THE ROLE OF NEW ANALYTICAL METHODS IN THE PRODUCTION OF AROMATIC HYDROCARBONS

By

L. VAJTA

Department of Chemical Technology, Technical University, Budapest

(Received December 9, 1969)

Investigations concerning hydrocarbon technology constitute a remarkable part of the research work done in the Institute for Chemical Technology of the Technical University of Budapest. These investigations are timely owing to the fact that the production of petrochemical feed stocks has just started in Hungary, raising of a number of chemical and technological problems.

We have realized during our research work that although the problems are of technological nature in accordance with the profile of our Institute, the work can only be effective if completed by fundamental research.

The nature of the necessary fundamental research varies with the problem to be solved. A great deal of analytical chemical research work is inevitable in connection with the development of chemical technology. The author of the present paper wishes to demonstrate by means of an example the great importance of the development and application of chemical analysis in chemical technological research. The work which will be dealt with in this paper has been made in close contact with other research groups which will be named later in this paper.

The fast development of the petrol industry in Hungary requires the organization and co-ordination of research. Accordingly, research work is done at three levels [1], in factory research laboratories, in industrial research institutes and in institutes of the Hungarian Academy of Sciences, or university institutes for fundamental research, though there are not sharp dividing lines, as will be illustrated by the examples given.

One of the important tasks of the petroleum industry in Hungary is to produce aromatic hydrocarbons from petrochemical raw materials [2]. According to the plans the large-scale industrial production of benzene,toluene and xylene mixtures on petrochemical basis starts in this year. The essence of the technology is that a hydrocarbon mixture containing high percentage of aromatic hydrocarbons is produced by the catalytic reformation of straight-run petrol, then aromatic hydrocarbons are extracted, and subjected to distillation. As the boiling points of meta- and para-xylene but slightly differ, they are separated by freezing out the latter (Fig. 1). Several analytical problems

Table 1

Report on the gas-chromatographic analysis of hydrocarbons

Place of sampling: Petrol reforming plant
Time of sampling: October 29, 8. 1969.
Sample: Straight-run petrol

Number	Component	Weight %	Note
1.	propane	—	
2.	i-butane	0.07	
3.	n-butane	0.47	
4.	2,2-dimethyl propane	—	
5.	2-methyl butane	1.04	
6.	n-pentane	1.63	
7.	2,2-dimethyl butane	0.04	
8.	2-methyl pentane+cyclopentane	1.40	ratio about 6 : 1
9.	3-methyl pentane	1.23	
10.	n-hexane	2.32	
11.	2,2-dimethyl pentane	0.05	
12.	2,4-dimethyl pentane	1.20	
13.	benzene	0.65	
14.	3,3-dimethyl pentane	0.06	
15.	cyclohexane	0.74	
16.	2 methyl hexane	1.44	
17.	2,3-dimethyl pentane	0.75	
18.	3-methyl hexane +1,1-dimethyl-cyclopentane	2.49	ratio about 6 : 1
19.	3-ethyl pentane	0.73	
20.	cis-1,3-dimethyl cyclopentane	0.32	
21.	trans-1,3-dimethyl cyclopentane	0.70	
22.	2,2,4-trimethyl pentane + 1,2-dimethyl cyclopentane	1.28	ratio about 1 : 1
23.	n-heptane	5.59	
24.	2,2-dimethyl hexane	0.05	
25.	cis-1,2-dimethyl cyclopentane	0.36	
26.	2,5-dimethyl hexane	0.35	
27.	methyl cyclohexane	3.06	
28.	2,4-dimethyl hexane	0.54	
29.	ethyl cyclopentane	1.08	
30.	2,2,3-trimethyl pentane	0.89	
31.	3,3-dimethyl hexane	0.10	

Number	Component	Weight %	Note
32.	toluene	1.72	
33.	unknown C_8 isomer	1.28	
34.	2,3-dimethyl hexane	0.55	
35.	2,3,3-trimethyl pentane	0.45	
36.	2-methyl heptane+3-methyl-3-ethyl pentane	2.49	
37.	4-methyl heptane	1.13	
38.	3-methyl heptane+3,4-dimethyl-hexane	2.52	
39.	unknown C_8 isomer	0.50	
40.	3-methyl-3-ethyl pentane	0.64	
41.	cis-1,3-dimethyl cyclohexane	1.53	
42.	trans 1,3-dimethyl cyclohexane	0.76	
43.	1,1-dimethyl cyclohexane	1.46	
44.	unknown C_8 isomer	0.19	
45.	n-octane	5.67	
46.	byciclo-heptane	1.22	
47.	2,2,4-trimethyl hexane	0.65	
48.	2,2,3-trimethyl hexane	0.33	
49.	2,2-dimethyl heptane	0.73	
50.	2,2-dimethyl heptane	0.48	
51.	1,2-dimethyl cyclohexane	0.42	
52.	2,6-dimethyl heptane + 4,4-dimethyl heptane	1.54	
53.	2,5 and 3,5-dimethyl heptane	1.22	
54.	ethyl-benzene	1.85	
55.	1,1,3-trimethyl cyclohexane	1.98	
56.	ethyl-cyclohexane	0.59	
57.	2,3,4-trimethyl hexane	0.33	
58.	meta-xylene	0.55	
59.	para-xylene	1.37	
60.	unknown C_9 isomer	0.65	
61.	2-methyl octane	0.51	
62.	unknown C_9 isomer	0.23	
63.	3-ethyl heptane	1.02	
64.	3,4-dimethyl heptane	0.83	
65.	3-methyl octane	0.52	
66.	ortho xylene	0.83	
67.	unknown C_9 isomer	1.23	
68.	unknown C_9 isomer	3.94	
69.	unknown C_9 isomer		
70.	unknown C_9 isomer		

Number	Component	Weight %	Note
71.	unknown C_9 isomer	3.94	
72.	unknown C_9 isomer		
73.	unknown C_9 isomer		
74.	unknown C_9 isomer		
75.	unknown C_9 isomer		
76.	unknown C_9 isomer		
77.	n-nonane	5.19	
78.	20 unknown C_{10} isomer	18.65	
79.	n-decane	1.56	
	Total	100.00	

Analysed by
Controlled by
Százhalombatta, October 30, 1969.

arose in connection with the research concerning this technology. Some of them could be solved by the application of the results of recent analytical investigations. In special cases, however, special research was required. These analytical problems arose in the following fields:

1. Determination of the hydrocarbon composition of straight-run petrol, reformed petrol, extract and raffinate obtained after extraction and distillation products.

2. Determination of hetero- and trace-elements in the products.

3. Studies on the catalyst in the new state and after use. Investigations in connection with the regeneration of the catalyst.

4. Methods for analysing waste waters from new plants.

The relevant methods of analysis have changed during the past few years. Methods which had earlier been used for research only became generally applied in industrial analysis. This development will be illustrated by some examples.

1. Determination of the hydrocarbon composition of straight-run petrol, reformed petrol, extract and raffinate obtained after extraction, and of distillation products

For estimating straight-run petrols, some time ago density, boiling-point curve, vapour pressure and water content, and — in the case of motor fuels — octane number were determined. Petrochemical applications demanded

Table 2

Report on the gas-chromatographic analysis of hydrocarbons

Place of sampling: Petrol reforming plant
Time of sampling: October 30, 8 h, 1(6).
Sample: Reformed petrol

Number	Component	Weight %	Note
1.	propane	—	
2.	i-butane	1.68	
3.	n-butane	2.50	
4.	2,2-dimethyl propane	—	
5.	2-methyl butane	3.90	
6.	n-pentane	2.64	
7.	2,2-dimethyl butane	0.76	
8.	2-methyl pentane + cyclopentane	3.56	ratio about 6 : 1
9.	3-methyl pentane	2.69	
10.	n-hexane	3.33	
11.	2,2-dimethyl pentane	0.21	
12.	2,4-dimethyl pentane	1.05	
13.	benzene	2.25	
14.	3,3-dimethyl pentane	0.45	
15.	cyclohexane	0.04	
16.	2-methyl hexane	2.50	
17.	2,3-dimethyl pentane	0.97	
18.	3-methyl hexane + 1,1-dimethyl cyclopentane	3.36	ratio about 4 : 1
19.	3-ethyl pentane	0.23	
20.	cis-1,3-dimethyl cyclopentane	0.50	
21.	trans-1,3-dimethyl cyclopentane	0.38	
22.	2,2,4-trimethyl pentane + 1,2-dimethyl cyclopentane	0.57	ratio about 3 : 1
23.	n-heptane	2.82	
24.	2,2-dimethyl hexane	0.32	
25.	cis-1,2-dimethyl cyclopentane	0.02	
26.	2,5-dimethyl hexane	0.03	
27.	methyl cyclohexane	0.59	
28.	2,4-dimethyl hexane	0.70	
29.	ethyl cyclopentane	0.18	
30.	2,2,3-trimethyl pentane	0.09	
31.	3,3-dimethyl hexane	0.24	

Number	Component	Weight %	Note
32.	toluene	9.22	
33.	unknown C_8 isomer	0.03	
34.	2,3-dimethyl hexane	0.50	
35.	2,3,3-trimethyl pentane	0.10	
36.	2-methyl heptane + 3-methyl-3-ethyl pentane	1.40	
37.	4-methyl heptane	0.84	
38.	3-methyl heptane + 3,4-dimethyl hexane	2.60	
39.	unknown C_8 isomer	0.09	
40.	3-methyl-3-ethyl pentane	0.15	
41.	cis-1,3-dimethyl cyclohexane	0.10	
42.	trans 1,3-dimethyl cyclohexane	0.12	
43.	1,1-dimethyl cyclohexane	0.14	
44.	unknown C_8 isomer	0.09	
45.	n-octane	2.10	
46.	bicyclo-heptane	0.03	
47.	2,2,4-trimethyl hexane	0.09	
48.	2,2,3-trimethyl hexane	0.17	
49.	2,2-dimethyl heptane	0.19	
50.	2,4-dimethyl heptane	0.32	
51.	1,2-dimethyl cyclohexane	0.15	
52.	2,5-dimethyl heptane + 4,4-dimethyl heptane	0.49	
53.	2,5 and 2,5-dimethyl heptane	0.84	
54.	ethyl-benzene	2.43	
55.	1,1,3-trimethyl cyclohexane	0.43	
56.	ethyl-cyclohexane	—	
57.	2,3,4-trimethyl hexane	0.06	
58.	meta-xylene	2.69	
59.	para-xylene	5.60	
60.	unknown C_9 isomer	0.30	
61.	2-methyl octane	0.52	
62.	unknown C_9 isomer	0.02	
63.	3-ethyl heptane	0.73	
64.	3,4-dimethyl heptane	0.82	
65.	3-methyl octane	0.65	
66.	ortho-xylene	3.67	
67.	unknown C_9 isomer	0.93	
68.	unknown C_9 isomer	2.26	
69.	unknown C_9 isomer		

Number	Component	Weight %	Note
70.	unknown C_9 isomer		
71.	unknown C_9 isomer		
72.	unknown C_9 isomer		
73.	unknown C_9 isomer	2.26	
74.	unknown C_9 isomer		
75.	unknown C_9 isomer		
76.	unknown C_9 isomer		
77.	n-nonane	1.08	
78.	20 unknown C_{10} isomer	15.24	
79.	n-decane	4.28	
	Total	100.00	

Analysed by
Controlled by
Százhalombatta, October 30, 1969.

the determination of the hydrocarbon composition as well. In connection with this problem gas chromatographic studies have been made in our Institute on fractions of different petroleum samples. The method which had earlier been used for research only, became widely used in industrial analytical laboratories. Thus, e.g. gas chromatography is used for the analysis of the raw material and reformate of the petrol reforming plant at the firm Dunai Kőolajipari Vállalat (Tables 1 and 2).

2. Determination of hetero- and trace elements in petrochemical products

Some time ago the technologist was interested in the determination of hetero- and trace-elements mainly in connection with the corrosion of metals. Tests such as copper-plate test and doctor test are no more used in petrochemical industry. New methods were required for the determination of the very important trace elements present in very small amount (5—10 ppb). In the refineries supplied with petroleum by railway tank cars lead contamination is of special importance. In our Institute activation analytical methods have been developed for the determination of trace elements [3]. At first, methods have been elaborated to the estimation of vanadium and aluminium in petroleum fractions. Trace elements were determined in various petroleum samples.

Other techniques which were elaborated at the institute Nagynyomású Kísérleti Intézet and other research institutes for petrochemistry, were also studied in our Institute and later accepted as factory standard at the trust Országos Kőolaj- és Gázipari Tröszt on the basis of these studies.

The determination of sodium and manganese in oil distillates by activation analysis has been worked out later in our Institute [4].

3. Studies on the catalyst in the new state and after use. Investigations in connection with the regeneration of the catalyst

Some years ago these investigations were restricted to the control of the effectiveness of the catalyst in pilot plant. During the studies the structure of the aluminium oxide carrier was determined by X-ray diffraction, the distribution of platinum by electron microscope.

The studies made in the Institute for Chemical Technology were concerned with the platinum catalyst on aluminium oxide carrier used in the production of aromatic hydrocarbons. By studying the changes connected with the reduction in the activity of aluminium oxide carrier [5], and changes in the distribution of platinum, the ageing of the catalyst could be followed and the state of the catalyst estimated from the technological point of view [6].

4. Methods for analysing waste waters from new plants

Some time ago absorption and adsorption methods were used for waste water analysis, which only resulted in total pollution of water.

As aromatic hydrocarbons are produced from the sulphur-containing petroleum from Romaskino, the analysis of wastes from plants working with sulphur-containing petroleum has been the main subject of our research. Ultraviolet spectrophotometry has been applied to the determination of sulphides, mercaptans and furfurol [7], and infrared spectrophotometry to that of hydrocarbons [8] in waste waters.

Naturally, the place and frequency of sampling and the analytical tasks have to be given in connection with the evaluation of the technology. These data must be complete, but it is not reasonable to demand an excessively great number of data, likely to increase costs and distract attention from the basic parameters. This principle is predominating in the research and also in the student education at our Institute. The scheme of continuous reforming equipments used for research and training is given in Fig. 2 (see also Table 3).

During the research work, in the field of chemical technology several analytical problems were encountered. Besides the techniques already mentioned, the use of thin layer chromatography is increasing. Investigations concerning this field are in progress at our Institute.

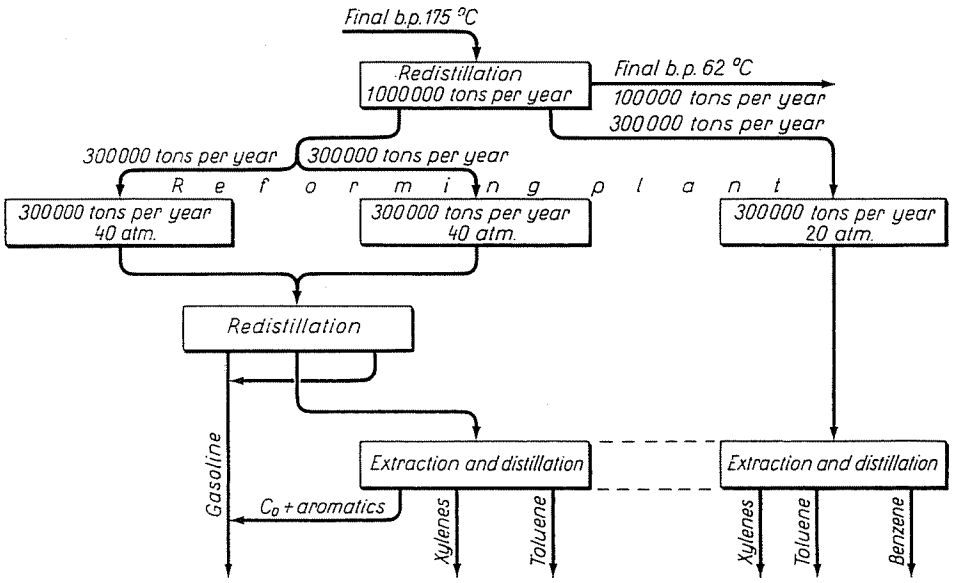

Fig. 1

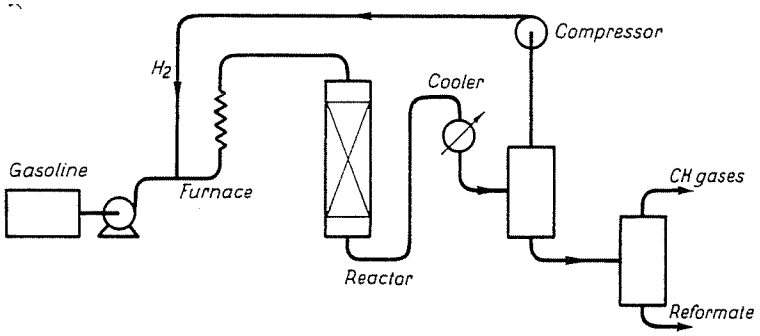

Fig. 2

Table 3

Sampling points of a laboratory reforming equipment

Sampling	Data to be determined
Petrol feed tank	density, distillation, hetero and frace elements, hydrocarbon composition
Hydrocarbon gases	hydrocarbon composition
Recycle gas	H_2, hydrocarbon composition
Reformate	density, distillation, hydrocarbon composition

The derivatograph has successfully been used for solving some complex analytical problems in connection with hydrocarbon technology [9, 10, 11].

One of the main characteristics of petrochemical technological research is the general application of modern analytical methods.

In this paper the author wished to demonstrate by some examples the close connection of chemical technological research with high-level analytical research. Technological research can only be successful if supported by the results of modern analytical chemistry.

Summary

A great number of analytical problems had to be solved during the research work done in the Institute for Chemical Technology in connection with hydrocarbon technology. The production of aromatic hydrocarbons on petrochemical basis necessitated research work for developing analytical methods and their application in chemical technology. These are the gas-chromatographic routine analysis of hydrocarbon mixtures, determination of hetero- and trace-elements by activation analysis, X-ray diffraction and electron-microscopic studies on catalysts, and determination of the impurities in waste waters by ultraviolet and infrared spectrophotometry.

Thin-layer chromatography and derivatography proved to be promising in solving analytical problems.

References

1. VAJTA, L.: Magyar Tudomány **9**, 569 (1962)
2. VAJTA, L.: Periodica Polytechnica Chem. Eng. **11**, 245 (1967)
3. VAJTA, L.—PÁLMAI, GY.—SZEBÉNYI, I.—TÓTH, G.: Periodica Polytechnica Chem. Eng. **11**, 275 (1967)
4. PÁLMAI, GY.—VAJTA, L.—SZEBÉNYI, I.—TÓTH, G.: Periodica Polytechnica Chem. Eng. **13**, 99 (1969)
5. VAJTA, L.—MOSER, M.—SZEBÉNYI, I.: Periodica Polytechnica Chem. Eng. **11**, 253 (1967)
6. VAJTA, L.—MÁNDY, T.—MOSER, M.—SCHAY, Z.—SZEBÉNYI, I.: Periodica Polytechnica Chem. Eng. **13**, 19 (1969)
7. VAJTA, I.—SZEBÉNYI, I.—HORVÁTH, M.—VERMES, E.: Periodica Polytechnica Chem. Eng. **10**, 309 (1966)
8. VAJTA, L.—SZEBÉNYI, I.—VERMES, E.: Periodica Polytechnica Chem. Eng. **11**, 235 (1967)
9. ADONYI, Z.: Periodica Polytechnica Chem. Eng. **10**, 325 (1966)
10. VAJTA, L.—ADONYI, Z.—VAJTA, L. S.: Acta Chimica Hung. **58**, 207 (1968)
11. VÁMOS, E.—ADONYI, Z.: Ipari Energiagazdálkodás **9**, 80 (1968)

Prof. Dr. László VAJTA Budapest XI., Budafoki út 8. Hungary