

POLYMETHYLBENZENES IN REFORMATES OBTAINED FROM NAPHTHA FRACTIONS

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Received May 25, 1974

Polymethylbenzenes — compounds characterized by having three or more methyl groups on a benzene ring — find an increasing importance as starting materials for the synthetic chemical industry. This is due to some advantageous properties of these compounds, e.g. the ring-substitution reaction rates of the polymethylbenzenes are much higher than those of benzene, toluene or even xylenes [1].

At the same time, the steric position of the methyl groups of the individual isomers results in high selectivity in case of chemical reactions.

The structure of polymethylbenzenes is generally suitable for the production of starting materials for heat resistant polymers and cross-linking agents, plasticizers and dyes. Presently the following three polymethylbenzenes are of industrial and commercial importance:

1,2,4 trimethylbenzene (pseudocumene)

1,3,5 trimethylbenzene (mesitylene)

1,2,4,5 tetramethylbenzene (durene)

The polymethylbenzene produced in the greatest quantity is pseudocumene, the world production of which was about 50,000 tons in 1970 [2].

In Fig. 1 utilization routes are shown for the three polymethylbenzenes mentioned [2].

Trimethylbenzenes and tetramethylbenzenes are known to be found in the liquid product of catalytic gasoline reforming [3]. In order to devise a scheme for the separation of polymethylbenzenes, the concentration of the compounds in these reformates must be known first and the optimum boiling ranges of feedstocks to be reformed must be determined.

As a consequence, the aim of the presented experimental work was to determine the concentration of polymethylbenzenes in reformates obtained from feedstocks with different boiling ranges. The effect of the temperature of reforming on trimethylbenzene formation was also studied.

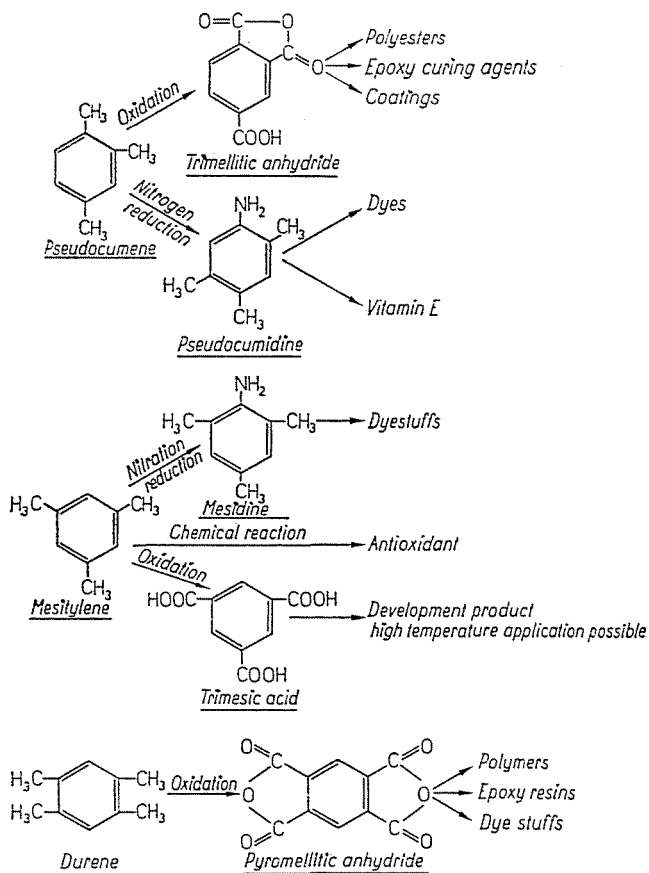


Fig. 1. Utilization routes of three polymethylbenzenes

Experimental

As starting material in the experiments a desulphurized naphtha of Romaskino origin was used, obtained from the feedstock of a reforming unit in the Danube Refinery, Százhalombatta. Three fractions obtained by laboratory distillation from this naphtha were used as feedstocks. Characteristic properties of the starting naphtha and the three fractions are given in Table 1. The experiments were first carried out in a high-pressure microreactor apparatus and then repeated in a larger experimental reactor system [4].

Microreactor was chosen because several experiments have been carried out also with pure model compounds and small quantities of these compounds were at disposal. At the same time, it was desirable to maintain the comparability between the experiments with naphtha fractions and pure model

Table 1
Properties of desulphurized feedstocks

	Straight-run naphtha of Romaskino origin (basic material)	Fraction distilled from base material			Straight-run naphtha from the Szény refinery
		A	B	C	
ASTM Distillation, °C					
Initial boiling point	75	100	126	154	82
10%	98	109	136	158	100
50%	129	128	147	165	130
90%	164	151	164	176	166
End point	185	164	178	189	188
Density, d_4^{20}	0.740	0.743	0.758	0.772	0.741
Hydrocarbon composition % by weight					
C ₈ paraffins	15.4	21.6	12.0	1.3	14.7
C ₉₊ paraffins	24.8	22.7	40.2	51.8	30.8
total paraffins	56.2	56.1	53.5	51.3	56.1
C ₈ naphthenes	8.6	11.6	6.9	1.6	8.1
C ₉ naphthenes	9.0	9.9	13.0	7.9	9.6
C ₁₀₊ naphthenes	7.0	3.9	11.2	20.7	9.5
total naphthenes	33.2	33.3	32.4	29.6	33.8
C ₈ aromatics	4.1	5.5	6.2	2.9	3.8
C ₉₊ aromatics	3.8	2.2	7.0	14.1	4.6
Trimethylbenzenes	1.1	0.6	1.6	3.3	0.9
total aromatics	10.3	10.4	13.9	17.0	9.8
total olefins	0.3	0.2	0.2	0.3	0.3
Per cent by weight of the basic material	100	30.6	22.1	12.1	—

compounds. The catalyst applied in all experiments was a commercial platinum catalyst, which is presently used in Hungarian reforming units. The micro-reactor had an inner diameter of 6.8 mm, therefore the commercial catalyst had to be crushed and the fraction with particle size 0.63 to 0.80 mm was filled into the reactor tube.

In case of the larger reactor, the catalyst was used in its original form.

Product gases were not recycled to the reactor in either case, but instead, hydrogen from a cylinder was led through the reactor.

The microreactor tube contained 2 ml of crushed catalyst, the experimental reactor had a catalyst volume of 100 ml. Because of the small size of the microreactor, in general no quantitative relationships valid for large scale operations can be established. For this reason, material balances were not

considered in the present work, although the liquid yields (reformate percentages by volume and by weight of feedstock) were determined.

However, in order to compare yields of our microreactor unit with those of the industrial plant, several runs were carried out with the same naphtha feedstock as used in the reforming plant in the Szőny refinery.

Of course, no parameter values completely equivalent to the large scale parameters could be set, as the industrial unit contained three adiabatic reactors connected in series, and our apparatus contained a single isothermic reactor. Hence, temperature drop and reheating could not be simulated. The test parameters were the following:

temperature:	500 °C
pressure:	32 kp/cm ²
liquid hourly space velocity:	2.2 ml/ml hour
gas/liquid ratio:	1380 ml/ml feed (H ₂ : CH mole ratio 11:1)

The industrial reformate and products of two microreactor runs are compared in Table 2. Table 1 shows the hydrocarbon composition of the naphtha feedstock.

Table 2 shows that beginning at isopropylbenzene, hence just in the range of C₉ aromatics, there is quite a good agreement between the industrial reformate and the two microreactor products. In spite of the great difference in size, our experiments permit to draw conclusions of quantitative rather than only of qualitative character.

Table 2

Composition of reformates from industrial and microreactor units

Component	Quantity in the reformate, per cent by weight		
	Industrial reformate	Microreactor product run No. 1	Microreactor product run No. 2
Methylbenzene	10.8	6.9	6.9
Ethylbenzene	3.7	2.5	3.1
1,3 and 1,4 dimethylbenzene	10.0	6.9	7.1
1,2 dimethylbenzene	4.1	2.8	2.9
Isopropylbenzene	0.4	0.5	0.4
n-propylbenzene	1.3	1.4	1.1
1,2,4 trimethylbenzene	5.0	4.4	4.5
1,3,5 trimethylbenzene	1.5	1.2	1.3
1,2,3 trimethylbenzene	1.6	1.6	1.8

In the reforming experiments, only the temperature was changed (between 470 and 530 °C), the other three parameters were held at the following constant values:

pressure: 30 kp/cm²
 liquid hourly space velocity: 3 ml/ml hour
 gas/liquid ratio: 1300 ml/ml feed

The value of the gas/liquid ratio corresponds to H₂ : CH mole ratios of 10.9 : 1, 9.2 : 1 and 10.2 : 1 in case of fractions A, B and C, respectively. The products of the reforming experiments were analyzed by a gas chromatographic method developed for this purpose at our Department [5].

Results

Table 3 shows the trimethylbenzene content of the reformates obtained from fractions A, B and C at different reforming temperatures in the micro-reactor. The data in Table 3 are represented in Figs. 2, 3 and 4. Fig. 2 shows that the reformat obtained from fraction A contains 4.5 to 5 per cent by weight of 1,2,4 trimethylbenzene, while the other two isomers are present

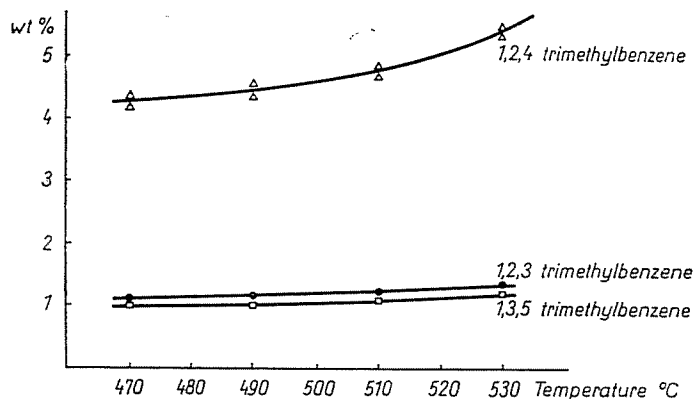


Fig. 2. Trimethylbenzenes in reformates obtained from fraction A in microreactor

in quantities of only about 1%. This can be explained by the fact that 1,2,4 trimethylbenzene has a far greater thermodynamic stability than the other two isomers. The rise of temperature slightly increases the 1,2,4 trimethylbenzene content of the reformat, but it practically does not affect the formation of the other two trimethylbenzenes.

Fig. 3 shows the trimethylbenzene content of the reformat obtained from fraction B at different temperatures. In this case, rising of the reforming temperature had a much more marked effect on the formation of 1,2,4 trimethylbenzene than in case of the first fraction.

The quantity of the other two isomers increased but slightly with the temperature.

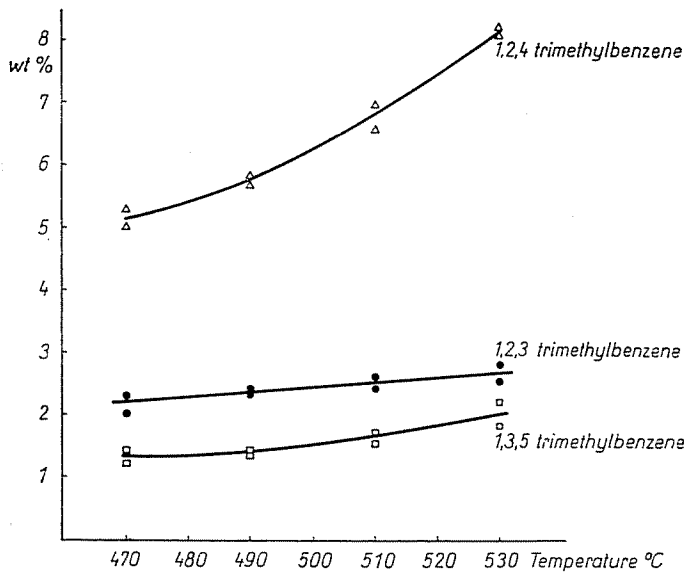


Fig. 3. Trimethylbenzenes in reformates obtained from fraction B in microreactor

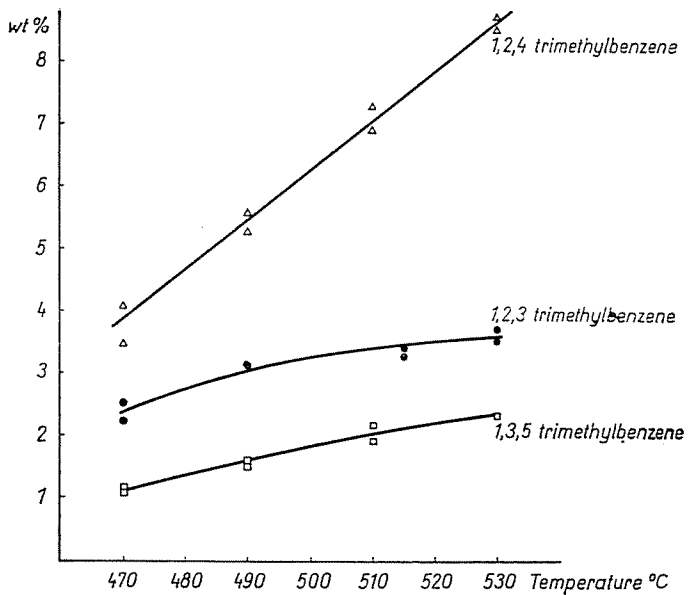


Fig. 4. Trimethylbenzenes in reformates obtained from fraction C in microreactor

Fig. 4 shows the results obtained with the highest boiling fraction. The effect of temperature increase is the most advantageous in this case. The reformat obtained at 530 °C had a 1,2,4 trimethylbenzene content of 8.7% by weight. The rise of temperature enhances also the formation of 1,3,5 and 1,2,3 trimethylbenzene, and the 1,2,3 trimethylbenzene (hemimellitene) content of the reformat is as high as 3% by weight.

Results of the experiments carried out in the larger reactor (100 ml volume of catalyst) are given in Table 4. Comparison of Tables 3 and 4 shows

Table 3

Concentration of trimethylbenzenes in reformates obtained in microreactor (catalyst volume: 2 ml)

Component	Percentage by weight of the reformat obtained from fraction											
	A				B				C			
	Reforming temperature, °C				Reforming temperature, °C				Reforming temperature, °C			
	470	490	510	530	470	490	510	530	470	490	510	530
1,2,4 trimethylbenzene	4.4	4.5	4.9	5.6	5.1	5.7	6.7	8.2	4.1	5.5	6.9	8.7
1,3,5 trimethylbenzene	1.0	1.0	1.1	1.3	1.2	1.4	1.5	1.8	1.1	1.5	1.9	2.3
1,2,3 trimethylbenzene	1.1	1.2	1.2	1.3	2.3	2.3	2.5	2.6	2.3	3.0	3.3	3.3

Table 4

Concentration of trimethylbenzenes in reformates obtained in a reactor containing 100 ml of catalyst

Component	Percentage by weight of the reformat obtained from fraction											
	A				B				C			
	Reforming temperature, °C				Reforming temperature, °C				Reforming temperature, °C			
	470	490	510	530	470	490	510	530	470	490	510	530
1,2,4 trimethylbenzene	4.8	4.9	5.1	5.3	4.8	4.9	6.2	7.2	4.1	6.0	7.0	7.8
1,3,5 trimethylbenzene	1.0	1.3	1.4	1.7	1.1	1.3	1.6	1.7	1.2	1.2	1.5	2.1
1,2,3 trimethylbenzene	1.2	1.4	1.4	1.5	1.6	2.1	2.2	2.3	2.2	2.3	2.4	2.7

a fair agreement between the results obtained in the latter case and in the microreactor. As an illustration, the trimethylbenzene content of the reformat obtained from fraction C in the larger reactor system is shown in Fig. 5.

The trimethylbenzene content of these reformates is very similar to those shown in Fig. 4. The trimethylbenzene yield is slightly lower than in case of the corresponding microreactor experiment.

The 1,2,4,5,- and 1,2,3,5 tetramethylbenzene contents of the reformates were also determined. These compounds were found in the experimental reformates in concentrations always below 1% by weight.

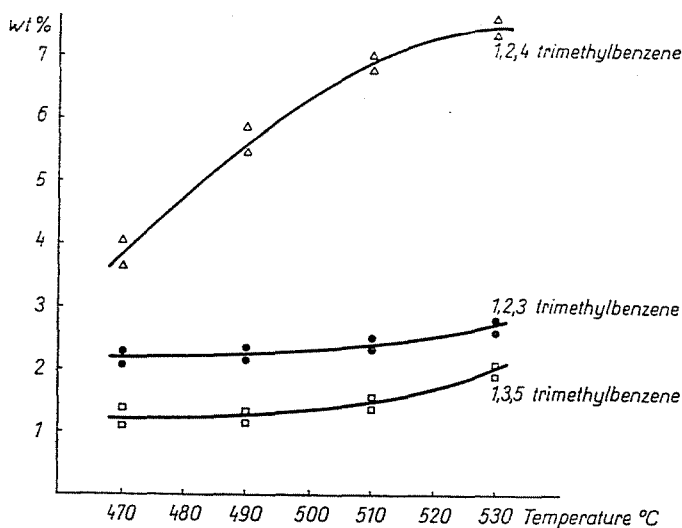


Fig. 5. Trimethylbenzenes in reformates obtained from fraction C in a reactor containing 100 ml of catalyst

Discussion

Two peculiarities were observed: the advantageous effect of the temperature rise on the trimethylbenzene yield (and especially on that of 1,2,4 trimethylbenzene), and the increase of this effect in case of the heavier fractions.

In order to study these effects in more detail, experiments have been carried out with different pure hydrocarbons; it was found that the quantity of alkylbenzenes formed by dehydrogenation of the corresponding alkylcyclohexanes did not increase at higher temperatures; on the contrary, the rise of temperature impaired the yield.

Experiments with pure n-nonane and n-decane showed, however, that the increase of temperature greatly enhanced the dehydrocyclization of paraffins and the formation of 1,2,4 trimethylbenzene.

Since C_9 paraffin hydrocarbons occur in naphthas in much greater concentrations than do trimethylcyclohexanes, the temperature rise is advantageous.

This influence is especially marked in the case of the higher boiling fractions because these contain more C_9 and heavier paraffins. In our case, for ins-

tance, the C_{9+} paraffin content of fractions A, B and C was 22.7, 40.2 and 51.8% by weight, respectively.

In case of the heavier fractions C_{10+} naphthenes may also yield trimethylbenzenes by hydrocracking and dehydroisomerization. Our experiments have shown that by reforming heavier naphtha fractions (boiling above 130 °C), reformates containing approximately 9% by weight 1,2,4 trimethylbenzene can be obtained.

Such streams can be considered as possible feedstocks for the production of 1,2,4 trimethylbenzene. As this compound is relatively easy to be separated by distillation from the reformat, the most suitable way for the production of other required polymethylbenzenes seems to be the separation of this compound and formation of other polymethylbenzenes by means of chemical conversion methods (isomerization, disproportionation, alkylation) from 1,2,4 trimethylbenzene as starting material.

Summary

Concentrations of tri- and tetramethylbenzenes in reformates obtained from three naphtha fractions at temperatures between 470 and 530 °C were determined. The experiments were carried out on a commercial Pt reforming catalyst in a microreactor and then repeated in a larger experimental reactor.

Higher boiling fractions gave better trimethylbenzene yields and higher temperatures enhanced trimethylbenzene formation especially in case of higher boiling fractions.

Max. 8.7 per cent by weight 1,2,4 trimethylbenzene was found in the reformat obtained at 530 °C from the fraction boiling at 154 to 189 °C. Tetramethylbenzene content of the reformates was always below 1% by weight. In the C_9 aromatics range, compositions of experimental reformates were in good agreement with an industrial reformat.

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