

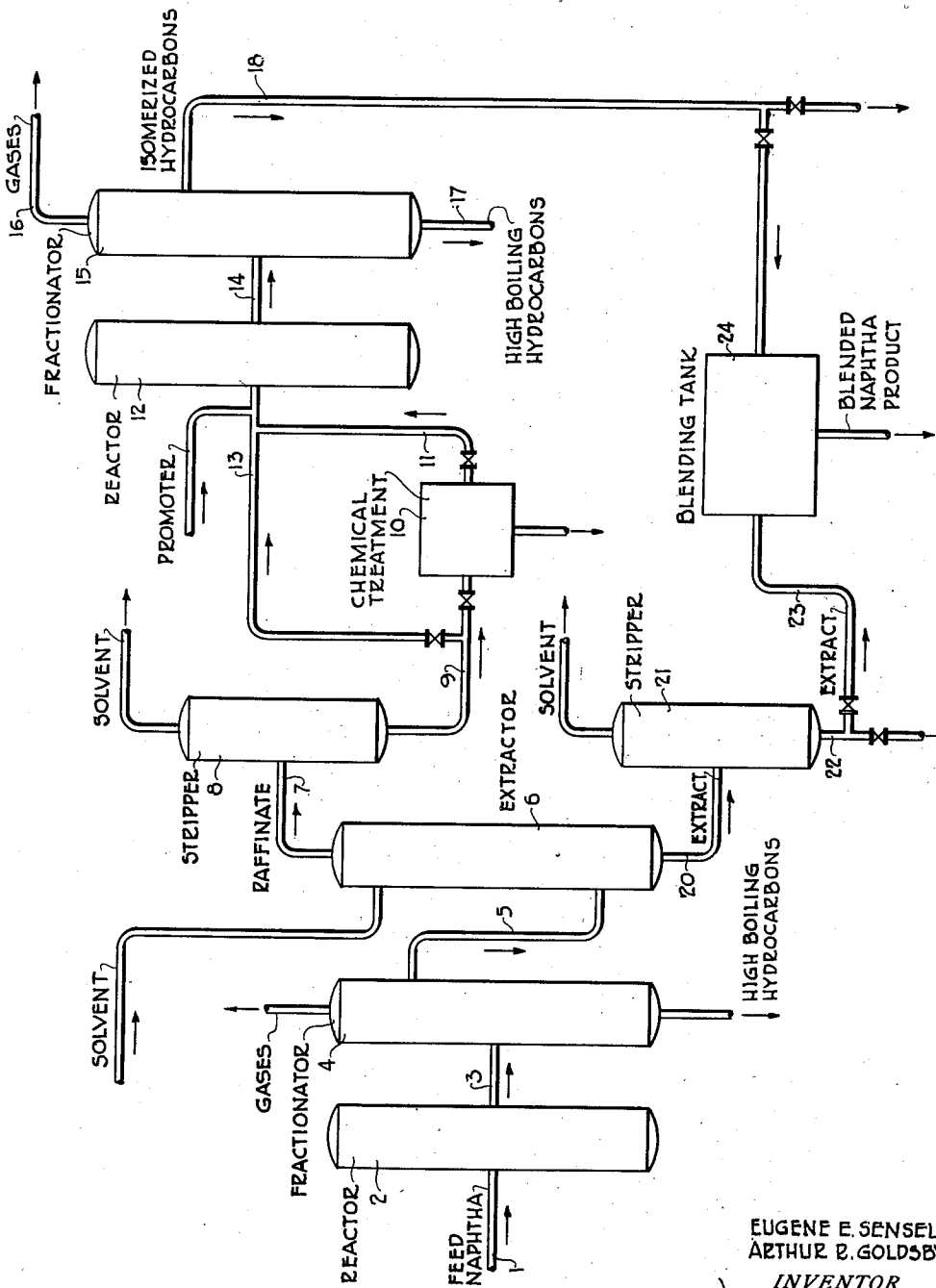
June 6, 1944.

E. E. SENSEL ET AL

2,350,834

CONVERSION OF HYDROCARBONS

Filed June 18, 1941



EUGENE E. SENSEL  
ARTHUR B. GOLDSBY  
INVENTOR

BY

*R. J. Dearbon*  
*Daniel Stuyker*  
ATTORNEY

## UNITED STATES PATENT OFFICE

2,350,834

## CONVERSION OF HYDROCARBONS

Eugene E. Sensel and Arthur R. Goldsby, Beacon, N. Y., assignors, by mesne assignments, to The Texas Company, New York, N. Y., a corporation of Delaware

Application June 18, 1941, Serial No. 398,531

4 Claims. (Cl. 260—683.5)

This invention relates to the conversion of hydrocarbons and has to do with the isomerization of hydrocarbons to form branched chain hydrocarbons and particularly has to do with the isomerization of saturated gasoline hydrocarbons.

The invention broadly contemplates treating a mixture of gasoline hydrocarbons, including aliphatic and alicyclic hydrocarbons, to remove alicyclic and other objectionable constituents which tend to cause catalyst deterioration during isomerization, and thereafter subjecting the gasoline hydrocarbons to isomerization in the substantial absence of alicyclic and other objectionable constituents whereby the isomerization reaction is effected at relatively low temperature to obtain substantial conversion of the paraffin constituents to isoparaffins.

Gasoline or naphtha usually comprises a mixture of saturated and unsaturated hydrocarbons. The saturated hydrocarbon constituents comprise paraffins and saturated naphthene hydrocarbons, while the unsaturated constituents comprise olefins including cyclo-olefins. In addition, aromatic hydrocarbons may be present, particularly if the hydrocarbon mixture is a cracked naphtha.

Aromatic and unsaturated hydrocarbons readily react with an isomerization catalyst such as an active metallic halide catalyst to form complexes or sludge thereby causing substantial catalyst deterioration. Consequently, it has been found desirable to remove aromatic and unsaturated hydrocarbons from the feed to an isomerization reaction.

The present invention has to do with the removal of both saturated and unsaturated alicyclic hydrocarbons from the feed to the isomerization reaction and particularly where it is desired to carry out the reaction at relatively low temperatures. At relatively high temperatures the presence of saturated alicyclic hydrocarbons, namely naphthene hydrocarbons, appears to impart a beneficial action. Thus, as disclosed in pending application, Serial No. 398,530 filed June 18, 1941, for Conversion of hydrocarbons, where the isomerization reaction is carried out under temperatures, for example, in the range 160° F. and above, in order to obtain high yields of isoparaffins it is desirable to effect the reaction in the presence of substantial amounts of naph-

thene hydrocarbons for the purpose of inhibiting cracking and side reactions which would otherwise occur at these relatively higher temperatures.

5 However, the present invention has to do with the discovery that in the low temperature isomerization of gasoline or naphtha, it is advantageous to remove naphthene hydrocarbons from the feed and thus effect the isomerization reaction in the substantial absence of such hydrocarbons as well as in the substantial absence of aromatic and olefinic hydrocarbons. In other words, for a low temperature operation, it is advantageous to select a feed stock which is essentially free from naphthenes.

10 For example, when isomerizing gasoline hydrocarbons in the substantial absence of naphthene hydrocarbons so as to obtain about 30 to 40% conversion of normal paraffins to isoparaffins it has been found that the reaction temperature can be maintained at least about 25° F. and in some cases as much as 100° F. or more, lower than the reaction temperature required where the feed contains naphthenes in substantial amount.

15 In practice the temperature of reaction may range from about 100 to 200° F., although the particular temperature employed will depend upon the nature of the catalyst, and the specific manner in which the reaction is carried out. It will also depend upon the nature of the paraffin feed to the reaction. Thus when the feed consists essentially of normal pentane and the reaction is effected with anhydrous aluminum chloride promoted with anhydrous hydrogen chloride but in the substantial absence of extraneous agents such as isobutane, the temperature may be about 100 to 130° F. for example.

20 The following conversion yields afford a comparison of the results obtained in the low temperature isomerization of normal pentane with aluminum chloride and hydrogen chloride; first in the absence of cyclohexane and, second, in the presence of cyclohexane, the naphthene being present in the latter case to the extent of about 25% by weight of the pentane feed to the reaction. The data were obtained in batch liquid phase experiments carried out at temperatures of 100, 130, 160 and 200° F. with a reaction time in each case of 4 hours. In each experi-

ment powdered anhydrous aluminum chloride of about 200 mesh was charged to a reaction vessel to the extent of 10% by weight of the feed hydrocarbon, the reaction being promoted by the addition of about 0.5 to 0.7% of hydrogen chloride by weight of the feed hydrocarbon.

	Temperatures, ° F.			
	100	130	160	200
<b>In the absence of cyclohexane:</b>				
Run No. ....	A	B	C	D
Total pentane converted to isopentane and other hydrocarbons, per cent by wt. of feed.....	12	54.5	97.2	95
Total isopentane obtained, per cent by wt. of normal pentane feed.....	11.5	41.9	22.9	20.5
Weight ratio of isopentane to normal pentane converted.....	.96	.77	.24	.22
<b>In the presence of 2% cyclohexane:</b>				
Run No. ....	E	F	G	H
Total pentane converted to isopentane and other hydrocarbons, per cent by wt. of feed.....	0	4	24	71
Total isopentane obtained, per cent by wt. of normal pentane feed.....	0	3	21.5	70.5
Weight ratio of isopentane to normal pentane converted.....		.75	.90	.99

As the foregoing data indicate, at reaction temperatures up to 130 and somewhat above, the conversion of normal pentane to isopentane and other hydrocarbons is substantially greater in the absence of the naphthene hydrocarbon. In fact there is little or no conversion in this temperature range in the presence of the naphthene. Moreover, in the lower portion of the reaction temperature range, for example, in the range 100 to about 120° F., the conversion product obtained in the absence of the naphthene consists essentially of isoparaffin, i. e., isopentane. However, at temperatures of 130° F. and above where the reaction is carried out in the absence of the naphthene hydrocarbon, the content of isopentane in the reaction product is proportionately less, falling off rather markedly at temperatures in the neighborhood of 160° F. due to cracking and side reactions with the formation of products other than isopentane.

As previously explained naphtha or other mixtures of gasoline hydrocarbons usually contain substantial amounts of naphthene hydrocarbons. In some instances, feed stocks may be selected from which an isomerization feed substantially free from naphthene constituents may be obtained by conventional methods of fractional distillation, including azeotropic distillation, or solvent extraction.

In other instances, the feed stocks may be of such nature or composition that other methods are better adapted to permit separating an isomerization feed substantially free from naphthene constituents. In this case the present invention contemplates subjecting the naphtha or gasoline stock to a catalytic conversion treatment for the purpose of converting the naphthene hydrocarbon constituents to aromatic and unsaturated hydrocarbons which are more readily separated from the paraffin hydrocarbons by distillation, extraction with solvents or by other methods.

For example, the hydrocarbon mixture containing naphthene constituents may be subjected to contact with a suitable dehydrogenation catalyst such as chromium oxide or molybdenum oxide advantageously disposed upon a supporting material such as alumina, and the contact effected under suitable conditions of temperature and pressure so as to obtain the desired

conversion of naphthene hydrocarbons. Thus, the reaction may be carried out at a temperature of about 900 to 1050° F. and under pressures ranging from atmospheric to substantially above atmospheric.

The reaction may be carried out in the substantial absence of extraneous hydrogen or hydrogen containing gases. On the other hand it may be advantageous to carry out the reaction in the presence of hydrogen under pressures in the range 200 to 600 pounds per square inch gauge. In such case hydrogen or hydrogen-containing gases produced in the reaction itself may be continuously recycled through the reaction zone.

For example, the reaction may be carried out employing a space velocity of about 0.5 to 1.0 (volumes of liquid feed measured at 60° F. per volume of catalyst). The light gases produced in the reaction and rich in hydrogen may be recycled at the rate of about 2500 cubic feet of gas per barrel of hydrocarbon feed to the reaction where the feed is a virgin naphtha, and may be as high as 10,000 cubic feet where the feed is a cracked naphtha.

If desired the products of reaction of the hydroforming reaction may be subjected to a hydrofining action in which the hydroformed products are passed to a separate reaction zone containing a hydroforming catalyst and maintained at a somewhat lower temperature so that the olefinic constituents are subjected to hydrogenation.

The catalytically converted naphtha resulting from the foregoing operations will comprise paraffin, aromatic and olefinic constituents, the naphthene constituents originally present in the initial feed having been converted to aromatic and other constituents as a result of the reaction.

After fractionation to remove normally gaseous constituents and also heavier hydrocarbons boiling above the motor fuel range the converted gasoline is subjected to a conventional extraction with a solvent such as liquid sulfur dioxide, dichloroethyl ether, furfural, nitrobenzene, etc., to effect a separation into extract and raffinate phases. The raffinate phase comprises paraffin hydrocarbons substantially free from naphthene, aromatic and unsaturated hydrocarbons while the extract phase comprises aromatic and unsaturated hydrocarbons. The extract phase after removal of the solvent will thus comprise gasoline hydrocarbons having a relatively high octane number, for example, about 80 to 100 and therefore, suitable as a blending stock for motor fuel.

The raffinate after removal of the solvent is then subjected to contact with an isomerization catalyst at a relatively low temperature in order to convert the paraffin constituents to isoparaffin hydrocarbons, thereby producing a mixture of gasoline hydrocarbons of high antiknock value.

The foregoing fractionation and solvent extraction operations may be modified to make provision for segregating from the converted naphtha a toluene fraction or concentrate where it is desired to segregate the toluene for some particular purpose.

If desired, the raffinate, prior to isomerization, may be subjected to a further chemical treatment in order to remove any remaining small quantities of aromatic and olefin constituents. For example, the raffinate, after removal of the solvent, may be subjected to treatment with sul-

furic acid followed by neutralization with caustic or other suitable alkaline material.

The accompanying drawing comprises a flow diagram illustrating one method of carrying out the reaction. Thus, referring to the drawing, a feed hydrocarbon such as gasoline or a gasoline fraction comprising a mixture of C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> hydrocarbons is conducted from a source not shown through a pipe 1 to a reactor 2 wherein the feed mixture is subjected to contact with a dehydrogenating or hydroforming catalyst under suitable conditions to effect conversion of naphthene hydrocarbons to aromatic hydrocarbons.

The resulting reaction mixture is conducted through a pipe 3 to a fractionator 4 wherein fixed or normally gaseous constituents are removed as a gaseous fraction from the top of the fractionator while hydrocarbons boiling above the motor fuel range are removed as a residual fraction from the bottom of the fractionator. As previously mentioned, in the case of a hydroforming reaction the gaseous fraction or any portion thereof rich in hydrogen removed from the top of the fractionator 4 may be recycled to the reactor 2.

A side stream comprising hydrocarbons of motor fuel boiling range is drawn off from the fractionator through a pipe 5. This side stream will comprise paraffin hydrocarbons together with unsaturated hydrocarbons and aromatic hydrocarbons including aromatic compounds formed as a result of the conversion of naphthenes in the reactor 2. This stream is conducted to an extractor 6 wherein it is subjected to extraction with a selective solvent such as already mentioned.

The resulting raffinate phase is drawn off through a pipe 7 to a stripper 8 wherein the solvent is stripped from the raffinate hydrocarbons, the solvent being recovered for reuse.

The solvent free raffinate is conducted through a pipe 9 to a chemical treating plant 10 wherein it is subjected to conventional acid and caustic treatments to remove any remaining traces of aromatic and unsaturated hydrocarbons.

The treated raffinate thereafter is conducted through a pipe 11 to a reactor 12. As indicated in the drawing the chemical treating step may be bypassed in which case the raffinate is conducted through a pipe 13 directly to the reactor 12.

In the reactor 12 the raffinate is subjected to contact with an isomerizing catalyst under isomerizing conditions including relatively low temperature conditions so as to obtain a substantial conversion of paraffin to isoparaffin hydrocarbons without substantial cracking.

The isomerization catalyst advantageously comprises aluminum chloride and hydrogen chloride and in which case the reaction is carried out at a temperature in the range about 100 to not in excess of about 130° F. Temperatures as low as 50° F. may be used, and temperatures higher than 130° F. may be used provided the reaction is carried out under conditions such that cracking and side reactions are avoided. The temperature will depend upon the feed hydrocarbon, that is, higher temperatures may be permissible with some stocks even though naphthene hydrocarbons are absent. Other metallic halides may be employed as, for example, aluminum bromide. Other hydrogen halides may be employed such as hydrogen bromide.

The isomerization reaction may also be carried out in either the gas or liquid phase, employing the catalyst in the form of a mass of solid particles or lumps, or in the form of a fluid mixture of powdered catalyst dissolved or suspended in a liquid medium such as metallic halide-hydrocarbon complex. The reaction may be carried out with finely divided solid catalyst suspended in vaporized hydrocarbons undergoing conversion.

In any case the isomerized hydrocarbon mixture is conducted through a pipe 14 to a fractionator 15. In the fractionating step gaseous hydrocarbons tending to accumulate in the reaction are removed through a pipe 16. These gases will comprise normally gaseous hydrocarbons such as normal butane and isobutane and some hydrogen as well as hydrogen chloride. If desired, a suitable proportion of the gaseous hydrocarbons such as isobutane or the hydrogen as well as the hydrogen chloride may be continuously recycled through the isomerization reactions zone for the purpose of facilitating the reaction and inhibiting the occurrence of cracking and side reactions.

High boiling hydrocarbons are drawn off from the bottom of the fractionator through a pipe 17, while a side stream including isomerized hydrocarbons boiling within the desired motor fuel boiling range is drawn off through a pipe 18.

Referring again to the extractor 6, the extract phase is drawn off through a pipe 20 and conducted to a stripper 21 wherein the solvent is recovered for reuse. The solvent free extract comprising aromatic and unsaturated hydrocarbons is drawn off through pipe 22 and may be subjected to further treatment for the purpose of stabilizing color and gum forming constituents. The extract hydrocarbons, as already indicated, comprise valuable gasoline hydrocarbons of relatively high octane number and this material is advantageously conducted all or in part through a pipe 23 to a tank 24 wherein it is blended in suitable proportion with the isomerized hydrocarbon mixture drawn off through pipe 18.

The arrangement of apparatus indicated in the drawing is merely diagrammatic and it is contemplated that in actual practice the arrangement of apparatus as well as the method of flow may be varied. For example, the dehydrogenation or hydroforming reactions and also the isomerization reaction may be carried out in a batch or continuous type of operation employing single or multistage reactors with provision for multiple injection of the feed and/or promoter to the reaction zone or zones.

The catalytic reactions may be carried out so as to permit either continuous concurrent or countercurrent flow of hydrocarbons undergoing treatment and a stream of catalyst in a reaction zone or zones.

An advantageous mode of carrying out the isomerization reaction involves the employment of a fluid type of operation wherein a substantial body of fluid containing the catalyst dissolved or suspended therein is maintained in a reaction zone with provision for continuous withdrawal of a stream of the reaction mixture and continuous recycling of the withdrawn stream to the reaction zone. Sufficient of the liquid mixture is recycled to impart thorough agitation to the reaction mixture within the reaction zone. If desired the paraffin feed may be introduced to the reaction zone in the form of a large number of separate streams simultaneously to the mass of reaction

mixture in such a way as to distribute the feed uniformly within and throughout the depth and cross-section of the fluid mass within the reaction zone.

Likewise the fractionating apparatus may be modified so as to effect any desired degree or type of fractionation at different stages in the process.

While specific examples of dehydrogenating and hydroforming catalysts have been mentioned, it is intended that other catalysts may be employed for this purpose. Additional examples of dehydrogenating catalysts which may be employed are metals such as silver, copper, iron, nickel, cobalt, aluminum, or alloys thereof, or sulfides or oxides of iron, nickel, cobalt, zinc, cadmium, aluminum, lead, bismuth, tin, vanadium, etc. Particularly effective catalysts consist of, or contain oxides or sulfides of the metals of the 6th group of the periodic system, namely, chromium, molybdenum, tungsten, uranium, selenium, tellurium and polonium. The catalysts may be used alone or in admixture with each other or deposited on solid carriers. Suitable carriers comprise silica, silicates, carbon, charcoal, etc.

Examples of hydroforming catalysts include, oxides of aluminum, boron, silicon, titanium, tin, molybdenum, selenium, tellurium, etc., also activated earths and clays, etc.

Also, if desired, the feed mixture prior to introduction to the reactor 2 may be subjected to chemical treatment for the purpose of removing sulfur compounds and other constituents which cause catalyst deterioration. However, it is contemplated that the hydroforming or other catalytic conversion carried out in the reactor 2 may be utilized to effect removal of sulfur and other impurities to a substantial extent. The removal of such impurities from the feed to the isomerization reaction is desirable from the standpoint of preventing catalyst deterioration.

The isomerized hydrocarbons or any portion thereof may be subjected to further refining or processing as desired. For example, the isomerized hydrocarbons together with promoter removed from the fractionator 15 may be passed directly to an alkylation unit wherein the isoparaffin hydrocarbons are caused to react with olefin hydrocarbons by contact with a metallic halide catalyst maintained under alkylating conditions. For example, an isopentane fraction of the isomerized hydrocarbons together with hydrogen chloride promoter may be passed to a suitable alkylation operation for reaction with an olefin such as triisobutylene in the presence of aluminum chloride catalyst to produce safety fuel.

While the preparation of a naphthene free gasoline for charging to the isomerization reaction has been described it is intended that individual gasoline hydrocarbons or various mixtures of such hydrocarbons including normal and isoparaffins and substantially free from naphthenes and other constituents may be prepared and subjected to isomerization. Provision may be made for recycling through the reaction unreacted hydrocarbon or any portion of the isomerized hydrocarbon mixture. Likewise provision may also be made for introducing extraneous paraffins including normal and isoparaffins and also extraneous gases including hydrogen to the feed to the isomerization reaction.

The hydrogen from the dehydrogenation reaction may advantageously be used in the isomerization reaction to decrease catalyst consumption and enable higher conversions to be obtained without substantial cracking.

In the above described experiments a reaction time of 4 hours is used. However, it is contemplated that a reaction time of 1 hour or less may be employed. For example, in continuous operations the reaction time may be about 5 to 15 minutes and as high as 2 hours or more.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of isomerizing gasoline hydrocarbons present in mixtures of straight chain and cycloparaffin hydrocarbons by the action of an isomerization catalyst selected from the group consisting of aluminum chloride and aluminum bromide in the presence of hydrogen halide promoter at relatively low temperatures, which comprises removing from the feed mixture at least a substantial portion of the cycloparaffin constituents present therein, and then subjecting residual straight chain paraffin constituents to contact with the catalyst under isomerizing conditions in the substantial absence of said cycloparaffin constituents and at a temperature in the range 100° F. to substantially below 160° F. such that the weight ratio of isoparaffin produced to normal paraffin converted is not substantially less than .77 and such that conversion of normal paraffin constituents to isoparaffins is substantially greater than that obtained under substantially similar conditions of reaction in the presence of said removed cycloparaffin hydrocarbons.

2. The method of isomerizing gasoline hydrocarbons present in mixtures of straight chain and cycloparaffin hydrocarbons by the action of an isomerization catalyst selected from the group consisting of aluminum chloride and aluminum bromide in the presence of hydrogen halide promoter at relatively low temperatures, which comprises removing from the feed mixture at least a substantial portion of the cycloparaffin constituents present therein, and then subjecting residual straight chain paraffin constituents to contact with the catalyst under isomerizing conditions in the substantial absence of said cycloparaffin constituents and at a temperature in the range about 100 to 130° F. such that the conversion of normal paraffin constituents to isoparaffins is substantially greater than that obtained under substantially similar conditions of reaction in the presence of said removed cycloparaffin hydrocarbons.

3. The method of isomerizing gasoline hydrocarbons present in mixtures of straight chain and cycloparaffin hydrocarbons by the action of an isomerization catalyst selected from the group consisting of aluminum chloride and aluminum bromide in the presence of hydrogen halide promoter at relatively low temperatures, which comprises obtaining a saturated gasoline fraction comprising straight chain and cycloparaffin hydrocarbons having from 5 to 7 carbon atoms per molecule, removing from said fraction substantially all of the cycloparaffin constituents present therein, and then subjecting residual straight chain paraffin constituents to contact with the catalyst under isomerizing conditions in the substantial absence of said cycloparaffin constituents and at a temperature in the range about 100 to 130° F. such that the conversion of normal paraffin constituents to isoparaffins is substantially greater than obtained under substantially sim-

ilar conditions of reaction in the presence of said removed cycloparaffin hydrocarbons.

4. The method of isomerizing gasoline hydrocarbons present in mixtures of straight chain and cycloparaffin hydrocarbons by the action of an isomerization catalyst selected from the group consisting of aluminum chloride and aluminum bromide in the presence of hydrogen halide promoter at relatively low temperatures, which comprises removing from the feed mixture at least a substantial portion of the cycloparaffin constituents present therein, and then subjecting resid-

ual straight chain paraffin constituents to contact with the catalyst under isomerizing conditions in the substantial absence of said cycloparaffin constituents at a temperature in the range not substantially above 130° F, such that conversion of normal paraffin constituents to isoparaffins is substantially greater than that obtained under substantially similar conditions of reaction in the presence of said removed cycloparaffin hydrocarbons.

EUGENE E. SENSEL.  
ARTHUR R. GOLDSBY.