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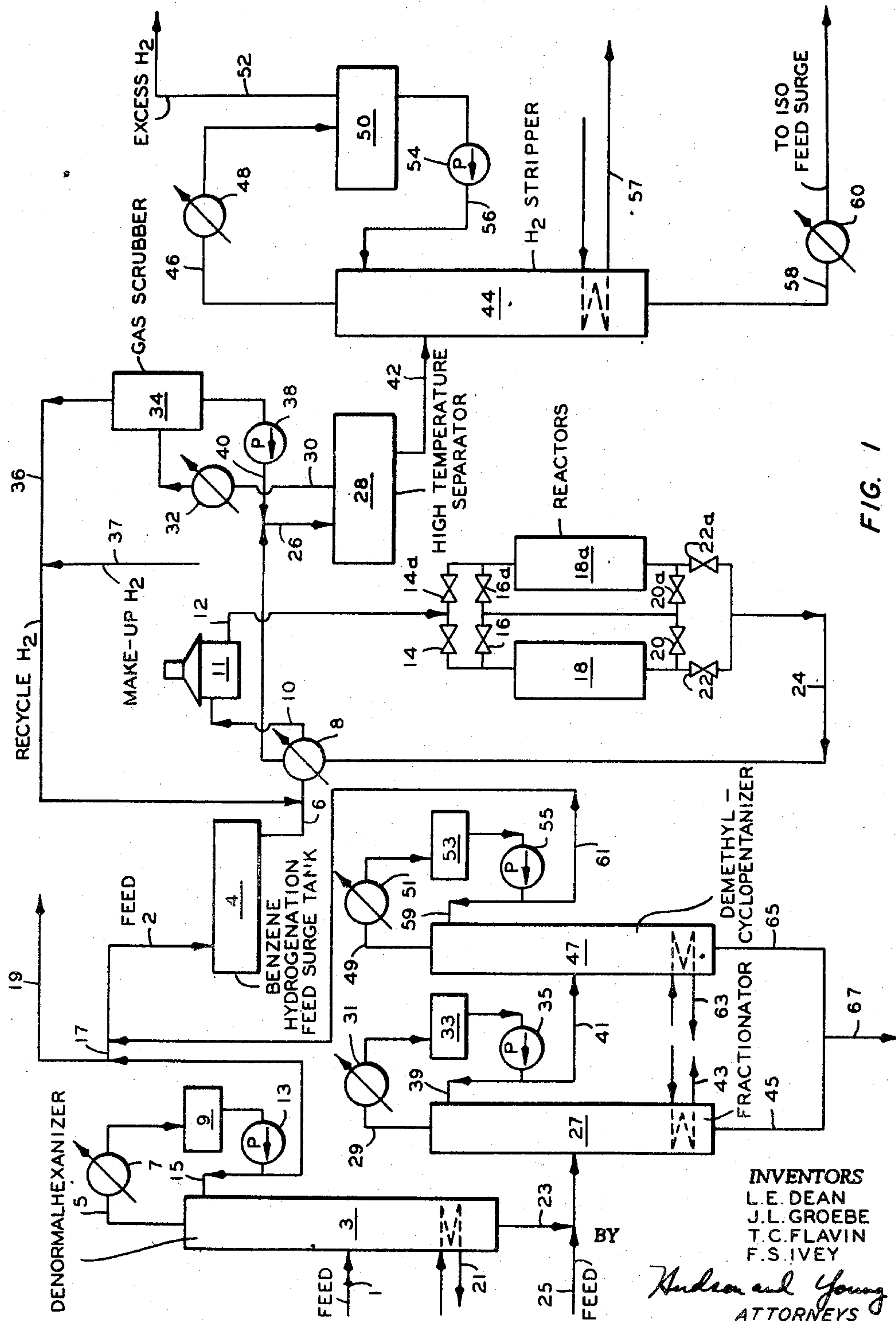
L. E. DEAN ET AL

2,953,606

PRODUCTION OF ISOHEXANE AND CYCLOHEXANE

Filed Nov. 25, 1957

3 Sheets-Sheet 1



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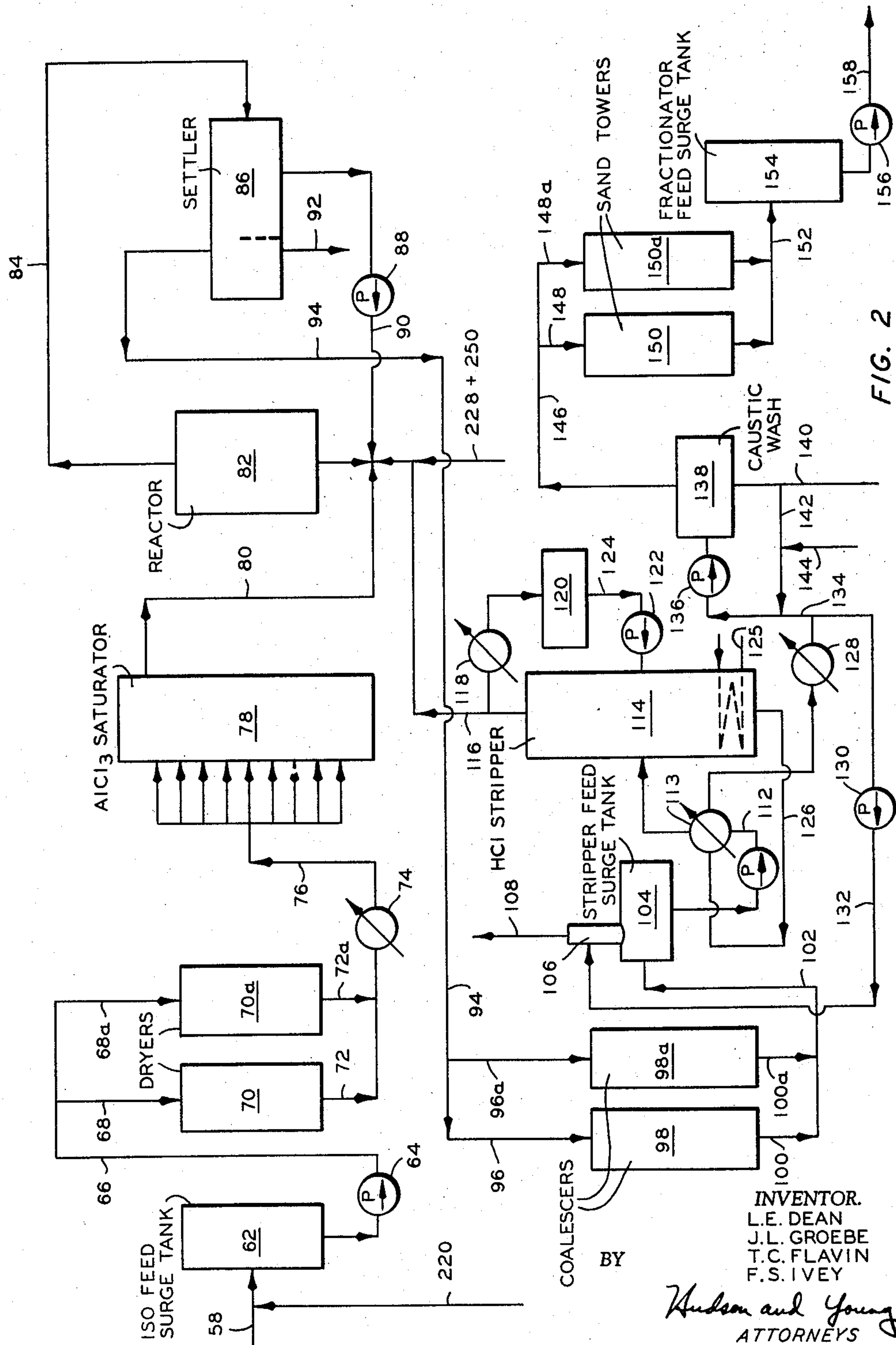


FIG. 2

INVENTOR.
L.E. DEAN
J.L. GROEBE
T.C. FLAVIN
F.S. IVEY

BY
Hudson and Young
ATTORNEYS

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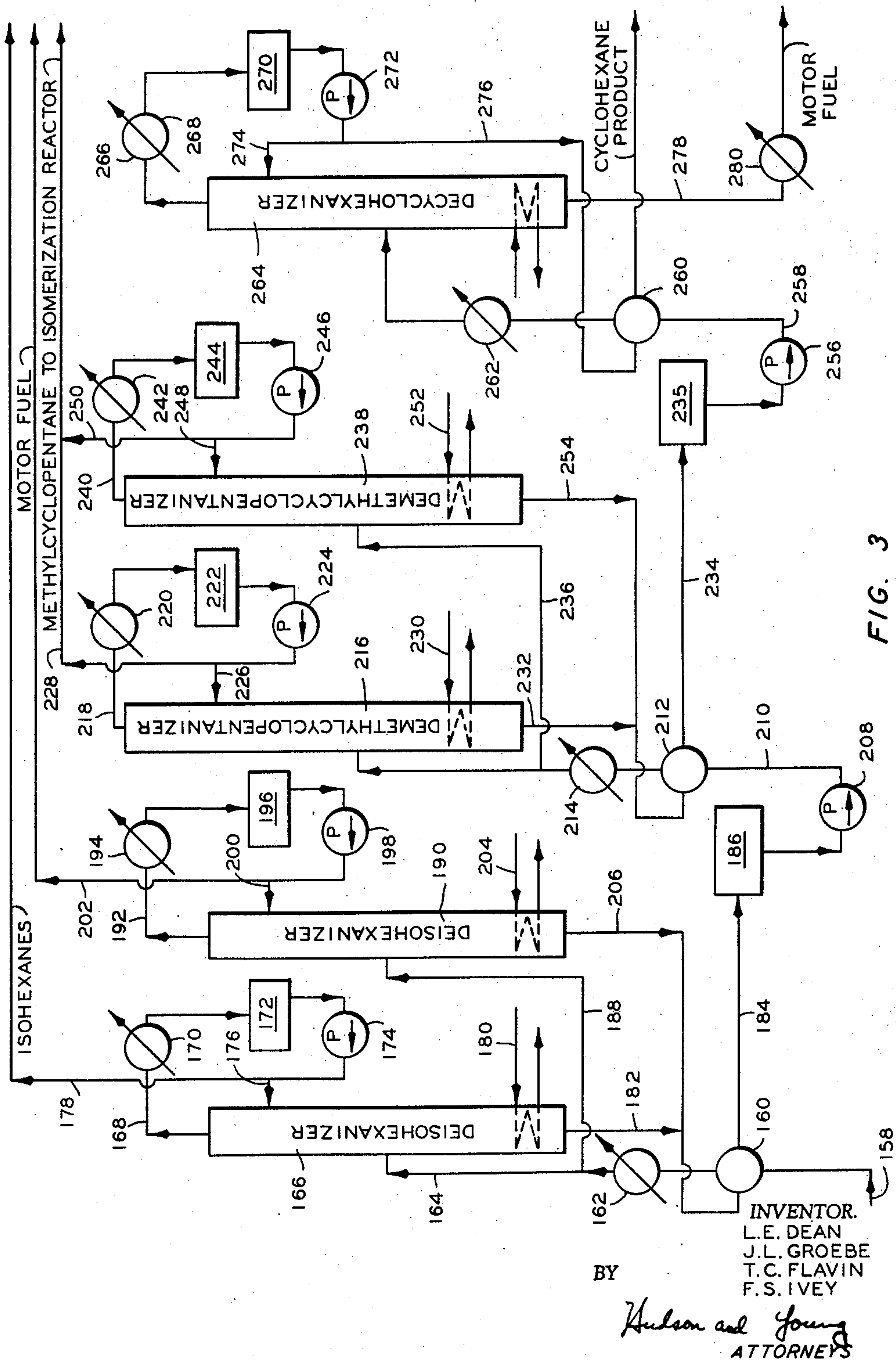


FIG. 3

BY

Hudson and Young
ATTORNEYS

INVENTOR.
L. E. DEAN
J. L. GROEBE
T. C. FLAVIN
F. S. IVEY

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PRODUCTION OF ISOHEXANE AND CYCLOHEXANE

Lloyd E. Dean, John L. Groebe, Fred S. Ivey, and Thomas C. Flavin, all of Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

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5 Claims. (Cl. 260-666)

This invention relates to an improved process for the conversion of hydrocarbons. In one aspect it relates to a process for the isomerization of normal acyclic and alkyl substituted alicyclic hydrocarbons having similar boiling points, such as normal hexane and methylcyclopentane. In another aspect it relates to a combination process for the isomerization of a feed material comprising normal hexane, methylcyclopentane and containing impurities, such as sulfur and benzene in the presence of a metal halide catalyst.

This application is a continuation-in-part of L. E. Dean et al., Serial No. 652,944, filed April 15, 1957, and now abandoned.

Various hydrocarbon fractions of petroleum contain large amounts of naphthenic compounds and normal paraffins. Many of these compounds are relatively useless in their original form; however, they can be converted to valuable materials which are useful in motor fuels or as starting materials in chemical processes. Thus, for example, normal hexane which has a low octane number can be converted to isohexanes which have high octane numbers and form valuable components of motor fuels. Also, for example a compound, such as methylcyclopentane can be converted to cyclohexane which is a starting material in the manufacture of nylon fibers.

It is an object of this invention to provide an improved process for the conversion of hydrocarbons.

Another object of this invention is to provide an improved process for increasing the octane number of components normally present in motor fuel.

Still another object of this invention is to provide an improved process for the isomerization of normally acyclic and substituted alicyclic hydrocarbons having similar boiling points.

Yet another object of this invention is to provide an improved process for the isomerization of a feed material comprising normal hexane and methylcyclopentane and containing benzene and sulfur as impurities.

These and other objects of the invention will become more readily apparent from the following detailed description and discussion.

The above objects are achieved broadly by contacting a feed material comprising a normal acyclic and an alkyl substituted alicyclic compound with a metal halide isomerization catalyst and a corresponding hydrogen halide under suitable conversion conditions whereby said compounds are isomerized.

In one aspect of the invention the feed material comprising a mixture of compounds of similar boiling points such as normal hexane and methylcyclopentane.

In another aspect of the invention the feed material which contains impurities, such as benzene and sulfur, is hydrogenated in the presence of a nickel catalyst whereby the benzene is converted to cyclohexane and the sulfur is converted to nickel sulfide after which said feed material is isomerized.

Isomerization of normally acyclic and alkyl substituted alicyclic hydrocarbons in the method of this invention

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is carried out usually at a temperature in the range of between about 90 F. and about 160° F., the particular temperature employed being dependent on the composition of the material to be converted. Various normal acyclic compounds can be isomerized, including normal butane, normal pentane, normal hexane, normal heptane, etc. The alkyl substituted alicyclic compounds which can be isomerized include methylcyclopentane which is isomerized to cyclohexane, 1,1-dimethylcyclopentane which is converted to methycyclohexane, and the like. Isomerization reaction is preferably carried out under sufficient pressure to provide a liquid phase reaction namely a pressure in the range between about 150 and about 300 p.s.i.g. The contact or residence time of the reactants in the reactor varies usually between about 0.1 and about 5 hrs.

The catalyst employed in carrying out isomerization comprise metal halides, such as aluminum chloride, aluminum bromide, boron trifluoride and the halides of such metals as zinc, tin, arsenic, antimony, zirconium, beryllium, titanium, iron, and the like. These catalysts are especially effective when present as complexes which are formed by interaction between the metal halides and hydrocarbons present in the reaction system. A particularly desirable isomerization catalyst is the complex of hydrocarbon with aluminum chloride. In addition to the catalyst it is desirable that the corresponding hydrogen halide be present in the reaction zone since this material maintains catalyst activity at a high level. The reaction rate and the conversion of the hydrocarbon feed is dependent on the amount of aluminum chloride in the aluminum chloride-hydrocarbon complex. Thus, to maintain a normal hexane conversion of about 55 percent, the catalyst complex should contain 60 to 62 percent aluminum chloride. However, the quantity of aluminum chloride in the complex can be varied over wide ranges to provide a corresponding range of feed reactant conversion. While the over-all activity of the catalyst is established by the aluminum chloride content, as stated, the presence of hydrogen chloride is required to provide a high activity. Usually the quantity of hydrogen chloride present is between about 2 and about 6 weight percent of the feed with about 4 weight percent being preferred. The hydrocarbon-to-catalyst ratio is also an important factor in the isomerization reaction rate and generally this ratio is maintained between about 0.8:1 and about 1.4:1 although ratios as high as 5 to 1 can be used if reaction temperatures are increased.

The removal of contaminants, namely benzene and sulfur, from the isomerization feed is effected by contacting said feed with a dehydrogenated nickel catalyst and hydrogen under suitable conditions of elevated temperature, usually between about 360 and about 500° F. Pressure does not appreciably affect the hydrogenation reaction and the actual pressure employed is established principally by the partial pressure of the hydrogen present. Usually the liquid hourly space velocity is between about 1 and about 3 cubic feet of liquid feed per cubic foot of catalyst per hour. Operation with an excess of hydrogen is preferred; therefore, it is desirable that more than the 3 mols necessary to convert each mol of benzene be present in the reaction zone. Preferably, the hydrogen concentration is such as to provide a hydrogen-to-benzene ratio of between about 4 and about 16 mols/mol.

As a result of the preceding operation benzene is hydrogenated and converted to cyclohexane, which is one of the desired products of the isomerization reaction; and the sulfur in the feed material reacts with the nickel catalyst, converting said catalyst to nickel sulfide. The latter reaction inactivates the catalyst, therefore, periodically it

is necessary to withdraw and dump the spent catalyst and add fresh catalyst to the system.

In order to more fully describe the invention in its various process steps and to provide a better understanding thereof, reference is had to the accompanying drawings of which Figure 1 is a diagrammatic illustration of the feed preparation unit and a benzene dehydrogenation unit, Figure 2 is a diagrammatic illustration of an isomerization unit and Figure 3 is a diagrammatic illustration of a unit for fractionating effluent from the isomerization unit.

Referring to Figure 1 a feed material comprising a mixture of isohexanes, normal hexane, benzene, methylcyclopentane and cyclohexane is introduced to a denormalhexanizer 3 through conduit 1. In the denormalhexanizer which is a conventional fractionating tower, the feed material is separated to provide an overhead product which is concentrated in normal hexane and also contains a substantial quantity of methylcyclopentane. This material is passed from tower 3 in the vapor state through conduit 5 and pump 7 into accumulator 9. Liquid is withdrawn from the accumulator through conduit 13 and utilized as reflux to the denormalhexanizer through conduit 15. A portion of the net accumulator liquid is removed as product; for example, for use as a solvent material, through conduit 19, and the remainder is passed through conduits 17 and 2, to the benzene hydrogenation feed surge tank 4.

The denormalhexanizer bottoms which comprise principally the heavier portions of the feed are removed through conduit 23 and combined with a second hydrocarbon feed stream through conduit 25. The latter stream is similar in composition to the denormalhexanizer bottoms. The combined streams are introduced to fractionator 27 wherein a separation between the components of the feed is carried out to again provide an overhead stream concentrated in normal hexane and methylcyclopentane. This material is passed from the fractionator through conduit 29 and condenser 31 into accumulator 33. The accumulated material is returned in part to the fractionator through pump 35 and conduit 39 and the remainder is introduced to demethylcyclopentanizer 47 through conduit 41. In the latter vessel a further refinement of the hydrocarbon feed is made whereby sulfur-containing materials are rejected from the bottom of the tower. The overhead material, which is concentrated in normal hexane and methylcyclopentane, is condensed with a portion being returned to the tower as reflux through conduit 59 and the remainder being combined with the overhead from the denormalhexanizer 3 through conduit 61. The bottoms from each of fractionator 27 and demethylcyclopentanizer 47 are joined through conduits 45 and 65 respectively to provide a combined stream which is withdrawn from the unit through conduits 67. Each of the fractionators are provided with reboiling means, namely 21, 43 and 63, to provide the heat necessary for the separation which is carried out in each tower. As a result of the aforescribed steps there is provided in the benzene hydrogenation feed surge tank 4 a hydrocarbon mixture comprising normal hexane, methylcyclopentane and a small amount of benzene, cyclohexane and various isohexanes. This material is removed from the feed surge tank and passed through conduit 6, where it is joined by a combined recycle and make-up hydrogen stream, then through exchanger 8 countercurrent to reactor effluent wherein preheat is added and then through conduit 10 into furnace 11 where the additional heat required to initiate the reaction is provided. The heated feed material leaves the furnace at a temperature of about 360° F., passes through conduit 12 and enters reactors 18 and 18a. The reactors are arranged so that the flow therethrough can be in series or in parallel, depending on whether or not a reactor is withdrawn from service. Generally it is desirable to carry out the hydrogenation reaction by passing the feed material through the reactors in series

with the feed first passing through the reactor which is next to be regenerated and then through the other reactor. It is possible to make either reactor first in the series by a suitable arrangement of valves 14, 14a, 16, 16a, 20, 20a, and 22 and 22a. In this specific embodiment valves 14, 20, 16a and 22a are open and valves 14a, 16, 22, and 20a are closed whereby the reactants flow through the reactor 18 and then through reactor 18a. Within the reactors the principal reaction is hydrogenation of benzene to form cyclohexane. This reaction is exothermic, therefore there is a temperature rise, usually of about 21° F. per mol percent of benzene in the fresh feed to the reactor. In the event that sulfur or sulfur-containing compounds are present in the feed material the sulfur reacts with the nickel catalyst converting the catalyst to nickel sulfide. Since nickel sulfide does not promote the hydrogenation reaction, removal of the sulfur from the feed in this manner in effect poisons the catalyst, which necessitates periodic shutdown of each reactor for removal of contaminated catalyst and addition of fresh catalyst.

The effluent from the reactors, now free from benzene and sulfur, but containing some light paraffins as a result of a minor amount of cracking passes through conduit 24 and exchanger 8 countercurrent to the feed to furnace 11 and then through conduit 26 into a high temperature separator 28. In this vessel the major portion of the hydrogen in the effluent, plus uncondensed lighter hydrocarbons are removed, passing from the separator through conduit 30. The vapors from the separator are passed through a partial condenser 32 and into a gas scrubber 34 wherein a portion of the hydrocarbons are separated from the hydrogen by condensation. The remaining gaseous material comprising about 85 mol per cent hydrogen is released from the scrubber through conduit 36 and combined with the feed to the hydrogenation unit as previously described. As required make-up hydrogen is introduced to the recycle hydrogen stream through conduit 37. The liquid material from gas scrubber 34 is returned to the high temperature separator through pump 38 and conduit 40. As necessary to maintain a more or less constant level in said separator the combined liquid is withdrawn therefrom through conduit 42 and introduced to hydrogen fractionator 44 supplied with heat through reboiler 57, wherein separation and recovery of the remaining hydrogen in this material is effected. The overhead from the stripper, which comprises principally hydrogen, with a small amount of light gaseous hydrocarbon passes through conduit 46 and partial condenser 48 into accumulator 50 from which hydrogen is withdrawn through conduit 52. Condensed overhead is returned to the stripper through pump 54 and conduit 56 as reflux. The bottoms from the hydrogen stripper comprising a stream now essentially free from hydrogen and light hydrocarbons are removed from the stripper through conduit 58, cooled in exchanger 60 and introduced to the isomerization feed surge tank 62. Before entering the isomerization feed surge tank the stripper bottoms effluent is combined through conduit 220 with a stream rich in methylcyclopentane obtained in a manner hereinafter described.

In the first stage of the isomerization step the feed material is removed from surge tank 62 through pump 64 and passed through conduit 66 into dryers 70 and 70a wherein any moisture present in the feed is removed. Normally the dryers are operated in parallel with one dryer being in operation while the other dryer is being regenerated or being emptied and filled with fresh drying agent. Various drying agents can be employed however, usually bauxite is preferred. The dried feed is passed through cooler 74 where the temperature is substantially reduced and then is passed through conduit 76 into aluminum chloride saturator 78. In this vessel the feed which can be introduced at various elevations contacts aluminum chloride crystals which are picked up and

carried with the feed through conduit 80 into an isomerization reactor 82. Before entering the reactor the catalyst concentration of the feed is increased by the addition of aluminum chloride hydrocarbon complex from settler 86. Hydrogen chloride is also added to the feed, through conduit 116. The principal reaction which takes place in the reactor is the isomerization of normal hexane to 2-methylpentane and methylcyclopentane to cyclohexane. In addition, three other isomers of normal hexane, neo-hexane, diisopropyl, and 3-methylpentane are also formed in varying quantities. The effluent from the reactor, comprising unreacted normal hexane, methylcyclopentane, cyclohexane and the various isohexanes is passed through conduit 84 and enters settler 86 wherein entrained catalyst complex is separated from the hydrocarbon material, the major portion of the settled catalyst complex being returned to the reactor through pump 88 and conduit 90. Inasmuch as the catalyst gradually loses its activity it is desirable that a portion of it be either periodically or continuously withdrawn from the system. For this purpose a baffle is provided in one end of settler 86 and separated catalyst is withdrawn continuously therefrom through conduit 92. Although a substantial separation of catalyst and hydrocarbon is effected in settler 86 of the hydrocarbon effluent therefrom still contains finely divided aluminum chloride-hydrocarbon complex and a major proportion of the hydrogen chloride. This stream is passed through conduit 94 into coalescers 98 and 98a for the purpose of effecting removal and recovery of these materials. As in the case of the isomerization feed dryers these vessels are operated in parallel with normally one vessel in operation while the other is being emptied and refilled with the coalescing and filtering medium. Various inert materials can be used for coalescing the catalyst, including sand, charcoal, and the like, however, bauxite is preferred for this purpose. The effluent from the coalescers, now substantially freed of aluminum chloride-hydrocarbon complex is introduced to hydrogen chloride stripper feed surge tank 104 through conduit 102. As previously stated, the effluent from the benzene hydrogenation contains small quantities of light gaseous hydrocarbons which are the result of cracking during the hydrogenation step. These materials are normally removed in the stripper along with said hydrogen chloride however, since the hydrogen chloride is recycled to the isomerization reactor eventually the light gases build up in the system. To prevent such a buildup venting of gases is provided through column 106 which is disposed on the stripper feed surge tank. In order to prevent loss of hydrogen chloride in this operation, bottoms from the hydrogen chloride stripper, comprising the main product stream (substantially free from HCl) are introduced to the top of column 106 through conduit 132. Hydrogen chloride in the vent gases is thus absorbed and returned to the stripper feed surge tank and the gases are passed from the system through conduit 108.

Accumulated material in the feed surge tank is removed therefrom through pump 110 and conduit 112, passed through exchanger 113 in indirect heat exchange with hydrogen chloride stripper bottoms and is introduced to hydrogen chloride stripper 114 wherein the major portion of the hydrogen chloride is separated from the reactor effluent. The overhead product from the stripper is a hydrogen chloride rich stream which, as previously noted, is returned in part to the isomerization reactor through conduit 116. The remainder of the stripper overhead is passed through condenser 118 and enters accumulator 120, from which it is withdrawn and returned to the stripper as reflux through pump 122 and conduit 124. Any heat required in the stripping operation is provided by reboiler 125 which is disposed in the bottom of stripper 114. The stripper bottoms product comprising principally the heavier hydrocarbon portion of the reactor effluent is removed therefrom through con-

duit 126, passed through exchanger 113 and cooler 128, conduit 134 and pump 136 and then introduced to caustic wash tank 138 wherein any remaining hydrogen chloride is neutralized. Provision is made to recycle caustic to the wash tank through conduit 142, with spent caustic being withdrawn through conduit 140 and fresh caustic being introduced, as required, through conduit 144. The caustic washed hydrocarbon product is then passed through conduit 146 to sand towers 150 and 150a to remove the caustic. These towers are also operated in parallel in order to provide for continuous operation during dumping and replacement of the sand contained therein. From the sand towers the product stream is introduced to the fractionator feed surge tank 154 through conduit 152.

The isomerization-fractionation system comprises a series of three fractionation stages, the first two stages each being carried out in two fractionators and the final stage being carried out in a single fractionator. In the first stage of this process material from surge tank 154 is passed through pump 156 and conduit 158 into a first fractionator 166. Before entering the fractionator the feed passes through two exchangers 160 and 162 being indirectly heated with the bottoms from fractionators 166 and 190 in the exchanger 160 and further heated with steam in exchanger 162. Fractionator 166 is the first fractionator in the series of two which are provided for the purpose of removing isohexanes from the isomerization reaction effluent.

A portion of the feed material is introduced to this fractionator through conduit 164. Within the fractionator a separation is carried out whereby an overhead product substantially free from normal hexane is provided. This material leaves the tower in the vapor state through conduit 168, is condensed in condenser 170 and passes into an accumulator 172. Accumulated liquid is withdrawn through pump 174, a portion is returned to the fractionator through conduit 176 as reflux and the remainder is yielded from the unit through conduit 178. The yielded material, which comprises essentially isohexanes, has a high octane value and is suitable for use as aviation fuel.

The remaining portion of the isomerization effluent is passed through conduit 188 and introduced to the second deisohexanizer 190. In this vessel it is necessary to provide a different separation from that carried out in fractionator 166. Due to the reaction equilibrium in the isomerization reactor and the composition of the feed provided thereto, it is not possible to convert all of the normal hexane present in the feed to the reactor even though recycle of this material is employed. As a result, it is necessary to yield a quantity of normal hexane from the unit. This is accomplished by operating deisohexanizer 190 to provide an overhead stream containing isohexanes and in addition any excess unconverted normal hexane. The overhead product from tower 190 is condensed and a portion is returned to this tower as reflux through conduit 200 with the remainder being yielded through conduit 202. Since the material in conduit 202 contains a substantial amount of normal hexane it has a lower octane number than the overhead product from tower 166 and therefore is suitable only for motor fuel.

The portion of the isomerization effluent which remains after the removal of normal hexane and isohexanes passes from the bottom of deisohexanizers 166 and 190, through conduits 182 and 206 respectively, through exchanger 160 and conduit 184 and then into accumulator 186. From this vessel the bottoms material is passed through pump 208 and conduit 210 to the second fractionation stage which is provided for the purpose of removing unconverted methylcyclopentane and normal hexane from the reaction effluent. Two fractionators 216 and 238 make up this stage.

The feed to these fractionators passes first through exchanger 212 in indirect heat exchange with the bottoms from the fractionators and then through exchanger 214

after which this material is divided with a portion being fed to each of the fractionators. The overhead product from the fractionators is treated in a conventional manner, namely condensed, a portion refluxed to the fractionators and the remainder yielded from the unit through conduits 228 and 250. The bottom streams are combined through conduits 232 and 254 and introduced through conduit 234 to accumulator 235. From this vessel the remaining effluent is passed to the remaining stage of the product fraction, namely to the decyclohexanizer 264. Before entering this vessel the accumulator material is preheated by passage through heat exchanger 260 countercurrent to the bottoms from vessel 264 and then through steam heater 262. The overhead vapors from the decyclohexanizer are condensed and split, with a portion being returned to the decyclohexanizer as reflux and the remainder being yielded as cyclohexane product through conduit 276. The remaining portion of the reaction effluent is withdrawn from the bottom of decyclohexanizer, cooled in exchanger 280 and yielded from the unit for use as motor fuel.

The following example is provided in illustration of an application of a preferred embodiment of the invention on a commercial scale.

EXAMPLE

Feed preparation

Flows:	Gal./day
Feed to denormalhexanizer (1) -----	238,460
Composition-----	Volume percent
Isohexanes -----	10.6
n-Hexane -----	53.3
Methylcyclopentane -----	20.0
Isoheptanes -----	2.8
Benzene -----	2.4
Cyclohexane -----	10.5
1-1, dimethylcyclopentane(+) -----	0.4
Denormalhexanizer overhead (17) -----	166,380
Composition-----	
Isohexanes -----	12.9
Methylcyclopentane -----	19.4
n-Hexane -----	63.9
Isoheptanes -----	0.2
Benzene -----	2.8
Cyclohexane -----	0.8
Denormalhexanizer bottoms (23) -----	44,080
Composition-----	
n-Hexane -----	6.4
Methylcyclopentane -----	22.8
Isoheptanes -----	14.3
Benzene -----	0.9
Cyclohexane -----	53.6
1-1, dimethylcyclopentane(+) -----	2.0
Feed to fractionator (23 and 25) -----	94,990
Composition-----	
Isohexanes -----	0.2
n-Hexane -----	9.4
Methylcyclopentane -----	17.7
Isoheptanes -----	12.5
Benzene -----	0.6
2,4-dimethylpentanecyclohexane -----	57.6
1-1, dimethylcyclopentane(+) -----	2.0
Fractionator overhead (41) -----	39,950
Composition-----	
Isohexanes -----	0.4
n-Hexane -----	22.5
Methylcyclopentane -----	42.0
Isoheptanes -----	10.1
Benzene -----	1.5
Cyclohexane -----	23.5
Demethylcyclopentanizer overhead (61) -----	25,730
Composition-----	
Isohexanes -----	0.7
n-Hexane -----	34.6
Methylcyclopentane -----	62.1
Isoheptanes -----	0.3
Benzene -----	2.3

Temperatures	°F.	
	Top	bottom
Denormalhexanizer (3) -----	230	265
Fractionator (27) -----	244	286
Demethylcyclopentanizer (47) -----	248	268

Pressures:	p.s.i.g.
Denormalhexanizer (3) -----	43
Fractionator (27) -----	45
Demethylcyclopentanizer (47) -----	42

Benzene hydrogenation

Flows:	Gal./day
Hydrocarbon feed to reactors (2) -----	259,000
Composition-----	Volume percent
n-Hexane -----	58.5
Methylcyclopentane -----	22.7
Benzene -----	2.8
Cyclohexane -----	1.8
Isohexanes -----	13.9
Isoheptanes -----	0.3
Hydrogen feed (plus recycle) (36 and 37) -----	9,310
Composition-----	
Hydrogen -----	mols/day 6252
Light paraffins -----	Volume percent 75.2
n-Hexane -----	do 15.5
Methylcyclopentane -----	do 2.8
Cyclohexane -----	do .4
Isohexanes -----	do 6.1
Feed to hydrogen stripper (42) -----	264,160
Composition-----	Volume percent
Light paraffins -----	1.4
n-Hexane -----	57.3
Methylcyclopentane -----	22.2
Cyclohexane -----	5.2
Isohexanes -----	13.6
Isoheptanes -----	0.3
Catalyst-----hydrated nickel oxide-----	108,000 lbs. in each reactor.
Temperatures:	° F.
Reactor feed (12) -----	380
Reactor effluent (24) -----	470
High temperature separator (28) -----	200
Gas scrubber (34) -----	105
Hydrogen stripper (44) -----	
Top -----	220
Bottom -----	325
Pressures:	p.s.i.g.
Reactor (18) -----	410
High temperature separator (28) -----	400
Gas scrubber (34) -----	395
Hydrogen stripper (44) -----	130

Isomerization unit

Flows:	Gal./day
Hydrocarbon feed to reactor (80, 228 and 250) -----	416,200
Composition-----	Volume percent
n-Hexane -----	63.1
Methylcyclopentane -----	18.2
Cyclohexane -----	3.8
Isohexanes -----	14.7
Isoheptanes -----	0.2
AlCl ₃ -complex catalyst to reactor (80 and 90) -----	299,830
HCl (recycle) to reactor (116) -----	19,700
Reactor effluene (84) -----	736,080
Composition-----	
n-Hexane -----	16.1
Methylcyclopentane -----	2.3
Cyclohexane -----	9.6
Isohexanes -----	28.0
Catalyst -----	40.9
HCl -----	2.7
Isoheptanes -----	0.1
1-1, dimethylcyclopentane(+) -----	0.3

Temperatures:	° F.
Hydrocarbon reactor feed (80) -----	80
Reactor effluent (84) -----	140
HCl stripper (114) -----	
Top -----	150
Bottom -----	355
Pressures:	p.s.i.g.
Reactor (82) -----	155
Coalescers (98 and 98a) -----	40
HCl stripper (bottom) (114) -----	190
Sand towers (150 and 150a) -----	153

Product fractionation

Flows:	Gal./day
Feed to Deisohexanizers (158) -----	413,340
Composition-----	Volume percent
n-Hexane -----	28.5
Methylcyclopentane -----	4.1
Cyclohexane -----	17.1
Isohexanes -----	49.6
Isoheptanes -----	0.2
1-1, dimethylcyclopentane(+) -----	0.5
Deisohexanizer (166) overhead (178) -----	108,720
Composition-----	
n-Hexane -----	8.9
Isohexanes -----	90.8
Methylcyclopentane -----	0.2
Cyclohexane -----	0.1
Deisohexanizer (190) overhead (202) -----	129,820
Composition-----	
n-Hexane -----	23.9
Isohexane -----	75.6
Methylcyclopentane -----	0.4
Cyclohexane -----	0.1
Feed to demethylcyclopentanizer (210) -----	175,300
Composition-----	
n-Hexane -----	44.1
Methylcyclopentane -----	9.3
Cyclohexane -----	40.2
Isohexanes -----	4.8
Isoheptanes -----	0.5
1-1, dimethylcyclopentane(+) -----	1.1

Product fractionation—Continued

Flows:	Gal./day
Demethylcyclopentanizer overhead (to isomerization unit) (228 and 250) -----	108,400
Composition—	
n-Hexane -----	71.3
Methylcyclopentane -----	15.0
Isohexanes -----	7.8
Cyclohexane -----	5.7
Isoheptanes -----	0.2
Feed to decyclohexanizer (258) -----	66,910
Composition—	
Cyclohexane -----	96.0
Methylcyclopentane -----	0.1
Isoheptanes -----	1.0
1-1, dimethylcyclopentane(+) -----	2.9
Cyclohexane product (276) -----	65,160
Composition—	
Cyclohexane -----	98.1
Isoheptanes -----	1.0
Methylcyclopentane -----	0.1
1-1, dimethylcyclopentane(+) -----	0.8
Decyclohexanizer bottoms to motor fuel (278) -----	1,770
Composition—	
Cyclohexane -----	20.7
1-1, dimethylcyclopentane(+) -----	79.3
Temperatures:	° F.
Feed to deisohexanizer (158) -----	240
Deisohexanizer (166)—	
Top -----	200
Bottom -----	248
Deisohexanizer (190)—	
Top -----	205
Bottom -----	255
Demethylcyclopentanizers (216 and 238)—	
Top -----	225
Bottom -----	265
Decyclohexanizer (264)—	
Top -----	258
Bottom -----	305
Pressures:	P.s.i.g.
Deisohexanizer (166) -----	40
Deisohexanizer (190) -----	40
Demethylcyclopentanizers (216 and 238) -----	40
Decyclohexanizer (264) -----	40

Having thus described the invention by providing a specific example thereof, it is to be understood that no undue limitations or restrictions are to be drawn by reason thereof, and that many variations and modifications are within the scope of the invention.

We claim:

1. A process for the isomerization of hydrocarbons which comprises contacting a hydrocarbon feed comprising normal hexane and methylcyclopentane in a reaction zone with an aluminum chloride-hydrocarbon complex catalyst and hydrogen chloride at a temperature of between about 90° F. and about 160° F. whereby the feed material is isomerized, introducing the reaction zone effluent to a settling zone wherein separation between hydrocarbons and catalyst is effected, recycling at least a portion of the catalyst to the reaction zone, passing the hydrocarbon phase from the settling zone to a coalescing zone wherein the removal of additional catalyst is effected by contacting with a catalyst coalescing medium selected from the group consisting of sand, charcoal, and bauxite, venting the hydrocarbon effluent from the coalescing zone to effect removal of light hydrocarbon gases, contacting the vented gases with absorbent obtained as hereinafter described whereby entrained hydrogen chloride is absorbed from said gases, combining absorbent and absorbed hydrogen chloride with the remaining liquid portion of the coalescing zone hydrocarbon effluent, passing the combined material to a hydrogen chloride stripping zone wherein the major portion of the hydrogen chloride is separated, removing and recycling stripped hydrogen chloride to the reaction zone, utilizing a portion of the stripped hydrocarbon material as said absorbent, passing the remainder of the stripped hydrocarbon through a caustic wash for the neutralization of any remaining hydrogen chloride, passing the caustic washed material through a sand tower for the removal of entrained caustic, then introducing said effluent to a series of fractionation zones wherein various components of said effluent are separated and recycling unreacted methylcyclopentane and normal hexane to the reaction zone.

2. A process for the isomerization of hydrocarbons which comprises contacting a hydrocarbon feed comprising normal hexane and methylcyclopentane and contain-

ing, as impurities, benzene and sulfur, with a hydrated nickel oxide hydrogenation catalyst in the presence of hydrogen at a temperature between about 300° F. and about 450° F. in a hydrogenation zone whereby the benzene in the feed material is hydrogenated to cyclohexane and the sulfur reacts with the nickel catalyst to form nickel sulfide, introducing the hydrogenation reaction zone effluent into a separation zone from which a gaseous material rich in hydrogen is vented, passing the vented material through a cooling zone and into a gas scrubbing zone for the separation of liquid and gas rich in hydrogen, returning the liquid from the scrubbing zone to the separation zone and the hydrogen-rich gas to the hydrogenation zone, introducing said combined liquids to a stripping zone wherein the remaining hydrogen is removed, said hydrogen also being recycled to the hydrogenation zone, passing the liquid from the stripping zone to an isomerization zone wherein this material is contacted with an aluminum chloride-hydrocarbon complex catalyst and hydrogen chloride at a temperature of between about 90° F. and about 160° F. whereby the feed material is isomerized, introducing the isomerization zone effluent to a settling zone wherein separation between hydrocarbons and catalyst is effected, recycling at least a portion of the catalyst to the isomerization zone, passing the hydrocarbon phase from the settling zone to a coalescing zone wherein the removal of additional catalyst is effected, venting the effluent from the coalescing zone to effect removal of light hydrocarbon gases, contacting the vented gases with an absorbent obtained as hereinafter described, whereby hydrogen chloride is absorbed from said gases, combining the absorbent and absorbed hydrogen chloride with the liquid portion of the coalescing effluent, passing the combined material to a hydrogen chloride stripping zone wherein the major portion of the hydrogen chloride is separated, removing and recycling stripped hydrogen chloride to the isomerization zone, utilizing a portion of the stripped hydrocarbon material as said absorbent, passing the remainder of the stripped hydrocarbon through a caustic wash for the neutralization of any remaining hydrogen chloride, passing the caustic-washed material through a sand tower for the removal of entrained caustic, then introducing said effluent to a series of fractionation zones wherein various components of said effluent are separated, and recycling unreacted methylcyclopentane and normal hexane to the reaction zone.

3. The process of claim 2 in which the isomerization effluent is divided into two portions, the first portion is fractionated to provide a product comprising essentially isohexanes, the second portion is fractionated to provide a product comprising essentially isohexanes and normal hexane, and the remainders of the two portions are combined and introduced to a series of fractionation zones wherein methylcyclopentane and cyclohexane are successively removed therefrom.

4. In a process for the isomerization of hydrocarbons which comprises contacting a hydrocarbon feed comprising an isomerizable hydrocarbon selected from the group consisting of isomerizable normal paraffins and naphthenes with an aluminum halide-hydrocarbon complex catalyst promoted by hydrogen halide, thereby isomerizing said hydrocarbon, and removing said catalyst from admixture with the thus treated hydrocarbon product, the improvement which comprises passing thus treated hydrocarbon product to a gas removal zone in which gaseous material is separated from the liquid hydrocarbon product and vented from the system, contacting the vented gases with an absorbent obtained as hereinafter described and thus effecting the absorption of hydrogen halide in said vent gas by said absorbent, mixing the resulting absorbent containing hydrogen halide with said liquid hydrocarbon product, passing the resulting mixture to a hydrogen halide stripping zone wherein hydrogen halide is removed from said hydrocarbon product by stripping, and

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returning part of the thus stripped hydrocarbon product to contact with said vented gas as hereinbefore described.

5. In a process for the isomerization of hydrocarbons which comprises contacting a hydrocarbon feed comprising normal hexane and methylcyclopentane with an aluminum chloride-hydrocarbon complex catalyst promoted by hydrogen chloride, thereby isomerizing said hydrocarbons, and removing most of said catalyst from admixture with the thus treated hydrocarbon mixture, the improvement which comprises passing thus purified hydrocarbon product to a coalescing zone wherein said hydrocarbon product is contacted with a catalyst coalescing medium selected from the group consisting of sand, charcoal, and bauxite and remaining traces of catalyst are coalesced and removed, passing thus treated hydrocarbon product to a gas removal zone in which gaseous material is separated from the liquid hydrocarbon product and vented from the system, contacting the vented gases with an absorbent obtained as hereinafter described

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and thus effecting the absorption of hydrogen chloride in said vent gas by said absorbent, mixing the resulting absorbent containing hydrogen chloride with said liquid hydrocarbon product, passing the resulting mixture to a hydrogen chloride stripping zone wherein hydrogen chloride is removed from said hydrocarbon product by stripping, returning part of the thus stripped hydrocarbon product to contact with said vented gas as hereinbefore described, and recovering isomerized hydrocarbons from the remainder of said hydrocarbon product.

References Cited in the file of this patent

UNITED STATES PATENTS

15	2,303,075	Frey	Nov. 24, 1942
	2,379,550	Sutton et al.	July 3, 1945
	2,381,439	D'ouville et al.	Aug. 7, 1945
	2,420,883	Johnson et al.	May 20, 1947
	2,755,317	Kassel	July 17, 1956