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CATALYTIC ISOMERIZATION OF OLEFINIC HYDROCARBONS

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This invention relates to the catalytic isomerization of olefinic hydrocarbons and more particularly to a process for the catalytic isomerization of olefin-containing gasoline to increase its anti-knock rating.

The process is particularly applicable to gasolines or naphthas containing an appreciable quantity of olefins, such as gasoline obtained by thermal cracking. Thermally cracked gasolines have an average octane rating considerably below that of the thermodynamic equilibrium value and a process tending towards the establishment of this equilibrium will be characterized by a considerable octane improvement.

In catalytic cracking the catalyst tends to produce some olefin isomerization and hence catalytically cracked gasolines have already been isomerized to some extent and thus do not show the improvement in octane number that is shown with thermally cracked gasolines when subjected to isomerization conditions. In addition, the lower the original octane rating of the charge the greater will be the increase upon isomerization.

The process of isomerization is particularly applicable to charge stocks characterized by a high olefin content, especially olefins of the non-branched type. Thermally cracked distillates and coke still gasolines are especially adaptable to this process, while olefinic polyform stocks, that is, gasolines cracked in the presence of light hydrocarbon gases, are not so improved by the process as the other charge stocks.

It is desirable to carry out the isomerization reaction alone while holding other reactions such as cracking, saturation, aromatization, treating and hydrogen transfer to a minimum. In the prior art processes of isomerization these other reactions have not been sufficiently suppressed. The catalysts and conditions described in these processes are of such a nature as to bring about side reactions. Also, those of the prior art processes which have been directed to gasolines have usually been concerned with improving the octane number from 55–60 to 65–68, while it is most desirable to increase thermally cracked stocks already having an octane number of 65–68 and upgrading them to 71–72.

The process of the present invention comprises passing the charging stock over a catalyst of alumina impregnated with anhydrous hydrogen chloride. The reaction conditions include a temperature range of from 300–600° C. and a space velocity of from 0.1 to 20 volumes of hydrocarbon per hour per volume of catalyst and pressures

from 0 to 200 pounds per square inch. Optimum results are obtained in the preferable range of 375–425° C., 0.3–1.3 space velocity and atmospheric pressure.

5 The process is characterized by liquid yields in excess of 95 per cent and usually 97–99 per cent. The reaction is almost entirely one of isomerization since there is very little cracking, saturation, aromatization, treating and hydrogen transfer. Octane numbers of thermally cracked stocks are increased substantially even with the higher octane rating charge stocks.

10 Further, the octane ratings of the leaded gasolines are correspondingly increased so that an isomerized leaded sample has a rating several units higher than an unisomerized sample containing the same amount of lead. Therefore, the process is not merely a substitute for tetraethyl lead but permits the reaching, with the stocks contemplated, of octane numbers impossible to obtain by leading alone.

15 The catalyst of the present invention is alumina which is maintained at a proper degree of activation by treating the alumina with anhydrous hydrogen chloride. The catalyst may be prepared as follows: 800 parts of alumina pellets were dried at 250° C. and after cooling to room temperature, anhydrous hydrogen chloride was passed through the pellets for two hours. Heat 20 was applied and the anhydrous hydrogen chloride passed through for another hour at which time the temperature was allowed to reach 400° C. The catalyst was then purged with nitrogen gas for about 15 minutes. The catalyst contained 25 about 4.0 volumes of hydrogen chloride per volume of catalyst.

30 As the catalyst is used, a deposit of carbonaceous material is laid down upon the catalyst surface, reducing its activity and necessitating periodic burn-offs. Burning-off can be accomplished with air, maintaining the burn-off temperature below the sintering temperature of the catalyst, about 1100° F. The catalyst will gradually lose activity if it is not periodically reactivated. Activation is accomplished by passing 1 to 20 volumes of anhydrous hydrogen chloride per volume of catalyst over the catalyst at room temperature and then gradually raising the temperature to that of the reaction. After the excess hydrogen chloride has been swept out with an inert gas, the hydrocarbon feed is passed over the catalyst. The physical shape of the alumina appears to have little effect upon the catalytic activity, 40 equally successful results having been obtained with $\frac{1}{8}$ inch pellets and with 8–14 mesh granules.

Table I summarizes data showing the gradual decrease of the catalyst activity when not periodically reactivated. Runs 1, 2 and 3 show the gradual decrease in octane improvement when the catalyst is burned off but not reactivated. Run 4 shows how the improvement returns to normal when the spent catalyst is reactivated with anhydrous hydrogen chloride.

Table I

	Run No			
	1	2	3	4
Throughput, vols. gasoline/vol. catalyst.....	9.2	9.3	9.2	9.5
Cycle No.....	1	2	3	4
Temperature, °C.....	400	400	400	400
Space velocity, hr. ⁻¹	0.5	0.5	0.5	0.5
Catalyst.....	(1)	(2)	(2)	(1)
Octane number increase:				
A. S. T. M. motor method, D357-43T.....	2.4	2.3	1.5	2.6
A. S. T. M. motor method, +1 cc. T. E. L.....	4.2	3.5	3.1	4.0
A. S. T. M. motor method, +3 cc. T. E. L.....	3.1	2.8	2.0	2.9

¹ Alumina-HCl
² Alumina

The length of the cycle between carbon burn-offs may be 10-30 volumes of charge per volume of catalyst, with very little sacrifice in octane improvement at 15-20 vol./vol. catalyst. The reactivation need not accompany each carbon burn-off. This small carbon deposit indicates very little side reaction such as cracking or dehydrogenation.

The use of the alumina catalyst activated with anhydrous hydrogen chloride invariably introduces a quantity of chlorine in the treated distillate which has a detrimental effect upon the lead susceptibility of the product. The isomerized product should be passed over a substance which will remove the chlorine without otherwise affecting the product. Bauxite at 200-500° C. and space velocities of 0.1-30 volumes of gasoline per hour per volume of bauxite is an effective means of removal of chlorine. All the results reported herein are for such dehalogenated products.

Example 1.—The ability of this catalyst to effect isomerization with the almost complete exclusion of any other side reaction is best shown by the treatment of n-octene-1. Three volumes of n-octene-1 were passed over one volume of 1/8 inch alumina pellets activated with anhydrous hydrogen chloride at a temperature of 400° C. and 0.5 vol./vol. hour space velocity. The resulting product was dehalogenated over bauxite at 280° C. and decolorized over clay at 250° C. The following data were obtained on the charge and the product:

Inspection	Charge	Product	Change
Per cent olefin.....	95.9	91.9	-4.0
Per cent paraffin and naphthene.....	4.1	8.1	+4.0
Octane numbers:			
A. S. T. M. motor method.....	36.7	74.9	+38.2
A. S. T. M. motor method + 3 cc. T. E. L.....	60.2	82.6	+22.4

The following examples show the use of this catalyst for gasolines. The charge stock in Examples 2, 3 and 4 was a debutanized thermally cracked gasoline having an A. S. T. M. boiling range of 110-390° F. The octane numbers of both charge and product were determined after normal butane had been added to yield a gasoline having a Reid vapor pressure of 10±1 pounds per square inch. The hydrocarbon analysis of the charge was approximately: olefins 42 per cent,

aromatics 9 per cent, paraffins and naphthenes 49 per cent, the bromine number was 58, and the average molecular weight was 107.

Example 2.—Thirteen volumes of gasoline were passed over one volume of 1/8 inch alumina pellets activated with anhydrous hydrogen chloride at a temperature of 400° C. and 0.5 vol./vol. hour space velocity. The resulting product was dehalogenated over bauxite at 280° C. and decolorized over clay at 250° C. The following A. S. T. M. motor method octane numbers were obtained on the blended 10 pound Reid vapor pressure gasolines:

	Charge	Product	Improvement
A. S. T. M. motor method.....	67.5	71.8	+4.3
A. S. T. M. motor method + 1 cc. T. E. L.....	74.3	78.9	+4.6
A. S. T. M. motor method + 3 cc. T. E. L.....	78.7	82.8	+4.1

After the run was completed, the catalyst was swept free of hydrocarbon gases with nitrogen. With the catalyst still at approximately 400° C., a slow stream of air was passed through the catalyst bed. The temperature of the catalyst at the air entrance rose to about 560° C. at which temperature the incoming air was shut off. The catalyst was allowed to cool to 500° C. and the process repeated. The high temperature regeneration zone worked its way gradually through the catalyst bed. After this zone had passed completely through the catalyst bed, addition of air only tended to cool the catalyst and no more carbon dioxide could be detected in the effluent gases.

Reactivation was accomplished by passing one to twenty volumes of anhydrous hydrogen chloride per volume of catalyst over the catalyst at 20-400° C. and over a period of one to six hours. In this case, ten volumes of anhydrous hydrogen chloride were used, taking three hours time. After two hours at room temperature, the temperature was raised to 400° C. during the third hour. At the end of that time, the excess hydrogen chloride was swept out with nitrogen and the isomerization of the charge stock begun.

Example 3.—Ten volumes of gasoline charge were passed over alumina granules of 8-14 mesh activated with anhydrous hydrogen chloride at the same conditions as Example 1. The following results were noted on the 10-lb. Reid vapor pressure gasolines:

	Charge	Product	Improvement
A. S. T. M. motor method.....	67.5	71.4	+3.9
A. S. T. M. motor method + 1 cc. T. E. L.....	74.3	77.9	+3.6
A. S. T. M. motor method + 3 cc. T. E. L.....	78.7	82.3	+3.6

The life of the catalyst was found to be satisfactory provided that the burn-off is controlled so that the catalyst is thoroughly cleaned yet not sintered.

Example 4.—Two hundred and sixty-five volumes of gasoline charge were passed over one volume of 1/8 inch alumina pellets under conditions comparable to the preceding examples. The catalyst was burned off and reactivated twenty-three times during the run. The length of each cycle between burn-offs was varied from nine to twenty-two volumes of charge per volume of

catalyst. The following octane improvements were obtained:

	Charge	Product	Im- provement
A. S. T. M. motor method.....	67.5-68.0	71.5-72.3	+3.8-4.6
A. S. T. M. motor method + 1 cc. T. E. L.....	74.3-74.5	78.1-79.1	+3.8-4.8
A. S. T. M. motor method + 3 cc. T. E. L.....	78.7-78.9	82.0-83.0	+3.5-4.3

There was no decline in catalyst activity in the latter cycles.

Example 5.—A gasoline having an A. S. T. M. distillation range 110–402° F., a bromine number of 35, and a hydrocarbon analysis of olefins 31 per cent, aromatics 23 per cent, and paraffins and naphthenes 46 per cent, and an average molecular weight of 137 was obtained by the rectification of the heavy bottoms obtained in the pressure tar separator from a thermal cracking plant. Nine volumes of this gasoline were passed over the $\frac{1}{8}$ inch alumina pellets activated with anhydrous hydrogen chloride. At a temperature of 400° C., atmospheric pressure and a space velocity of 0.5 hr.⁻¹, the following octane rating changes were obtained:

	Charge	Product	Im- provement
A. S. T. M. motor method.....	67.6	70.2	+2.6
A. S. T. M. motor method + 1 cc. T. E. L.....	72.7	77.1	+4.4
A. S. T. M. motor method + 3 cc. T. E. L.....	77.7	81.1	+3.4

Example 6.—A series of runs were made on a debutanized polyform gasoline, having an A. S. T. M. distillation range 91–430° F., a bromine number of 40.5, a hydrocarbon analysis of olefins 28.4 per cent, aromatics 16.8 per cent, and paraffins and naphthenes 54.8 per cent, and an average molecular weight of 109, using alumina granules of 8–14 mesh activated with anhydrous hydrogen chloride as catalyst. At 400° C., atmospheric pressure, and 0.5 hr.⁻¹ space velocity, the following results were obtained:

	Run No.			
	1	2	3	4
Octane No. increase:				
A. S. T. M. motor method.....	2.2	2.3	2.3	2.3
A. S. T. M. motor method + 3 cc. T. E. L.....	2.1	1.9	2.0	2.5

The octane rating of this charge stock was:

A. S. T. M. motor method=72.5

A. S. T. M. motor method+3 cc. T. E. L.=82.7

In the examples cited above the hydrocarbon analysis and the bromine number showed very little change, under proper conditions less than 10 per cent of their original value, giving adequate proof that the improvements obtained are the result of the isomerization of the olefins.

It will be understood that the catalyst of the present invention is alumina activated by anhydrous hydrogen chloride and not aluminum chloride, since no measurable amount of aluminum chloride is formed by reaction.

Thus we have described a new and useful invention for the isomerization of olefin hydrocarbons, particularly in thermally cracked gasolines, for the improvement of octane number

therein, by passing the charge over a catalyst comprising alumina which has been impregnated with anhydrous hydrogen chloride. The resulting isomerization and increased octane number are the only substantial changes in the gasoline and there is no measurable cracking, saturation, aromatization, treating or hydrogen transfer.

What we claim is:

1. A method for isomerizing olefin hydrocarbons which comprises passing said hydrocarbons at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride.

2. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride.

3. A method for isomerizing olefin hydrocarbons which comprises passing said hydrocarbons at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride, at a space velocity of from 0.1 to 20 volumes of said hydrocarbon per hour per volume of catalyst.

4. A method for isomerizing olefin hydrocarbons which comprises passing said hydrocarbons at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride at a space velocity of from 0.1 to 20 volumes of said hydrocarbon per hour per volume of catalyst at a pressure not in excess of 200 pounds per square inch.

5. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 375° to 425° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride.

6. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 375° to 425° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride at a space velocity of from 0.3 to 1.3 volumes of gasoline per hour per volume of catalyst and at substantially atmospheric pressure.

7. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with about 4 volumes of anhydrous hydrogen chloride per volume of alumina.

8. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline over a catalyst comprising alumina which has been dried and impregnated with anhydrous hydrogen chloride for several hours at a temperature of from room temperature to 400° C.

9. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride, interrupting the passage of gasoline periodically and passing oxygen over the catalyst to remove carbon deposited thereon.

10. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride, interrupting the passage of gasoline periodically, passing oxygen over the catalyst, subsequently passing anhydrous hydrogen chlo-

ride over the catalyst and resuming the passing of the gasoline.

11. A method for increasing the octane rating of an olefinic gasoline comprising isomerizing the olefins by passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride and leaving the other constituents substantially unaffected.

12. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride and subsequently removing any chlorine from said gasoline.

13. A method for increasing the octane number of thermally cracked gasoline comprising passing said gasoline at a temperature of from 300° to 600° C. over a catalyst comprising alumina impregnated with anhydrous hydrogen chloride and subsequently removing any chlorine from said gasoline by passing said gasoline over bauxite at 200-500° C. and a space velocity of 0.1 to 30 volumes of gasoline per volume of bauxite per hour.

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