

Oct. 27, 1942.

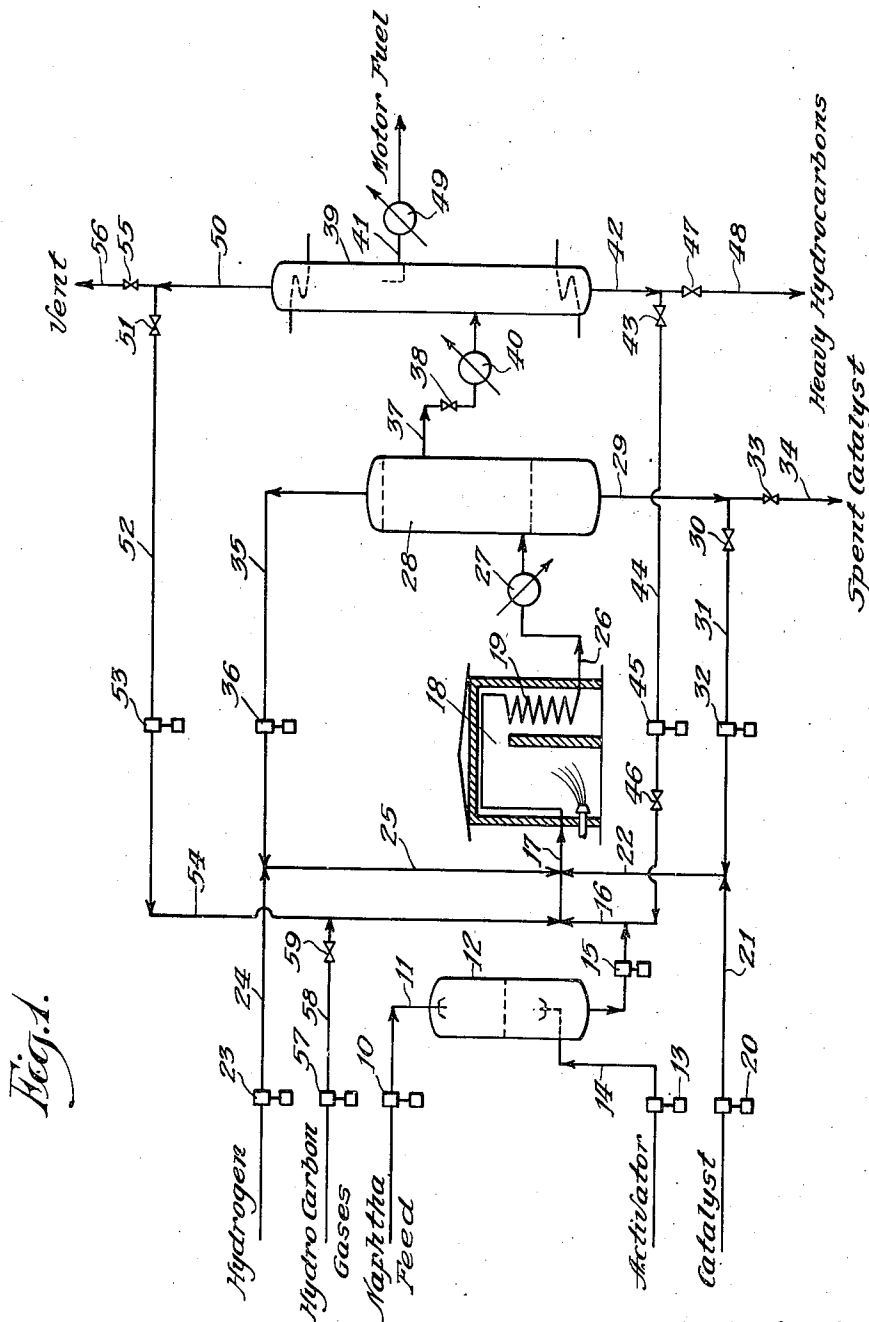
B. L. EVERING ET AL

2,300,249

CATALYTIC CONVERSION PROCESS

Filed Oct. 14, 1940

2 Sheets-Sheet 1



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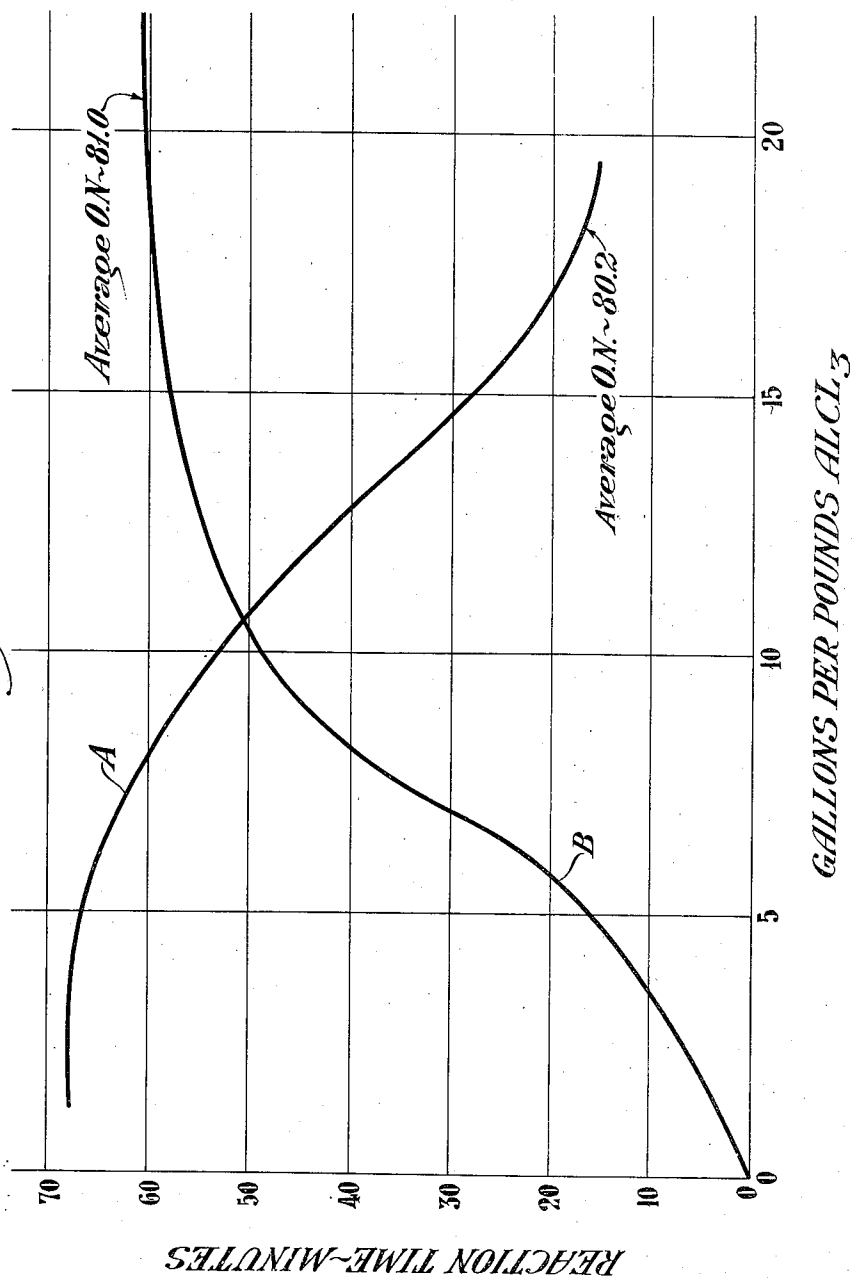
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2 Sheets-Sheet 2

Fig. 2.



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UNITED STATES PATENT OFFICE

2,300,249

CATALYTIC CONVERSION PROCESS

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Application October 14, 1940, Serial No. 361,022

8 Claims. (Cl. 196—78)

This invention relates to the catalytic conversion of hydrocarbons and more particularly to a process for the conversion of hydrocarbons involving the use of an active aluminum halide catalyst. Still more specifically, it relates to a conversion process of this type in which the catalyst is an active liquid aluminum halide-hydrocarbon complex having an exceptionally long life.

It is well-known that the branched-chain paraffin hydrocarbons and naphthas containing them in substantial proportions are very valuable as motor fuels and particularly as airplane fuels because of their high antiknock values, freedom from gum-forming tendencies and high heat content per unit weight of fuel. It has been proposed to produce such naphthas from substantially saturated liquid fractions which are rich in straight-chain paraffin hydrocarbons by the action of aluminum chloride or other active aluminum halide catalysts in the presence of an activator such as hydrogen chloride, and we have described a particularly advantageous process of this type in our co-pending application Serial No. 308,480, filed December 9, 1939, of which this application is a continuation-in-part.

In carrying out the conversion of straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons on a refinery scale it is extremely advantageous that the process be continuous and this fact makes it very desirable to have the catalyst in liquid form, so that it can be pumped readily through pipes, tubes and other apparatus. It has, of course, long been known that aluminum chloride in the presence of a hydrocarbon such as an olefinic or aromatic hydrocarbon under conversion conditions will gradually, and sometimes very rapidly, be converted into an aluminum chloride-hydrocarbon complex which is a liquid and retains a portion of the activity of the original aluminum chloride. However, such complexes are rapidly degraded under the usual reaction conditions to an inactive sludge and this degradation has been a major factor in limiting the commercial use of aluminum chloride in hydrocarbon conversion processes.

We have found that hydrocarbon conversion processes, and particularly the production of branched-chain paraffin hydrocarbons from

straight-chain paraffin hydrocarbons can be carried out most effectively in the presence of an active liquid aluminum halide-hydrocarbon complex produced by the action of an aluminum halide such as anhydrous aluminum chloride on highly branched paraffin hydrocarbons in the presence of an activator such as hydrogen chloride at a relatively low temperature, and that such complexes exhibit the unexpected property of increasing in activity with use.

It is an object of our invention to provide an economical hydrocarbon conversion process particularly adapted to the production of high antiknock motor fuel fractions in the presence of an unusually effective liquid aluminum halide catalyst. Another object is to provide a process whereby naphthas having low antiknock values due to their content of straight-chain paraffin hydrocarbons are converted into high antiknock motor fuel fractions in the presence of an active aluminum halide catalyst derived from highly branched paraffin hydrocarbons. A still further object is to provide a continuous process of the type described in which the naphtha to be converted and a liquid aluminum halide-hydrocarbon complex catalyst are continuously and concurrently passed through an elongated reaction zone. Other objects, advantages and uses of our invention will appear from the following detailed description thereof read in conjunction with the drawings, which form a part of this specification, and in which:

Figure 1 shows in a schematic manner an apparatus suitable for carrying out our invention, and

Figure 2 is a graph of the results obtained in comparable experiments demonstrating in part the advantages derived from operating in accordance with our invention.

The active liquid aluminum halide-hydrocarbon complex utilized in accordance with our invention is prepared by the action of an aluminum halide catalyst, such as anhydrous aluminum chloride or aluminum bromide, and an activator affording a hydrogen halide on a substantially saturated fraction containing predominantly at least one paraffin hydrocarbon having at least two side chains at a temperature in the range from about 50° F. to about 175° F. Preferably this liquid catalyst complex in prepared

from aluminum chloride and a substantially saturated fraction containing paraffin hydrocarbons having at least six carbon atoms and two side chains per molecule. Suitable saturated fractions are for example the hydrogenated polymers and co-polymers of olefins having less than six carbon atoms per molecule, namely, ethylene, propylene and the butylenes and amylenes, and the products of alkylation of isobutane and of isopentane with olefins of the class described. These fractions are very rich in highly branched paraffin hydrocarbons, the hydrogenated polymers of isobutylene, for example, being rich in so-called iso-octane (2,2,4-trimethylpentane). While certain alkylation products also contain this and other similar hydrocarbons, we prefer to prepare our complex from a fraction rich in iso-octane, although less volatile fractions rich in hydrogenated trimers and even heavier polymers of isobutylene are also effective in producing the desired complex.

In one case an aluminum chloride-hydrocarbon complex was prepared by stirring together at atmospheric pressure a quantity of anhydrous aluminum chloride with an excess of commercial iso-octane at 120° F. to 140° F. until a liquid complex resulted. During the complex formation large amounts of isobutane were produced and the remaining hydrocarbon liquid contained 50% of material boiling higher than the end point of the original iso-octane. This heavy material is suitable for safety fuel while the isobutane can be utilized readily in an alkylation process, for example. The complex itself can be decanted from the unreacted aluminum chloride, which can be ultimately converted in its entirety to the complex by further treatment with additional quantities of iso-octane. The viscosity of the complex catalyst produced was less than that of S. A. E. 50 lubricating oil and it could be easily pumped through pipes, towers or any form of contacting equipment. A complex catalyst prepared by the action of anhydrous aluminum chloride on a light naphtha fraction rich in straight-chain paraffin hydrocarbons, on the other hand, at a temperature above 200° F., which is necessary in order that the complex may be formed in a reasonable time, was much less fluid. As will be shown hereinafter, the activity of the complex prepared from iso-octane increased very markedly with use while that from the light naphtha gradually declined.

The active liquid aluminum halide-hydrocarbon complex is particularly useful in reactions involving the production of branched-chain from straight-chain paraffin hydrocarbons, although it can also be used in the alkylation of isobutane or isopentane with normally gaseous olefins and for the catalytic polymerization of such olefins under suitable conditions. In one of its most important aspects our invention comprises contacting an admixture of a substantially saturated naphtha rich in straight-chain paraffin hydrocarbons, an active liquid aluminum halide-hydrocarbon complex prepared from a highly branched paraffin hydrocarbon as described above and an activator affording a hydrogen halide under the reaction conditions in a reaction zone maintained at a temperature in the range from about 100° F. to about 450° F. and a superatmospheric pressure sufficient to maintain the naphtha largely in the liquid phase. Under these conditions a large proportion of the straight-chain paraffin hydrocarbons in the naphtha are converted to branched-chain paraffin hydrocarbons

and a fraction rich in branched-chain paraffin hydrocarbons comprising a high antiknock motor fuel fraction is separated from the products. This process is referred to herein as "isomerization," although some changes in molecular weight occur simultaneously with the molecular rearrangement.

The feed stock to our isomerization process can be any substantially saturated naphtha rich in straight-chain paraffin hydrocarbons. For example, it can be a relatively pure, normally liquid straight-chain paraffin hydrocarbon such as normal pentane, normal hexane or normal heptane, but generally predominantly straight-run naphthas such as those from Michigan, Pennsylvania or Mid-Continent crude oil are preferred since they are much more readily available. Another excellent feed stock is the highly paraffinic naphtha produced by the Fischer-Tropsch process from carbon monoxide and hydrogen. Natural gasoline fractions and so-called "distillates" are also suitable and are plentiful and inexpensive in some production areas. It is very important that the feed stock be free or almost free from aromatic hydrocarbons since they have been found to reduce the activity of the catalyst to a very marked degree, and consequently to limit seriously the amount of conversion obtained per unit weight of catalyst. Our preferred feed stock therefore contains less than about 5% and preferably 0.5-1.0% or less of aromatic hydrocarbons. In many cases a preliminary solvent extraction step or other treatment is necessary or desirable to reduce the aromatic content of the feed. Olefinic hydrocarbons are also undesirable and should not be present in more than very small amounts, while cyclo-paraffinic or naphthenic hydrocarbons can be tolerated in considerable quantities. Nevertheless, the feed stock should preferably contain at least 50% of paraffin hydrocarbons and those containing at least 80% of paraffin hydrocarbons are especially desirable.

In general the naphtha feed stock should have a boiling range within the range from about 100° F. to about 500° F., although naphthas having an initial boiling point as low as about 30° F. and including about 25% to 30% by weight of butanes may be used. A particularly suitable naphtha feed is one prepared by the distillation and fractionation of a straight-run or natural gasoline stock to produce a light naphtha having an initial boiling point in the range from about 30° F. to about 90° F. or higher and an end point in the range from about 145° F. to about 158° F., preferably about 152° F. Substantially all of the aromatic hydrocarbons and most of the naphthenic hydrocarbons such as cyclohexane are excluded from this fraction and it is very rich in straight-chain paraffin hydrocarbons. Under special circumstances it may be desirable to use a light naphtha fraction boiling within a still narrower range.

The concentration of aluminum halide-hydrocarbon complex catalyst present in the reaction zone can vary within wide limits depending primarily upon the temperature, reaction time and catalyst activity. Generally the catalyst concentration will be within the range from about 5% to about 30% by weight of the liquid hydrocarbons present, based on the aluminum halide content of the complex, although larger or smaller amounts can be used if the other conditions are controlled in accordance therewith. It will be understood that the actual catalyst consumption

will be considerably lower since the complex re-

tains its activity for a considerable period of time and is preferably recycled to the reaction zone.

The activator supplied to the reaction zone is a substance affording a hydrogen halide under the conditions prevailing therein, which can be either a hydrogen halide itself such as hydrogen chloride or hydrogen bromide, or it can be carbon tetrachloride or one of the alkyl halides such as methyl chloride or bromide, ethyl chloride or bromide, etc. In general, the chlorinated and brominated hydrocarbons, particularly the more volatile ones, are suitable, and even water can be used since a hydrogen halide will be generated therefrom by reaction with the catalyst, but this is not preferred since the catalyst is thus deactivated more rapidly than would otherwise be the case. Preferably the amount of activator used is sufficient to supply a concentration in the reaction zone of about 1 to 2 mols of hydrogen halide per mol of aluminum halide, which will usually be in the range from about 0.1% to about 15.0% by weight, based on the reacting hydrocarbons present. The activator used in the preparation of the complex catalyst can be any of those indicated above, with the exception of water, which is undesirable for the reasons pointed out. Hydrogen chloride, however, is the preferred activator in all cases because of its availability and low cost.

The isomerization reaction is preferably carried out in the presence of free hydrogen, as disclosed in our application Serial No. 308,480, for the reason that the hydrogen greatly assists in increasing the yield of valuable hydrocarbon products per unit weight of catalyst. In this case the hydrogen is supplied under a pressure in the range from about 250 to about 3000 pounds per square inch and preferably at a pressure in the range from about 500 to about 1500 pounds per square inch. Relatively pure hydrogen is, of course, particularly suitable but in the plant operation of our process hydrogen containing impurities such as methane is available at much lower cost and can be used effectively as long as the hydrogen content of the gas is above about 50 mol per cent, in which case the hydrogen pressure previously mentioned would be the hydrogen partial pressure rather than the total gas pressure. It is also preferred that the hydrogen should be largely dissolved in the naphtha, particularly when our process is operated on a continuous basis. Generally the amount of free hydrogen present is less than about 50 volumes of gaseous hydrogen measured at 60° F. per volume of liquid naphtha and preferably it lies in the range from about 10 to 25 volumes of hydrogen per volume of naphtha, although under some circumstances smaller amounts can be used.

Another important variable which influences the course of the reaction is temperature. In general temperatures ranging from about 100° F. to about 450° F. are suitable, although different reaction times and amounts of catalyst are almost imperative in order that economically practicable results may be obtained at various temperatures. Usually we prefer to carry out the reaction in the range from about 200° F. to about 350° F. in order that it may proceed rapidly and without drastic over-treatment. In the upper portion of the broad temperature range specified the tendency toward decomposition into normally gaseous hydrocarbons such as isobutane can be inhibited by supplying a relatively small quantity of one of the butanes to the reaction zone.

It is apparent that the isomerization process above described can be carried out either batchwise or continuously, although we greatly prefer continuous concurrent flow of the naphtha feed and the active liquid aluminum halide catalyst. Certain portions of the apparatus must obviously be constructed of corrosion-resistant material to prevent rapid deterioration thereof from active halogen compounds present. Many suitable types of apparatus can be designed readily by one skilled in the art, but our invention will be described in detail in connection with only one of these, as illustrated in Figure 1, to which reference is now made.

The naphtha feed is introduced into the system by means of pump 10 and line 11 and passes into a chamber 12 in which it is mixed with a gaseous activator such as hydrogen chloride supplied by pump 13 through line 14. In the arrangement shown only that portion of the activator which dissolves in the naphtha is allowed to escape from chamber 12 and in the case of hydrogen chloride this is sufficient, as shown by the following data on the solubility of hydrogen chloride in a light naphtha at various temperatures and pressures:

Table I

HCl pressure	Weight percent HCl in light naphtha		
	58° F.	215° F.	336° F.
8 lbs./in. ²			
25 lbs./in. ²	0.4		
35 lbs./in. ²			0.35
85 lbs./in. ²		0.8	
135 lbs./in. ²	8.3	2.0	
150 lbs./in. ²			2.3
185 lbs./in. ²	14.4		
185 lbs./in. ²		5.3	
205 lbs./in. ²	22.6		
			3.9

However, the activator can be mixed directly with the feed stock or otherwise introduced into the system and these methods are, of course, used in connection with normally liquid activators. When very high pressures are to be used in carrying out the isomerization reaction the pressure in chamber 12 is preferably maintained in an intermediate range, for instance, 200 to 300 pounds per square inch or less. This pressure is controlled so as to supply enough activator to give the desired concentration when considered with the activator in the recycle streams described below.

The naphtha now containing dissolved activator is passed through pump 15 and lines 16 and 17 into a reaction zone 18 which, as shown, is a heated elongated coil 19 maintained at the desired reaction temperature. A pressure vessel, including stirring equipment may be substituted for reaction zone 18 but the form shown or a modification thereof using heat exchange with steam, diphenyl or other heat-transferring fluid, is preferred for continuous operation. In order to maintain the necessary agitation between the catalyst and the other reactants it is necessary that the velocity through coil 19 shall be great enough to insure turbulent flow. Knockhole mixers or other baffle arrangements may be inserted in coil 19 at several places to aid in achieving this result. The liquid aluminum halide-hydrocarbon complex prepared as hereinabove specified is supplied to line 17 and mixed therein with the feed stock by means of pump 20 and lines 21 and 22, and when hydrogen is used, as we prefer,

it is likewise introduced into line 17 through compressor 23 and lines 24 and 25.

The entire reaction mixture from coil 19 passes through line 26 and cooler 27 to a separator 28 in which the aluminum halide-hydrocarbon complex settles out as a lower layer and is continuously withdrawn through line 29. This complex or a major portion thereof is preferably recycled to line 17 through valve 30, line 31, pump 32 and line 22. If desired, however, all of the complex or any portion thereof can be withdrawn from the system through valve 33 and line 34. The complex withdrawn can, of course, be regenerated and the aluminum halide recovered therefrom used to make more complex and reintroduced into the system through pump 20, or a portion thereof can be treated with water or otherwise to furnish hydrogen halide for use as activator in the process.

The remainder of the products from coil 19 consists essentially of free hydrogen, if that substance has been supplied to the reaction, hydrogen halide, naphtha rich in branched-chain paraffin hydrocarbons and possibly some normally gaseous paraffins such as isobutane formed during the reaction. These are allowed to stratify in separator 28 so that a gaseous phase forms above the liquid hydrocarbon layer. When hydrogen has been used the pressure within separator 28 is preferably maintained as close as possible to the reaction pressure existing within coil 19, although it is obvious that there will be some pressure drop in transferring the reactants from coil 19 to separator 28. In this case the temperature of separation depends to a very considerable extent upon the character of the feed stock and the pressure, but generally it will lie within the range from about 50° F. to about 150° F., under which conditions very substantial quantities of free hydrogen formerly in solution are released as a gas. This hydrogen-rich gas is withdrawn from the top of separator 28 and returned to the reaction zone 18 by means of line 35, pump 36, line 25 and line 17. If hydrogen has not been used, however, the pressure in separator 28 is preferably substantially reduced and the temperature is maintained at a somewhat higher value so that the gas recycled through line 35 will consist essentially of gaseous paraffins such as isobutane, together with some activator.

The hydrocarbon layer is removed from separator 28 through line 37 and valve 38 and introduced into fractionating tower 39 through a heater 40. Valve 38 is preferably of the pressure-reducing type adjusted to the desired fractionating pressure. Fractionating tower 39 can be of any conventional design and, as shown, is provided with a side stream outlet 41 for the withdrawal of those hydrocarbons having the desired boiling range. If it is desired to remove a closely selected high antiknock fraction such as a fraction rich in neohexane, the bottoms will contain considerable amounts of unconverted naphtha and are recycled to the reaction zone 18 through line 42, valve 43, line 44, pump 45, valve 46 and lines 16 and 17. If substantially all of the material boiling in the motor fuel range is withdrawn as a side stream, however, the relatively heavy bottom fraction may be withdrawn from the system through valve 47 and line 48, although this also can be recycled. The desired product in line 41 is passed through a cooler 49 to storage or for other treatment and the more volatile material containing, for example, gases having less than five carbon

atoms per molecule and possibly additional free hydrogen and some hydrogen halide, is withdrawn as an overhead through line 50. This gaseous fraction is preferably recycled to line 17 through valve 51, line 52, pump 53 and line 54. In order that inert gases may be prevented from accumulating in the system, however, a portion of the material in line 50 may be vented either intermittently or continuously through valve 55 and line 56. In that case free hydrogen and/or hydrogen halide can be recovered from vent gases. Alternatively, the hydrogen halide can be removed from the products by a caustic washing step or the like prior to their introduction into heater 40 and fractionating tower 39.

As previously mentioned, small amounts of normal butane or isobutane can be supplied to reaction zone 18 when the reaction temperature is relatively high, for instance, 300° F. to 450° F. and this can be done by means of pump 57, line 58, valve 59 and lines 54 and 17. Generally, however, this expedient will be unnecessary when operation has been carried out for a period of time since sufficient isobutane will be formed and recycled through line 35 and/or line 52 to act as an inhibitor effective in suppressing the formation of further quantities of isobutane.

It is apparent from the above that we have described a novel method of isomerizing paraffinic naphthas to produce high antiknock motor fuel fractions by the use of a liquid aluminum halide-hydrocarbon complex which is particularly adapted to continuous plant operation.

In order to illustrate the unusual property of the aluminum halide-hydrocarbon complex catalysts prepared as already described an experiment was carried out, herein called "Run 1" to determine the effectiveness of catalysts of this type. In Run 1 the particular catalyst used was prepared by the action of anhydrous aluminum chloride and hydrogen chloride at atmospheric pressure and about 120° F. to 140° F. on commercial iso-octane, which is a product consisting essentially of the hydrogenated polymers and co-polymers of the butylenes. Since no continuous apparatus was available a number of successive tests were made under typical conditions, using the same charge of catalyst, the length of each test being determined by the time in which the bomb pressure dropped a predetermined amount, since it had been previously noticed that this was related to the extent of octane number improvement of the naphtha feed, although the proper reaction time cannot be determined accurately in all cases under experimental conditions. In this experiment the naphtha feed was a sample of light virgin naphtha derived from Mid-Continent crude oil boiling between 110° F. and 153° F. and having an octane number of 67.5 (CFR-M). The pertinent data for Run 1 are shown in Table II. It will be noted that in the first six portions of this run the amount of aluminum chloride in the catalyst was 98.5 gms., whereas thereafter it was 74.5 gms. This reduction in the amount of catalyst was due to the fact that it was at first thought that the amount of aluminum chloride in the complex was about 45% whereas it was actually 62.6%, as discovered by subsequent analysis, and the amount of complex was therefore reduced during Run 1 to make it correspond more nearly to Run 2 described below. However, perusal of the data will indicate clearly that the activity of the catalyst increases very markedly with use.

Table II

Run 1	Light naphtha	AlCl ₃ in iso-octane complex	HCl	Initial H ₂ pressure	Temperature	Pressure	Reaction time	H ₂ consumed	HCl consumed	Propane produced	Isobutane produced	Liquid yield No.	Octane (CFR-M)	Increase in O. N.
	Grams	Grams	Grams	#/in. ³	°F.	#/in. ³	Hours	Feet ³	Grams		Grams			
A.....	655	98.5	20.0	600	320	1200	0.55	0.11	8.5	None	11.7	Not deter.	72.8	5.3
B.....	608	98.5	13.8	600	326	980	1.10	0.32	-0.2	None	16.9	do.	76.8	9.3
C.....	608	98.5	13.8	600	326	940	1.10	0.32	0.8	None	15.1	do.	78.9	11.4
D.....	608	98.5	13.8	600	330	920	1.10	0.41	-1.7	None	16.7	do.	80.9	13.4
E.....	608	98.5	13.8	600	328	930	1.10	0.57	4.6	None	13.6	do.	82.0	14.5
F.....	608	98.5	13.8	600	330	920	0.85	0.48	-0.2	None	11.9	do.	82.0	14.5
G.....	608	74.5	13.8	600	330	940	0.85	0.40	0.5	None	12.6	do.	82.5	15.0
H.....	608	74.5	13.8	600	333	940	0.88	0.44	1.2	None	14.2	do.	82.4	14.9
I.....	608	74.5	13.3	600	334	930	0.78	0.51	-0.5	None	12.3	do.	81.7	14.2
J.....	608	74.5	13.8	600	333	950	0.75	0.47	-1.0	None	11.7	do.	81.5	14.0
K.....	608	74.5	13.8	600	330	940	0.55	0.33	-1.1	None	8.8	do.	81.2	13.7
L.....	608	74.5	13.8	600	328	980	0.25	0.18	2.6	None	7.9	do.	80.1	12.6
M.....	608	74.5	13.8	600	330	980	0.25	0.18	-0.3	None	4.2	do.	79.7	12.2
Totals.....	6,751		185.6				10.1	4.72	13.2	None	157.6	98.4%	80.2	12.7
Average.....	520		14.3	600	330	965	0.78	0.36	1.0	None	12.1	98.4%	80.2	12.7

It will be observed that the reaction time required to increase the antiknock value of the feed to an average of 80.2 octane number gradually decreased from more than 1 hour to approximately 15 minutes and that the catalyst obviously was not exhausted at the end of the run. In Figure 2 curve A shows the approximate relationship of reaction time plotted against the yield of product per pound of aluminum chloride in the catalyst. Another important feature not shown is that the catalyst complex remaining at the end of this run had a viscosity of only 75 second Saybolt at 300° F., as compared with a viscosity under similar conditions of 42 seconds for the fresh complex, thus demonstrating that the increase in viscosity with use is relatively small and that the complex can be used for a long period of time while retaining its pumpability.

In order to demonstrate the difference between the results obtained using aluminum halide-hydrocarbon complex according to our invention and using anhydrous aluminum chloride Run 2 was made which was similar to Run 1 and the results are shown in Table III.

It will be noted that the reaction time in this case leveled off at a considerably higher value than in the case of Run 1 and this is shown by curve B of Figure 2. Furthermore, the complex formed during Run 2 became more and more viscous until it approached the limits of pumpability.

These results show conclusively the unexpected and advantageous behavior of aluminum halide-hydrocarbon complexes of the type hereinabove described in a continuous process for the isomerization of the straight-chain paraffin hydrocarbons in a saturated naphtha. Many modifications of our invention and of the apparatus shown herein for carrying out the same will be apparent to those skilled in the art and they will be able to supply numerous details not herein described nor illustrated in the drawings. We do not desire therefore to be limited to the specific modifications and examples used in illustrating our invention but only by the scope of the appended claims.

We claim:

1. The process of producing a high antiknock

Table III

Run 2	Light naphtha	AlCl ₃	HCl	Initial H ₂ pressure	Temperature	Pressure	Reaction time	H ₂ consumed	HCl consumed	Propane produced	Isobutane produced	Liquid yield	Octane No (CFR-M)	Increase in O. N.
	Grams	Grams	Grams	#/in. ³	°F.	#/in. ³	Hours	Feet ³	Grams		Grams			
A.....	655	70.3	20.0	600	305	950	0.83	0.10	8.3	None	12.5	Not deter.	79.9	12.4
B.....	492		13.9	600	310	900	0.23	0.22	5.2	None	13.2	do.	82.0	14.5
C.....	492		13.9	600	305	850	0.10	0.21	2.2	None	18.6	do.	79.5	12.0
D.....	508		13.8	600	325	925	0.28	0.19	2.5	None	12.0	do.	82.1	14.6
E.....	490		13.9	600	330	950	0.45	0.20	0.5	None	12.5	do.	79.8	12.3
F.....	504		13.9	600	328	950	0.66	0.42	1.2	None	11.2	do.	81.7	14.2
G.....	504		13.9	600	330	950	0.75	0.42	2.1	None	16.0	do.	81.8	14.3
H.....	504		13.9	600	330	950	0.87	0.24	3.2	None	17.4	do.	81.5	14.0
I.....	504		13.8	600	334	925	0.88	0.43	1.3	None	15.4	do.	80.9	13.4
J.....	502		13.8	600	332	925	0.92	0.46	1.4	None	18.1	do.	80.9	13.4
K.....	500		13.9	600	334	925	0.92	0.44	1.7	None	19.6	do.	80.9	13.4
L.....	504		13.9	600	333	925	0.75	0.37	1.6	None	14.8	do.	80.7	13.2
M.....	505		13.8	600	334	925	1.00	0.49	0.9	None	21.0	do.	81.7	14.2
N.....	506		13.9	600	333	925	0.97	0.33	-0.1	None	26.0	do.	82.0	14.5
O.....	504		13.9	600	333	925	0.83	0.39	-0.5	None	17.2	do.	80.7	13.2
P.....	505		13.8	600	334	900	1.00	0.35	-0.3	None	20.0	do.	80.8	13.3
Q.....	504		14.0	600	332	925	1.00	0.33	-0.3	None	18.5	do.	80.9	13.4
R.....	508		13.8	600	331	925	0.97	0.43	-0.1	None	19.6	do.	81.0	13.5
S.....	506		13.8	600	331	925	0.97	0.40	0.2	None	16.5	do.	80.9	13.4
T.....	508		14.0	600	332	925	1.00	0.44	0.2	None	23.9	do.	80.6	13.1
Totals before correction.....			284.6				14.78	6.86	31.2	None	344.0	96.0%	81.0	13.5
Corrected totals.....	10,205	70.3					14.78	6.86	31.2	9.0	218.6	97.7	81.0	13.5
Average.....	512		14.2	600	330	925	0.74	0.34	1.56	None	10.9	97.7	81.0	13.5

In Run 2 the reaction time required to raise the octane number of the stock on the average to 81 gradually increased from less than 0.1 hour to about 1 hour and remained substantially constant at the latter value for a considerable period.

motor fuel fraction from a substantially saturated naphtha rich in straight-chain paraffin hydrocarbons which comprises contacting in a reaction zone maintained at a temperature in the range from about 100° F. to about 450° F. and

a pressure in the range from about 250 to about 3000 pounds per square inch an admixture of said naphtha, an activator affording a hydrogen halide and an active liquid aluminum halide-hydrocarbon complex prepared by the action of an aluminum halide catalyst and an activator affording a hydrogen halide on a substantially saturated fraction containing predominantly at least one paraffin hydrocarbon having at least two side chains at a temperature in the range from about 50° F. to about 175° F., removing the products from said reaction zone, and separating said high antiknock motor fuel fraction from said products.

2. The process in claim 1 wherein said active liquid complex is prepared from a substantially saturated fraction containing hydrocarbons having at least six carbon atoms per molecule selected from the group consisting of hydrogenated polymers and copolymers of olefins having less than six carbon atoms per molecule, and the products of alkylation of isobutane and of isopentane with olefins having less than six carbon atoms per molecule.

3. The process of claim 1 wherein said substantially saturated fraction is rich in hydrogenated polymers of isobutylene.

4. The process of claim 1 wherein the temperature in said reaction zone is in the range from about 200° F. to about 350° F.

5. The process of claim 1 wherein said aluminum halide catalyst is aluminum chloride and said activator is hydrogen chloride.

6. In a continuous process for producing a high antiknock motor fuel fraction from a substantially saturated naphtha rich in straight-chain paraffin hydrocarbons, the step comprising passing an admixture of said naphtha, an activator affording a hydrogen halide and an active liquid aluminum chloride hydrocarbon com-

plex through an elongated reaction zone maintained at a temperature in the range from about 100° F. to about 450° F. and a superatmospheric pressure sufficient to maintain said naphtha substantially in the liquid phase, said complex being prepared by the action of anhydrous aluminum chloride and an activator affording a hydrogen halide on a substantially saturated fraction rich in at least one paraffin hydrocarbon having at least two side chains and at least six carbon atoms per molecule at a temperature in the range from about 50° F. to about 175° F.

7. The process of claim 6 including the additional steps of removing the products from said reaction zone, separating aluminum chloride-hydrocarbon complex from said products, and recycling at least a portion of said separated complex to said reaction zone.

8. In a continuous process for producing a high antiknock motor fuel fraction from a substantially saturated naphtha rich in straight-chain paraffin hydrocarbons, the steps comprising passing an admixture of said naphtha, an active liquid aluminum chloride-hydrocarbon complex, hydrogen chloride and free hydrogen through an elongated reaction zone maintained at a temperature in the range from about 200° F. to about 350° F. and under a pressure in the range from about 250 to about 3000 pounds per square inch, said complex being prepared by the action of anhydrous aluminum chloride and hydrogen chloride on a substantially saturated fraction rich in iso-octane at a temperature in the range from about 75° F. to about 150° F., separating a hydrocarbon-containing portion from said products and recovering said motor fuel fraction from said hydrocarbon-containing portion.

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