PRODUCTION OF AROMATIC HYDROCARBONS ON A PETROCHEMICAL BASIS

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The raw materials for petrochemical processes are supplied by the petroleum and gas industries. Natural products form one part of these raw materials, the other part consists of products, or by-products of petroleum processing.

Aromatic hydrocarbons were produced in the past by high temperature coking of coal. An ever growing importance is now accorded to aromatic compounds manufactured from petrochemical products.

The task set before the Hungarian petroleum processing industry is the realization of the manufacture of aromatic products on a basis of petrochemical raw materials. In order to study this question it was advisable first to review the basic materials that the petroleum and gas industries were called to furnish for the chemical industry. The standing committees for Petroleum and Gas Industrie of COMECON have composed a list of such raw materials, by-products and products (cf. *Table 1)*. As is shown in this Table, from the point of view of the manufacture of aromatic compounds the hydrocarbons with 6, 7 and 8 carbon atoms can be considered as raw materials, i.e. the processing of the light gasoline fraction will provide these raw materials.

When basic stocks of petroleum processing are considered as quantities available then it is to be seen that petroleum to be processed according to the third and fourth Five Year Plans will come from abroad in continuously increasing quantities (cf. *Table 2)*.

Thus, imported crudes must be considered first. The crudes delivered through the Friendship pipeline are Romaskino type oils, for which distillation equilibrium curves [2] are shown in *Figs 1* and *2*. *Table 3* shows the hydrocarbon composition of the fraction between first boiling point and 200 °C of Romaskino crudes [3].

The data of this Table show that the content of aromatic compounds in the gasoline of Romaskino origin is 13.39 per cent but only 4.1 per cent is the proportion of the C_6 and C_8 aromatic compounds present. Therefore, it is imperative, from the point of view of production of aromatic substances, that the naphthene hydrocarbons be converted through dehydrogenation into

Table 1

Basic substances, by-products, and products manufactured by the petroleum and gas industries for utilization by the chemical industry

Number of carbon atoms	Paraffins		Olefins		Naphthenes	Aromatic compounds
	n	i	n	i		
1	methane					
2	ethane		ethylene			
3	propane		propylene			
4	butane	butane	buthylene	buthylene		
5	pentane	pentane				
6	—	—	—	—	cyclohexane	benzene
7	—	—	—	—	—	toluene
8	—	—	—	—	—	xylenes and ethyl-benzene
9, and more			gasoline for pyrolysis			
9, and more			petroleum			
9, and more	paraffin					
9, and more		other liquid products				

aromatic structures. The naphthene content of the gasoline fraction is 27.97 per cent, of which round about 10 per cent is composed of C_6 and C_8 hydrocarbons. Finally the n-heptane content, present as 3.89 per cent, must not be forgotten as this too can be considered as a basis for aromatic compounds, these being obtainable from it through dehydrocyclization.

Table 2

Petroleum processing, in million metric tons per year

	1965	1970	1975
Hungarian	1.8	2.0	2.5
Imports	2.1	4.0	6.5
Total to be produced	3.9	6.0	9.0

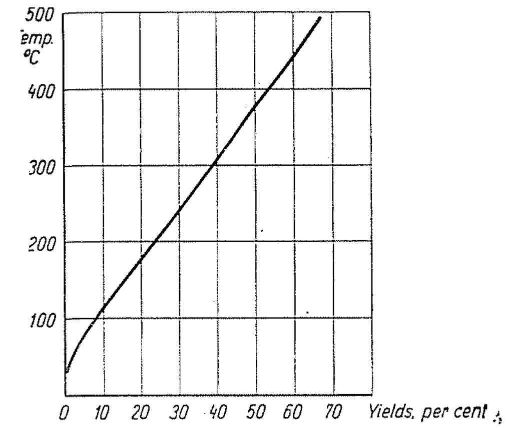

Fig. 1. Romaskino, devonian crudes from D_1 and D_2 horizons. Equilibrium distillation curve

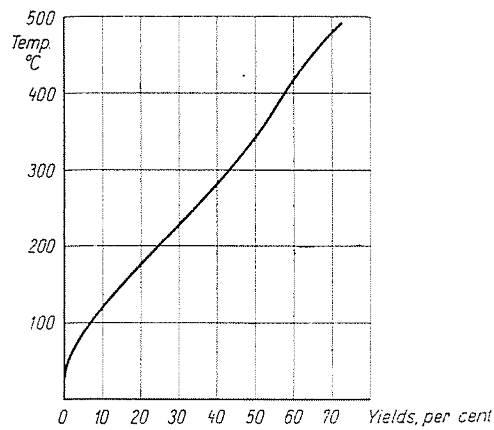

Fig. 2. Romaskino, devonian crude from D_3 horizon. Equilibrium distillation curve

Having taken stock of these raw materials, production of aromatic substances is envisaged in two refineries in Hungary.

Manufacture of aromatic compounds at the Dunai Kőolajipari Vállalat (Danube Refining Co.)

If 6 million tons (metric) of Romaskino type petroleum are processed by the Danube Refining Co., then about 180,000 tons of BTX aromatics might be produced. The yields to be expected are shown in *Table 4.*

Table 3

Hydrocarbons in the gasoline fraction between first boiling point and 200 °C from Romaskino oil

Hydrocarbon	Per cent of gasoline
1. Aromatic compounds	13.39
Benzene	0.43
Toluene	1.14
Xylenes, and ethyl benzene	2.59
C_9	3.62
C_{10}	2.97
C_{11}	2.64
2. Naphthenes	27.97
cyclo-Pentane	traces
Methyl-cyclo-pentane	1.87
cyclo-Hexane	0.63
Dimethyl-cyclo-pentanes	1.85
Methyl-cyclo-hexane	4.34
Trimethyl-cyclo-pentanes	1.50
Dimethyl-cyclo-hexanes	2.34
C_9	5.60
C_{10}	4.14
C_{11}	3.40
higher than C_{12}	2.30
3. Paraffin-hydrocarbons	58.64
i-Pentane	0.35
i-Hexanes	3.93
i-Heptanes	3.80
n-Pentane	2.15
n-Hexane	0.98
n-Heptane	3.89
n-Octane	5.43
C_9	6.52
C_{10}	7.88
C_{11}	8.48
C_{12}	8.68
higher than C_{12}	6.55

Table 4

Division of the close fractions of Romaskino gasoline

Temp. of separation, °C	Yields, % by weight	Quantity of straight run gasoline won from 6 million tons of crude oil
First drop ... 62	2.7	162.000
62...105	4.6	276.000
105...140	5.3	318.000
140...175	5.5	330.000

In view of the above figures, the yield of aromatic compounds can be expected to be the following:

Benzene	30.000 tons
Toluene	60.000 tons
o-Xylene, p-Xylene, Ethylbenzene	30.000 tons
m-xylene	45.000 tons

Reforming will be carried out in three reforming units each of 300.000 tons capacity; the technological flow sheet is given in *Fig. 3*. Attention should be paid to the saturation reactor marked (17) provided for the elimination of trace quantities of unsaturated compounds. The stock to be processed in the reforming plant will be made available by secondary re-distillation of 1 million ton per year capacity. Two reforming units will be operated at 40 atm, the third, the benzene producing unit, at 20 atm. Aromatic compounds will be won by extraction with diethylene glycol from the reformate; benzene, toluene, and the mixture of xylenes will be won by fractionation [4] (cf. *Fig. 4*). The first reforming plant will be put into operation in 1968, together with the extraction of the aromatic compounds. In this plant the catalyst AP—56 of U.S.S.R. origin will be used; for relevant data cf. *Table 5*.

Several aromatic compounds will not be available in amounts to satisfy demand in Hungary, some will be produced in excess of demand. Thus e.g. toluene will be produced several times in excess, whereas production will furnish less benzene than is needed. Therefore, the establishment of a desalkylation plant of 30.000 tons capacity is the subject of a study. The separation of xylene isomers will be carried out in the conventional way; o-xylene, ethylbenzene, and m-xylene, p-xylene mixtures, respectively, will be fractionated, p-xylene will be separated by freezing.

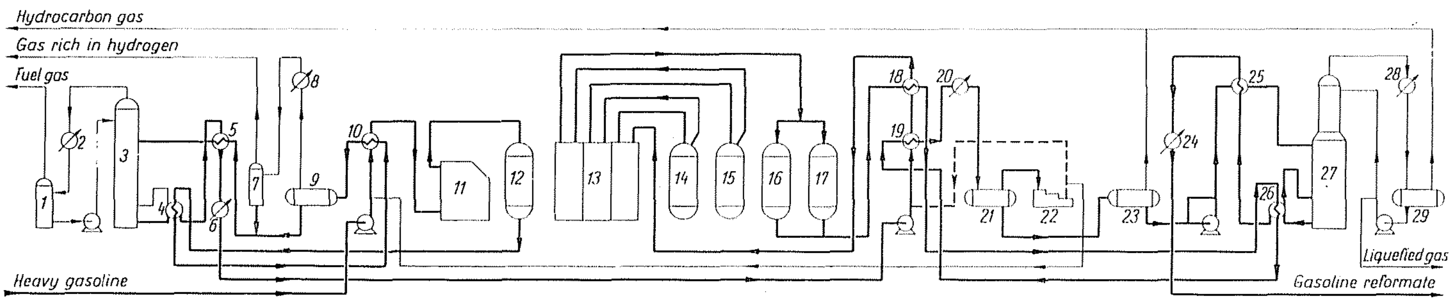

Fig. 3. Flow sheet of the reforming plant

1 Reflux tank
2 Condenser
3 Boiler column
4 Reboiler
5 Heat exchanger
6 Condenser
7 Cold separator
8 Condenser
9 Hot separator
10 Heat exchanger
11 Tubular oven
12 Desulphuration reactor
13 Tubular oven
14, 15, 16, (17) Reforming reactors
18, 19 Heat exchangers
20 Condenser
21 High pressure separation
22 Circulation compressor
23 Low pressure separation
24 Condenser
25 Heat exchanger
26 Reboiler
27 Stabilizer column
28 Condenser
29 Reflux tank

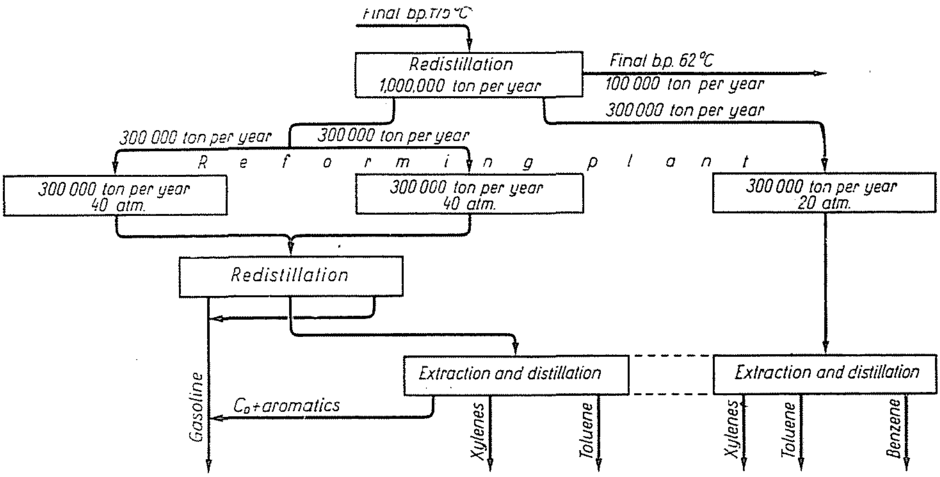

Fig. 4. Scheme of production targets of aromatic hydrocarbons and of motor benzine, in the case of the capacity increase to 6 million tons per year of the Dunai Kőolajipari Vállalat.

Table 5

Results of tests with Catalyst AP-56. U.S.S.R.

Shape of particles	rodlets
Dimensions (diameter and length)	2.9 by 5.6 mm
Specific surface, m^2 per gramme	165
Weight per volume, kg per litre	0.660
Paraffin content, per cent by weight	0.56
Fluorine content, per cent by weight	0.3
Chlorine	nil
Iron	0.017
Na_2O	0.006
Moisture heated to 1200 °C	8.3

Production of aromatic compounds at the Tiszai Kőolajipari Vállalat (Tisza Refining Co.)

Scheduled for a start after 1975, another 6 million ton refinery capacity is planned for the processing of Romaskino crudes. This refinery will be operated in close technological contact with the TISZA Chemical Combine. We think that the 62...105 fraction, the benzene fraction, about 280.000 tons per year, will be the pyrolysis basis of the Tisza Chemical Combine (TVK); this makes the production of about 100 to 110 thousand tons of ethylene possible. The about 60 to 80 thousand tons of green oil will be returned to the refinery where it will undergo hydro-refining and will be processed, through extraction with diethylene glycol, or with sulfolan, to benzene. In a catalytic reforming unit and a diethylene glycol or sulfolan extraction unit the toluene-xylene fraction will be processed to aromatic products. After the separation of the aromatic products, the complete separation of the xylenes is contemplated. From the aromatic compounds, toluene and m-xylene will be, initially, added to gasoline to raise its octane rating, the other products i.e. benzene, o-xylene, p-xylene, ethylbenzene will be available as raw materials of the chemical industry.

Summary

From a comparison of the technologies of the two Hungarian refinery plants it can be gathered that whereas the Duna Refining Co. will use the reforming process for the production of aromatic compounds, the Tisza Petroleum Co. will resort in part to reforming and in part to pyrolysis and processing of pyro-condensates. The total production of aromatic compounds of the two plants with a 300.000 ton desalkylation unit included, will yield, when operated at full capacity, the following:

Benzene	80.000 tons
Toluene	90.000
o-Xylene	24.000
Ethylbenzene	20.000
p-Xylene	16.000
m-Xylene	90.000

As is to be seen from the foregoing, aromatics production planned for the petroleum industry will utilize the relevant results of Hungarian research effort in this field.

References

1. Minutes of the XXII. Session. COMECON Standing Committe for Petroleum and Gas Industries.

2. N'efti S. S. S. R. Gos. Nauchno-T'ekhnichesko'e Izd., Leningrad 1958, pp 446—447.

3. loc. cit. pp 299.

4. VAJTA, L.: Development of the manufacture of petrochemical primary substances in Hungary. Magyar Kémikusok Lapja **5**, 27 (1966).

5. VAJTA, L., SIKLÓS, P., POZSGAI, T.: Studies on the determination of yields of pyrolysis gazoline in the production of ethylene. Chem. Eng. **9**, 145 (1965).

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