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PROCESS FOR PRODUCING MONONUCLEAR AROMATICS

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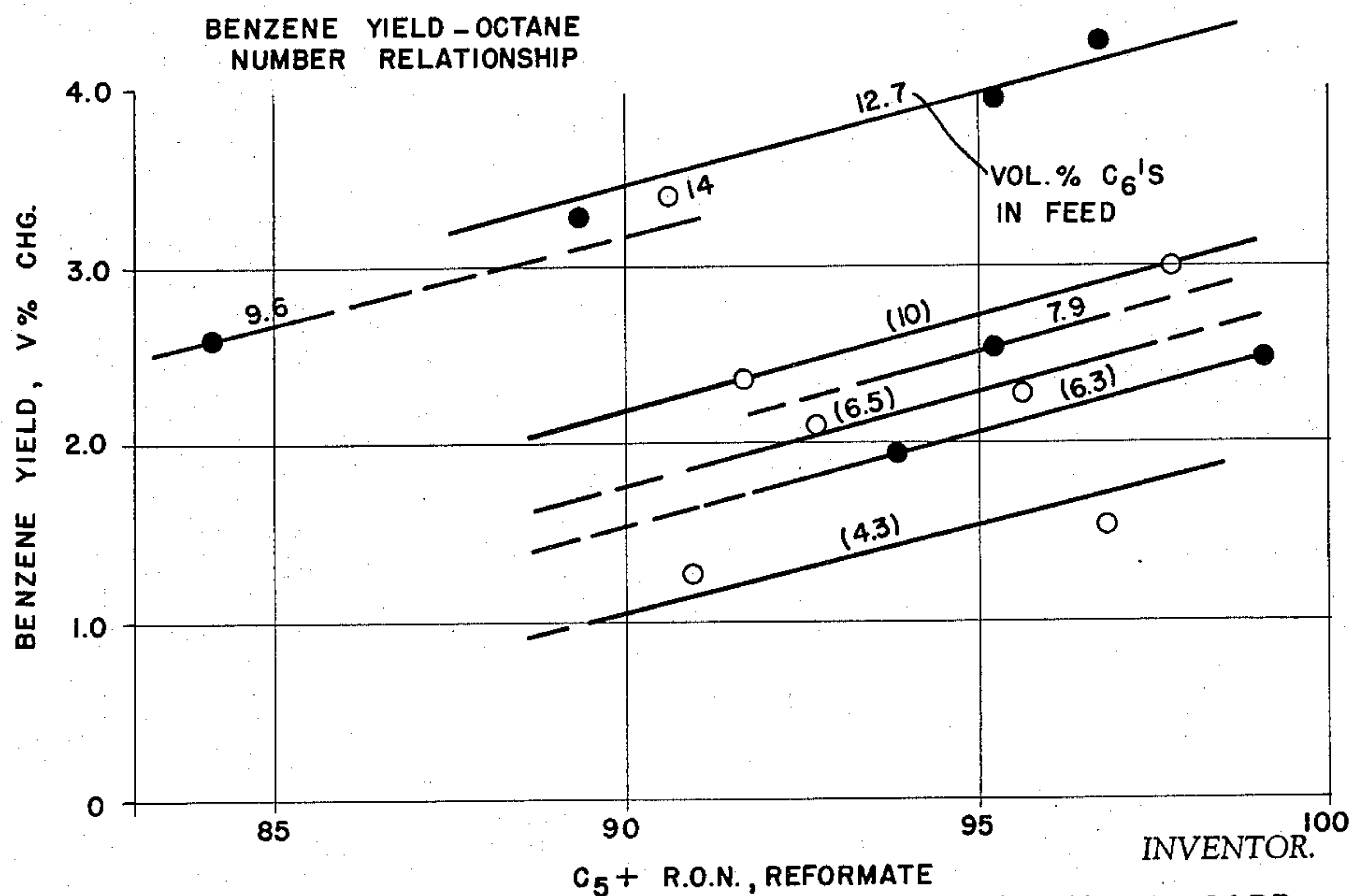
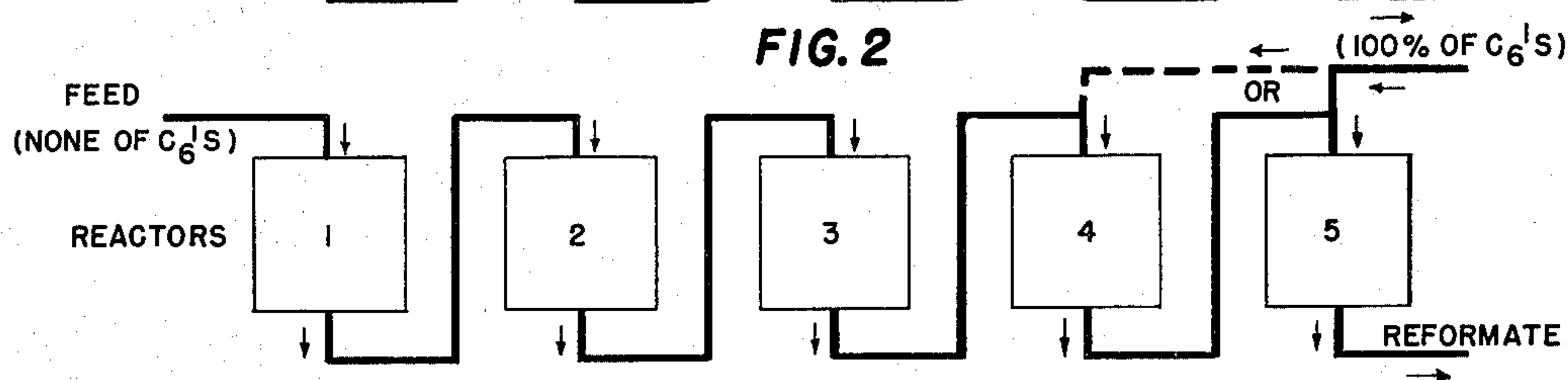
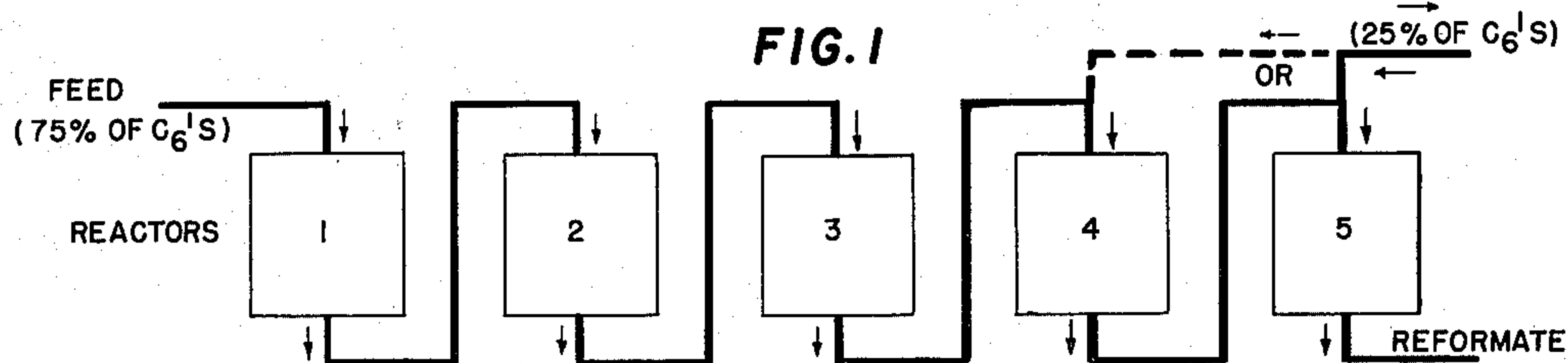
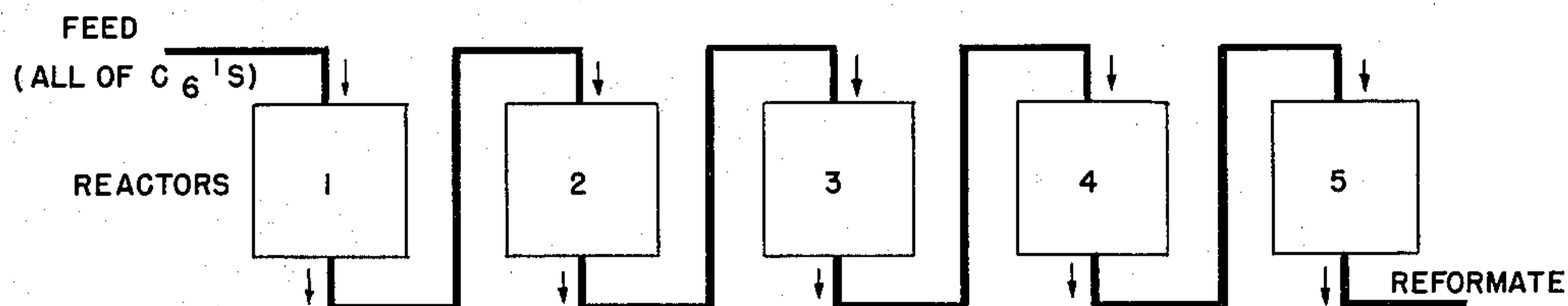


FIG. 4

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1

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## PROCESS FOR PRODUCING MONONUCLEAR AROMATICS

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This invention relates to a process for treating hydrocarbons boiling within the naphtha boiling range by a series of reforming reactions to increase the content of aromatic hydrocarbons in the resulting product. More particularly, this invention relates to a method of manufacturing benzene and homologues thereof by the catalytic reforming of petroleum portions rich in six-carbon atom hydrocarbons wherein a portion and preferably all of the  $C_6$  hydrocarbons in the feed stock are separated and introduced at an intermediate point in a series of reactors. Even more specifically, the invention encompasses a method of producing benzene from naphthas by separating the  $C_6$  portion from the naphtha, subjecting the balance of the feed to reforming under aromatization conditions in at least one initial reaction zone and conducting the effluent reformed feed, admixed with at least 25% by volume of the  $C_6$  portion and preferably 100% by volume of the  $C_6$  portion, to at least one and preferably two subsequent reforming zones to produce a reformat having an unexpected increase in content of benzene.

It is common practice in the reforming art to produce benzene by catalytically reforming a petroleum naphtha, including all of the  $C_6$  components in one or more reaction zones to produce a reformat from which benzene may be separated by extraction, distillation or other means. Reforming is applied to heavy naphtha fuel portions to increase the aromaticity and also the octane number thereof. It is usual to conduct such reactions in a series of complex thermal and/or catalytic reactors, which necessarily results in certain losses due to carbonization and conversion into products outside the desired boiling range. One known method is to pass a preheated hydrocarbon charge through a catalyst chamber having a plurality of appropriate catalyst beds connected to each other or connected and/or separated by suitable heating zones to cause successive catalytic reactions in accordance with the catalysts used to increase the content of aromatic hydrocarbons therein.

In these conventional catalytic processes the yields of aromatics or, more specifically, benzene can be increased by increasing the total  $C_6$  hydrocarbon content of the fresh feed, by increasing reactor temperatures and by decreasing the total pressure or space velocity. Adjustment of reactor temperatures, pressure or space velocities in the indicated directions also tends to increase the octane number of the total reformat, but it is well recognized that such changes in operation are quite costly, both from an initial-investment and an operating-cost viewpoint. In accordance with the present invention, means are provided for increasing the production of aromatic-type hydrocarbons from a specified amount of feed stock which, when the feed-stock constituents other than  $C_6$  hydrocarbons are reformed at practical levels for these process variables, is simple, economically practical and superior to conventional practice.

Accordingly, it becomes a primary object of this invention to provide a process for producing increased yields of aromatic-type hydrocarbons from feed stock containing six-carbon-atom components.

Another object of the invention is to provide a process for manufacturing benzene and homologues thereof by catalytically reforming petroleum naphthas rich in  $C_6$  hydrocarbon components wherein a portion or all of the

2

$C_6$  hydrocarbons in the feed stock are separated and introduced at an intermediate or terminal reaction zone in a series of interconnected reaction zones.

Still another object of this invention is to provide a process for the manufacture of benzene from naphthas wherein the  $C_6$  hydrocarbon components are removed from the feed, the feed is subjected to reforming in at least one reaction zone and the  $C_6$  components are added to the reformed feed passing to a subsequent reaction zone, in an amount ranging from 25% to 100% by volume of the  $C_6$  components separated or present, and the combined product is fractionated to recover increased yields of benzene.

These and other objects of the invention will be described or become apparent as the invention is developed herein.

The drawings are diagrammatic illustrations showing in FIGURE I conventional reforming reactors connected in series; FIGURE II one embodiment of the invention wherein about 25% by volume of the  $C_6$  hydrocarbon components are added to the last, or next to the last, or both, of the last reactors in the series; and FIGURE III a similar arrangement with that of FIGURE II wherein all of the  $C_6$  hydrocarbon components are added to the next to the last, or both, of the last reactors in a series of reforming units.

FIGURE IV is a graph showing the benzene yield-octane number relationship for different volume percents of  $C_6$  hydrocarbons in the feed for conventional reforming operation.

Based on a study of data from commercial and bench-scale units, it has been found in accordance with this invention that benzene yield can be related to the amount of  $C_6$  hydrocarbons in the feed stock and the  $C_5+$  research octane number (clear) of the reformat when all the  $C_6$ 's are fed to the head reactor and when operating conditions are consistent with practical levels for reforming. The correlation developed is as follows for benzene yield,  $y$ , in volume percent on charge naphtha:

$$y=0.21x+0.10z-8.5$$

where  $x$  is the volume percent  $C_6$ 's in the feed and  $z$  is the  $C_5+$ R.O.N. of the reformat. The standard error for this formula is  $\pm 0.19$  and the 95% confidence limits are  $\pm 0.41$ . A comparison of all data with the final equation for benzene yield shows that the average deviation is about 0.25. In addition to the straight-line relationships, it is also assumed that the benzene yield is 1.0% with no  $C_6$ 's in the feed and at a 95 R.O.N. reformat. This is obtained by extrapolation of the data to 0%  $C_6$ 's in the feed.

Using this formula as a basis for comparison with other cases wherein  $C_6$ 's are fed to reactors other than the first, it is possible to evaluate the effect of adding the  $C_6$ 's in different ways to the series of reactors. The case wherein 75% of the  $C_6$ 's were fed to the first reactor and 25% to the fifth reactor (at the proper temperature) resulted in a benzene yield of 3.74 v. percent at the R.O.N. of 84 and for  $x=12.4$  v. percent. The calculated  $y$  for the case of all  $C_6$ 's to the front reactor was 2.56 v. percent. This meant that this method of handling the  $C_6$ 's resulted in an increase in benzene yield of 50%.

The case wherein all the  $C_6$ 's were fed to the fifth reactor resulted in a benzene yield of 3.38 v. percent at a R.O.N. of 8.12 and for  $x=13.7$  v. percent. The calculated  $y$  for the case wherein all the  $C_6$ 's were fed to the head reactor was 2.5%. The effect of processing the  $C_6$ 's in the fifth reactor increased the benzene yield by 35%. These increased yields represent those from specific tests and the increases are not necessarily the maximum values obtainable. Methods of improving the yields further are discussed later.



In order to demonstrate the foregoing concepts, a series of experiments are reported in the following Table I;

Y was found to depend considerably on the increase in total C<sub>6</sub> hydrocarbon in the fresh feed, the reaction tem-

TABLE I  
Benzene production data from reformers

Run No.-----	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Feed, ° F-----	A (210-394)		B (185-376)			C (203-394)		A' (140-410)		D (188-394)		B		
Avg. temp., ° F-----	890	913	917	904	914	895	910	872	910	883	907	890	905	916
Pressure, p.s.i.g-----	350	350	350	350	350	350	350	320	320	350	350	290	290	290
H <sub>2</sub> /HC-----	5.8	5.5	5.7	5.7	5.6	6.2	6.2	4.0	4.0	6.0	5.9	3.6	3.6	3.3
LVHSV-----	2.0	1.1	1.5	2.0	1.0	2.0	2.0	1.5	1.5	2	2	1.9	1.9	1.9
C <sub>5</sub> +yield, v. percent-----	83.4	74.4	78.9	83.6	74.6	81.4	78.6	83.6	79.1	85.1	78.0	86	81.1	75.1
R.O.N., clear-----	93.9	99.1	95.2	89.3	96.8	92.6	95.6	91.2	97.8	91.0	96.9	84.1	90.6	95.0
C <sub>6</sub> 's in feed, v. percent-----	<sup>1</sup> (6.25)	(6.25)	12.7	12.7	12.7	(6.5)		(10)		(4.3)		9.63	14.0	7.93
C <sub>6</sub> yield, v. percent-----	10.0	11.0	16.2	16.7	17.0					7.1	9.5	11.96	14.2	11.0
C <sub>6</sub> H <sub>6</sub> yield, v. percent C <sub>6</sub> 's in feed-----			30.9	26.0	33.4							27	24	32
C <sub>6</sub> H <sub>6</sub> yield, v. percent-----	1.97	2.44	3.93	3.30	4.25	2.10	2.31	2.35	3.01	1.22	1.55	2.56	3.41	2.56
Predicted C <sub>6</sub> H <sub>6</sub> yield from equation, v. percent-----	2.21	2.73	3.70	3.11	3.86	2.13	2.43	2.73	3.39	1.51	2.10	out	3.51	2.69

<sup>1</sup> Parentheses mean estimated values from data correlations.

The experiments shown in Table I disclose that benzene yields are closely tied to the available C<sub>6</sub> hydrocarbons in the case where all of the C<sub>6</sub> hydrocarbons are fed to the first reactor as part of the reformer feed stock as illustrated by FIGURE 1. More important is the showing that by the application of the equation developed in accordance with this invention, the predicted (calculated) and actual values of the benzene yield are shown to be in close agreement. These data also show that in such conventional operations in order to improve the benzene yield, the following factors are important:

(1) *Increase in the total C<sub>6</sub> hydrocarbon content of the fresh naphtha feed.*—The most important of the C<sub>6</sub> hydrocarbons are cyclohexane and methylcyclopentane. These components usually increase with increase in C<sub>6</sub> hydrocarbon quantity and constitute from about 35 to 40% of the total C<sub>6</sub> hydrocarbons present. It becomes apparent from the data that several reasons may be assigned for this effect. These particular naphthenes are converted to benzene much more rapidly than are the paraffin hydrocarbons. Furthermore, the equilibria of the system benzene-cyclohexane-methylcyclohexane are more favorable for high benzene contents, that is, in the order of 75-100%, whereas the equilibria for the entire C<sub>6</sub> hydrocarbon system and hydrogen do not favor high benzene contents. The level of the latter benzene contents at equilibrium is found to range from about 5 to 25% at normal operating conditions. Also, the rates of the cyclization reaction are slow compared to the rates of dehydrogenation reactions.

(2) *Increase in reactor temperatures.*—As seen from the data in Table I, the driving force for higher benzene yield is increased with temperature. Both hydrocracking and aromatization rates are increased with temperature. Under these circumstances, it becomes apparent that the benzene yield can have a maximum as a function of temperature at constant levels of the other factors or reaction conditions. Actually the location of the optimum temperature for the reaction may be above or below the economic maximum reforming temperature.

(3) *Decrease in total pressure.*—From the data it is seen that since dehydrogenation rates are increased and hydrocracking rates are decreased with a decrease in pressure, it is desirable to operate at the lowest pressure possible consistent with reforming economics.

(4) *Decrease in space velocity, S.*—It is seen that the space velocity does not affect the initial reaction rates, but it does control the extent of conversion. From these experiments it is concluded that the space velocity should not be below about 1.5 to 2.0. Any decrease in space velocity will increase the hydrocracking and dehydrogenation yields but will not affect the hydrocracking and dehydrogenation rates. From this it is possible to calculate the optimum space velocity for the greatest benzene yield as indicated by the equation infra. The value of

perature increases and decreases in total pressure. Accordingly, it is not possible to accurately generalize as to the effect of decrease in space velocity. However, reaction temperature increases, decreases in total pressure and decreases in space velocity are synonymous with increasing octane number of the whole reformat.

In accordance with this invention, it was found that at the proper levels of these four factors, supra, further increases in the benzene yield over and above expectations can be obtained by processing all or part of the available C<sub>6</sub> hydrocarbons in the final reactor, or the final two reactors, at space velocities of 10 and 5, respectively. The term "space velocity" as used herein is defined as the pounds of liquid hydrocarbon feed per hour per pound of catalyst in the reactors used. By operating in this manner the amount of C<sub>6</sub> hydrocarbons produced from the non-C<sub>6</sub> hydrocarbons can be controlled and/or maximized. Also, the dehydrogenation can be maximized while at the same time hydrocracking of the C<sub>6</sub> hydrocarbons is kept at a minimum.

It has been found that by the proper selection of reaction conditions, optimum increases in benzene yield and octane number can be obtained. The first reactor or first reactors in the series can operate at any desired temperature whenever there is no appreciable content of C<sub>6</sub> hydrocarbons in the feed, that is, in the order of less than 1.0%. The higher the severity of treatment in the first reactor or reactors operating in the substantial absence of C<sub>6</sub> hydrocarbons, the higher the amount of C<sub>6</sub> hydrocarbons produced from the non-C<sub>6</sub> hydrocarbons present. However, the temperature of the final reactor or reactors operating at a space velocity of about 10 must be at a value of about 920° F. and less than 940° F.

In order to demonstrate these discoveries, the following specific examples are given with the operating conditions and results summarized in Table II.

#### EXAMPLE I

A reformer feed stock containing 75% v. of the total C<sub>6</sub> hydrocarbons was processed successively through five reforming reactors in series as illustrated in FIGURE 1. An ultraformer catalyst was used in each reactor and the operating pressure was 290 p.s.i.g. The remainder of the C<sub>6</sub> hydrocarbons, amounting to about 25% v. of the total feed was charged, along with the effluent products from the fourth reactor, to the fifth reactor in the series. The research octane number (clear) of the total C<sub>5</sub>+ product was 84.0 and the benzene production amounted to 3.74% v. of the total feed. As calculated by the equation (supra), if all of the C<sub>6</sub> hydrocarbons had been included in the feed stock in accordance with conventional practice, the benzene yield at 84.0 octane number severity would have been only 2.56% v. based on the total feed. The 3.74% v. yield found represented a 50% increase in benzene yield.



5  
EXAMPLE II

In this experiment only the C<sub>7</sub>-and-heavier hydrocarbons were charged to and passed through the first four reactors in a series, and all of the C<sub>6</sub> hydrocarbons were charged to the fifth reactor along with the total products from the fourth reactor. This operation is illustrated in FIGURE 3. The research octane number (clear) of the reformed product from the fifth reactor was 81.2 and the benzene yield was 3.38% v. based on the total feed. Had all of the C<sub>6</sub> hydrocarbons been included in the feed to the first reactor, and the conditions been maintained to yield a product having an octane number of 81.2, the (calculated) benzene yield would have been only 2.5% v. The 3.38% v. obtained represented a 35% increase in benzene yield over conventional practice.

EXAMPLE III

The process carried out in Example II was repeated using different cuts of the reformer feed-stock, and processing conditions at an 86.8 RON severity. This resulted in a benzene yield of 3.20 which is over 30% more than would be obtained using conventional practice.

The results are tabulated as follows:

TABLE II  
Benzene production in tail reformer-reactor

Example No.	1			2			3		
	1-4 (Fig. 2)	5 (Fig. 2)	Over-all	1-4 (Fig. 3)	5 (Fig. 3)	Over-all	1-4 (Fig. 3)	5 (Fig. 3)	Over-all
Feed naphtha	C <sub>7</sub> HC's and heavier+75% of total C <sub>6</sub> HC's.	25% of total C <sub>6</sub> HC's.		C <sub>7</sub> and heavier HC's.	C <sub>6</sub> HC's.		C <sub>7</sub> and heavier HC's.	C <sub>6</sub> HC's.	
Catalyst, wt., g.	44.7			111.3	26.2		111.3	26.2	
Catalyst, vol., ml.	55.0			120.0	30.0		120.0	30.0	
Reactor temp. ° F.:									
Top		929		926	926		950	942	
Avg.	890	928		885	923		905	941	913
Block		930		928	931		945	940	
LW HSV, lb./hr./lb.	1.9 (LVHSV)	11.36		2.74	12.6	2.56	2.70	12.6	2.52
H <sub>2</sub> /HC (mol/mol)	3.6	3.28		4.2			4.2		3.66
Charge data liquid:									
G./hr.	508.1			302.1	44.1	346.2	300.4	44.1	
Sp. gr.	0.7764			0.7491	0.6916		0.7491	0.6916	
Hydrogen:									
s.c.f.h.	12.5			9.31			9.31		
G./hr.	31.8			23.6			23.6		
Total g./hr.	539.9				369.8				368.1
Recovery:									
Liquid (unstab'd)			97.6			90.0			86.6
Gas (s.c.f.h.)			12.88			12.41			14.25
Total g./hr.			539.9			369.8			368.1
True C <sub>5</sub> + yield:									
V. percent chg.			96.7			85.1			81.6
W. percent chg.			97.3			89.1			85.8
C <sub>5</sub> + R.O.N. (clear)			84.0			81.2			86.8
+3 ml. TEL/gal.			96.5			95.0			97.2
Benzene yield (v. percent chg.).			3.74			3.38			3.20

Table III give the characteristics of the feed stocks used herein.

TABLE III  
Summary of feedstock data

Feed Identification (Table I)	A	B	C	D
Boiling range	(210-394°)	(185-876°)	(204-394°)	(188-394°)
Mixture	17 sour/83 sweet-sour.			
Sp. gr.	0.7616	0.7511	0.7527	0.7547
Percent sulfur	Desulf.	Ca. 0.01	Desulf.	0.0004
Paraffins, v. percent		35.1		
Naphthenes		55.4		
Aromatics		9.5		
ASTM distillation, ° F				
IBP	210	185	202	188
5	223	205	214	221
10	235	210	219	230
20	246	220	226	241
30	256	228	234	250
40	267	238	243	260
50	281	251	253	272
60	294	269	266	286
70	310	287	284	302
80	328	308	309	320
90	348	332	340	343
95	363	350	358	360
EP	394	376	394	394

6

This invention is not to be confined to any particular reforming or hydroforming reactor or processing technique aside from the manipulations described. The process is applicable to all reforming or hydroforming techniques wherein petroleum naphthas are subjected to a reforming technique to yield liquid products boiling within the naphtha or motor gasoline boiling range and possessing improved octane numbers, improved engine cleanliness characteristics and increased content of aromatics. The invention is applicable to hydroforming a naphtha feed stock at elevated pressures of from about 15 to 1000 pounds per square inch and at temperatures ranging from about 750° to 1050° F. in the presence of a solid catalyst having reforming characteristics and in the presence of hydrogen. By reforming and hydroforming reactions is meant those reactions such as hydrogenation, hydrocracking, aromatization, cyclization, paraffin and naphthene isomerization and dehydrogenation. Many of the known solid catalysts include supported metals such as platinum and palladium, as well as the oxides and sulfides of metals of Group VI of the periodic table. Oxides and sulfides of molybdenum, chromium, vanadium and tungsten are particularly suitable for the reaction when

supported on a material of high surface area such as alumina-containing adsorptive supports, the various activated aluminas, alumina gels, silica-alumina compositions, zinc aluminate spinel, etc.

The naphtha vapors may be passed through reactors which contain the catalyst as a dense fluidized bed or in a fixed bed. If the fluidized technique is used, spent catalyst is withdrawn continuously from the dense phase in each reaction zone and passed to a separate regeneration zone where reactivation is accomplished by treatment with an oxidizing atmosphere to burn off carbonaceous deposits. All of the inherent advantages of the fluid technique may be utilized in the instant process. Where static catalyst bed reactors are used, it is necessary from time to time to replace the catalyst bed as inactivation progresses. The presence or absence of small amounts of water in the reaction environments is optional to the present process.

This invention is, accordingly, directed to the process of reforming liquid hydrocarbon mixtures containing six-carbon-atom hydrocarbons to produce a reformat of increased octane number wherein the hydrocarbon mixtures



are subjected to successive contact with a reforming catalyst in a series of reactors by separating a portion of said six-carbon-atom hydrocarbons from the feed mixture, subjecting the residue to reforming in a first reactor, mixing the portion so separated with the reformed product, subjecting the resulting mixture to reforming in a subsequent reactor in the series, and separating the combined reformate. The invention applies to feed mixtures containing a sufficient amount of  $C_6$  hydrocarbons which are reformable into those types of hydrocarbons which exhibit increased research octane numbers and are generally aromatic in nature. It is desirable that the  $C_6+$  hydrocarbons contain a substantial portion of cyclic aliphatic hydrocarbons such as cyclohexane and methylcyclopentane. Best results are obtained when the  $C_6+$  hydrocarbons contain at least about 35 to 40 volume percent of cyclohexane and methylcyclohexane. The method of this invention finds particular utility when the severity level of the reforming reactions is established or maintained to produce a  $C_5+$  reformate having a R.O.N. of about 85, wherein the yield of aromatics produced is equal to about 0.21 of the volume of  $C_6+$  hydrocarbons separately introduced plus 0.10 of said  $C_5+$  R.O.N. minus 8.5. In general, naphthas boiling in the range of about 180° F. to about 400° F. and containing a substantial volume of paraffinic and naphthenic hydrocarbons are particularly susceptible to the process of this invention.

The conditions of pressure, temperature and space velocity may be varied within rather broad limits to attain the results of increased R.O.N. and aromaticity found. The exact conditions of operation will depend to a degree on the feed used, the degree of improvement desired, the nature of the catalyst and the efficiency of the reaction zones or processing techniques employed.

A series of reaction zones are used because the reforming reaction is exothermic and the effluent products from each zone are preferably reheated between zones to the desired reaction temperature. The reaction zones through which the  $C_5$  and lighter hydrocarbons pass are operated at an average temperature of about 750° F. to 850° F. using hydrogen-to-hydrocarbon mole ratios of about 1 to 8 with total pressures of about 200 to 500 p.s.i.g. and overall space velocities of about 1.0 to 4 lb./hr./lb. The subsequent or last reaction zones are operated at slightly different conditions as appears hereinafter.

In general, when two reaction zones are used in sequence and 25 volume percent of the  $C_6+$  hydrocarbons are introduced in the second zone, the second zone should be maintained at an average temperature of about 850° to 960° F. under pressures of about 200 to 500 p.s.i.g. using space velocities of about 2 to 12 where the first zone is operative at 750–850° F. as previously stated. The preferred conditions for this type of operation in the second zone are an average temperature of 920° to 940° F., 25 to 350 p.s.i.g. 5 to 10 space velocity using a catalyst consisting essentially of about 0.3 to 0.7 wt. percent of platinum deposited on a carrier composed of alumina. Where three or more, up to five, reaction zones are used, it is expedient to use incremental increases in severity of operation from the first to last zone. In such instances, where 25 volume percent of the  $C_6+$  hydrocarbons are introduced into the last or next to last reaction zone in the series, the following conditions will apply to these latter zones; temperature 920° to 940° F., pressure 250 to 350 p.s.i.g., space velocity 5 to 10 using the above-described catalyst. Where more than 25 volume percent, up to 100 volume percent, of the separated  $C_6+$  hydrocarbons are introduced in the next to last or last reaction zones in the series, the same conditions may be used. Preheating between zones is operated under conditions to maintain the average temperatures within the foregoing stated values.

While the invention has been described in relation to certain specific embodiments thereof, it should be under-

stood that such embodiments are illustrative only and not by way of limitation. Various modifications of the invention and alternate procedures using different conditions will become apparent from the description herein to those skilled in this art without departing from the scope of the claims.

What is claimed is:

1. In the process of reforming naphthas boiling in the range of about 180° to 400° F., containing a substantial volume of paraffinic and naphthenic hydrocarbons, wherein said naphthas are subjected to contact with a reforming catalyst in a successive series of reaction zones, the improvement comprising separating, from said naphthas, a fraction of  $C_6$  and higher molecular weight hydrocarbons, containing at least about 35 to 40 volume percent of cyclohexane and methylcyclohexane, subjecting the remaining naphthas to reforming in said succession of reaction zones at a reforming severity to produce a  $C_5+$  R.O.N. reformate product of at least about 85, mixing said separated  $C_6$  fraction with the effluent reaction products from said succession of reaction zones, subjecting the mixture to contact with a reforming catalyst in at least one last reaction zone, maintained at an average temperature of about 850° to 960° F., a pressure of 200 to 500 p.s.i., and a space velocity of 2 to 12, whereby the yield of aromatic hydrocarbons follows the correlation:

$$Y=0.2X+0.10Z-8.5$$

where Y is the yield of benzene, X is the volume percent of  $C_6$  hydrocarbons in the naphtha, and Z is the  $C_5+$  R.O.N. of the reformate product.

2. The process, in accordance with claim 1, in which said succession of reaction zones is maintained at a temperature of about 750° to 850° F., a pressure of about 200 to 500 p.s.i., the hydrogen/hydrocarbon mole ratio is 1:1 to 1:8 and the space velocity is 1.0 to 4.0.

3. The process, in accordance with claim 1, in which said  $C_6$  fraction contains at least about 25 volume percent of the  $C_6$  and higher hydrocarbons present in said naphtha.

4. The process of reforming naphthas, boiling in the range of about 180° F. to 400° F., containing at least about 35 volume percent of  $C_6$  and higher molecular weight hydrocarbons of paraffinic and naphthenic nature, which comprises separating about 25 volume percent of said  $C_6$  fraction from said naphthas, subjecting the remaining portion of said naphthas to reforming in the presence of a platinum-alumina catalyst in a succession of reaction zones maintained at a temperature of about 750° to 850° F., a pressure of about 200 to 500 p.s.i., a  $H_2/HC$  ratio of 1:1 to 1:8 and a space velocity of about 1.0 to 4.0, reheating the effluent products from each reaction zone before passage to the next succeeding reaction zone, mixing said separated  $C_6$  fraction with the preheated effluent from the next to last of said reaction zones, passing the mixture to the last of said reaction zones, maintaining said last reaction zone at a temperature of about 920° to 940° F., a pressure of about 250 to 350 p.s.i.g., and a space velocity of 5 to 10 whereby the yield of aromatic hydrocarbons follows the correlation:

$$Y=0.2X+0.10Z-8.5$$

where Y is the yield of benzene, X is the volume percent of  $C_6$  hydrocarbons in the naphtha, and Z is the  $C_5+$  R.O.N. of the reformate product and recovering a reformed product having an enhanced benzene content and increased octane number.

5. The process, in accordance with claim 4, in which the  $C_6$  fraction contains about 35 to 40% of cyclohexane and methylcyclohexane.



6. The process, in accordance with claim 4, in which the separated  $C_6$  fraction is mixed with the preheated effluent from the second to the last of said reaction zones and the last two reaction zones in the series are maintained, under the conditions of said last reaction zone.

5

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 2,995,509

August 8, 1961

Norman L. Carr

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 26, for "100° " read -- 100% --; column 2, line 64, for "8.12" read -- 81.2 --; columns 3 and 4, TABLE I, column 15, line 6 thereof, for "95.0" read -- 95.2 --.

Signed and sealed this 27th day of March 1962.

(SEAL)

Attest:

ERNEST W. SWIDER  
Attesting Officer

DAVID L. LADD  
Commissioner of Patents