REFORMING OF NAPHTHA FRACTIONS ON A PLATINUM-RHENIUM CATALYST

By

I. Szebényi, G. Széchy and L. Isaák*

Department of Chemical Technology, Technical University, Budapest

Bimetallic platinum-rhenium type catalysts have been used in catalytic reforming on a commercial scale since 1969. Their advantages are already well-known and their use becomes more and more widespread [1]. Platinum-rhenium type catalysts have been introduced also in Hungary. The revamped catalytic reforming unit at the Komárom Refinery Co. started production with a bimetallic (Engelhard E-601) catalyst, and the introduction of this type of catalysts is also planned at the Danube Refinery Co. [2]

With these developments in view, it has been aimed in this work at studying the possible yields of aromatics in laboratory scale reforming with the use of an industrial platinum-rhenium-catalyst (at the relatively low pressure made possible by this catalyst) from feedstocks of the three reforming units of the Danube Refinery Co.

Special attention was paid to the individual C_9 and C_{10} aromatic compounds, as some of these may become valuable petrochemical feedstocks [3, 4], and the long-range Hungarian plan for aromatics production takes also the separation and production of these compounds in consideration [5].

Our relatively short experimental runs do not give possibility for the study of the yield stability, but offer informations concerning the yields of the individual aromatics, especially those of C_9 and C_{10} aromatics.

The experiments were carried out on a commercial Engelhard E-601 platinum-rhenium catalyst in a "twin-reactor" (a small pilot plant apparatus) manufactured at the High-Pressure Research Institute [6]. This equipment differs basically from the commercial reforming technology — beside the several orders of magnitude in size — by that the reforming process occurs in a single isothermic reactor as against the series connected adiabatic reactors of a commercial reforming plant where reheating is also possible. In spite of this significant difference, the "twin-reactor" has been shown to give product compositions approaching those from commercial reforming operations and to suit studying the yields in catalytic reforming [6].

* Danube Refinery Co., Százhalombatta.

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Experimental

45 cc. of aluminium granules were placed into the lower part of the reactor where the feed is evaporated and heated to the desired temperature. Above the aluminium, 50 cc. (39.3 g) of the catalyst were filled in and the remaining volume of the reactor was filled with inert ceramic granules.

For the experiments electrolytic hydrogen was used. The oxygen contamination of the gas was hydrogenated on a Leuna 7748 palladium catalyst and subsequently dried on an Erszorb 4 molecular sieve bed (made by Erdő-kémia, Hungary). The catalyst filled into the reactor was activated in situ and pretreated according to the instructions of the manufacturer. The pretreatment was followed by an equilibration period of 80 hours consisting of feeding undesulphurized naphtha. The actual runs were begun after the equilibration period.

Equilibration was needed to moderate the high initial activity experienced with platinum-rhenium catalysts, manifest by reduced liquid product yields [7].

In the experiments, temperature and liquid hourly space velocity were varied as these parameters are relatively simple to control in commercial plants. The measurements were carried out at 470, 500 and 530 °C and at each of these temperatures at liquid hourly space velocities of 1, 2 and 3 vol/vol.hour. The pressure was maintained at 15 kp/cm², the hydrogen to hydrocarbon mole ratio at 5 : 1 in all experiments. The properties of the three feeds are listed in Table 1.

After adjusting the required values of temperature and space velocity, the apparatus was run for two hours at unchanged parameters to achieve stabilization of the system. The samples were always taken only after this period of stabilization. The samples were analyzed by gas chromatography. The individual C_9 and C_{10} aromatics were determined by the gas chromatographic method developed at the Department of Chemical Technology [8].

Results

The naphtha fraction boiling between 73 and 113 °C is reformed for the production of benzene and toluene at the Danube Refinery. The results of our reforming experiments carried out with this fraction are shown in Table 2.

Some of the results of the commercial reforming operations with the same feedstock at the Danube Refinery with a $Pt-Al_2O_3$ type catalyst are also shown in Table 2 for comparison.

The advantages of the reduced operating pressure and the use of the E-601 catalyst are clearly manifest. Comparison of the commercial results with those of the laboratory run carried out at 470 °C and space velocity 2 vol/vol. hour (meaning less severe reforming conditions both in terms of temperature and space velocity), shows the benzene and toluene yields to exceed by 4 and 6% by weight, resp., that of the commercial operation carried out with AP-56 catalyst.

Table 1

Feed properties

Density g/ml (at 20 °C)	0.708	0.748	0.747
ASTM Destillation, °C			
IBP	73	112	78
10%	78	120	104
50%	85	126	143
90%	100	138	172
EP	113	145	184
Hydrocarbon group composition			
(% by vol.)			
paraffins	73.7	64.4	61.8
naphthenes	22.1	26.0	27.5
aromatics	4.2	9.6	10.7
Hydrocarbon composition, (% by wt.)			
propane	0.0	0.0	0.0
n-butane	0.0	0.0	0.0
iso + cyclo-butanes	0.1	0.1	0.0
iso + cyclo-pentanes	1.6	0.1	0.2
n-pentane	1.8	0.1	0.3
iso + cyclo-hexanes	27.2	0.1	7.8
n-hexane	15.3	0.1	5.7
benzene	2.0	0.1	1.5
iso + cyclo-heptanes	30.2	9.1	10.3
n-heptane	14.5	5.3	5.3
toluene	3.2	3.6	1.5
iso + cyclo-octanes	2.7	32.1	8.4
n-octanes	1.1	15.7	4.1
ethyl-benzene	0.0	0.0	0.0
meta + para-xylenes	0.1	5.7	2.1
ortho-xylene	0.1	1.7	2.5
iso + cyclo-nonanes	0.3	18.7	12.4
n-nonane	0.1	5.2	7.7
iso + cyclo-decanes	0.0	2.3	12.6
n-decane	0.0	0.1	6.9
iso + cyclo-undecanes	0.0	0.0	4.2
heavier aromatics	0.0	0.1	4.9
n-undecane	0.0	0.0	1.6
Sulphur content, ppm	1	1	1

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Table 2

Reforming of naphtha fraction boiling between 73 and 113 °C

Laboratory reforming conditions
Pressure = 15 kp/cm²
Hydrogen-hydrocarbon mole ratio = 5 : 1
Catalyst: E-601

Commercial reforming conditions
Pressure = 20 kp/cm²
Hydrogen-hydrocarbon mole ratio = 5.4 : 1
Catalyst: AP-56

Type of reforming	Laboratory reforming									Commercial reforming
Temperature of reforming °C	470			500			530			485
LHSV, vol/vol. h.	1	2	3	1	2	3	1	2	3	1.8
Component	Yield percentage by weight of charge									
benzene	16.0	13.8	11.0	22.9	17.6	15.0	25.4	21.3	16.6	9.1
toluene	23.0	22.3	19.8	29.0	26.0	24.1	33.9	31.6	29.4	16.0
ethyl-benzene	0.8	0.6	0.6	1.0	1.1	1.1	1.6	1.5	1.6	1.0
para-xylene										
meta-xylene	1.4	1.2	1.0	2.1	1.9	1.8	2.9	2.6	2.3	
ortho-xylene	1.0	0.9	0.7	1.3	1.3	1.3	1.7	1.7	1.9	0.4*
Total C_8 aromatics	3.2	2.7	2.4	4.4	4.4	4.2	6.3	5.7	5.7	1.4
Total C_{9+} aromatics	0.3	0.2	0.2	0.4	0.4	0.6	0.5	0.6	0.7	
Total aromatics	42.5	38.9	33.3	57.3	48.4	43.8	66.2	59.1	52.4	26.5
C_{5+} yield	81.5	85.4	87.3	77.9	81.6	85.1	74.3	77.4	81.8	

* Summed amount of ortho-xylene and higher aromatics.

It is also clear from Table 2 that the yield of C_9 and higher aromatics is very small (practically insignificant) in these reformates. Consequently, the phenomenon that aromatics with a given number of carbon atoms are formed only from compounds having the same or a greater number of carbon atoms, can be observed in this case, too.

The laboratory results obtained by reforming the 112 to 145 °C boiling range fraction are summarized in Table 3. This fraction has been reformed on Engelhard E-301 catalyst at the Danube Refinery, for the production of toluene and xylenes. Comparing the laboratory results and the commercial reforming as for the previous fraction, the advantages of reduced operating pressure are clearly demonstrated. The yield of total aromatics obtained in commercial operation is about 4% by weight smaller than the yield from laboratory reforming performed at milder conditions (470 °C and 2 vol/vol.hour) than those of the commercial operation. This yield increase is originated mainly in the increase of the amount of C_9 and higher aromatics, while the amount of C_6-C_8 aromatics is about the same in the commercial operation and the laboratory run chosen for comparison.

The results of laboratory reforming show that with the use of the E-601 catalyst at operating temperatures above 500 °C it is possible to conduct the

Table 3

Reforming of naphtha fraction boiling between 112 and 145 °C

Laboratory reforming conditions
Pressure = 15 kp/cm²
hydrogen-hydrocarbon mole ratio = 5 : 1
Catalyst: E-601

Commercial reforming conditions
Pressure = 31 kp/cm²
hydrogen-hydrocarbon mole ratio = 5.2 : 1
Catalyst: E-301

Type of reforming	Laboratory reforming									Commercial reforming
Temperature of reforming, °C	470			500			530			485
LHSV, vol/vol. h.	1	2	3	1	2	3	1	2	3	1.8
Component	Yield percentage by weight of charge									
benzene	0.4	0.2	0.2	1.2	0.7	0.5	2.6	1.8	1.2	0.3
toluene	12.3	11.4	10.4	15.6	13.9	12.7	18.4	16.8	15.2	10.7
ethyl-benzene	5.7	4.9	4.9	5.3	5.7	5.8	4.5	6.1	5.3	20.0
para-xylene	5.6	4.0	3.9	7.4	6.5	5.4	7.7	7.0	7.0	
meta-xylene	13.4	11.2	10.0	15.6	14.4	13.2	16.2	16.0	15.8	
ortho-xylene	7.5	5.6	5.5	9.2	8.8	7.6	8.2	8.1	8.5	6.4
isopropyl-benzene	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.1	
n-propyl-benzene	0.5	0.4	0.5	0.5	0.5	0.5	0.2	0.4	0.4	
meta- and para-ethyl-toluene	3.7	2.8	2.7	4.0	4.1	3.9	3.3	4.0	4.2	
o-ethyl-toluene	0.7	1.0	0.6	0.6	0.8	0.9	0.4	0.7	0.7	
1,3,5-trimethyl-benzene (mesitylene)	1.6	1.1	0.8	2.1	1.7	1.4	2.0	2.0	1.7	
1,2,4-trimethyl-benzene (pseudocumene)	5.8	5.2	4.2	5.9	6.3	5.9	5.0	5.7	5.7	
1,2,3-trimethyl-benzene (hemimellitene)	1.3	1.1	1.0	1.1	1.4	1.4	0.8	1.1	1.3	
n-buthyl- and 1,3-diethyl-benzene	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
1-methyl-2-n-propyl-benzene	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	
1,2-dimethyl-4-ethyl-benzene + indane	0.5	0.4	0.4	0.5	0.5	0.5	0.4	0.4	0.5	
1,2-dimethyl-3-ethyl-benzene	0.1	0.1	0.1	0.1	0.1	0.1	—	0.1	0.2	
1,2,4,5-tetramethyl-benzene (durene)	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.1	
1,2,3,5-tetramethyl-benzene (isodurene)	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	
5-methyl-indane	—	—	—	0.1	—	—	0.1	—	0.1	
1,2,3,4-tetramethyl-benzene (prehnitene)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Total C_8 aromatics	32.1	25.8	24.3	37.4	35.4	31.9	36.7	37.2	36.6	26.4
Total C_9 aromatics	13.7	11.8	10.0	14.3	14.9	14.2	11.8	14.0	14.1	8.5
Total C_{10} aromatics	1.3	1.1	0.8	1.5	1.4	1.3	1.2	1.2	1.4	
Total aromatics	59.8	50.3	45.7	70.0	66.3	60.6	70.7	71.0	68.5	45.9
C_{5+} yield	82.5	86.5	88.9	78.3	82.2	85.7	75.0	78.1	82.0	

reforming operation at high space velocities without decreasing the yields of C_8 aromatics. This fraction gives already significant amounts of C_9 aromatics while the amount of C_{10} aromatics remains small, corresponding to the boiling range of the feed.

In the temperature range of 470 to 500 °C the distribution of the individual aromatics changes but very slightly, only the absolute yields of aromatics increase with increasing temperature. The dealkylation occurring at higher temperatures modifies this nearly constant aromatics distribution, but not significantly. The yield of C_9 aromatics slightly decreases at temperatures above 500 °C, if the space velocity is 1 vol/vol.hour.

Decreasing the space velocity from 2 to 1 vol/vol.hour the amount of C_9 aromatics does not increase further, but the yields of the aromatics with smaller carbon numbers still increase and thus the distribution of aromatics is shifted towards the aromatic hydrocarbons with less than 9 C atoms.

At 530 °C the effect of dealkylation is manifest at all the three space velocities studied: the amount of C_9 aromatics does not reach the values measured at 500 °C, in spite of the higher yields of total aromatics. At 530°C and at a space velocity of 1 vol/vol.hour not only the dealkylation of C_9 aromatics becomes significant but also that of C_8 aromatics starts.

In Table 4 the distributions of C_8 and C_9 aromatics measured in our laboratory runs were compared with the thermodynamic equilibrium distribution [9]. The distribution of the C_8, and especially that of the C_9 alkylbenzenes are seen not to be far from the equilibrium distribution already at the mildest reforming conditions studied (470 °C and 3 vol/vol.hour). At 470 °C, with increasing residence time, the composition of the reformate even better approaches the equilibrium, although some fluctuations may be observed. At 530 °C, even with the shortest residence time studied, the product composition is very close to the thermodynamic equilibrium. Looking at Table 4, a characteristic feature mentioned earlier becomes apparent; namely that the distribution of aromatic isomers having the same carbon number depends only slightly on the conditions of reforming, because the distribution corresponds more or less to the thermodynamic equilibrium in the whole parameter range of commercial reforming operations. The only exception worth mentioning is ethyl-benzene, the distribution of which differs significantly from the equilibrium value under mild reforming conditions and approaches the equilibrium only in more severe reforming.

Corresponding to the equilibrium value, 1,2,4-trimethyl-benzene has always a dominating position among the C_9 aromatics.

From this fraction, according to its end point at 145 °C, only small quantities (max. 1.5% by weight) of C_{10} aromatics are formed. The quantities of C_{10} aromatics practically do not change with the temperature. The distribution of these compounds will be discussed later, in connection with the results obtained in reforming the naphtha boiling between 78 and 184 °C.

Table 4

Experimental and thermodynamic equilibrium distribution of C_8 and C_9 aromatics

	Thermodynamic Equilibrium distribution, % by weight (9)		Experimental distribution, % by weight			
			at 470 °C			at 530 °C
	at 470 °C	at 530 °C	LHSV: 1 vol/vol. h.	2 vol/vol. h.	3 vol/vol. h.	3 vol/vol. h.
C_8 aromatics						
ethyl-benzene	9.2	10.0	17.8	19.0	20.2	14.5
meta-xylene	47.0	46.6	41.7	43.6	41.2	43.2
para-xylene	21.2	20.4	17.2	15.6	16.0	19.1
ortho-xylene	22.6	23.0	23.3	21.8	22.6	23.2
	100.0	100.0	100.0	100.0	100.0	100.0
C_9 aromatics						
isopropyl-benzene	1.2	1.3	0.7	1.7	2.0	0.7
n-propyl-benzene	3.5	3.9	3.6	3.4	5.0	2.8
meta- and para-ethyl-toluene	28.0	31.5	27.1	23.9	27.0	29.8
o-ethyl-toluene	7.6	8.2	5.1	8.4	6.0	5.1
1,3,5-trimethyl-benzene (mesitylene)	13.5	11.5	11.7	9.3	8.0	12.0
1,2,4-trimethyl-benzene (pseudocumene)	37.2	34.2	42.4	44.0	42.0	40.4
1,2,3-trimethyl-benzene (hemimellitene)	9.0	9.4	9.4	9.3	10.0	9.2
	100.0	100.0	100.0	100.0	100.0	100.0

The naphtha having the broad boiling range of 78 to 184 °C is reformed on AP-64 platinum-alumina catalyst at the Danube Refinery for the production of a high octane motor-gasoline blending component. Among the feeds studied, this naphtha gives the highest quantities of C_9-C_{10} aromatics (Table 5). This is quite obvious from considering the boiling range and especially the end point of this naphtha. It is seen in Table 5 that in reforming this feed at 500 °C and a space velocity of 2 vol/vol.hour, the yield of C_9 aromatics amounts to 20.9 by weight of the feed, that is, to one-third of the total aromatics yield. Under the same reforming conditions the added yields of C_9 and C_{10} aromatics account for a little more than the half of the total aromatics. Concerning the distribution of C_9 aromatics, the same statements can be made as mentioned earlier on the fraction boiling between 112 and 145 °C.

From this naphtha, a significant amount of C_{10} aromatics was formed. Among the compounds identified individually, n-butyl- and 1,3-diethyl-benzene, further 1,2-dimethyl-4-ethyl-benzene can be found in the greatest quantities in the reformate. This latter compound could not be completely separated from indane (thus their quantities were given jointly) but it was possible to establish that indane accounts for a small portion of the joint amount, of a quantity less than 1% by weight in the samples shown in Table 5.

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Table 5

Reforming of naphtha fraction boiling between 78 and 184 °C

Laboratory reforming conditions
Pressure = 15 kp/cm²
Hydrogen-hydrocarbon mole ratio = 5 : 1
Catalyst: E-601

Temperature of reforming, °C	470			500			530		
LHSV, vol/vol. h.	1	2	3	1	2	3	1	2	3
Component	Yield percentage by weight of charge								
benzene	3.3	2.5	2.6	4.6	4.2	3.7	6.7	5.4	4.5
toluene	8.3	6.6	6.6	12.0	10.3	9.3	15.6	13.3	11.4
ethyl-benzene	2.4	2.0	1.8	2.3	2.5	2.3	2.6	2.4	2.6
para-xylene	2.0	1.3	1.5	2.9	2.3	2.0	3.7	3.1	2.5
meta-xylene	5.5	4.7	3.6	6.6	5.6	5.2	8.2	7.0	6.1
ortho-xylene	3.0	2.1	1.3	3.3	3.3	3.0	4.3	4.1	4.0
isopropyl-benzene	0.3	0.3	0.3	0.3	0.3	0.4	0.1	0.2	0.3
n-propyl-benzene	1.4	1.4	1.3	1.3	1.6	1.6	0.7	1.1	1.4
meta- and para-ethyl-toluene	5.0	3.8	3.9	6.0	6.0	5.5	6.0	6.5	6.0
o-ethyl-toluene	1.4	1.7	1.7	1.5	1.8	1.9	1.0	1.3	1.5
1,3,5-trimethyl-benzene (mesitylene)	2.0	1.5	1.5	2.8	2.4	2.2	2.7	2.4	2.0
1,2,4-trimethyl-benzene (pseudocumene)	6.1	5.3	4.8	7.0	7.0	5.9	7.5	7.2	6.0
1,2,3-trimethyl-benzene (hemimellitene)	2.0	2.2	2.3	1.3	1.8	2.0	1.3	1.4	1.6
n-buthyl- and 1,3-diethyl-benzene	2.6	2.5	2.7	2.0	2.7	2.7	0.8	1.5	1.5
1-methyl-2-n-propyl-benzene	1.3	0.6	0.6	1.0	1.3	1.0	0.7	1.1	0.9
1,2-dimethyl-4-ethyl-benzene + indane	3.4	2.7	3.1	2.2	3.1	3.0	1.8	2.4	2.6
1,2-dimethyl-3-ethyl-benzene	0.6	0.6	0.6	0.4	0.6	0.4	0.3	0.2	0.4
1,2,4,5-tetramethyl-benzene (durene)	0.9	0.9	0.7	1.0	0.9	0.7	0.6	0.7	0.7
1,2,3,5-tetramethyl-benzene (isodurene)	1.1	1.1	1.2	1.2	1.3	1.1	0.9	1.1	1.0
5-methyl-indane	0.1	0.3	0.3	0.3	0.2	0.3	0.2	0.2	0.5
1,2,3,4-tetramethyl-benzene (prehnitene)	0.6	0.6	0.5	1.1	1.0	1.4	0.8	1.0	1.0
Total C₈ aromatics	12.9	10.2	8.1	15.1	13.7	12.5	18.8	16.6	15.1
Total C₉ aromatics	18.2	16.2	15.8	20.2	20.9	19.5	19.3	19.9	18.8
Total C₁₀ aromatics+indane	10.6	9.3	9.7	9.2	11.1	10.6	6.1	8.2	8.6
Total aromatics	53.3	44.8	42.8	61.1	60.2	55.5	66.5	63.4	58.4
C₅₊ yield	82.8	86.3	89.1	78.5	82.3	86.1	75.0	78.5	82.3

1,2-dimethyl-4-ethyl-benzene has a significant position among the C_{10} aromatics of a "typical" reformate, also according to [4].

The compound with the greatest importance among C_{10} aromatics as a petrochemical feedstock is durene; its yield does not exceed max. 1% by weight.

The effect of dealkylation can be very clearly observed in case of this feed having a broad boiling range and features completely similar to those mentioned previously in connection with the fraction boiling between 112 and 145 °C. This effect is demonstrated in Fig. 1. In case of both fractions, the maximum
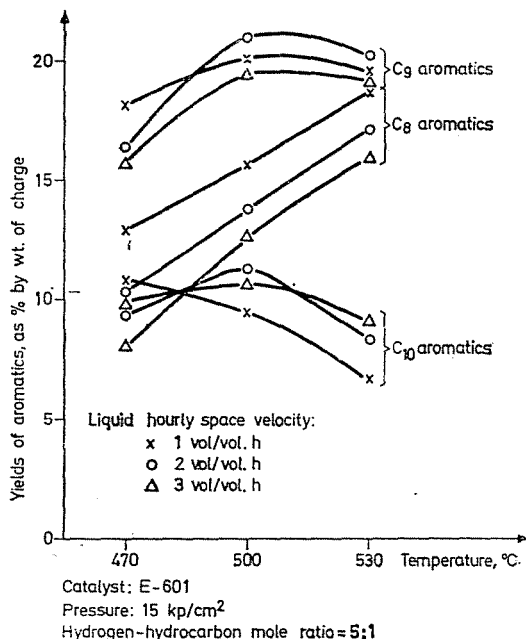
Fig. 1. Yields of C_8, C_9 and C_{10} aromatics from reforming the naphtha fraction boiling between 78 and 184 °C

yield of C_9 and C_{10} aromatics can be realized by reforming at 500 °C and at a space velocity of 2 vol/vol.hour. The choice of more severe reforming conditions (either as a higher temperature or as a lower space velocity) enhances dealkylation and thus, the yield of C_9-C_{10} aromatics decreases while the amount of C_6-C_8 aromatics and also the yield of total aromatics increases. It should be emphasized that the yield of total aromatics is above 60% by weight under severe reforming conditions. This is a quite high value, especially if the wide boiling range of the feed is considered.

Acknowledgements

Summary

Naphtha fractions were reformed in a laboratory apparatus on E-601 platinum-rhenium catalyst in the parameter range of commercial reforming.

The advantages of the reduced operating pressure (15 kp/cm² in this work) made possible by the use of the bimetallic catalyst are numerically demonstrated not only in the yields of $C_7 - C_8$, but also in those of $C_9 - C_{10}$ aromatics.

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Prof. Imre SZEBÉNYI ⎫
dr. Gábor SZÉCHY   ⎬ H-1521 Budapest

László ISAÁK   Dunai Kőolajipari Vállalat,
                       2443 Százhalombatta, Pf. 1. Hungary