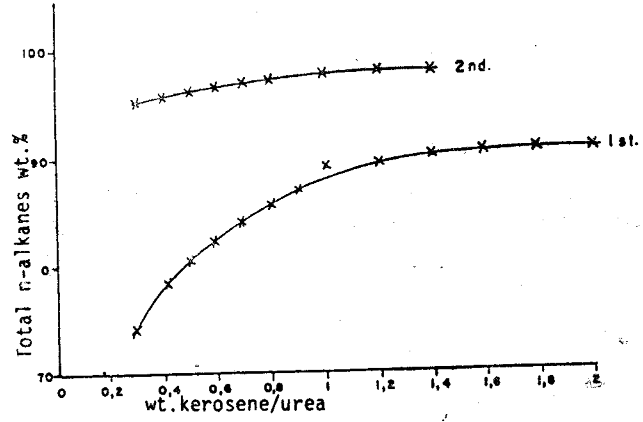
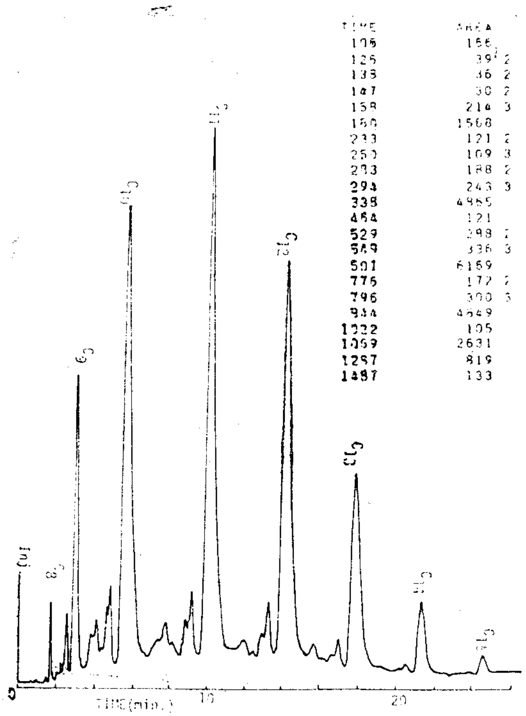


Figure 2. Change of total n-alkane weight percent in the first and second urea adducation with the weight ratio of kerosene to urea.

The gas chromatogram of the liquid phase was given in Figure 8. The weight percentage of individual n-alkanes in the mixture of unadducted liquid phase in the successive separation was given in Table 2.

The reverse case was seen in this successive separation higher n-alkanes ratio decreased while lower n-alkanes ratio increased.



TIME	AREA	
105	156	
125	39	2
133	36	2
147	30	2
158	214	3
160	1568	
233	121	2
250	109	3
283	188	2
294	243	3
338	4965	
454	121	
529	298	2
569	336	3
591	6159	
776	172	2
796	390	3
934	4549	
1022	105	
1059	2631	
1257	819	
1487	133	

Figure 3. Gas chromatogram of first urea adduct of kerosne. Temperature program 60°–120° at 4°C min^{-1} with nitrogen carrier gas flow rate 30 $ml.min^{-1}$.

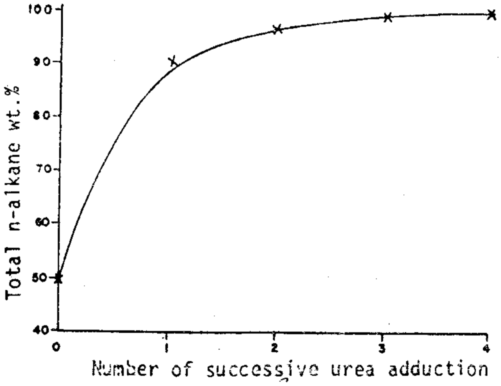
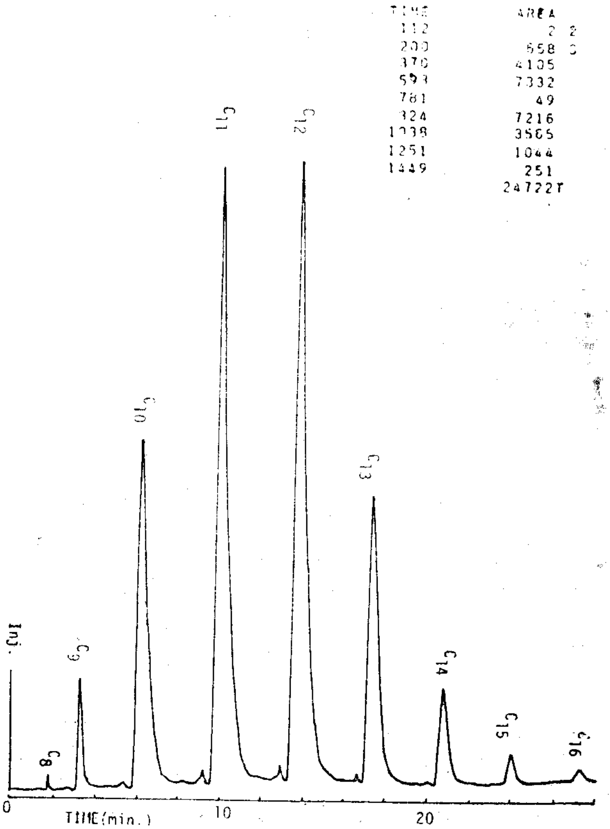


Figure 4. Weight percent on n-Alkanes separated by successive urea adduction from kerosene.



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TIME         AREA
 112            2  2
 200          658  3
 370         4105
 593         7332
 781           49
 924         7216
1038         3565
1251         1044
1449          251
            24722T
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Figure 5. Gas chromatogram of final (4th.) urea adduct of kerosene. Temperature program 60°-120° at 4°C $\min^{-1}$ with nitrogen carrier gas flow rate 30 ml.min^{-1}.

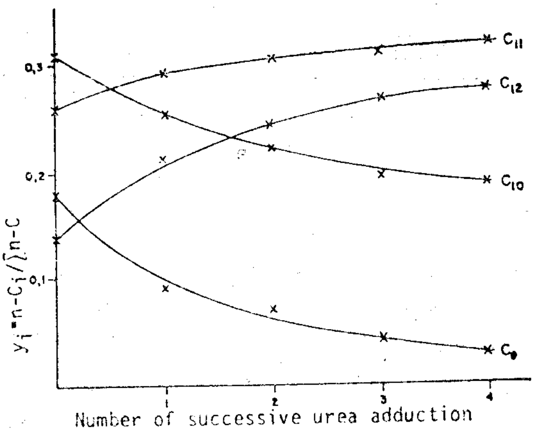


Figure 6. Change of some n-alkanes mol fraction in the urea adducts with the successive adduction.

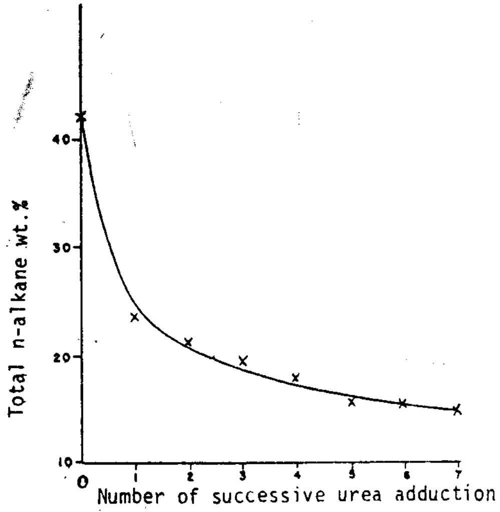


Figure 7. Weight percent of n-alkanes in the liquid phase of successive urea adduction from kerosene.

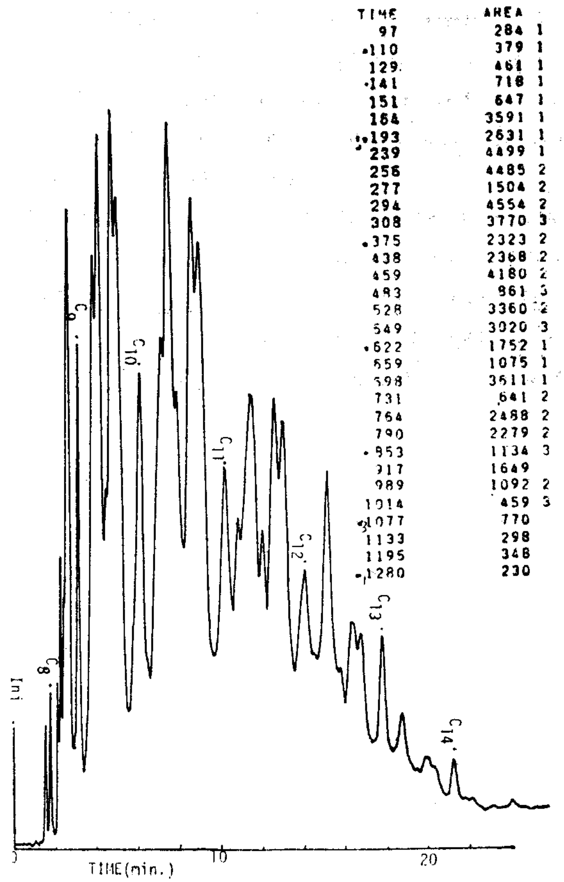
Table 2. n-Alkanes Weight % Composition in the Unadducted Liquid Phases in the Successive Urea Adduction (Liquid Phase/Urea Weight Ratio is 0.6)

wt. % of n-alkanes in	1 st.	2 nd.	3 rd.	4 th.	5 th.	6 th.	7 th.
$n-C_8$				0.496	0.501	0.540	0.603
$n-C_9$	1.095	1.12	1.223	3.127	3.314	3.972	3.955
$n-C_{10}$	5.194	8.233	7.338	6.164	5.650	4.807	4.00
n_{11}	10.741	7.464	6.299	4.446	3.986	2.934	2.792
$n-C_{12}$	3.417	2.200	1.860	1.590	1.490	1.400	1.100
$n-C_{13}$	2.165	1.700	1.440	1.110	1.030	0.993	0.976
$n-C_{14}$	1.254	1.180	1.144	0.935	0.700	0.508	0.414
Σ n-C %	23.870	21.897	19.304	17.863	15.771	15.154	14.485

CONCLUSION

It is possible to separate n-alkanes from kerosene with high purity by successive adduction with urea, but overall efficiency is low As the number of adduction increases in the successive adduction higher n-alkanes ratio increases in the adduct.

It is not possible to remove n-alkanes comletely from unadducted branched chain alkanes. Because no adduction formed after a certain concentration of n-alkanes in branched chain alkanes.



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   TIME          AREA
     97           284 1
  •110            379 1
   129            461 1
  •141            718 1
   151            647 1
   164           3591 1
 ••193           2631 1
  •239           4499 1
   256           4485 2
   277           1504 2
   294           4554 2
   308           3770 3
  •375           2323 2
   438           2368 2
   459           4180 2
   493            961 3
   528           3360 2
   549           3020 3
  •622           1752 1
   659           1075 1
   598           3611 1
   731            641 2
   764           2488 2
   790           2279 2
  •953           1134 3
   917           1649
   989           1092 2
  1014            459 3
 •1077            770
  1133            298
  1195            348
 •1280            230
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Figure 8. Gas chromatogram of urea unadducted part of kerosene (branched chain alkanes). Temperature program 60°–120° at 1°C min^{-1} ^{1} with nitrogen carrier gas flow rate 30 ml.min^{-1}.

RFFERENCES

ANGLA, B., Ann Chim., (12) 4, 639 (1945).

BENGEN, M.F., German Patent application OZ 123 438 (Marcih 18, 1940).

BRECK, D.W., Zeolite, Molecular Sieves., John Wiley Sons İnc., New York (1974)

CORVİNİ, G., CLARK, K.R., BRANCROFT, W.G., Proc. Gas Gas Cond. Conf., (1975).

DIETZ, W.A., J of Gas. Chrom., 5, 68–71., (1967).

FETTERLY, I.C., Petroleum Refiner., 34 No 4, 134–137 (April 1955).

FETTERLY, L.C., U.S. Patents 2, 569, 986 and 2, 578, 054 (1951).

FRITZ, B., Eur. Chem. News. Norm. Paraf. Suppl., 29–31 (1966).

GEORGESCU, M., et al., Rev. Chim. (Bucharest)., 25(12) 1030–4 (1974).

HOPPE, A., FRANZ, H., Petroleum Refiner., 36(5) 221–24 (1957).

LIEDHOLM, G.E., et.al., Ger.Pat.1.119, 440 (Dec. 14.1961).

MİTROFANOX, M.G., et al., Khim Tekhnol Topl. Masel., 18(8) 8–9 (1973).

NAOKI, YATA et al., Bull., Japan .Petrol. Ins., 8,7–12 (1966).

REDLICH, O., GABLE, C.M., et.al., J. Am. Chem. Soc., 72, 4153 (1950).

SMITH, A.F., J. Chem. Phys., 18, 150–51 (1950).

ZIMMERSCHIED, W.J., et. al., Ind. Eng. Chem., 42, 1300 (1950).