

May 16, 1972

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3,663,426

UPGRADING OF REFORMATE WITH A TELLURIUM-FAUJACITE CATALYST

Filed Nov. 14, 1969

6 Sheets-Sheet 1

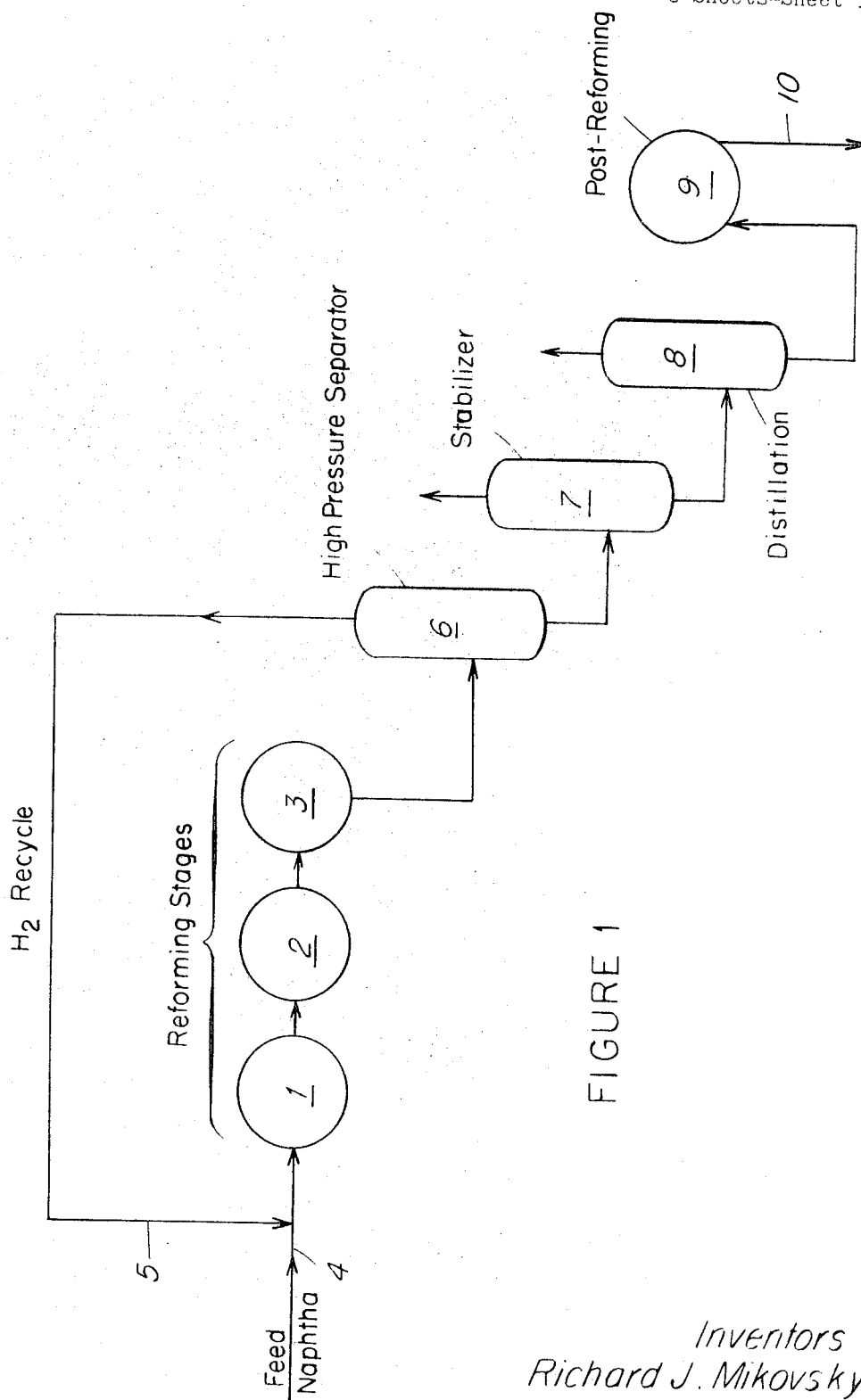


FIGURE 1

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6 Sheets-Sheet 2

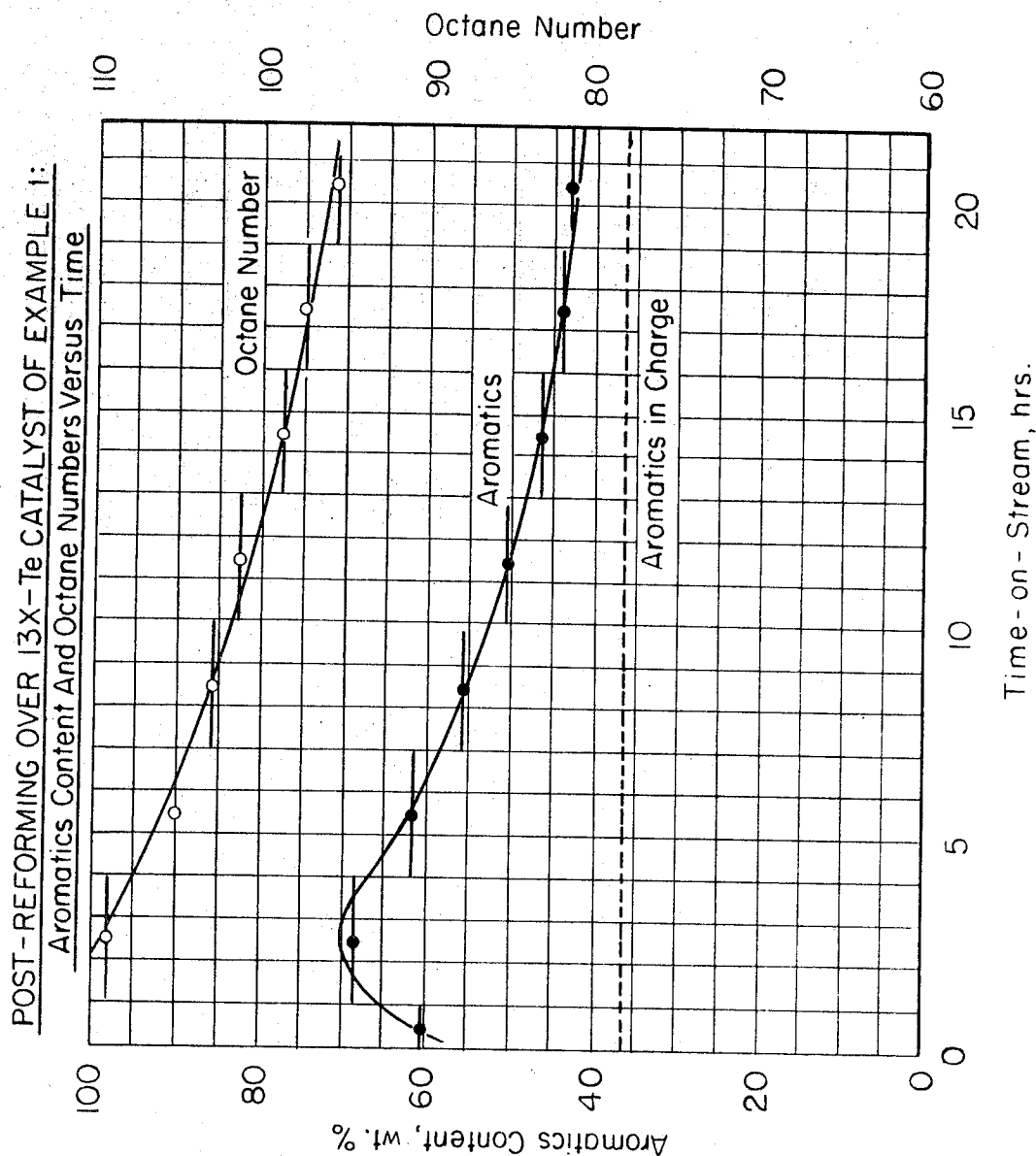


FIGURE 2

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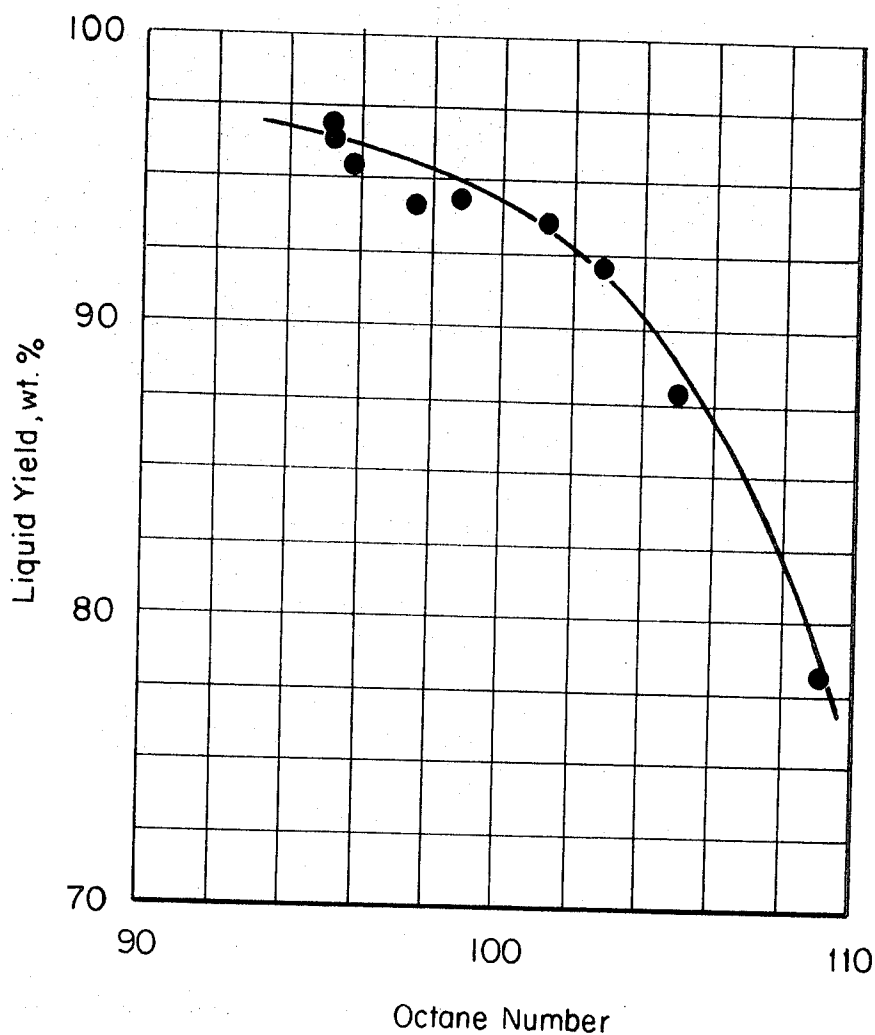
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FIGURE 3

POST-REFORMING OVER 13X-Te CATALYST OF EXAMPLE 1:

Liquid-Yield / Octane-Number Relationship



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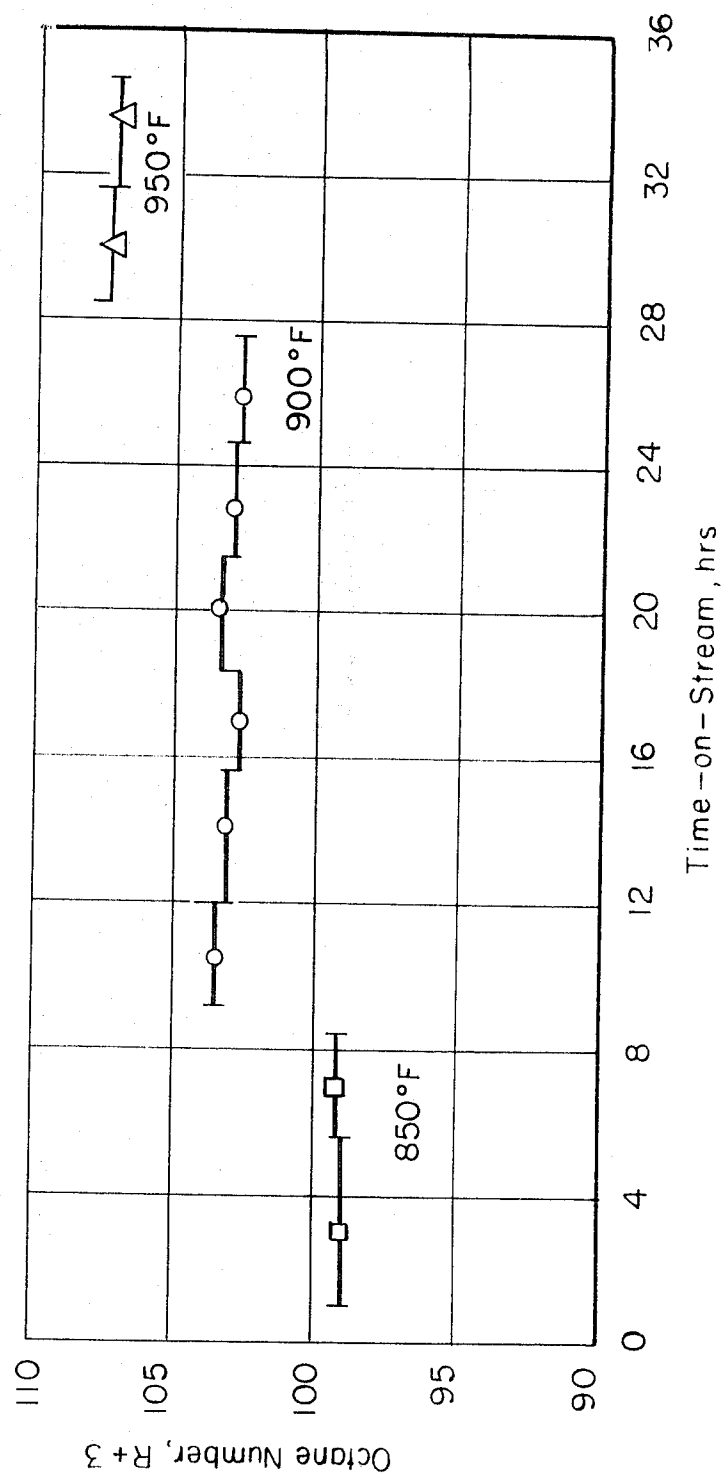
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FIGURE 4

POST-REFORMING OVER $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ CATALYST OF EXAMPLE 2:

Octane Numbers of Liquid Products



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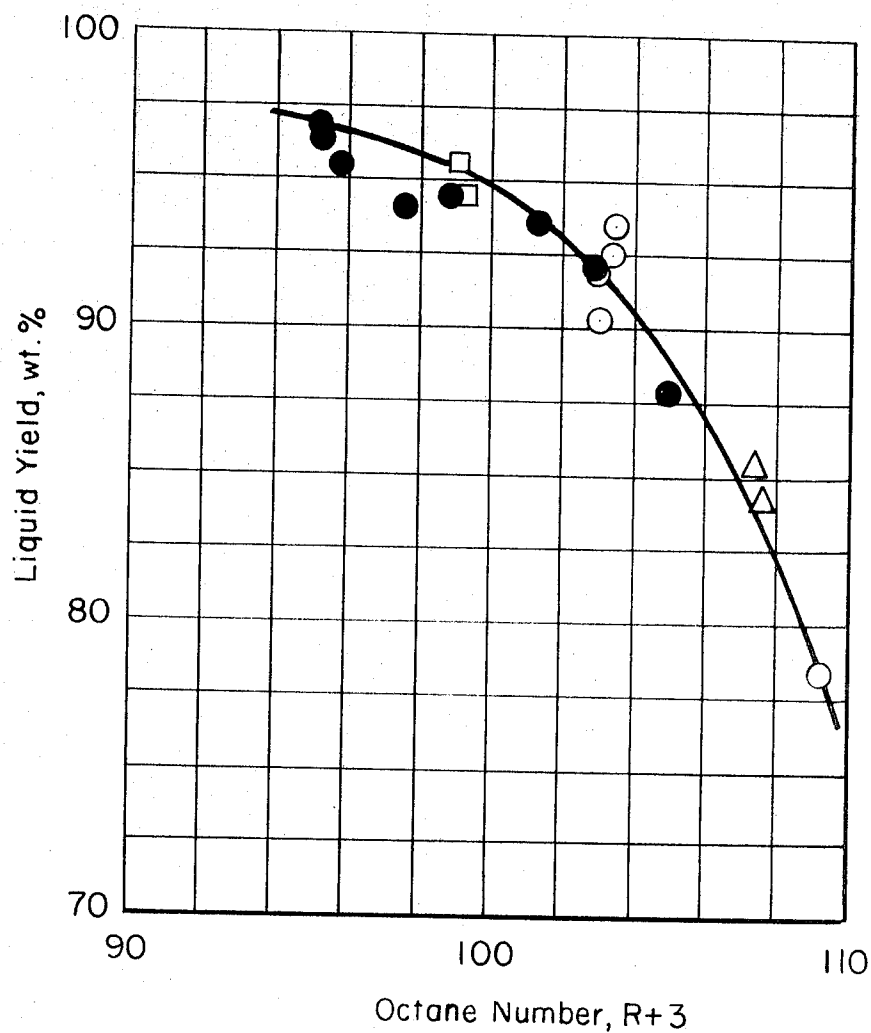
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FIGURE 5

POST-REFORMING OVER AROMATIZATION CATALYSTS OF EXAMPLES 1 AND 2

Yield-Octane-Relation

- = $\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3$, 850°F
- = $\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3$, 900°F
- △ = $\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3$, 950°F
- = 13X-Te, 850°F



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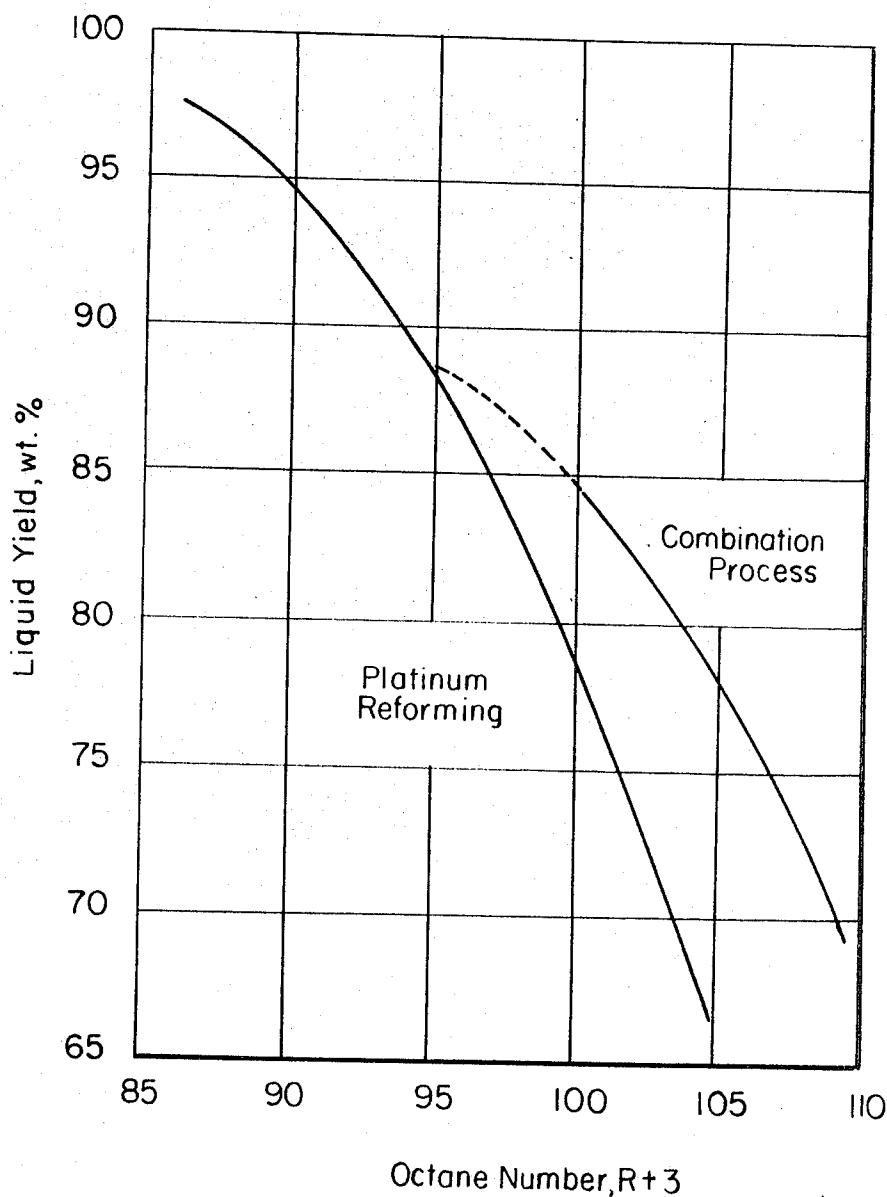
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FIGURE 6

YIELD ADVANTAGE: PLATINUM REFORMING ALONE
VERSUS PLATINUM REFORMING FOLLOWED BY POST-
REFORMING TO SAME O.N.



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9 Claims

ABSTRACT OF THE DISCLOSURE

Naphtha is reformed over a noble metal catalyst to effect a desired degree of naphthene aromatization and then subjected to a post-reforming step in which paraffins in the reformat are aromatized over a dehydrocyclization catalyst.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a reforming process, and in particular to a combination reforming process designed to improve yields by taking advantage of the selective dehydrocyclization capability of non-noble metal dehydrocyclization catalysts.

Description of prior art

The low-octane character of paraffins, especially n-paraffins, relative to aromatics has long been recognized, and various proposals have been advanced for removing n-paraffins from reformat to yield a gasoline having a higher octane rating than the reformat. In U.S. Pat. 2,952,014 it is proposed to selectively sorb n-paraffins out of reformat by contacting the reformat with a molecular sieve capable, by reason of its pore size, of sorbing no reformat components other than n-paraffins. In British Pat. 1,129,381 the reformat is subjected to hydrocracking over a similarly size-selective molecular sieve catalyst, with the consequence that n-paraffin, and no other reformat component, is converted to easily separable material.

SUMMARY OF THE INVENTION

According to the present invention reformat obtained by subjecting a naphtha, under reforming conditions, to the action of a noble metal reforming catalyst is contacted in a post-reforming operation with a dehydrocyclization catalyst whereby paraffins in the reformat are converted to relatively high-octane aromatics with better selectivity than the noble-metal catalyst.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The reforming catalyst is preferably a conventional platinum-on-alumina catalyst typically containing 0.3–0.6% weight platinum and up to about 1% weight halogen, preferably chloride. The conditions of contact between the naphtha feed and the catalyst usually comprise a temperature in the range 600 to 1000° F., a pressure in the range 100 to 1000 p.s.i., a liquid hourly space velocity in the range 0.1 to 10 and an H₂/HC mol ratio in the range 1 to 20. The reforming may be carried out as a fixed bed, moving bed or fluidized bed operation, although for purposes of brevity it will be described in this specification principally in terms of a three-reactor fixed bed installation.

As is known, the principal reactions brought about by reforming over a platinum catalyst are dehydrogenation of cyclohexanes to aromatics, isomerization of alkylcyclopentanes to cyclohexanes, isomerization and dehydrocyclization of paraffins and, inevitably and undesir-

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ably, some cracking. As the severity of the reforming operation increases, the extent to which all these reactions proceed increases, with the consequence that the liquid yield falls (due to the destruction of normally-liquid components by the cracking) whilst the octane number of the liquid product rises. A compromise must therefore be effected in selecting conditions of reforming, the accepted product octane value being determined by the yield loss which can be tolerated.

According to the present invention, the need for such a compromise is largely eliminated by conducting the reforming at relatively low severity, whilst still permitting substantial progress of those octane-increasing reactions particularly effectively catalyzed by platinum. In particular, conversion of both 5- and 6-membered naphthenes to aromatics is permitted to go to substantial completion (naphthene extinction). The reformat is then subjected to a post-reforming step in which the paraffin component of the reformer charge, which component has been less modified by the reforming conditions, is dehydrocyclized to aromatics.

The catalyst used in the post-reforming step is one having high selectivity for dehydrocyclization of paraffins, which have at least 6 consecutive carbon atoms. The preferred catalysts are chromia-alumina and tellurium-impregnated synthetic faujasite, but other catalysts having dehydrocyclization activity such as the oxides of molybdenum, tungsten, vanadium, cerium, thorium, neodymium and samarium, and mixtures of one or more of these may be employed (in association with a suitable carrier, such as alumina).

In the presently preferred manner of practising the invention, the naphthene-depleted reformat, optionally after deisohexanization and/or stabilization by C₅-hydrocarbon removal, is subjected to a single-pass, fixed-bed contact with the dehydrocyclization catalyst, that catalyst being either a Cr₂O₃/Al₂O₃ catalyst typically containing about 10% weight Cr₂O₃ on a support of γ -alumina; or being an alkali-metal form, such as the sodium form, of zeolite X loaded with 6% by weight (of the composite) of tellurium.

The extent to which the reformat is depleted in naphthenes may, as mentioned above, amount to naphthene extinction; but a small naphthene content can be tolerated in the post-reforming stage. Thus we have achieved excellent post-reforming stage performance with a reformat having a naphthene content of 1.5%, although at naphthene contents of the order of 10% performance falls off badly. The precise extent to which residual reformat naphthenes affect post-reforming performance depends, naturally, on the particular conditions selected for the particular post-reforming operation.

Best results are obtained by operation at a temperature in the range 850 to 1100° F., a liquid hourly space velocity in the range 0.05 to 2.0, and under a hydrogen pressure in the range 0.1 to 5.0 atm. The selectivity for dehydrocyclization of the preferred catalysts is at its highest at a prevailing hydrogen pressure of 1 atm. or less, and the hydrogen pressure applied in the post-reforming step is therefore such as will, after taking account of reactor back-pressure, provide for contacting of catalyst and reformat at a pressure of about 1 atm. in at least part of the catalyst bed.

BRIEF DESCRIPTION OF THE DRAWING

Referring to FIG. 1, a reforming unit comprising stages 1, 2, and 3 is supplied with naphtha reformer feed via line 4; the feed is introduced into reformer stage 1 together with recycle hydrogen supplied via line 5. The effluent from reformer stage 3, typically at a temperature of 900° F., is subjected to separation (H₂ from reformat) at reformer pressure in high pressure separator 6;

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the H_2 is recycled. The liquid product from high pressure separator 6 is fed to stabilizer 7, in which normally gaseous hydrocarbons, including butane, are flashed off. The stabilized reformate is then optionally led to distillation column 8 in which hydrocarbons boiling below n-hexane and having less than the succession of 6 carbon atoms required for dehydrocyclization are fractionated off. The liquid product from the distillation is then fed to post-reforming reactor 9 and the post-reforming product from that reactor—characterized by substantial replacement of feed paraffins by aromatics—is taken off via conduit 10.

In order that the invention may be still more clearly understood, the following examples are provided by way of illustration of preferred embodiments.

EXAMPLE 1

A C_6 -290° F. Kuwait naphtha, analyzing 8.1 wt. percent aromatics, 17.2 wt. percent naphthenes and 74.7 wt. percent paraffins, was passed under reforming conditions (900° F. inlet, 250 p.s.i.g., 1.2 LHSV, and 7.5 H_2/HC mol ratio) through a three-reactor reformer in contact with a commercial reforming catalyst. The catalyst comprised 0.35% weight platinum on a support of eta alumina and had a surface area of 377 m.²/gm. and a chloride content of 0.42% weight. The raw liquid product had an octane number ($C_5 + (R+3)$) of 94.5, and contained 1.5 wt. percent naphthenes and 36.4 wt. percent aromatics. Octane number was determined in accordance with ASTM standard D-2699-68.

The post-reforming was conducted at a liquid hourly space velocity of 0.10, a temperature of 850° F., an H_2 /hydrocarbon mol ratio of 4.0, and an overall pressure approximately atmospheric. The catalyst was prepared by ball milling together, for 4 hours, Linde Zeolite 13X (sodium form) and elemental tellurium in proportions calculated to yield a composite containing about 6 wt. percent Te. The composite was pretreated for 18 hours in flowing hydrogen at 1000° F. before use. A chromatographic analysis of the charge and of the liquid products at various time intervals is presented in Table I, whilst data regarding the octane number of liquid product is presented in Table II. Information from these tables is represented graphically in FIGS. 2 and 3, which show, respectively, Aromatics Content and Octane Number versus Time and Liquid Yield/Octane Number Relationship.

TABLE I.—POST-REFORMING OVER 13X-Te CATALYST OF EXAMPLE I—CHROMATOGRAPHIC ANALYSES OF CHARGE AND LIQUID PRODUCTS

Sample	Charge	1		2		3		4		5		6		7	
		1-4 hrs.	4-7 hrs.	7-10 hrs.	10-13 hrs.	13-16 hrs.	16-19 hrs.	19-22 hrs.							
Weight percent:															
C_1 - C_5	8.4	10.7	13.3	12.8	10.9	10.9	8.3	9.5							
C_6 + non-aromatics.....	55.2	20.9	25.0	31.6	38.9	42.9	47.7	47.3							
Benzene.....	4.6	12.8	11.2	10.6	7.8	6.5	6.3	6.0							
Toluene.....	14.4	36.1	29.5	24.4	21.5	19.7	17.6	17.1							
C_8 aromatics.....	13.9	17.8	18.6	18.0	17.8	16.8	16.8	15.9							
C_9 aromatics.....	3.5	1.7	2.4	2.6	3.1	3.3	3.3	4.2							

TABLE II.—POST-REFORMING OVER 13X-Te CATALYST OF EXAMPLE I—OCTANE NUMBERS (R+3) OF LIQUID PRODUCTS

Period:	Time (hrs.)	Research Octane Number
1.....	1-4	109.2
2.....	4-7	105
3.....	7-10	102.8
4.....	10-13	101.3
5.....	13-16	98.8
6.....	16-19	97.6
7.....	19-22	95.8

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From these data, it is clear that a surprising upgrading of the reformate, at rather high yield, was effected during the first few periods of on-stream time, the catalyst requiring regeneration after 20-25 hours service.

Additional runs performed with the same charge stock and otherwise identical conditions indicated that catalyst aging is decreased by hydrogen dilution of the charge and also by operating at relatively low temperatures.

EXAMPLE II

Using the same charge stock as in Example I, and carrying out the initial reforming under the same conditions as in that example, a post-reforming operation was carried out using, in contrast to the tellurium catalyst of that example, a chromia-alumina catalyst containing 10.4% Cr_2O_3 , 0.44% K_2O and 0.39% CeO_2 and made by method of Archibald and Greensfelder.¹ The post-reforming was carried out under conditions of space velocity, pressure and hydrogen dilution the same as those of the post-reforming of Example I, but three runs were made, at temperatures of 850, 900 and 950° F., respectively. The relationship between octane number of liquid product and time-on-stream is shown in FIG. 4. The relationship between liquid yield and product octane number is shown in FIG. 5. Consideration of these two figures shows, as might be expected, that increasing octane number is associated with increasing severity of operation and with decreased liquid yield. However, despite the loss of liquid yield and expense of the increased severity the operations shown in FIGS. 4 and 5 compare highly favorably with a straight reforming operation devoid of any post reforming step.

This favorable comparison is illustrated in FIG. 6 in which the fall-off in liquid yield associated with the increasing severity necessary to attain a given octane value product is shown to be far less marked for a "combination process in accordance with the invention" than for Pt-reforming alone. Typical analyses conforming with the curves of FIG. 6 are shown in Table III in respect of two target octane values, viz 100 and 105 (both leaded research octane values, 3 cc. TEL/US gal.).

¹ Archibald, R. C., and Greensfelder, B. S., Ind. & Eng. Chem., 37, 356 (1945).

TABLE III.—COMPARISON OF Pt-REFORMING ALONE WITH Pt-REFORMING COMBINED WITH Cr_2O_3/Al_2O_3 POST-REFORMING

	Pt-reforming	Combina-tion process	Δ
I. C_5 ON(R+3)=100:			
65 H_2 , wt. percent.....	1.2	2.1	+0.9
Coke, wt. percent.....	0	0.4	+0.4
C_1 - C_5 , wt. percent.....	13.9	9.0	-4.9
iC_4 , wt. percent.....	4.8	3.1	-1.7
nC_4 , wt. percent.....	4.1	2.6	-1.5
C_6 +s, wt. percent.....	76.0	82.8	+6.8
C_6 +s, vol. percent.....	71.7	78.1	+6.4
II. C_5 ON(R+3)=105:			
70 H_2 , wt. percent.....	1.4	3.0	+1.6
Coke, wt. percent.....	0	0.4	+0.4
C_1 - C_5 , wt. percent.....	20.8	11.7	-9.1
iC_4 , wt. percent.....	6.9	3.1	-3.8
nC_4 , wt. percent.....	5.6	2.5	-3.1
C_6 +s, wt. percent.....	65.3	79.3	+14.0
C_6 +s, vol. percent.....	59.9	72.7	+12.8

¹ Gravities were estimated.

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It can be seen from the close coincidence between those curves of FIG. 5 which show post-reforming over a chromia-alumina catalyst and that which shows post-reforming over a 13X-Te catalyst that the comparison depicted in FIG. 6 holds good irrespective of which of the preferred catalysts is employed for the "combination process."

It will therefore be appreciated that by means of the invention the three-fold advantage is achieved that (i) the initial platinum reforming step need only be conducted at the severity necessary to achieve substantial, preferably complete, conversion of naphthenes, thus prolonging reforming catalyst life; (ii) the paraffins, which are permitted largely to survive this reforming, are more selectively converted into desired high-octane gasoline components than by straight reforming; and (iii) the diminution in yield associated with the prior art practices of simply separating off the reformate paraffins, or converting them to non-gasolen products, is avoided.

What is claimed is:

1. Reforming process comprising contacting a charge naphtha, under reforming conditions, with a platinum metal-containing reforming catalyst until at least a major portion of the naphthenes have been aromatized in said charge, the resulting reformate being then contacted with a tellurium-impregnated synthetic faujasite aromatization catalyst, to increase the octane number of said reformate by aromatization of paraffins, at a temperature in the range 800 to 1100° F., a liquid hourly space velocity in the range 0.5 to 2.0 and a hydrogen partial pressure in the range 0.1 to 5.0 atmospheres.

2. Process according to claim 1 wherein the faujasite is an alkali-metal faujasite.

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3. Process according to claim 2 wherein the aromatization catalyst contains about 1 to 11 weight percent tellurium.

4. Process according to claim 3 wherein said catalyst contains about 6 weight percent tellurium.

5. Process according to claim 1 wherein the synthetic faujasite is zeolite X.

6. Process according to claim 3 wherein the aromatization catalyst is pretreated in flowing hydrogen at about 1000° F. before use.

7. Process according to claim 1 wherein said resulting reformate contains no more than about 1.5 weight percent naphthenes.

8. Process according to claim 1 wherein said hydrogen partial pressure is no more than 1.0 atmosphere.

9. Process according to claim 1 wherein the hydrogen/hydrocarbon mol ratio during said aromatization of paraffins is about 4.0.

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HERBERT LEVINE, Primary Examiner

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208—135, 136, Dig. 2