TECHNOLOGICAL RESEARCH ON THE PRODUCTION OF PETROCHEMICAL AROMATICS

By

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Nearly ten years ago I was given the task of heading a group of experts to develop a proposal for establishing the production of petrochemical aromatics in Hungary. This study [1] has been the basis of the development initiated later and still in progress. In this study we proposed to construct a facility consisting of six plants.

The conception of producing petrochemical aromatics does not refer to all aromatics produced on a petroleum basis; it only refers to the BTX aromatics (benzene, toluene, xylene, including ethyl benzene). Similarly, the extraction of the native aromatics content of the corresponding fractions does not fall under the heading of producing petrochemical aromatics.

In practice there are two possible ways for producing petrochemical aromatics: the production from catalytic reformates and the utilization of the liquid products of pyrolysis — in practice, of naphtha pyrolysis — for the production of aromatics.

The production of aromatics — while of great significance and fraught with numerous problems — represents only a relatively small fraction of the petrochemical material flow in petroleum processing.

The Shankey diagram prepared in connection with the central petrochemical target program (Fig. 1) is illustrative of these two above-mentioned variants of aromatics production. It also shows that the present problems of petrochemical development are based on the naphtha flow, a relatively small percentage of the processed petroleum into which the flow of liquid products of pyrolysis is recirculated.

At the time of this study we already were able to look back on considerable domestic research acivities; these served as the basis of our work. This research had been started surprisingly long ago at the Department of Chemical Technology of the Technical University Budapest. Already in 1919 Pfeiffer and Zechmeister [2] reported on obtaining aromatic products in the thermal decomposition of dynamo oil (spindle oil) and numerous other lubricating oils in the 550 to 675°C range; in their view these could be of value for producing the BTX aromatics.

In the Department of Chemical Technology research on aromatics was started with great impetus after World War II, both through the liquid pyrol-

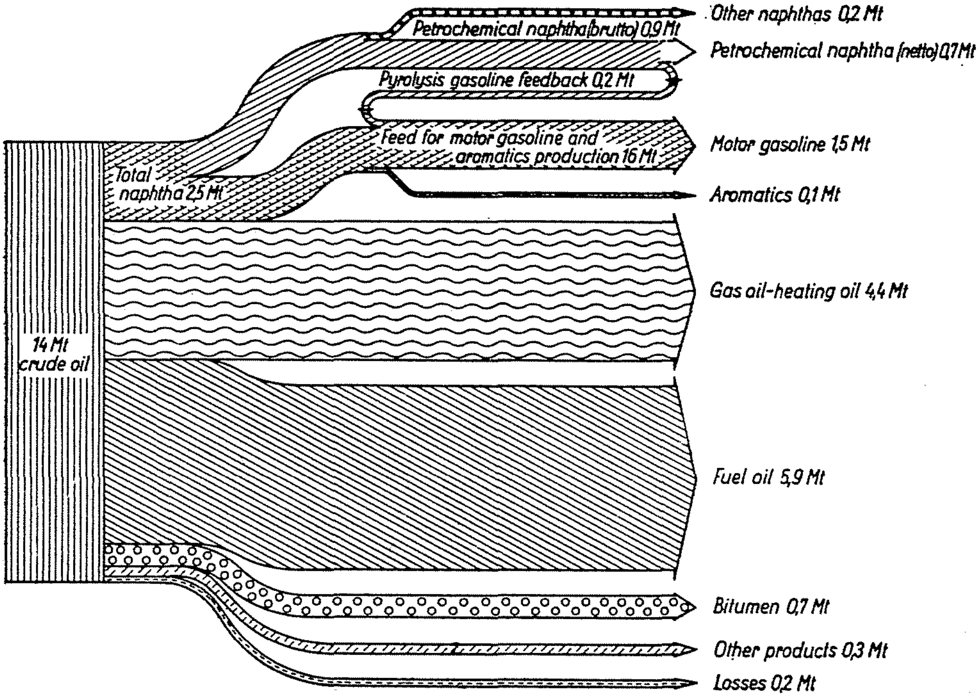

Fig. 1. Main material flows of the petroleum processing industry in 1980

ysis products [3] and by processing catalytic reformates [4—5]. The volume of this work was much greater in the Institute and later in the NAKI Institute than reflected by the still available publications.

However, it became necessary to modernize the directions of research with respect to the process of gasoline reformation with platinum catalysis which grew rapidly in importance after 1949.

The decisive aspect of the proposal for the domestic production of petrochemical aromatics was predominant import of technological plants and processes since generally accepted considerations disencouraged their domestic development.

Co-operation with the corresponding Soviet research institutes and the already initiated introduction of the reforming technology with platinum catalysts represented a valuable assistance in establishing our technology.

Although we imported the plants and processes for the domestic production of petrochemical aromatics we were continuously faced by many problems which required intensive research for their elucidation. These problems were extremely varied; here I should like to report on our experiences gained in some of them.

Research to gain information on the basic material

The problems connected with the basic material formed the first group of problems. Earlier a small number of tests — distillation properties, characterizing factor, corrosion properties, salt content etc. — sufficed to characterize the mineral oils and gasolines.

Today the determination of the chemical composition has gained in importance in petroleum and gasoline testing but the determination of individual components is attempted in the fractions with lower carbon atom numbers alone. With the increase of the carbon atom number the number of the possible components grows; this is a well-known fact. In paraffin hydrocarbons the number of possible isomers is 335 in the fraction up to C_{12}.

Therefore, from a technological point of view, the system of so-called group determinations is used. These methods have also progressed very definitely. In general, the fraction up to C_5 is tested separately on a chromatograph. In fractions containing C_6 and larger molecules the aromatic content is first analysed by the FIA method.

Previous to further analysis, the aromatic parts must be removed, either chemically by sulphonation with P_2O_5 and H_2SO_4 or by adsorption on silica gel [6].

In the obtained mixture of saturated CH hydrocarbons the naphthene content is determined by graphic statistical structure analysis, e.g. by the method of refraction intercept [7].

Tests with temperature programmed gas chromatographs have acquired even more significance [8]. They serve a double purpose: the determination of the real boiling point curves of these gasoline fractions, which can be of help in calculating the equilibrium distillation curve, and the determination of individual hydrocarbons in the substances freed of aromatics, at least up to C_9 (nonane). In higher hydrocarbons the individual hydrocarbons can be determined by mass spectrometry.

It might be said that this analysis needs to be carried out but once and this is not a very big task; however, all over the world and also in Hungary, the petroleum industry characteristically processes variable types of petroleum. Our processing industry has treated eight types of petroleum in the past three years. True, only three of these were significant but no identical chemical composition can be expected even when processing petroleum from the same field. Table 1 shows the gasoline yields of two important layers of the Romaskino petroleum, which is the most important for us, and the compositions of the gasolines [9]. The gasoline yield of the petroleum is very different between the two layers (24 and 17%). The hydrocarbon composition is even more divergent: naphthene hydrocarbon contents is 29%, and 23%, respectively. I stress the naphthene hydrocarbon content because the naphthene content is crucial from the point of view of engine fuel production and petrochemistry, since it can raise problems or yield advantages in further processing. If the gasoline is subjected to catalytic reforming the higher naphthene content is favourable; in the olefins-oriented pyrolysis it naturally raises technological problems. Considering the fact that not only Romaskino petroleum will enter the pipeline oil, constant fundamental analysis is required even if the gross composition of the oil does not change. The table also shows that not only do the two layers show a divergence but the percentage of ring structure compounds, that is of naphthene and aromatic compounds, increases towards the higher boiling points within one and the same gasoline fraction. Therefore, in testing a light gasoline fraction and a heavy gasoline fraction of the Romaskino gasoline (Table 2) one may find a naphthene content of 24 to 28% in the heavy gasoline and of 16 to 19% in the light gasoline. This is not a very significant difference in itself; however, when looking at the gas chromatogram of these gasolines with a view to the domestic production of benzene, the cyclohexane content is seen to be 3% in one case and 10% in the other.

Table 1

Hydrocarbon group composition of the gasoline fractions of Romaskino petroleum strata

Temperature limits of distillation, °C	Yield (petroleum), %	d_4^{20}	Hydrocarbon content in %		
			Aromatics	Naphthenes	Paraffins
Romaskino petroleum, Pasijsk stratum Initial boiling point:					
60	4.1	0.6380	—	—	100
60– 95	4.4	0.7000	3	26	71
95–122	3.1	0.7346	8	27	65
122–150	4.6	0.7532	13	30	57
150–200	7.8	0.7791	19	31	50
Final boiling point:					
200	24.0	0.7318	10	29	61
Romaskino petroleum, uglanosnyj stratum Initial boiling point:					
62	2.2	0.6478	—	—	100
62– 95	2.6	0.6958	1	18	81
95–122	3.0	0.7203	2	23	75
122–150	3.4	0.7427	9	23	68
150–200	6.2	0.7800	14	27	59
Final boiling point:					
200	17.4	0.7300	8	23	69

Therefore in our proposal for a facility consisting of six plants, the first plant in the technological order was a gasoline redistilling plant to furnish gasolines with a defined range of boiling points and a not very variable hydrocarbon composition for the processing plants.

Table 2

Analysis data for heavy and light gasoline fractions from Romaskino

Analytical data	Heavy gasoline fraction Basic material for Reformer I	Light gasoline fraction Basic material for Reformer II
Density g/ml	0.727—0.735	0.694—0.699
Index of refraction $n^{D}20$	1.4105—1.4130	1.3918—1.3943
Distillation test		
Initial boiling point °C	72—80	66—68
5% dist. °C	91—95	69—72
10% „	95—102	70—73
20% „	102—110	71—74
30% „	108—115	74—75
40% „	110—120	75—76
50% „	112—122	77—78
60% „	122—130	79—80
70% „	124—135	81—82
80% „	130—140	85—86
90% „	138—145	91—94
95% „	141—148	96—98
Final boiling point °C	150—160	103—105
Water content ppm	90—110	87—100
Sulphur content ppm	150—250	80—95
Lead content ppb	1—5	
Hydrocarbon group comp. (PONA) % by wt.		
Paraffins	62—68	74—79
Olefins	0.2—0.6	0.1—0.2
Naphthenes	24—28	16—19
Aromatics	8—10	5—7
Octane number F_1	47—51	55—58
Gas chromatographic analysis data		
Paraffins % by wt.		
C_3	traces	0.03—0.06
iC_4	0.1—0.2	0.06—0.09
nC_4	0.4—0.6	0.09—0.12
iC_5	0.8—1.1	0.1—0.5
nC_5	1.7—1.9	0.4—2.1
C_6	6—8	40.6—43.3
C_7	10—17	27—29
C_8	15—23	1.7—2.8
C_9+	11—29	—
Naphthenes % by wt.		
C_5	0.1—0.4	0.4—0.9
C_6	2.5—2.8	9.6—9.7
C_7	6.2—9.5	10.6—11.4
C_8	7.3—11.5	1.2—1.5
C_9	5.5—6.2	—
C_{10}	2—3	—
Aromatics % by wt.		
Benzene	0.9—1.2	2.3—2.5
Toluene	2.8—3.1	1.9—2.2
o.-xylene	0.4—1.1	—
Ethyl benzene + m.p.-xylenes	2.9—3.8	0.1—0.2
Higher aromatics	0.5—2.0	—
Average molecular weight	105—115	92—97

Research for determining the trace elements

Catalytic reforming necessitated to test the trace element content in our petroleum and petroleum products. Trace elements are substances which occur in petroleum in concentrations of 10 to 110 ppm or sometimes several times 10 ppb. The problem of hetero and trace elements is gaining in importance for petroleum and its products, from a technological and product application point of view. The problem of hetero atoms has been solved by the hydrogenating refining previous to catalytic reforming but the problem of trace elements requires our continued attention. According to our present knowledge, petroleum contains about twenty trace elements, in addition to corrosion

Table 3

Trace element contaminations in petroleum

Element	Petroleum	Corrosion	Catalyst
		contamination	
Aluminium	Á	—	Á
Arsenic			
Barium	R	—	—
Boron	R	—	—
Calcium	Á	—	—
Chlorine	Á	Á	—
Chromium	Á	Á	a
Cobalt	R	—	a
Copper	Á	Á	Á
Nickel	—	a	Á
Iron	Á	Á	—
Lead	a	Á	—
Manganese	R	—	—
Molybdenum	R	—	a
Fluorine	Á	Á	R
Nitrogen	Á	Á	—
Phosphorus	—	—	a
Silicon	Á	Á	Á
Sodium	Á	Á	—
Sulphur	Á	Á	—
Vanadium	Á	Á	a
Zinc	—	Á	—

Á	generally
a	occasionally
R	rarely

contaminations and components introduced during the processing from the catalysts [11] (Table 3).

Our research was directed towards gaining information on the trace element content of our petroleum and petroleum product grades. We have developed a method to test petroleum and gasoline for trace elements by an X-ray fluorescence method [12], also suitable for determining the lead content in ethylated gasoline. The tests included the determination of the V, Fe, Ni, Cu. Mn content of Hungarian petroleum grades.

Activation analysis was another method of research for trace elements [13]. With an extension of this method we were able to determine the trace element balance for V, Al, Na and Mn at the Duna Petroleum Plant [14] (Table 4).

Table 4

Distribution of trace elements, Duna Enterprise for Petroleum Processing

Sample	Vanadium, ppm	Aluminium, ppm	Sodium, ppm	Manganese, ppm
Petroleum	91	2.0	12.5	0.10
Light gasoline	0.01	1.2 1.5	3.0	0.07
Heavy gasoline	0.02	1.2	2.1	0.05
Petroleum	0.01	1.1	1.3	0.10
Light gas oil	0.02	1.0	0.7	0.03
Heavy gas oil	0.02 0.08	1.1	0.7	0.04
Mazout	163 162	2.6	21.8	0.15
Vacuum gas oil	0.02 0.05	0.9	0.14	0.04
Light POD	0.01	0.7	0.32	0.04
Medium POD	0.01	1.2 1.0	0.88 0.76	0.04
Heavy POD	0.99 0.65	1.3	0.78	0.03
Goudron	267 305	3.7 4.1	34 39	0.20 0.23

Research on reforming catalysts

Catalytic reforming is based on the reaction of dehydrogenation of naphthenes on a platinum catalyst — studied and developed by ZELINSZKY and co-workers [15] — and being an endothermal reaction with an increase of the molecule number, it could be carried out suitably at low pressures. In some reforming plants low pressure is actually used (regenerative type reforming plants) but here regeneration is required very frequently because of the coking of the catalyst. The investment costs are high and that is why we selected the semi-regenerative type with a medium hydrogen pressure (in spite of the reaction with an increase of the molecule number) because here the life of the catalyst between two consecutive periods of regeneration is prolonged.

The reforming processes with platinum catalyst introduced in Hungary employ two types of catalyst: one with 0.35 per cent by weight of platinum and another with a higher platinum content of 0.56 per cent by weight. Against expectations, the conversion properties of the catalyst with less platinum content were better.

To elucidate these conditions and obtain information on the catalysts, research was started on these substances. The platinum carrier of the reforming catalysts is gamma alumina. However, gamma-alumina is not simply a carrier, it also acts as a catalyst. The grade of reforming basic materials is progressively gaining in paraffins content, due to the quality modification of petroleum production. The gamma alumina as suitable catalyst carrier has the general properties of high specific surface, porosity etc. It also has to carry out isomerisation; to this end in its production acid centers must be established.

The possibility of establishing acid centers can be interpreted by crystal chemistry. Gamma alumina has a spinel-type crystal structure (Fig. 2). In the elementary cell of spinel ($Mg_8Al_{16}O_{32}$) 32 cubically arranged oxygen ions form the anion skeleton. The 16 aluminium ions are located on the octahedral positions between the layers and the 8 magnesium ions in the tetrahedra positions.

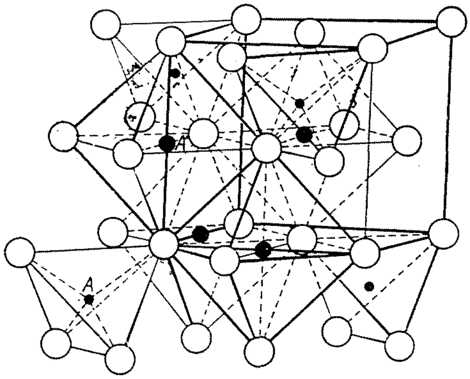

Fig. 2. The structure of spinel

The elementary cell of gamma aluminium oxide is formed by 32 oxygen ions and only 21 and 1/3 aluminium ions. Accordingly, vacancies exist in the ion grid of the catalyst. These vacancies are distributed statistically among the 24 catalyst ion positions and represent a structure porosity. In gamma aluminium oxide derived from boehmite the aluminium ions occupy mainly octahedral positions [16—18].

Gamma aluminium oxide contains varying amounts of strongly bonded water which is partly incorporated in the structure.

The surface concentration of aluminium ions can vary locally within wide limits. On spots with high aluminium concentration a defective co-ordination may also appear on heating, with an oxygen or hydrogen ion leaving the tetrahedral position. These defectively co-ordinated, aluminium-rich locations may act as electron acceptors, as Lewis acids and the proton of the bonded water may act as a protonic acid, a Brönstedt acid in the system.

These acid positions are only formed when the coverage by OH groups is very slight, a great amount of water acts as a poison on the catalyst.

The activity of the aluminium oxide catalyst in the isomerisation reaction can be increased when haloid ions also participate in the formation of the acid positions.

On a halogen-activated catalyst, reforming reactions proceed at lower temperatures. A similar good result is achieved by introducing halogens in the course of reforming or regeneration, e.g. in the shape of carbon tetrachloride.

The surface and the pore structure are very important in utilizing aluminium oxides as catalyst carriers. Aluminium oxides are aggregates of small primary particles (25 to 200 Å). The size and type of these particles determine the surface characteristics. The primary particles of gamma aluminium oxide are arranged irregularly. On prolonged heating the size of the primary particles grows. During initial growth the smallest particles diffuse into the adjacent particles and coalesce with them [20].

Platinum catalyzes the hydrogenating–dehydrogenating reactions. Its most important role is the catalysis of the dehydrogenation of naphthene hydrocarbons. In gasoline reforming in a suitable hydrogen atmosphere, platinum checkes the noxious deposition of coke, by hydrogenating the cracked products. In this way the catalyst life is increased. The catalysts contain a few tenths of per cent by weight of platinum. For this small amount of platinum to represent a sufficiency of active positions the diameter of the platinum crystallites must be small and uniformly arranged on the whole catalyst surface.

The catalyst testing methods mentioned in literature have the common feature to mainly indirectly testing the relationship between the structure and the process of exhaustion.

Our Institute wished to test the catalysts by a direct method, namely electron optical study. It shortly appeared that this task surpassed our resources and we asked for the assistance of MR. ELEMÉR SZÁDECZKY-KARDOSS, Academician, of the Geochemical Research Laboratory of the Hungarian Academy of Sciences; he and MR. GYÖRGY PANTÓ gave us every assistance in our work.

We also contacted several research stations abroad, among them the Tokyo laboratory of the JEOL firm and the electron optical laboratory of the Technical University of Graz.

We had to surmount many obstacles in our several years' research. For instance, the platinum crystallites of reforming catalysts are not only few in number but also small in size (only a few Å).

In the carrier itself — gamma aluminium oxide — the elementary particle has a size of about 100 Å. True, during use the platinum crystallites agglomerate and the irregularly arranged elementary gamma aluminium oxide particles coalesce. Our first task consisted in establishing a method of specimen preparation.

We used completely fresh catalysts and variously carbonized RD-150 C catalysts in our tests; they had been taken from the experimental reactor of the High Pressure Research Institute, with 2.6 to 23% carbon contents. We were able, accordingly, to study the morphology of largely exhausted catalysts.

We also studied the platinum distribution on the AP-56 catalyst.

In the course of our research the electron optical methods and measuring tools also developed. A complete logical sequence of direct testing was established, starting with the light microscope and proceeding through the electron microscope's field of resolution with the aid of the scanning electron microscope, and terminating by electron microprobe analysis.

The combined electron optical studies served to define the character of the pores, their size and morphology as well as the laws of microstructural composition of the catalysts and their variation on new and exhausted catalysts, i.e. as a function of their use. We determined the linear platinum content and its distribution, the linear distribution and amount of contaminants deposited on the catalyst, e.g. of carbon.

We shall follow the methodology of research not in the temporal sequence of research, but in the order of resolution of the electron optical methods. Fig. 3 gives a scanning electron micrograph of the catalyst RD-150, in ×100 magnification. Fig. 4 shows the same catalyst (×5000) with a very plastic presentation of the aluminium oxide aggregates and the pores. Because of the smaller resolution as compared with the electron microscope, Fig. 5 (×25,000) only detects the larger particles which compose the aggregates; in Fig. 6 (×45,000) the arrangement and morphology of the pores are readily discernible.

The electron microscopic shots at smaller magnifications show aggregates of primary particles of the gamma aluminium oxide carrier, arranged irregularly with various orientations. A new catalyst sample RD-150 is shown in Fig. 7 (×16,000); its primary particles are uniformly small. Fig. 8 (×16,000) shows the same catalyst after use with 2.6% carbon content; the primary particles are agglomerated. Fig. 9 shows the increase of the average particle

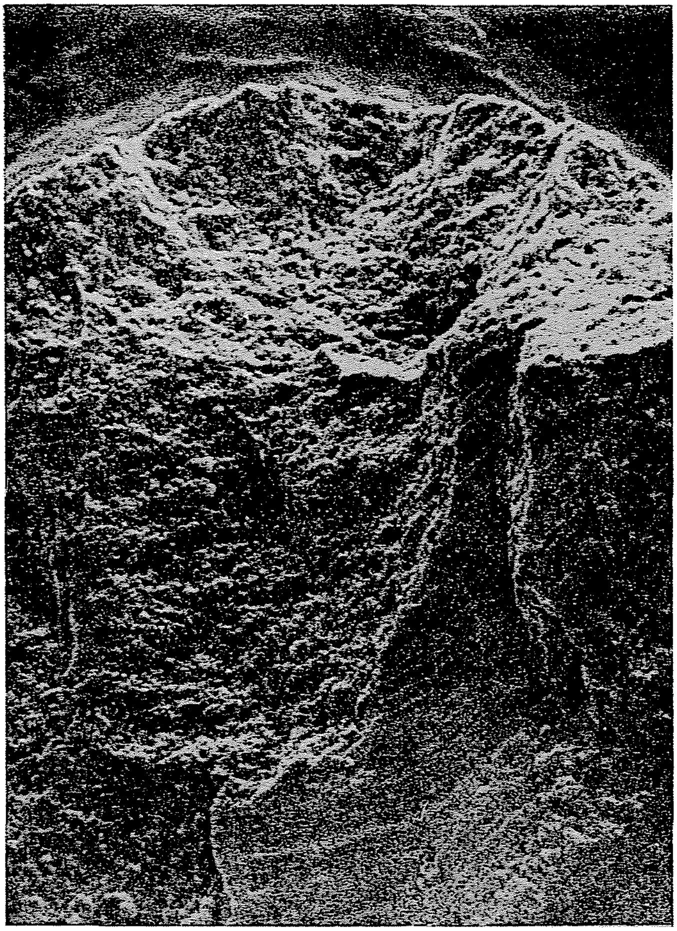

Fig. 3. Scanning electron micrograph of the catalyst RD-150 C. ×100

size in the full specimen section for 6.1% carbon content, after further use (×16,000).

In electron microscopic studies an increase of resolution permits a further investigation of the variation of the morphology of gamma aluminium oxide particles in the microscopic range [21].

Fig. 10 (×110,000) shows the microstructure of the fresh specimen, Fig. 11 a used specimen similarly to the previous series, and Fig. 12 an exhausted catalyst specimen with 6.1% carbon content. In the specimen used for a shorter period the size increase of the tabular grains is readily visible together with the evolution of the internal structure; in further use this evolution proceeds further.

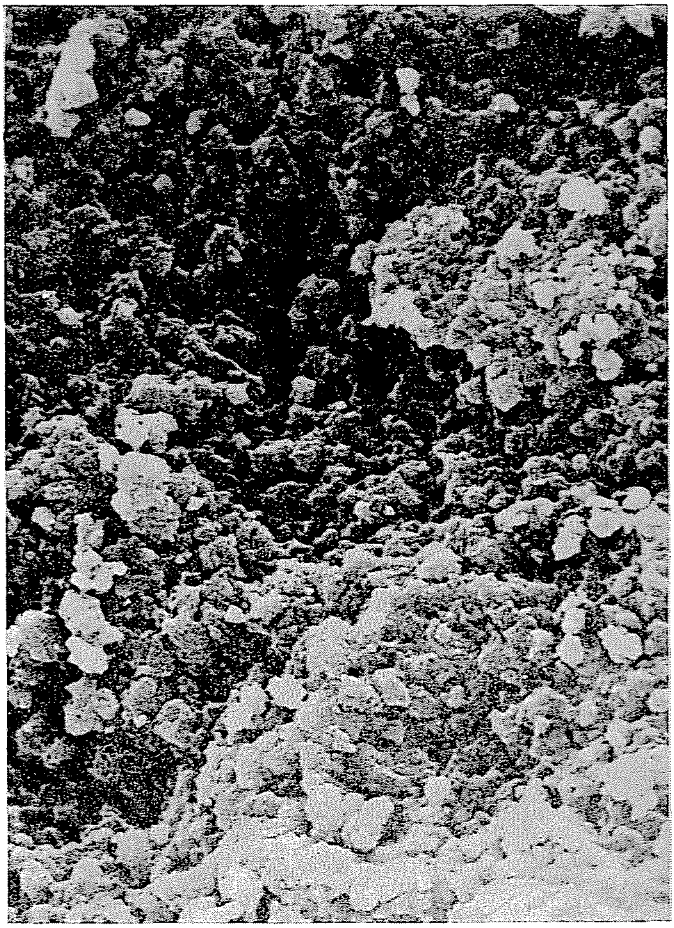

Fig. 4. Scanning electron micrograph of the catalyst RD-150 C. ×5000

At higher resolutions (×180,000) the platinum particles are discernible (Fig. 13). In Fig. 14 the platinum agglomeration during use appears. In these two shots platinum was also identified by X-ray micro-diffraction (Recordings of the University of Graz).

The resolution may further be increased by a photographic magnification of the electron microscopic picture (Fig. 15). An electron micrograph on a domestic Philips electron microscope shows the pore structure and the platinum particles (×1,000,000) [22].

Electron microprobe analysis is very suitable for comparing the two types of catalysts used in Hungary for platinum content and distribution (Fig. 16). Platinum concentration and its uniformity of distribution has been studied further on several catalyst grains (Figs 17, 18) [23].

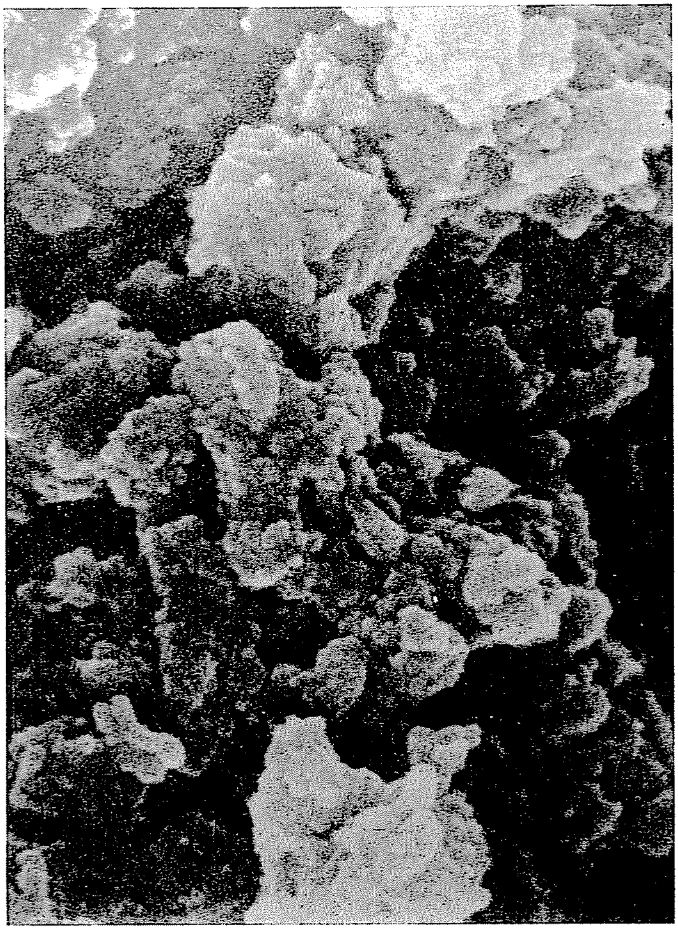

Fig. 5. Scanning electron micrograph of the catalyst RD-150 C. ×25,000

On the specimens from the experimental reactor, the carbon deposit can be checked also by electron microprobe analysis for carbon content and for its linear distribution (Fig. 19).

The evaluation of the results of direct electron optical studies is in good agreement with the results obtained in the High Pressure Research Institute by indirect methods — X-ray diffraction and chemosorption. The relationships discovered in this research are readily interpreted and utilized in plant practice. The apparent contradiction between the platinum contents and activities of the two catalysts have been solved by electron optical studies. A comparison of the conversion curves of the two catalysts in the same reforming plant has also supported our test results. Fig. 20 shows the conversion

Fig. 6. Scanning electron micrograph of the catalyst RD-150 C. 45,000 ×

curves of the catalyst with higher platinum content, in three adiabatic reactors connected in series in this system. Fig. 21 for the catalyst with smaller platinum content, indicates in the same reformer a more intensive conversion, a dehydrocyclization of the paraffin hydrocarbons and a lower paraffin and higher aromatics content of the reformate.

We are of the view that our method of studying catalysts by electron optical instruments could be developed and extended further.

Already at the inital stage of our catalyst research, the application of thermoanalytical methods has also been attempted. Unfortunately, the derivatograph at our disposal proved to be unsuitable to give results of sufficient sensitivity and accuracy showing the changes in the catalyst occurring

Fig. 7. Electron micrograph of the catalyst RD-150 C before use. ×16,000

at thermal effects. This was the reason why we have disregarded the further application of these methods for several years. Recently, in co-operation with the Department of General and Analytical Chemistry of the Technical University Budapest, from among the meanwhile further perfected thermoanalytical methods differential dynamic calorimetry has come into prominence. On the basis of preliminary experiments carried out on gasoline reforming platinum catalysts, we have established, that differential dynamic calorimetry (quantative DTA) is–in most cases– much more suitable for the study of the thermic processes taking place in catalysts, than the traditional methods because of its greater sensitivity and accuracy. This method already known from literature offers the following valuable advantages to us: it is quantitative,

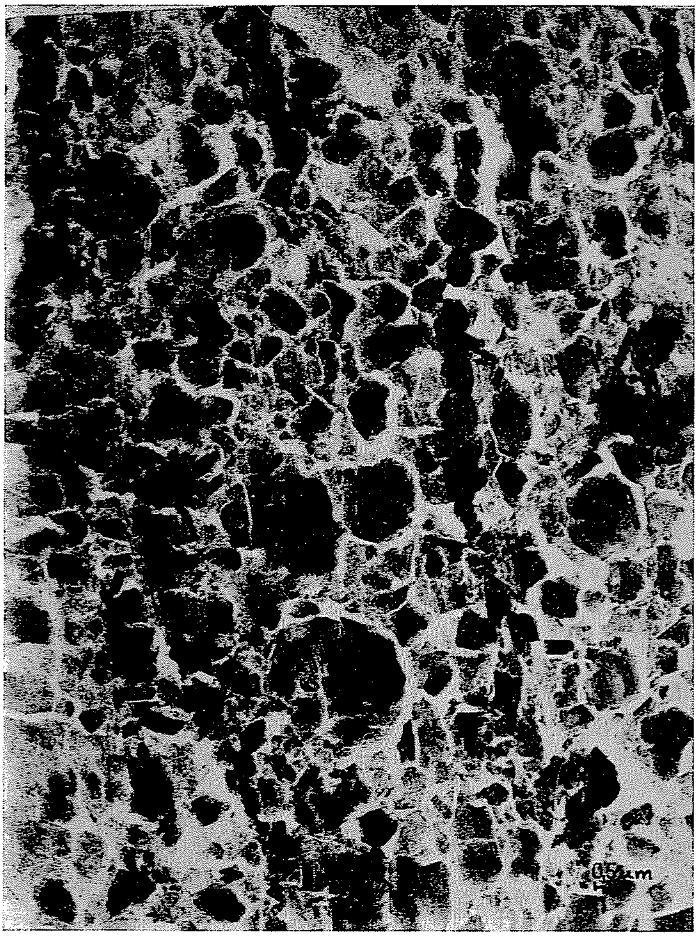

Fig. 8. Electron micrograph of the catalyst RD-150 C with 2.6% C content. ×16,000

its resolution is better than 10°/cm, its baseline stability is excellent, and in the small quantity of sample required for the measurement (1—10 mg), the thermal effects proceed more completely, thus the sensitivity of the method is very great. While the liberated amount of heat is calculated with a comparatively great error in case of DTA, this quantity can be measured here with a deviation of 2—3%. As an example, Fig. 22 shows the thermograms of

1. regenerated and chlorinated RD-150C,
2. used RD-150C,
3. fresh RD-150C catalyst samples.

The arrows in Fig. 22 point to places of the characteristic thermal transformations. We should like to use differential dynamic calorimetry mainly for great-accuracy thermal investigation of desulphurization catalysts.

Fig. 9. Electron micrograph of the catalyst RD-150-C with 6.1% C content. ×16,000

The collectively endothermal reactions can be characterized in the individual adiabatic reactors by the temperature profiles and the temperature decrease within the reactors.

Practically, the reactors are not perfectly adiabatic, they have a certain heat loss. Although this loss causes no technological problems with suitable thermal insulation, higher local heat losses may occur and these may lead to reactor-technological and reactor-structural problems. In such cases checks with infrared photography have proved valuable.

Catalyst research is still going on and it has served as a basis for developing regenerative and reactivating processes in combination with the technological tests, to produce significant progress of the complete technology [24].

Fig. 10. Electron micrograph of the catalyst RD-150 C before use. ×110,000

Fig. 11. Electron micrograph of the catalyst RD-150 C with 2.6% C content. ×110,000

Fig. 12. Electron micrograph of the catalyst RD-150 C with 6.1% C content. ×110,000

Fig. 13. Electron micrograph of the catalyst RD-150 C with 2.6% C content. ×180,000

Fig. 14. Electron micrograph of the catalyst RD-150 C with 6.1% C content. ×180,000

Fig. 15. Electron micrograph of the catalyst RD-150 C with 0.0% C content. ×1,000,000

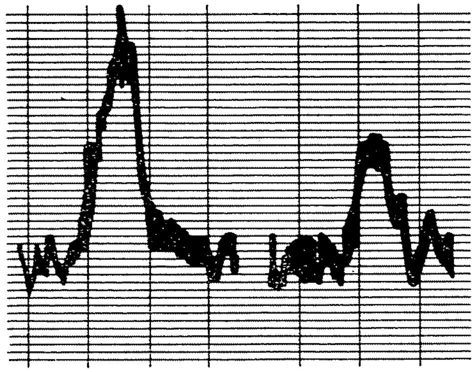

Fig. 16. Electron microprobe recordings of the Pt contents of AP-56 and RD-150 C

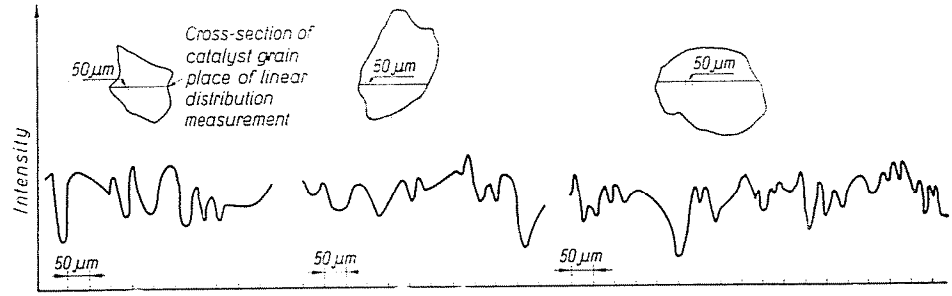

Fig. 17. Electron microprobe recording of the linear Pt content in AP-56

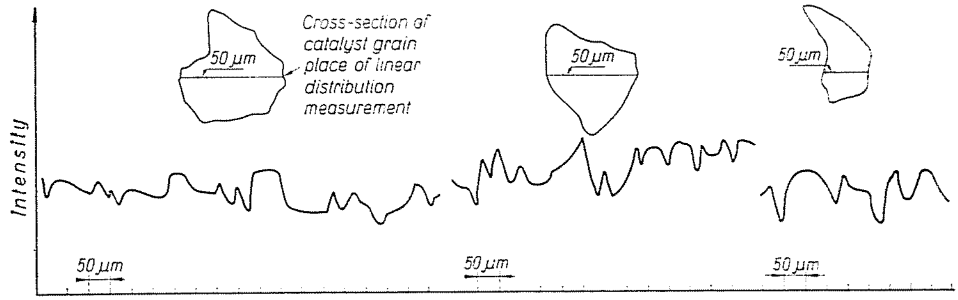

Fig. 18. Electron microprobe recording of the linear Pt content in RD-150 C

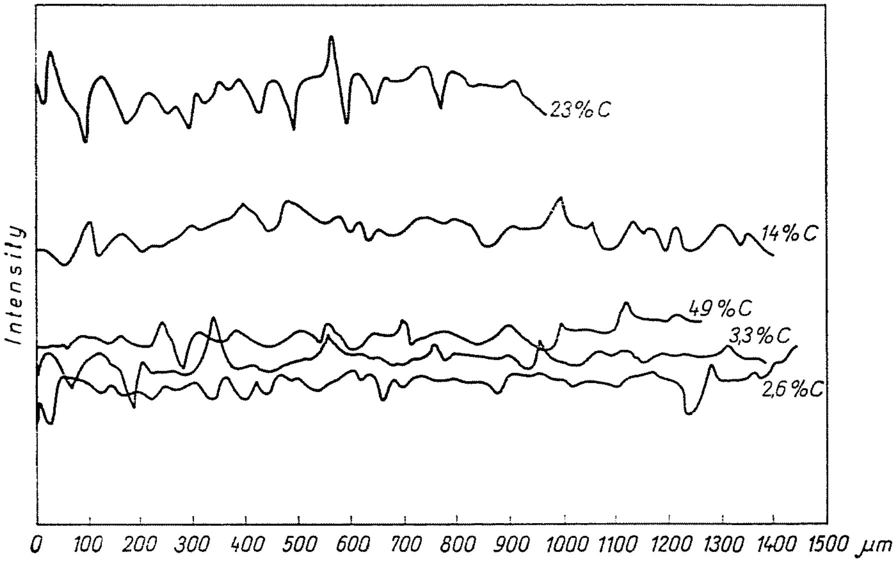

Fig. 19. C content of used RD-150 C catalysts, electron microprobe recording

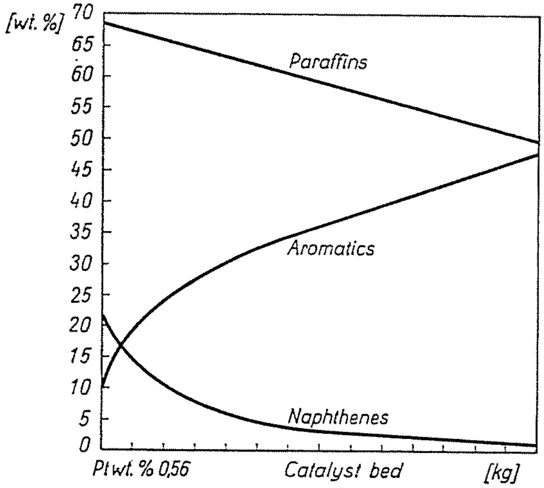

Fig. 20. Conversion with 0.56% by wt. platinum catalyst

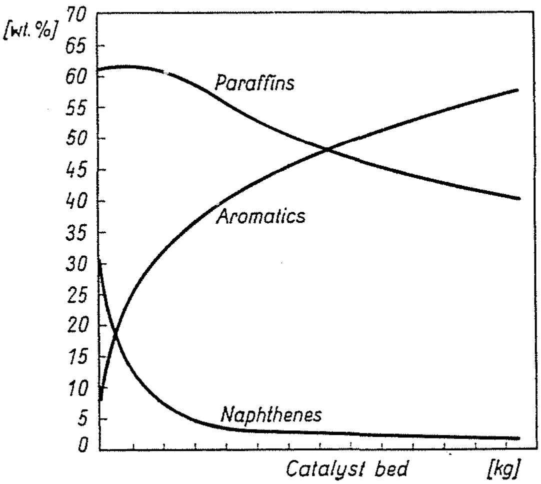

Fig. 21. Conversion with 0.35% by wt. platinum catalyst

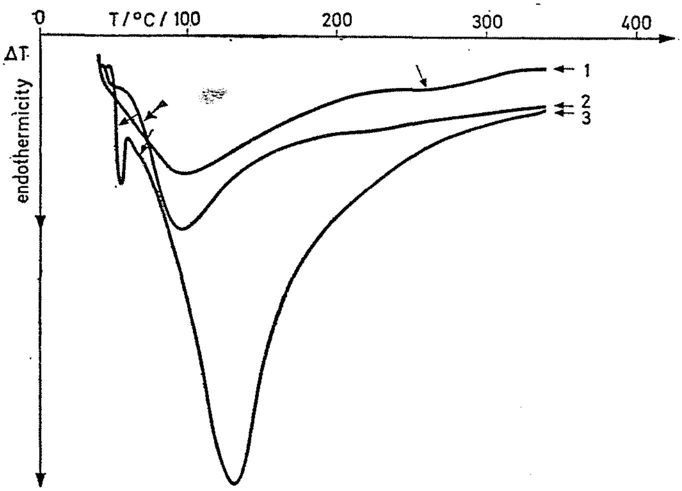

Fig. 22. Thermograms of gasoline reforming catalysts

The production of aromatics from pyrolysis-gasoline

In our research on catalytic reformation we kept in mind the work on the liquid products of naphtha pyrolysis. For research purposes we set up a continuous experimental facility for pyrolysis (since no domestic pyrolysis plant existed as yet). There we determined the amounts of liquid products (pyrolysis-gasoline) obtained from Romaskino gasoline; naturally the yields of the other products were measured also.

Pyrolysis-gasoline is, however, a by-product. The pyrolysis plants are optimized for the production of olefins. That is why we collected not only the experiences from our own equipment but also carried out further research on pyrolysis-gasolines purchased from pyrolysis plants abroad (in the GDR, in Czechoslovakia and Austria) [25].

The pyrolysis gasolines have a high aromatics content. They cannot be used — even as a component of motor gasoline — without removal of dienes, and previous to the extraction of aromatics, removal of olefins.

Therefore our research was extended to the composition and refining of pyrolysis gasoline [26, 27]. Although the significance of two-stage pyrolysis-gasoline hydrogenation was recognized already at the start of the tests, our research included some other refining possibilities for commercial pyrolysis gasolines, e.g. thermal polymerization, refining with phosphoric acid and sulphuric acid and the Gray process [28].

The *Gray Process* consisted of a catalytic refining of thermally cracked gasoline in the vapour phase; the activated bleaching earths catalyzed the polymerization of diolefins and about 10 to 15% polymer and a corresponding amount of gasoline with a corresponding potential resin content was obtained.

This research was carried out only for completeness sake. However, it proved useful after the start of domestic gasoline pyrolysis. The process was developed further and a montmorillonit from *Nagytétény*, activated with sulphuric acid, was used as catalyst; this yielded a suitable raffinate already in the liquid phase, at low temperatures (80°C) [29]. Pyrolysis gasoline refined in this way is a valuable bleinding component for motor gasoline.

Table 5

Aromatics percentage of pyrolysis gasolines

	Present refined pyrolysis gasoline, %	Mild pyrolysis	Severe pyrolysis
		refining by one-stage hydrogenation, %	
Benzene	40	24	39
Toluene	26	17	18
C_8 aromatics	8	9	7
C_6 to C_8 aromatics	74	50	64

Both the catalytic reformate and the pyrolysis gasoline can be used as basic materials in the production of aromatics. The aromatic hydrocarbons are separated from the mixture by solvent extraction. Only an olefin-free mixture may be used for extraction, expecially with the solvent diethylene glycol, in use in our plants.

The two kinds of origin cause significant differences in the quality of the basic material (Table 5).

Our present research is directed towards developing an optimal technology for the production of aromatics from pyrolysis gasoline.

The quality of petrochemical aromatics

The quality of petrochemical aromatics is much better than that of aromatic hydrocarbons produced from coal. Table 6 presents the qualities of the commercial scale benzene and toluene products of the Duna Enterprise of Petroleum Processing. According to chromatographic tests the benzene is 99.98 to 99.99% grade and toluene is of a similar purity. The absence of sulphur compounds is another great advantage of petrochemical aromatics; this is due to the desulphurization of the base gasoline before reforming.

Table 6

Quality data for benzene and toluene

Tested characteristic	Test method	Test data	
		Benzene	Toluene
Density 20°C	ASTM D-891	0.879	0.867
First drop °C	ASTM D-850	79.75	110.15
Dry point °C	ASTM D-850	80.15	110.80
Range of distillation °C		0.40	0.65
Point of crystallization °C	ASTM D-852	5.45	—
Level number	ASTM D-848	1	1.5
H_2SO_4 test	ASTM D-853	0.05	0.08
H_2S, SO_2 content	ASTM D-853	none	none
Corrosion test	ASTM D-849	negative	negative
Chromatographic composition:			
Benzene % by wt.		99.98	—
Toluene % by wt.		—	99.97
Paraffins % by wt.		0.02	0.03

Connection with the technology of motor gasoline manufacture

Technological research on petrochemical aromatics cannot be separated from the technology of motor gasoline manufacture [30]. The octane numbers

Table 7

Octane numbers of C_6 to C_8 hydrocarbons

Paraffins			Olefins		
Name	MON	RON	Name	MON	RON
Hexane	26.4	24.8	Hexane(2)	78	89
Heptane	0	0	Heptene(2)	—	70
2-methyl-hexane	45	—			
2,3-dimethyl-pentane	89	88.5			
2,2,3-trimethyl-butane	+0.18	+0.5			
octane	−17	−19	Octene(1)	34.7	38.7
2-methyl-heptane	23.8	21.7	octene(2)	56.5	56.3
2-2-dimethyl-hexane	77.4	72.4	octene(3)	68.1	72.5
3,3-dimethyl-hexane	83.4	75.5	octene(4)	74.3	73.3
2-methyl-3-ethyl-pentane	88.1	87.3	2,4,4-trimethyl-pentane		
2,2,3-trimethyl-pentane	99.9	+0.31		86.0	100
2,2,4-trimethyl-pentane	100.0	100.0			
2,3,3-trimethyl-pentane	99.4	+0.16			
2,2,3,3-tetra-methylbutane	103.0				

Naphthenes			Aromatics		
Name	MON	RON	Name	MON	RON
C_6 cyclohexane	78.6	83	Benzene	+0.73	100
C_7 methyl-cyclohexane	73	74.8	Toluene	+0.07	100
C_8					
propyl-cyclopentane	28.1	31.2	o-xylene	100	100
i-propyl-cyclopentane	77.2	81.1	m-xylene	100	100
ethyl-cyclohexane	40.8	45.6	p-xylene	100	100
1,2-dimethyl-cyclohexane	78.8	80.9	ethylbenzene	97.9	+0.2

of BTX aromatics are very favourable (Table 7). In the paraffin series the octane numbers of paraffins with seven carbon atoms vary from 0 to 89 but toluene with seven carbon atoms has an octane number of 100.

In Hungary, the research objectives for motor gasoline manufacturing technologies and aromatics production technologies must involve that the compression ratio of the engines in our rapidly increasing car park is still on the increase, i.e. we have to produce gasoline with increasing octane numbers, with a simultaneous reduction of lead alkyl addition.

The requirements on modern motor gasolines include a considerable percentage of aromatic hydrocarbons; this aspect must be considered today and in future.

Recent lines of research

As can be seen from Fig. 1, petrochemical activities are based essentially on a narrow gasoline fraction. According to the preliminary plans for petrochemical integration, the COMECON countries will increase their ethylene production 7 to 8 times to 1990, with an increase of petroleum processing to 250 to 300%.

It is a very dangerous situation when an extraordinarily widely branching industrial activity is based on a raw material represented by a narrow, strictly defined range; one may be exposed to the lack of this basic material or to considerable price increases.

It seems self-evident that research should be extended to the use of higher molecular products as row materials, but not forgetting the natural gas. Some decades ago the Reppe synthesis formed the base reactions of the organic synthetic large-scale operations and acetylene chemistry is likely to occupy again a certain restricted position for a prolonged period.

On the basis of these considerations and from the general conclusion apparent in chemical technology that the limits of parameters develop very rapidly, our Institute has taken up plasma reactor studies at extremely high temperatures (2 to 3000°K) to gather some fundamental knowledge in case the above-mentioned problem should be raised.

The Presidium of the Hungarian Academy of Sciences discussed last year the situation of organic chemical research in Hungary and has arrived at some decisions. These refer to petrochemical research and the following formulation is used in this respect: "Due to the correct conception of buying licences for the bulk of industrial petrochemical technologies from abroad, fundamental petrochemical research is restricted in its scope as compared with the previous plans and its directions are modified." The conclusions embodied in this resolution show the experiences gained in the production of petrochemical aromatics. The fundamental research results have within a short period contributed to the elucidation of technological problems; the research which initially was only intended to discover the causal connections soon yielded development results. In the plants built for the production of petrochemical aromatics the research results permitted achievements much superior to the ratings guaranteed by the equipment producers. Today our research results contribute to technological progress at the vendors' of the technology [31, 32]. The economic success of these results is very considerable, but instead of reckoning up the millions of forints I consider it more important to declare that this research really turned the purchased technological complex into our own, and transformed the production of petrochemical aromatics into an organic part of the Hungarian science of chemical technology which is capable of independent developments.

It was also my task to organize the widely branching research. The competent research institutes — the Hungarian Oil and Gas Research Institute, the High Pressure Research Institute — the plant research stations, technologists and the producing plants themselves actively participated in this work; this is of course indispensable in technological research.

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Summary

Scientific research in the field of the production of petrochemical aromatics has a long history in Hungary. With the commencement of the production of aromatics this subject has much grown in importance.

Research has been going on to determine the hydrocarbon structure of the basic materials and their trace element contents. The direct testing of catalysts of the platinum type by electron optical methods (scanning electron microscopy, electron microscopy and electron microprobe analysis) is a novel method. Its results show a good agreement with the results of classical indirect testing. Our research was also extended to the production of aromatics from pyrolysis gasoline.

Finally, the complex problem of aromatic hydrocarbons and motor gasolines with high octance numbers is discussed.

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* In Hungarian
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