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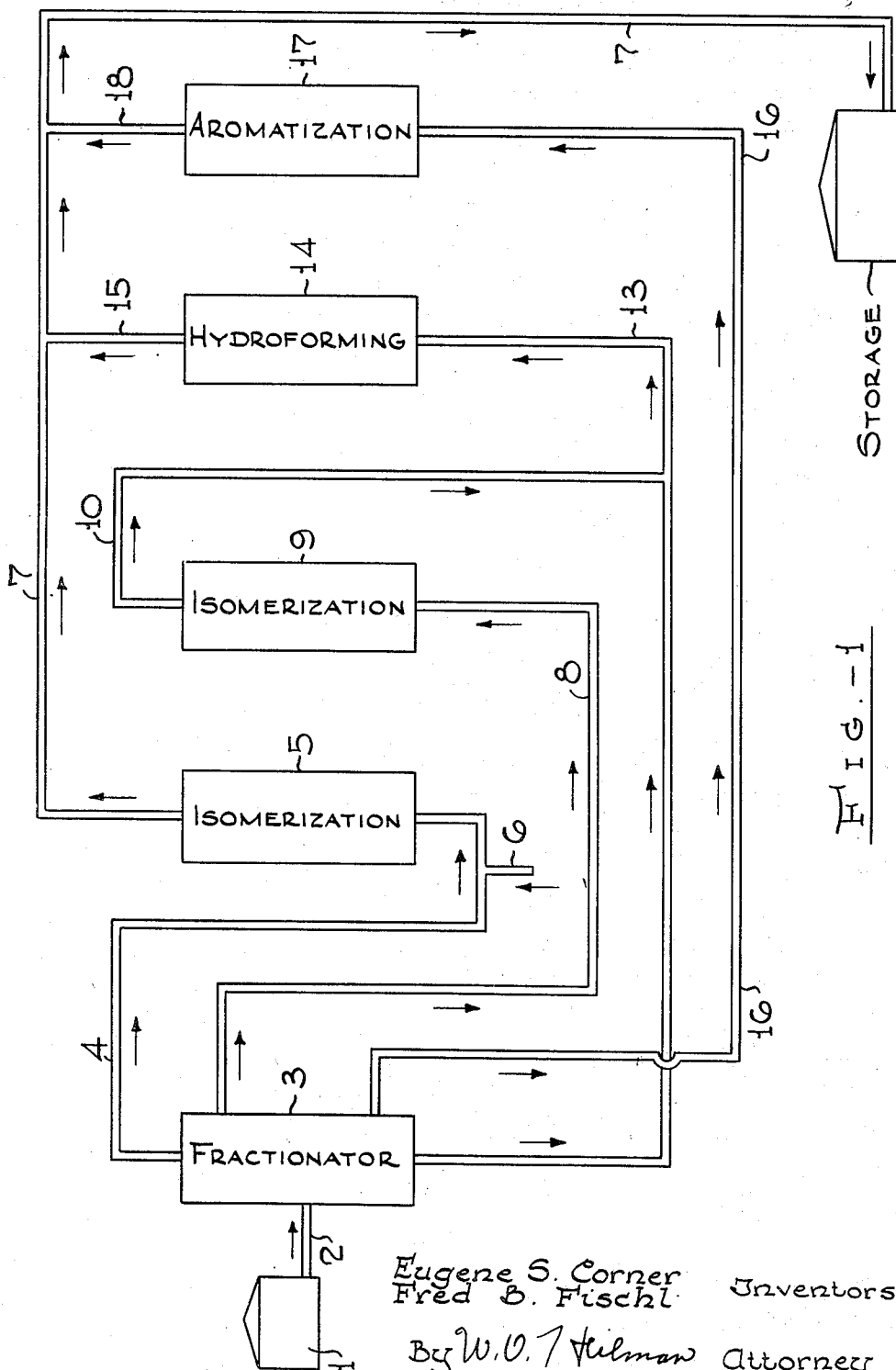
E. S. CORNER ET AL

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PROCESS FOR IMPROVING THE OCTANE NUMBER OF LIGHT NAPHTHAS

Filed Jan. 18, 1950

2 Sheets-Sheet 1



Eugene S. Corner
Fred B. Fischl. Inventors

By W. O. 7 Hilman Attorney

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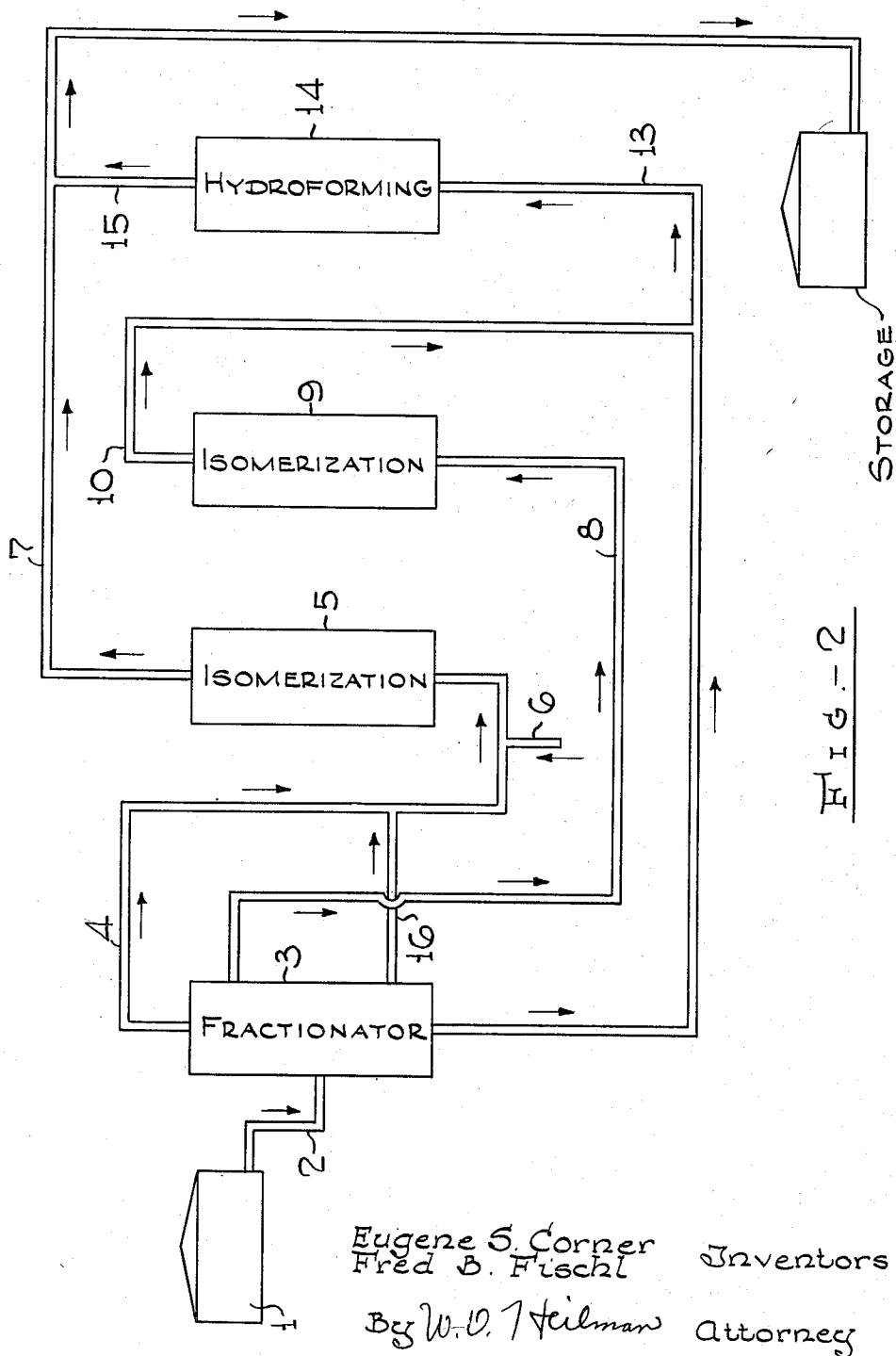
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Eugene S. Corner
Fred B. Fischl
Inventors

By W. D. Heilman
Attorney

UNITED STATES PATENT OFFICE

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PROCESS FOR IMPROVING THE OCTANE
NUMBER OF LIGHT NAPHTHASEugene S. Corner, Maplewood, and Fred B. Fischl,
Rahway, N. J., assignors to Standard Oil De-
velopment Company, a corporation of Delaware

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3 Claims. (Cl. 196—50)

1

This invention relates to the treatment of hydrocarbon oils boiling substantially in the gasoline boiling range for the purpose of producing therefrom fuels of improved octane number. The invention is more particularly concerned with a flexible combination of fractionation and catalytic treatments whereby the nature and severity of the respective catalytic treatments are adjusted according to the characteristics of the particular fraction treated so that a fuel of optimum quality may be produced. The catalytic treatments in question are catalytic hydroforming and catalytic isomerization and catalytic aromatization.

The term "hydroforming" wherever used in the specification and claims shall be understood to mean any process of subjecting material consisting essentially of hydrocarbons substantially boiling in the gasoline range to treatment at an elevated pressure above about 50 lbs./sq. in. at a temperature in excess of 500° F. and in the presence of catalysts and added hydrogen containing gas to produce a dehydrogenated or otherwise chemically reconstructed product, for example, of anti-knock characteristics superior to those of the starting material. By the term "chemically reconstructed" is meant something more than the mere removal of impurities or ordinary finishing treatments. The amount of added hydrogen containing gas is in the range from 1000 and 5000 cubic feet per barrel, preferably from 1500 and 3000 cubic feet per barrel of feed. In the hydroforming reaction, various reactions occur, for example, reactions such as dehydrogenation, aromatization or cyclization, cracking, hydrocracking, hydrogenation, desulfurization and alkylation, all or some of which may occur to a greater or lesser extent during the process. Hydrogen is one of the products of the hydroforming reaction.

The term "catalytic isomerization" wherever used in the specification and claims shall be understood to mean any process of subjecting materials consisting essentially of hydrocarbons substantially boiling in the gasoline range to heat treatment in the liquid or vapor phase and in the presence of a catalytic material to produce a product containing isomeric forms of the hydrocarbons.

The term "catalytic aromatization" wherever used in the specification and claims shall be understood to mean any process of subjecting materials consisting essentially of hydrocarbons substantially boiling in the gasoline range to heat treatment at a temperature in excess of 500° F. and in the presence of solid catalysts whereby cyclodehydrogenation reactions predominate to obtain a product having greater aromatic content and anti-knock characteristics superior to those of the starting material. A low pressure should be employed in aromatization, for ex-

2

ample, a pressure in the range from 0 to 50 lbs./sq. in. gage, preferably a pressure approaching atmospheric. Optimum aromatization and conversion are obtained in the absence of added hydrogen. However, small amounts of hydrogen or hydrogen-rich gas such as from 0 to 1000 cubic feet per barrel of feed may be introduced for the purpose of lowering the carbon deposition on the catalyst.

In accordance with the present invention, a hydrocarbon oil boiling in the gasoline range, such as light naphtha for example, is fractionated into four fractions and each of these fractions is subjected to one or more of the various catalytic treatments best suited to give the maximum increase in anti-knock value of the particular fraction. The manner in which the process is carried out will be more fully understood from the following description in connection with the accompanying drawings in which Figure 1 is a diagrammatic view of one type of suitable apparatus showing the lines of flow and Figure 2 is a diagrammatic view of a second embodiment of the present invention.

Referring to the drawing, a virgin naphtha from source 1 is passed by line 2 to distillation zone 3, where it is subjected to fractionation conditions to yield an overhead fraction boiling up to 158° F., a light side cut boiling from 158 to 200° F., a heavy side cut boiling from 200 to 211° F. and a bottoms fraction boiling above 211° F. The overhead fraction is passed by line 4 to reaction zone 5 which contains anhydrous aluminum chloride, aluminum chloride-hydrocarbon, sludge, aluminum bromide, or other isomerization catalysts.

Reaction zone 5 is maintained under isomerization conditions. When employing aluminum chloride catalyst, the pressure may be between 50 and 300 lbs./sq. in. and the average temperature between 120 and 250° F. Small amounts of hydrogen and anhydrous hydrogen chloride or other catalyst modifiers and activators such as water may be introduced through line 6. Reaction products leave reaction zone 5 through line 7.

A light side stream fraction boiling at 158 to 200° F. is removed from distillation zone 3 through line 8. This fraction contains large amounts of alkyl-cyclopentanes, cyclohexanes, and methylhexanes. This fraction is passed to isomerization reaction zone 9 similar in all respects to reaction zone 5. In reaction zone 9 the C₅ naphthenes are converted to C₆ naphthenes which are very effective feed stocks for the hydroforming reaction. The isomerized materials are removed overhead from tower 9 through line 10 and combined with the bottoms from tower 3 boiling above 211° F. This mixture is then introduced by line 13 into hydroforming reaction zone 14. Reaction zone 14 is maintained under

3

pressure between 50 and 500 lbs./sq. in. preferably between 150 and 400 lbs./sq. in. and at a temperature between 800 and 1050° F., preferably between 900 and 1000° F. The rate of flow of the mixture through the reaction zone is between 0.2 and 5 volumes of liquid per volume of catalyst per hour. Rates between 0.3 and 3.0 volumes of liquid feed per volume of catalyst per hour are preferred in most cases. An amount of gas containing free hydrogen should be introduced along with the liquid mixture ranging between 1000 and 5000 cubic feet of gas per barrel of liquid feed, preferably between 1500 and 3000 cubic feet. The gas should contain between 20 and 90 mol percent of free hydrogen preferably between 50 and 80 mol percent. The catalyst in reaction zone 14 may comprise any one or more of the many materials which promote hydroforming. Among these may be mentioned compounds such as the oxides or sulfides or the metals of the 4th, 5th, 6th and 8th, groups of the periodic system, especially the oxides of vanadium, molybdenum, chromium, tungsten, cobalt and nickel. These compounds may be used alone in various mixtures or combinations with each other or in combination with carriers or supporting materials, such as alumina, alumina gel, peptized alumina gel, zinc alumina spinel, various types of clays, etc. Particularly suitable catalysts are mixtures of aluminum and chromium oxides, aluminum and molybdenum oxides, aluminum and vanadium oxides, in which the active metal oxide preferably comprises from 1 to 50% by weight of the mixture. Products leave reaction zone 14 through line 15 and are combined with the products leaving reaction zone 5 through line 7.

Returning now to distillation zone 3, a heavy side stream fraction boiling between 200 and 211° F. is removed through line 16 and passed to aromatization reaction zone 17. Reaction zone 17 is maintained under relatively low pressure, preferably atmospheric but not above about 50 lbs./sq. in. gage and at a temperature between 800 and 1050° F., preferably between 900 and 1000° F. A suitable catalyst for this reaction is a mixture of chromium and aluminum oxides, preferably containing promoters such as potassium and cerium oxides. Products from this reaction zone are removed through line 18 and combined with the products removed from reaction zones 5 and 14 flowing through line 7. The combined effluents from reaction zones 5, 14 and 17 are passed to storage and yield a motor fuel of optimum anti-knock properties.

In alternate embodiment of the invention, referred to in Figure 2, the heavy side cut B. P. 200–211° F. in line 4 is combined with the overhead fraction in line 4 and the combined streams are isomerized in reaction zone 5. In this embodiment of the invention the aromatization reaction zone 17 of Figure 1 is omitted and the side cut of 200–211° F. boiling point, consisting predominantly of low octane number normal heptane, is converted to high octane number isomers in isomerization zone 5. The effluents from isomerization zone 5 and hydroforming zone 14 flowing through lines 7 and 15 respectively are combined to form the final motor fuel of high anti-knock quality.

The following data illustrate the advantages to be obtained according to this invention:

A light virgin naphtha was fractionated into 4 fractions, the first boiling up to 158° F. and containing cyclopentane and normal and

4

branched hexanes; a second, boiling between 158 and 200° F. and containing alkylcyclopentanes, cyclohexanes, and methylhexanes; a third fraction boiling between 200 and 211° F. comprising normal heptane and a bottoms fraction consisting of virgin naphtha boiling above 211° F. The fraction boiling up to 158° F. consists almost entirely of normal and branched hexanes which have very poor hydroforming characteristics with the result that conventional hydroforming of this fraction is undesirable since the hydrocarbons are not converted readily to aromatics and give excessive dry gas yields at elevated pressures as is illustrated by the following data:

TABLE A

Hydroforming of isomeric hexanes at 215 p. s. i. g.

[90 ZnO₂.Al₂O₃—10 MoO₃ catalyst; 900° F.; 2.1–2.6 H₂/HC mol ratio; 1.0 v./v.hr.; 1.0 hr. periods.]

Hydrocarbon.....	n-Hexane	2-Methylpentane	2,3-Dimethylbutane	2,2-Dimethylbutane
Conversion, Percent.....	11	13	18	9.0
Selectivities, Wt. Percent:				
Aromatics.....	11	6.2	0.0	10
Olefins.....	3.7	18	11	3.8
Gas.....	84	84	86	80
Carbon.....	1.6	1.5	3.3	6.3
Yields:				
Aromatics, Vol. Percent.....	1.3	0.6	0	0.7
Olefins, Vol. Percent.....	0.6	1.1	1.9	0.4
Gas, Wt. Percent.....	8.9	11	15	7.2
Carbon, Wt. Percent.....	0.2	0.2	0.6	0.6

The fraction boiling between 158 and 200° F. contains a large percentage of alkylcyclopentanes and is upgraded most effectively by isomerizing the C₅ naphthenes to C₆ naphthenes, the latter possessing very superior hydroforming characteristics. To show the effect of isomerization prior to hydroforming, a light East Texas naphtha fraction boiling between 150 and 200° F. was passed over a catalyst consisting of 90% Al₂O₃.ZnO and 10% MoO₃ at a temperature of 950° F., at a rate of flow of 0.75 volume of feed per volume of catalyst per hour and in the presence of 2.5 moles of hydrogen per mol of hydrocarbon. The following data were obtained:

TABLE B

Effect of isomerization prior to hydroforming on upgrading of a light East Texas naphtha

[Boiling range 150–200° F.; 90 ZnO.Al₂O₃—10 MoO₃ catalyst; 950° F. 0.75 v./v. hr.; 2.5 H₂/HC mol ratio; 2–4 hr. periods.]

Isomerization ¹	No	Yes	No	Yes
Pressure, p. s. i. g.....	50	50	215	215
Conversion, Percent.....	44	64	41	56
Selectivities, Wt. Percent:				
Aromatics.....	55	74	64	79
Olefins.....	20	6.0	7.7	2.3
Gas.....	18	17	27	17
Carbon.....	7.0	2.9	1.5	1.4
Yields:				
Aromatics, wt. Percent.....	20	38	21	37
Olefins, Vol. Percent.....	8.5	3.6	3.1	1.3
Gas, wt. Percent.....	8.0	10	11	9.5
Carbon, wt. Percent.....	3.1	1.8	0.6	0.8
Q ₄ —Liquid Yield, Vol. Percent.....	86	84	87	87
Feed.....	87.0	94.2	83.0	93.0
O. N.—CFR-Res.....	14.5	21.7	10.5	20.5

¹ AlCl₃ catalyst; 150° F.; 50 lbs./sq. in. gauge anhydrous hydrogen chloride; 10 hr. period; 99 vol. percent yield.

The above data show that when the fraction boiling between 150 and 200° F. was isomerized prior to hydroforming a 10.5 CFR—Research Oc-

tane Number advantage was obtained over hydroforming without isomerization. Furthermore, the combination process resulted in a marked reduction in carbon formation at 50 lbs./sq. in. gage.

The fraction boiling between 200 and 211° F. (nearly pure normal heptane) was aromatized by passing it at relatively low pressures over a chromia-alumina catalyst promoted with potassium and cerium oxides having the following composition:

10.3% Cr₂O₃
89.7% Al₂O₃
1.04% potassium oxide
0.4% cerium oxide

The results obtained by this process are compared with those obtained by hydroforming the same fraction at 215 lbs./sq. in. over the alumina zinc molybdena catalysts used in the hydroforming of the fraction boiling between 150 and 200° F. The results obtained are shown in the following table:

TABLE C

Comparison of aromatization and hydroforming of n-heptane over promoted chromia-alumina and alumina-zinc-molybdena catalysts

[1.0 v./v. hr.; 1.0-1.5 hr. periods.]

Process.....	Aromatization			Hydroforming
Catalyst.....	Cr/Al*	Cr/Al*	Cr/Al*	Mo/Zn/Al**
Temperature, °F.....	900	900	950	900
Pressure, p. s. i. g.....	0	0	50	215
H ₂ /HC, Mol Ratio.....	0	2.2	*2.5	*2.5
Conversion, percent.....	52	27	15	23
Selectivities, Wt. percent:				
Aromatics.....	71	46	8.1	29
Olefins.....	17	38	53	6.0
Gas.....	10	15	38	63
Carbon.....	1.8	1.1	1.2	1.9
Yields:				
Aromatics, vol. percent.....	30	9.6	0.9	5.1
Olefins, vol. percent.....	8.5	10.0	7.6	1.3
Gas, wt percent.....	5.2	3.9	5.5	15
Carbon, wt. percent.....	0.9	0.3	0.2	0.4

*10.3 Cr₂O₃-89.7 Al₂O₃+1.04% K and 0.4% Ce.

**90 Al₂O₃. ZnO-10 MoO₃.

* Equivalent to approximately 2,500 cu. ft. of hydrogen per barrel of liquid feed.

The above data indicate that the chromia-alumina catalyst is more than twice as active under low pressure aromatization conditions as the alumina-molybdena catalyst under conventional hydroforming conditions at high pressure and is more selective to aromatics as shown by aromatic selectivities of 71 and 29% respectively. The additional advantage of the chromia-alumina catalyst is its low dry gas selectivity (10 weight per-

cent at atmospheric pressure as compared with 63% for the alumina molybdena catalyst at 215 lbs./sq. in. gage). The data also show that the addition of relatively large amounts of hydrogen, for example 2200-2500 cubic feet per barrel of feed in aromatization decreases both conversion and selectivity to aromatics. The data also show that better results are obtained when the pressure is maintained less than 50 lbs./sq. in.

The nature and objects of the present invention having been thus fully set forth, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. Process for improving the anti-knock value of light virgin naphtha as motor fuel which comprises fractionating the naphtha into a hexane fraction boiling up to 158° F., an alkylcyclopentane fraction boiling 158 to 200° F., a normal heptane fraction boiling 200 to 211° F., and a heavy naphtha fraction boiling above 211° F., isomerizing the hexane fraction, isomerizing the alkylcyclopentane fraction, combining the isomerized alkylcyclopentane fraction with the heavy naphtha fraction, hydroforming the combined fraction, aromatizing the normal heptane fraction and combining the isomerized normal hexane fraction, and the aromatized and hydroformed fractions as the final improved motor fuel.

2. Process according to claim 1 in which the isomerization steps are carried out in the presence of an aluminum chloride catalyst in which the aromatization step is carried out at a temperature in the range 900° to 1000° F., and substantially atmospheric pressure, in the presence of a chromia-alumina catalyst, and in which the hydroforming step is carried out at a pressure in the range from about 150 to 400 pounds per square inch gage at 900-1000° F. in the presence of an alumina-molybdena catalyst.

3. Process according to claim 2 in which the chromia-alumina catalyst is promoted with potassium and cerium oxides.

EUGENE S. CORNER.

FRED B. FISCHL.

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