ALKYL-AROMATIC COMPOUNDS
IN GASOLINE-REFORMATION PRODUCTS

By

L. ACKERMANN, I. SZEBÉNYI and E. VERMES

Department of Chemical Technology, Technical University, Budapest

The aim of this work was to study the hitherto unutilized reserves in aromatics of the Hungarian petroleum industry, with special respect to C_9 and C_{10} aromatic compounds. For this purpose data relevant to an estimation of the quantities of industrially utilizable compounds likely to be recovered from the products of aromatization plant have been gathered. Therefore optimum conditions of testing had to be determined and adequate methods of identification had to be worked out with special regard to the character of the Hungarian reformates.

While formerly the demand of industrial aromatic products was met almost exclusively from coal tars, at present most of these compounds are obtained by catalytic reforming, but the importance of the products of gasoline pyrolysis is also steadily increasing.

One factor that necessitates increased aromatics production is the prevention of air pollution, as motor gasolines of lower lead content need more aromatics to compensante for octane loss.

In Hungary, petrochemical production of aromatic compounds is in a state of development. At the Komárom Petroleum Co. 150 000 metric tons of gasoline are reformed yearly, since 1964; the Duna Petroleum Co. began reforming in 1969 with an annual output of 300 000 tons [1]. The extraction unit was started in 1970 and is now producing 8600 tons of benzene and 22 000 tons of toluene per year. By putting additional reforming units on stream, a further increase of the production of aromatics can be expected. In the Duna Petroleum plant, after its completion, besides benzene and toluene, about 140 000 tons of xylene and of ethyl-benzene will be produced yearly.

The main purpose of our studies was the quantitative determination of these individual C_9 and C_{10} aromatic compounds the recovery of which from reformates may be important because they are useful industrial raw materials, are present in sufficient concentrations, and can be separated by an economically feasible technology.

Of the C_9 and C_{10} aromatics durene, pseudo-cumene, and mesitylene are industrially interesting. Cumene, prehnitene and cymene can be mentioned in this category respectively among the aromatic C_9 and C_{10} compounds. Pseudo-cumene is the compound which offers the greatest variety of applications, thus this is the industrially most important one. It is used mainly as a plasticizer of alkyd-resin coatings, varnishes, and modified polyesters. Its conversion into trimellitic acid or acid anhydride gives a starting material for insecticide and fungicide manufacture.

Trimellitic acid anhydride, besides the dianhydride of pyromellitic acid obtained from durene, is a primary compound in the manufacture of polyimides which have good electrical and mechanical properties, are unaffected by exposure to radiation, and are stable over a wide range of temperature. Thus their importance in the aircraft industry as well as in the construction of spacecraft and satellites exposed to cosmic radiation is appreciable.

The esters of polyvalent alcohols with trimesinic acid produced of mesitylene are suitable for the manufacture of resins. The trimesinic acid esters can be used as plasticizers of e.g. vinyl resins.

From a mixture of the C_9 and C_{10} aromatic compounds only pseudo-cumene can directly be recovered by distillation. Pseudo-cumene boiling at 169 °C is separated from hemi-mellitene boiling at 176 °C on a column of 100 theoretical plates, and from o-ethyl-toluene boiling at 165 °C on a column of 150 plates. The purity of pseudo-cumene thus separated is 95 per cent [2].

Owing to their identical boiling points, a mixture of mesitylene and o-ethyl-toluene will separate from other aromatics in a fractionation process, but the mesitylene can be separated of the binary mixture by crystallization at low temperature.

Durene having a freezing point of 80°C can be separated by fractionating crystallization after having distilled off the naphthalene fraction.

Several authors have studied the C_9 and C_{10} aromatics, their separation and their qualitative and quantitative analysis. Almost all of them had chosen an approach different from those adopted by others. In the course of their work they used analytical distillation and solid-liquid chromatography. Within the scope of this report the discussion of all the various techniques would be impossible, only some examples will be mentioned.

SOPOV et al. [3] combined gas and liquid chromatography with infrared spectrophotometry, whereby they achieved the identification of 34 individual aromatic compounds. KHAN-MALEK [4] produced three fractions by the distillation of samples, in the fractions 50 compounds could be identified by gas chromatography using stationary phases having various polarities. QUADER and KRISHNA [5] separated the sample to be tested on silica gel, whereby four fractions were obtained, the aromatic fraction was separated by distillation. For the identification ultraviolet and infrared spectrometry as well as gas

chromatography were used. MALINOVSKA [6] used two stationary phases of different polarities in gas chromatography. Also gas chromatography was the technique used by KOLBIN et al. [7], PATEROK and PILARCZYK [8], DEMEN-TEVA and NAUMOVA [9], TA-CHUANG LO CHANG and KARR [10], and many others.

In addition to gas chromatography, for the purpose of identification infrared spectroscopy is also used, usually as a supplementary method. This was the technique adopted also by the authors in the study of the reformates produced by the Duna, and the Komárom Petroleum Companies. The instruments used were a gas chromatograph Type CHROM 3, and infrared spectro-photometers UNICAM Sp-200, and UR-20.

The first task was to select a suitable stationary phase for gas chromatography. In the beginning 10 per cent Apiezon-L on firebrick support was used. Comparison of the obtained chromatograms with those produced with a packing made with 10 per cent polar polyethylene-glycol adipate (PEGA) stationary phase on Rysorb support showed, in so far as more peaks were recorded, that the latter packing gave better separation, quite as expected. Another advantage of a polar absorbent was that this emphasized the distinction between aromatic and other compounds by a greater difference in the relative retention times, in consequence, overlappings were reduced to a minimum: the non-aromatics were eluted before the aromatic compounds. There was, however, one exception: retention of benzene was nearly the same as that of isononanes. Among paraffins, retention of n-decane, and that of compounds with more carbon atoms, was shown to exceed that of toluene, but, since the amount of the former was negligible because of the upper boiling-point limit of the reformed fraction, no interference occurred.

The identification of peaks was first attempted on the basis of data found in a publication of SOPOV et al. [3]. These authors have given relative retention values for a number of aromatic compounds on PEGA at various temperatures. Checking some values given for 120°C by means of standard compounds, quite significant divergences were found, and a more thorough study of the data suggested that some of them did not satisfy the basic principles of gas chromatographic theory. Hence, some other method of identification had to be found.

By experiments with a packing that contained 25 per cent APIEZON-L liquid phase on the support, for the separation of coal-tar aromatics, TA-CHUANG LO CHANG and KARR [10] have found that plotting the logarithms of the relative retentions of alkyl-benzenes against the boiling point of the respective compounds, the points for compounds having the same number of carbon atoms in the alkyl-chain will define a straight line. Checking this correlation with standard compounds, it was found to be valid also for PEGA, thus it afforded a method for the identification of the individual peaks. Since

in the case of the C_9 and C_{10} aromatics the number of isomers is very great and the boiling points of these but slightly differ, several compounds may exhibit common peaks. Therefore various data from the literature and infrared spectrophotometry were used in deciding which of the compounds are likely to be present and which one is present in the highest amount.

A great number of compounds being involved of which pure standards were lacking, no calibration for quantitative estimations could be resorted to, thus we fell back upon the method of 100 per cent, i.e. the respective peak areas in the entire chromatogram were established and expressed as percentages, considered as percentages by weight. In case of a homologous series of compounds using a flame-ionisation detector, the accuracy of this method is not worse than ±5 per cent [11].

After having identified the peaks, chromatograms could be made with temperature programming, since the change of temperature did not affect the sequence of alution of hydrocarbons of the same type, in our case that of aromatics. Thus also the peaks of lower boiling non-aromatics emerged distinctly on the chromatograms and the time of one run did not exceed 60 to 70 minutes.

Experimental conditions were as follows:

Detection: flame ionisation.

Length of column: 360 cm.

Diameter of column: 6 mm.

Temperature: from 60° to 120 °C.

Carrier gas flow: 50 to 60 ml of N_2 per minute.

Sample: 0.1 microliter.

On the basis of our results it could be established that the composition of samples from the same refinery but collected at various times did not show significant deviations.

Total aromatic content of samples from the Komárom Petroleum Co. varied between 55.5 to 59.3 per cent, these figures for samples from the Duna Petroleum Co. were at 44.9 and 48.7 per cent, that is by about 10 per cent lower than the former.

Highest and lowest values of C_9 and C_{10} aromatic compounds expressed as percentages of the total aromatic content in the Komárom samples were 44.2 and 47.1, respectively; the corresponding figures in the Duna samples were 39.9 and 45.7.

Data for three samples of the two refineries each are given in Table 1.

The average distribution of the aromatic compounds was found to be as shown in Table 2. Among the industrially utilizable aromatic compounds discussed, pseudocumene is to be found in greater quantities, about 10 per cent of the total aromatic content, while mesitylene accounts for 2 to 3 per cent, and durene for about 1 per cent.

Table 1

Distribution (percentage by weight) of aromatic compounds in various reformates

	Komárom samples			Duna samples		
	363/70	364/70	365/70	K-90/70	K-92/70	K-97/70
Total aromatics	57.5	55.5	59.3	44.9	48.7	48.4
C_6...C_8 aromatics	31.6	30.1	31.4	27.0	27.2	26.3
C_{9+} aromatics	25.9	25.4	27.9	17.9	21.5	22.1
Pseudo-cumene	6.0	5.6	6.2	4.6	5.5	5.6
Mesitylene	1.4	1.2	1.3	1.8	1.6	1.7
Hemimellitene	1.9	1.6	1.7	1.4	1.3	1.4
Durene	0.6	0.7	0.5	0.4	0.6	0.5

Table 2

Average distribution of aromatic compounds in samples from the Komárom Petroleum Co., and from the Duna Petroleum Co.

	Komárom samples	Duna samples
	percentage by weight	
Total aromatic content	57.4	47.3
C_6...C_8 aromatics	31.0	26.8
C_{9+} aromatics	26.4	20.5
Pseudo-cumene	5.9	5.2
Mesitylene	1.3	1.7
Hemimellitene	1.7	1.4
Durene	0.6	0.5

In a further stage of our analytical studies, exploratory runs were made with a 50 meter capillary column coated with Squalan (50 000 theoretical plates). As expected, separations were better than those obtained with packed columns. On the basis of literature data checked with some standard compounds, in one of the reformates 33 various alkyl-benzenes could be identified. The advantage of a capillary column was evident, since with a few exceptions, these compounds were eluted as completely resoluted peaks.

At Szőny the yearly output of reformates is 110 000 tons, at Százhalombatta some 250 000 tons are produced. For pseudo-cumene, calculated at

5 per cent, this makes 19 000 tons per year in Hungary. For mesitylene, only 5 to 6 thousand tons can be predicted.

The final conclusion could be drawn that the recovery of pseudo-cumene might be of interest since this can be achieved with a comparatively simpler technology than that of other aromatics, the quantities involved are appreciable, and the field of applications open to this compound is wide enough.

Recovery of pseudo-cumene, and its use in its own right, is a problem in the foreground of interest all over the world, thus efforts in this direction would certainly deserve consideration also in Hungary.

Summary

The concentration of aromatic compounds of potential industrial interest, present in reformates produced in Hungary was studied in order to estimate the amount to be expected from the recovery. Gas chromatographic method combined with infrared spectrometry has been developed for testing reformates.

It has been found that of the industrially utilizable C_{9+} aromatics the pseudo-cumene is present in highest concentration in the reformates tested, amounting to as much as 10 per cent of total aromatics, while these figures for mesitylene and durene are 2 to 3 and 1 per cent, respectively.

References

1. SCHLER, Ö.: Kőolaj és Földgáz **4**, 348 (1971) (in Hungarian).
2. RUDZIECKA, M.—SZNAJDER, J.—TRESZCZANOVICZ, F.: Premysl Chemiczny **46**, 57 (1967).
3. SOPOV, D.—DANKOV, S.: Neftekimia **4**, 798 (1965).
4. KHAN-MALEK, H.: Journ. Intern. Etude Méthodes Séparation Immédiate Chromatogr., Paris, 1961, p. 141. (Publ. 1962).
5. QUADER, S. A.—KRISHNA, M. G.: Brennstoff-Chemie **46**, 168 (1965).
6. MALINOVSKA, K.: Chem. Anal. (Warsaw) **9**, 353 (1964).
7. KOLBIN, M. A.—MAMAEVA, K. N.—ULANOV, A. N.: Neftepererabotka i Neftekimia Nauk, Tekn. Sb. No. 10. 17 (1965).
8. PATEROK, N.—PILARCZYK, H.: Chem. Anal. (Warsaw) **10**, 1227 (1965).
9. DEMENTEVA, M. J.—NAUMOVA, T. J.: Kim. i Teknol. Topliv i Masel **10**, 52 (1965).
10. TA-CHUANG LO CHANG—KARR, C.: Anal. Chim. Acta **21**, 474 (1959).
11. HALÁSZ, I.—SCHNEIDER, W.: Anal. Chem. **33**, 978 (1961).

Dr. László ACKERMANN
Dr. Imre SZEBÉNYI   Budapest XI., Budafoki út 8, Hungary
Dr. Etelka VERMES