

Feb. 24, 1953

F. E. CONDON
METHOD OF ISOMERIZING PARAFFINS WITH
ALUMINUM HALIDES AND CIS-DECALIN

2,629,754

Filed Dec. 17, 1948

2 SHEETS--SHEET 1

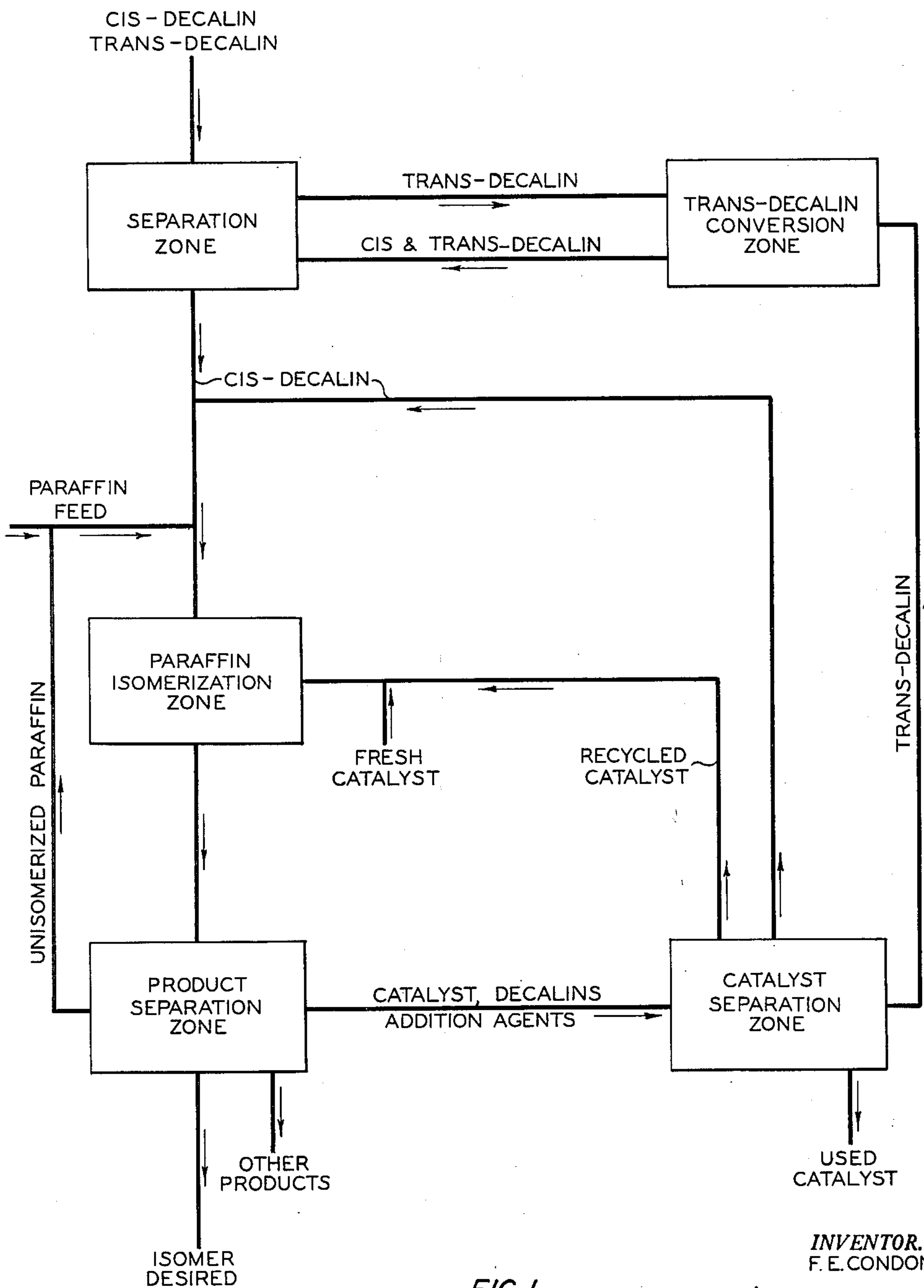


FIG. 1

BY

Hudson & Young

ATTORNEYS

INVENTOR.
F. E. CONDON

Feb. 24, 1953

F. E. CONDON
METHOD OF ISOMERIZING PARAFFINS WITH
ALUMINUM HALIDES AND CIS-DECALIN

2,629,754

Filed Dec. 17, 1948

2 SHEETS—SHEET 2

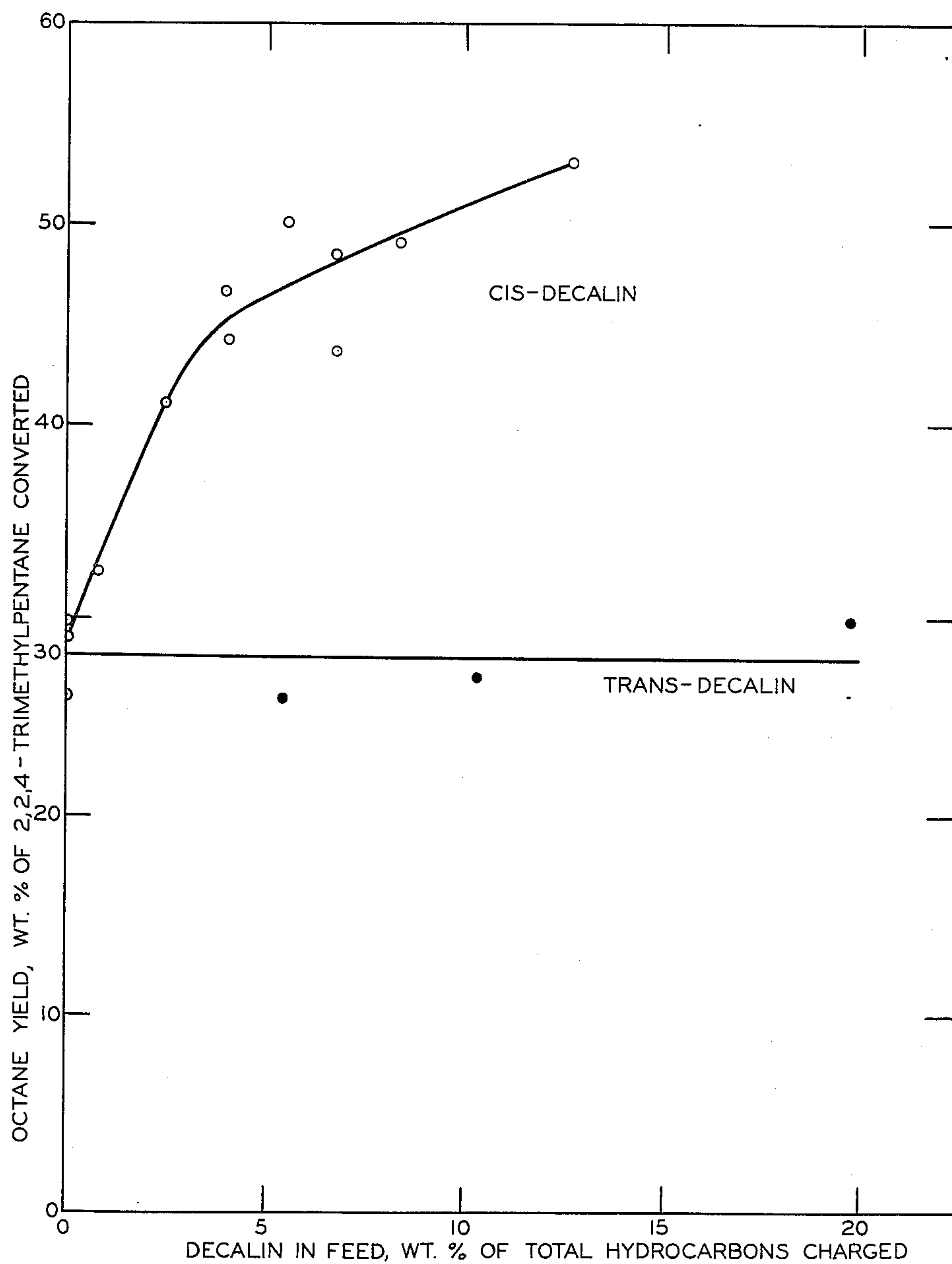


FIG. 2

INVENTOR.
F. E. CONDON

BY *Hudson & Young*

ATTORNEYS

UNITED STATES PATENT OFFICE

2,629,754

METHOD OF ISOMERIZING PARAFFINS
WITH ALUMINUM HALIDES AND CIS-
DECALINFrancis E. Condon, Bartlesville, Okla., assignor
to Phillips Petroleum Company, a corporation
of Delaware

Application December 17, 1948, Serial No. 65,905

7 Claims. (Cl. 260—683.5)

1

The present invention relates to the isomerization of a hydrocarbon. In one of its embodiments, the invention relates to the isomerization of a paraffin hydrocarbon.

The importance of processes for the isomerization of hydrocarbons, generally, for example, the paraffin hydrocarbons, is well recognized in the art of producing motor fuels as well as in the chemical synthesis fields. Many different processes involving various conditions of isomerization and different catalysts have been set forth.

In respect of the art of producing motor fuels it has been desired constantly to increase not only the yields of isomerized hydrocarbons, produced in any particular process, but also the percentage of the specifically desirable isomer or isomers obtained. Therefore, any change in existing processes which will decidedly increase either the total yield of isomer produced or increase the percentage of the desirable isomer or isomers in the product obtained is constantly sought for and constitutes an important advance in the art. As fully set forth below, the process of this invention accomplishes a decidedly large increase in the ultimate yield of isomerized hydrocarbons obtainable in a prior art process, that is, it increases the percentage of the desirable isomer or isomers in the product mixture.

As stated, the isomerization of hydrocarbons, for example, paraffin hydrocarbons, is well known in the art. Catalysts which have been employed for this reaction are also well known and include, among others, Friedels-Crafts catalysts, for example, aluminum chloride, aluminum bromide, and the like.

Hydrocarbons isomerized by the prior processes include among others, the paraffin hydrocarbons, branched-chain paraffin hydrocarbons, and the like. Of particular present importance to the art are the branched-chain paraffin hydrocarbons which possess or exhibit high octane number or value in use as motor fuels. Therefore, the present invention will be described in connection with its application to the production of certain highly desirable branched-chain paraffin hydrocarbons and its application to the production of other isomer hydrocarbons will be obvious to those versed in the hydrocarbon art or the chemical art from a reading of this specification and its appended claims.

As stated, it is known to isomerize a paraffin hydrocarbon or a branched-chain paraffin hydrocarbon employing a Friedels-Crafts type catalyst, for example a metal halide isomerization catalyst such as aluminum chloride, aluminum bromide, zirconium chloride, zinc chloride, etc. Now it also has been known to employ certain reaction modifying agents which inhibit side reactions. Among those which have been recommended to be employed is decalin, that is, decahydronaphthalene.

2

Ordinarily available decalin contains both cis- and trans-decalin. Thus, the recommended use of decalin in the prior art has been a recommendation of the use of both the cis- and trans- forms of decalin. In any event, to my present knowledge, the art has not distinguished between the isomers of decalin in respect of its use as a modifier for the isomerization of hydrocarbons.

According to this invention it has been found that of the components of decalin it is the cis-decalin which is solely responsible for the modifier effect of decalin as heretofore recommended for the catalytic isomerization of hydrocarbons. Thus, according to this invention it has been found that trans-decalin exhibits or possesses practically no modifier effect in the catalytic isomerization of hydrocarbons and, therefore, when it is present merely dilutes the cis-decalin.

Therefore, as a result of these findings and according to the present invention, there is provided a process for the isomerization of isomerizable hydrocarbons, for example, paraffin hydrocarbons, and more particularly branched-chain paraffin hydrocarbons, having at least four carbon atoms to the molecule, under isomerization conditions in presence of an isomerization catalyst and a modifier consisting essentially of cis-decalin.

Still, according to this invention, it has also been found that when 2,2,4-trimethylpentane is isomerized it is converted substantially to the octanes, 2,2,3-, 2,3,3- and 2,3,4-trimethylpentanes. Thus, of the octanes obtained upon the isomerization of 2,2,4-trimethylpentane, 91% consisted of the three just enumerated.

It is known that the research octane numbers of 2,2,3-, 2,3,3-, and 2,3,4-trimethylpentanes are superior to that of 2,2,4-trimethylpentane and accordingly the importance of the application of the process of the present invention can be appreciated readily. It is also known that in the synthesis of triptane (2,2,3-trimethylbutane) 2,2,3-, and 2,3,3-trimethylpentanes are catalytically hydrogenolyzed. The importance of triptane as a super-fuel component further emphasizes the value of the present invention to the chemical synthesis art.

The process of the present invention is applicable with advantage to the isomerization of 2,2,4-trimethylpentane to the other trimethylpentanes e. g. 2,2,3-, 2,3,3- and 2,3,4-trimethylpentanes and, therefore, it will be described with reference to said isomerization.

According to a modification of the present invention and as illustrated diagrammatically in Figure 1 of the drawing, commercially available decalin is separated by fractional distillation into a cis-decalin fraction (B. P. 194.6° C.) and a trans-decalin fraction (B. P. 185.5° C.). The trans-decalin which previously diluted cis-decalin, can now be converted to cis-decalin, as here-

3

inafter set forth, and used to cause said advantageous effect as one of the features of this invention.

The cis-decalin is now admixed with 2,2,4-trimethylpentane and contacted with aluminum chloride in a paraffin isomerization zone under usual conditions of isomerization well known in the art. To promote the reaction, an alkyl halide, an olefin or the like, and/or a hydrogen halide may also be present in the reaction mixture. The use of such reaction-promoting addition agents, commonly called catalyst activators, is well known in the isomerization art.

Following completion of the isomerization reaction, the reaction mass is passed to a product separation zone. The catalyst is separated employing standard procedures and the hydrocarbons are fractionally distilled.

The reaction mass consists of catalyst, isomerized 2,2,4-trimethylpentane, some other hydrocarbons and cis- and trans-decalins. Some of the cis-decalin undergoes a change to the trans-form during the reaction. The unisomerized 2,2,4-trimethylpentane is recycled to the isomerization zone, the other hydrocarbons are removed from the system, the cis-decalin is used to further modify additional isomerization and, as a feature of the invention, the trans-decalin is converted to the cis- form and also used to modify additional isomerization in the isomerization zone.

Used catalyst is reused, all or in part, or withdrawn from the system, as desired. The conversion of trans- to cis-decalin can be effected advantageously by dehydrogenation to naphthalene, hydrogenation, and recovery of the cis-isomer. This is accomplished in the "trans-decalin conversion zone." The dehydrogenation and hydrogenation can be accomplished by known methods. Thus, the dehydrogenation can be effected in presence of a nickel, or chromia-alumina, catalyst at an elevated temperature. The hydrogenation can be effected in presence of a nickel, cobalt, copper or platinum catalyst at an elevated pressure the temperature being maintained, preferably, below about 100° C. to favor the yield of the cis-isomer.

The quantity of cis-decalin admixed with the hydrocarbon feed can be varied. Even small amounts of cis-decalin, say 0.1 per cent by weight of the hydrocarbon in the feed, can be used to advantage to effect an increase in the yield of octanes, but increased yields of octanes are obtained with increasing amounts of cis-decalin up to about 15 per cent by weight. Little advantage now appears to be gained by using more than about 15 per cent by weight of cis-decalin in the hydrocarbon feed. Thus, according to the invention the preferred range for the quantity of cis-decalin to be used is 0.1 per cent to 15 per cent by weight of the hydrocarbon feed, although a quantity without this range would yield to a lesser or to a greater extent the beneficial results of the invention. In any event the particular quantity of cis-decalin that will be the optimum under any set of operating conditions can be arrived at only by balancing the many various factors involved against the octane yield improvement. In general, the considerations and conditions discussed in this specification are operative for other hydrocarbon isomerization reactions in each of which the many various factors will and can be balanced by mere routine test by one versed in the art. In the isomerization of 2,2,4-trimethylpentane it has been found that

4

quantities of cis-decalin of at least about 4% may be considered as an optimum from this viewpoint. However, from other considerations, it may be found that quantities even up to 50% cis-decalin by weight of the hydrocarbon feed will be considered as optimum because use of this quantity will result in improved yields of desired isomers greater than those obtained with lesser quantities of cis-decalin.

It is to be noted from the graph in Figure 2 that even a very small proportion of cis-decalin increased very considerably the total 2,2,4-trimethylpentane isomerized to other branched-chain octanes whereas the trans-decalin gave no practically significant increase.

The quantity of aluminum halide used will also depend upon a consideration of the various factors. The yield of octanes appears to be substantially independent of the quantity of catalyst used, at least in the range of from about 2% to about 13% by weight of the 2,2,4-trimethylpentane. The aluminum halide can be used as such or as a sludge or aluminum halide-hydrocarbon complex. The various catalysts are well known in the art as are the promoters and their use.

Contact time for the reaction will vary depending upon other conditions. A time in the range of from about 1 to about 500 minutes now appears to be desirable. In one run according to the invention about 10% of 2,2,4-trimethylpentane was converted by about 10% of aluminum bromide and 10% cis-decalin in about 2 hours at 26° C. No promoter was used in this run.

A temperature in the range of from about minus 30° C. to about plus 50° C., preferably from about minus 10° C. to about 30° C. is operative in the invention. Within the recited ranges of temperature, I have found that a yield of about 29% octanes from 2,2,4-trimethylpentane, obtained with aluminum bromide at 26° C. could be increased to double this value, namely to 52%, if the temperature was maintained at about 1° C. Thus, it is seen that lower temperatures tend to increase yield. However, the temperature cannot be too low if a high rate of reaction is desired. Therefore, to determine the desired temperature, consideration must be given to the rate of reaction at that temperature. The increase in yield with decrease in temperature from 26° C. to 1° C. is shown in Table I.

TABLE I

Run Number.....	1	2
55 Temperature, °C.....	26	1
Contact Time, Hours.....	2.3	2.8
Aluminum Bromide, Weight percent of 2,2,4-Trimethylpentane.....	7.1	2.5
Feed Composition, Weight Percent:		
2,2,4-Trimethylpentane.....	100.0	100.0
Cis-decalin.....	0.0	0.0
60 Product Composition, Weight Percent:		
Isobutane.....	3.17	0.69
Isopentane.....	0.90	0.17
C ₆ and C ₇	3.3	1.1
2,2,4-Trimethylpentane.....	78.83	92.24
Other Octanes.....	6.2	4.0
C ₉ and Heavier.....	7.6	1.8
Catalyst Sludge Oil.....		
65 Yield, Weight Percent of 2,2,4-Trimethylpentane Converted:		
Isobutane.....	15.2	3.9
Isopentane.....	4.3	2.2
C ₆ and C ₇	15.6	14.2
Octanes.....	29	52
C ₉ and Heavier.....	36	23
Catalyst Sludge Oil.....		
70 Total Conversion, Weight Percent of 2,2,4-Trimethylpentane Feed.....	21.2	7.8
Yield of Octanes, Weight Percent of 2,2,4-Trimethylpentane Charged.....	6.2	4.1
Yield of Octanes, Weight Percent of 2,2,4-Trimethylpentane Converted.....	29	52

5

While the reaction appears to be essentially independent of pressure, a pressure sufficient to maintain liquid the hydrocarbons in the reaction zone is employed.

The increase of the desired octanes which can be obtained by the use of cis-decalin, according to this invention, is clearly evident from Table II. When no cis-decalin was used, the yield in octanes of the 2,2,4-trimethylpentane converted was 29%. When cis-decalin was used in increasing amounts this value was 44%, 43.5%, 53.6% and 65% respectively.

TABLE II

Run Number	3	4	5	6
Temperature, °C.	26	26	26	26
Contact Time, Hours	2.0	2.0	2.0	5.0
Aluminum Bromide, Weight Percent of 2,2,4-Trimethylpentane	9.5	9.7	9.4	12.1
Feed Composition, Weight Percent:				
2,2,4-Trimethylpentane	95.9	93.2	87.1	66.7
Cis-decalin	4.1	6.8	12.9	33.3
Product Composition, Weight Percent:				
Isobutane	2.01	2.61	1.74	1.735
Isopentane	0.16	0.36	0.29	0.028
C ₆ and C ₇	1.2	1.2	0.79	Trace
2,2,4-Trimethylpentane	86.42	80.33	76.28	58.8
Other Octanes	4.2	5.6	5.8	5.14
C ₉ and Heavier	4.66	7.4	13.4	33.0
Catalyst Sludge Oil	1.35	2.5	1.7	1.3
Yield, Weight Percent of 2,2,4-Trimethylpentane Converted:				
Isobutane	21.2	20.3	16.1	22
Isopentane	1.75	2.8	2.7	0.35
C ₆ and C ₇	13	9.3	7.3	Trace
Octanes	44	43.5	53.6	65
C ₉ and Heavier	6	4.7	4.6	0
Catalyst Sludge Oil	14	19.4	15.7	12.7
Total Conversion, Weight Percent of 2,2,4-Trimethylpentane Feed	9.9	13.8	12.4	13.8
Yield of Octanes, Weight Percent of 2,2,4-Trimethylpentane Charged	4.4	6.0	6.7	9.0
Yield of Octanes, Weight Percent of 2,2,4-Trimethylpentane Converted	44	43.5	53.6	65

Variation and modification are possible within the scope of the appended claims to the invention the essence of which is that cis-decalin, has been found to be the essential isomerization reaction improver in decalin.

I claim:

1. A process for the isomerization of an isomerizable hydrocarbon which comprises subjecting decalin to fractionation to separate a cis-decalin fraction and a trans-decalin fraction therefrom, combining the cis-decalin fraction with said hydrocarbon and subjecting the combined stream under isomerization conditions to the action of an isomerization catalyst, processing the resulting reaction mass to separate from it isomerized hydrocarbon as a product of the process, catalyst and cis-decalin, trans-decalin formed from cis-decalin during the isomerization, any by-products which are separated from

6

the process, and unreacted hydrocarbon, converting the trans-decalin to cis-decalin, and passing the cis-decalin, the unreacted hydrocarbon and the catalyst to the isomerization step.

2. The process of claim 1 wherein the hydrocarbon is 2,2,4-trimethylpentane, the catalyst is an aluminum halide, the temperature is within the range minus 30° C. to plus 50° C., a pressure sufficient to maintain the reaction substantially in the liquid phase is employed and the cis-decalin in the isomerization step is present in a quantity within the range of 0.1%–15% by weight of the hydrocarbons.

3. The process of claim 2 wherein the aluminum halide is aluminum chloride and is present in a quantity within the range of 2%–13% by weight of the hydrocarbon.

4. The process of claim 2 wherein the aluminum halide is aluminum bromide and is present in a quantity within the range of 2%–13% by weight of the hydrocarbon.

5. A process for the isomerization of an isomerizable paraffin hydrocarbon having at least four carbon atoms per molecule which comprises subjecting said hydrocarbon under isomerization conditions to the action of an aluminum halide catalyst and a reaction improver consisting essentially of cis-decalin, recovering trans-decalin formed during the isomerization reaction, converting said trans-decalin to cis-decalin, and reusing said cis-decalin, thus obtained, in the process.

6. The process of claim 5 wherein the hydrocarbon is 2,2,4-trimethylpentane, the aluminum halide is aluminum chloride, the reaction is effected at a temperature within the range minus 30° C. to plus 50° C. at a pressure sufficient to maintain the reactants in the liquid phase and the cis-decalin is present in a quantity of 0.1%–15% by weight of the hydrocarbon.

7. The process of claim 5 wherein the aluminum halide is aluminum bromide.

FRANCIS E. CONDON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,434,437	Ross	Jan. 13, 1948
2,438,421	Sensel et al.	Mar. 23, 1948
2,468,746	Greensfelder et al.	May 3, 1949
2,475,358	Moore et al.	July 5, 1949

OTHER REFERENCES

New Dictionary of Chemistry, page 167.
Richter's Organic Chemistry, page 171.
In re Thomas, 630 O. G. 1095.