

Oct. 30, 1945.

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CATALYTIC ISOMERIZATION OF HYDROCARBONS

Original Filed Aug. 12, 1939

2 Sheets-Sheet 1

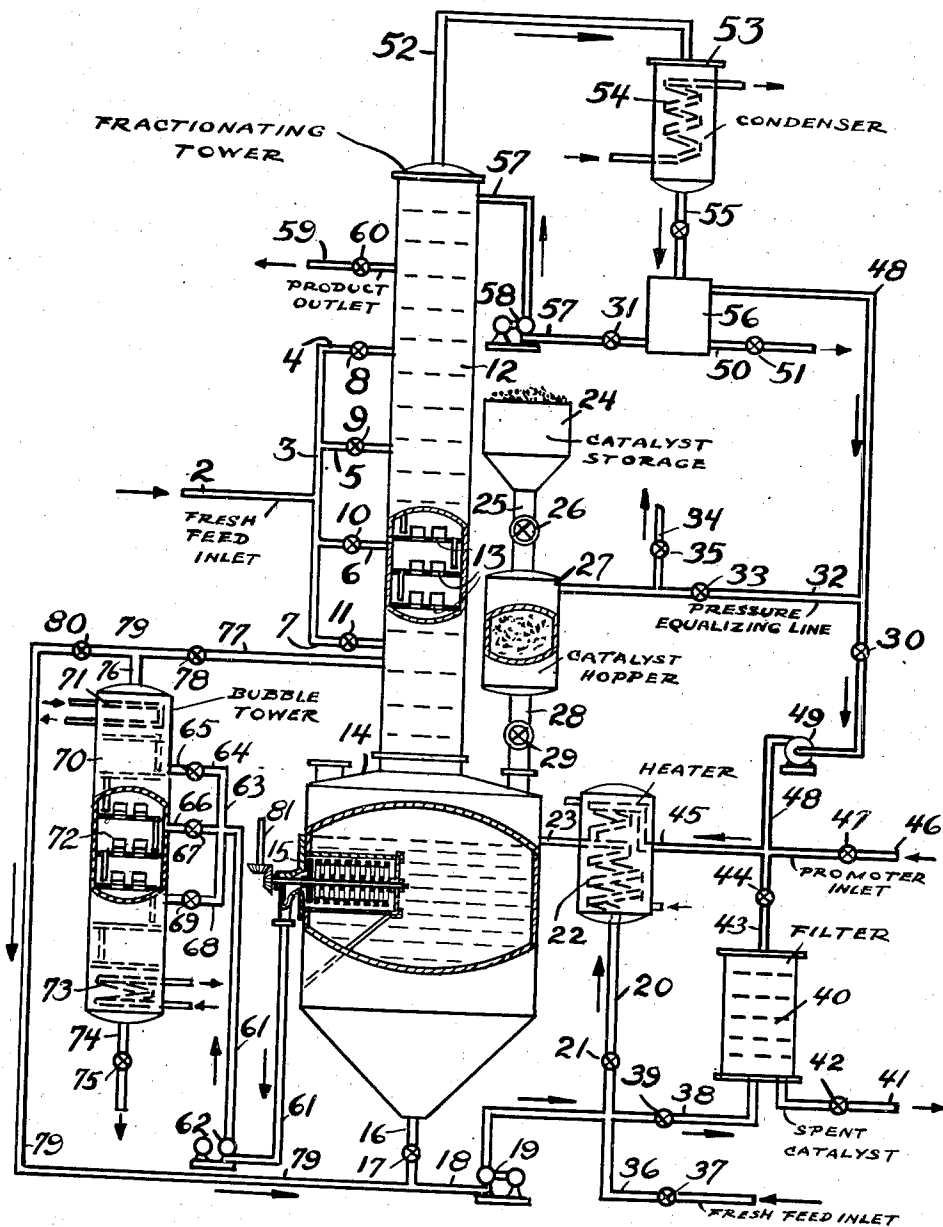


FIG.-1

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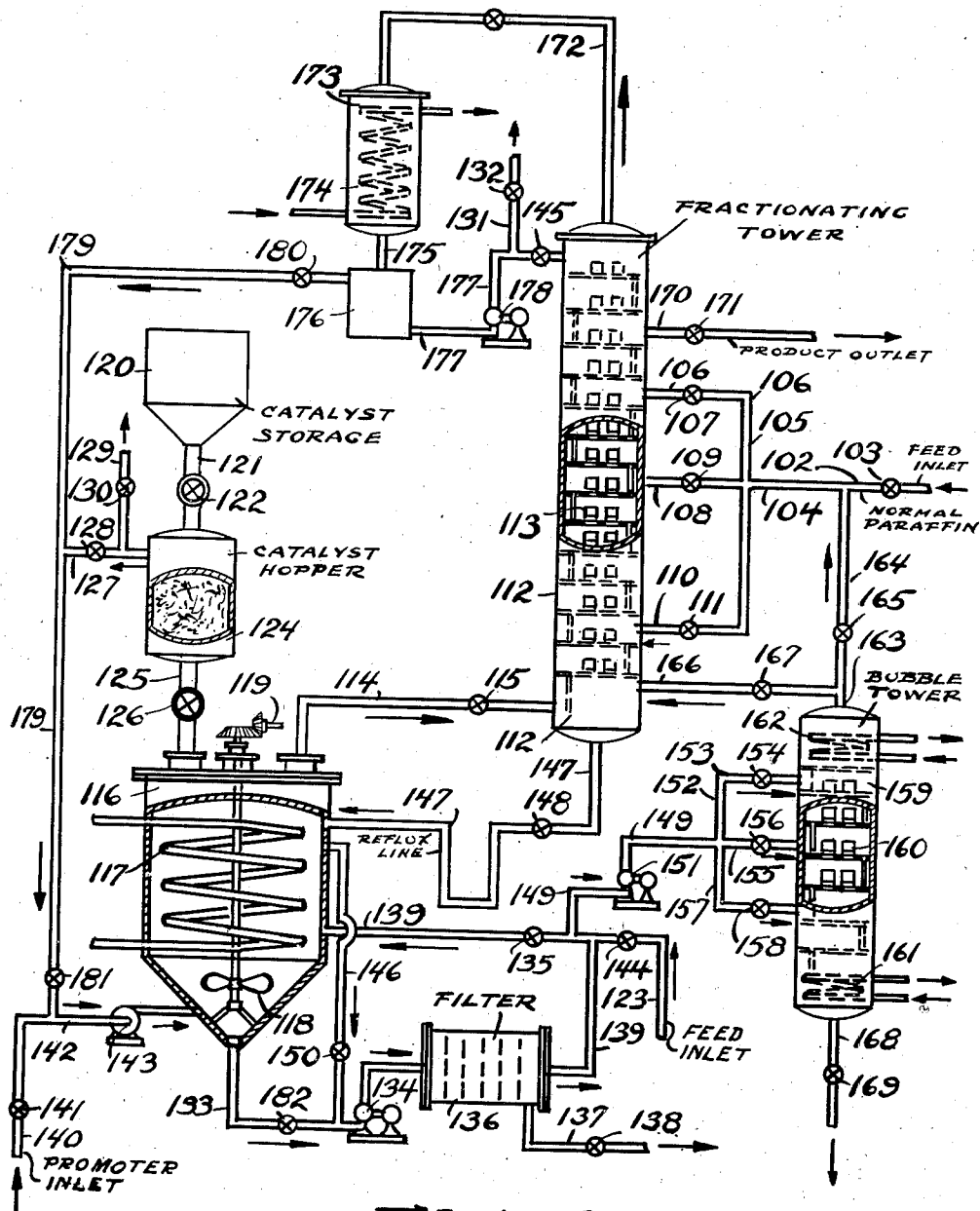


FIG.-2

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UNITED STATES PATENT OFFICE

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CATALYTIC ISOMERIZATION OF
HYDROCARBONS

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Original application August 12, 1939, Serial No.
289,867. Divided and this application May 26,
1942, Serial No. 444,505

4 Claims. (Cl. 260—683.5)

This application is a division of Serial No. 289,-
867, filed August 12, 1939.

This invention relates to a process for produc-
ing branched chain hydrocarbons from normal or
straight chain hydrocarbons.

It is known that hydrocarbons in the presence
of certain catalysts, such as aluminum chloride,
aluminum bromide and the like, are isomerized
to produce hydrocarbons of different physical and
chemical properties from those originally con-
tacted with the catalyst although containing the
same number of carbon atoms per molecule. It
is known that this reaction is reversible and that
quantitative yields of the desired isomer are sel-
dom, if ever, obtained.

It is an object of the present invention to iso-
merize hydrocarbons, particularly paraffin hydro-
carbons, to produce isomers thereof under con-
ditions such that the ultimate yields of the
desired isomers amount to almost quantitative
proportions. The conditions necessary to accom-
plish this result will be more fully hereinafter
described.

It is a further object of the invention to carry
out such a process in the liquid phase and to so
construct the apparatus useful in the process so
as to be able to carry out the process in a contin-
uous manner with a maximum conversion of the
feed stock into highly useful products.

It is a further object of the invention to iso-
merize straight chain paraffins containing at least
four carbon atoms so as to produce maximum
practical yields of branched chain paraffinic hy-
drocarbons which find particularly suitable uses
as motor fuel constituents or, more recently, as
reactants in the alkylation reactions involving
the reaction of isoparaffins with olefins to pro-
duce high octane number gasoline petroleum
mixtures.

In order to accomplish the above specified ob-
jects as well as others which will be readily appar-
ent to those skilled in the art upon attaining a
fuller understanding of the invention to be more
fully hereinafter described, normally liquid
straight chain paraffins or normally gaseous
straight chain paraffins which have been sub-
jected to sufficient pressure to maintain them in
the liquid phase, for example, normal butane, are
conducted continuously into a still pot or indi-
rectly into a still column from whence they reach
the still pot where they are contacted with a suit-
able isomerization catalyst, for example, the hal-
ides of certain metals of group III of the periodic
system, either with or without small amounts of
promoters, such as water, the hydrogen halides,

for example, hydrogen bromide or hydrogen chlo-
ride, or substances equivalent thereto, such as the
alkyl halides, methyl, ethyl, propyl, and butyl
chlorides and bromides under suitable tempera-
ture and pressure conditions. Alternatively, the
normal paraffinic hydrocarbons may be fed into a
fractionating column whose reboiler contains the
required isomerization catalyst. As the reaction
proceeds in the bottom of the fractionating col-
umn or in the still pot, as the case may be, iso-
meric paraffinic hydrocarbons are formed which
in turn have a lower boiling point than the cor-
responding straight chain isomers from which
they are formed.

A more complete understanding of the opera-
tion of the present invention can be attained by
reference to the accompanying diagrammatic
views in sectional elevation of two embodiments
of the concept of the present invention. Fig-
ures 1 and 2 will be more fully hereinafter de-
scribed.

As one embodiment of the invention, pure
straight chain paraffin hydrocarbons may be em-
ployed as the feed stock for the process of the
reaction. For example, normal butane, normal
pentane, normal hexane, normal heptane and the
like, as pure compounds, may be subjected to the
isomerization treatment as hereinafter more fully
described. However, it is to be distinctly under-
stood that the process of the present invention
equally as well applies to the treatment of mix-
tures of hydrocarbons predominantly composed
of straight chain paraffinic constituents, for ex-
ample, straight run naphthas of low octane num-
ber, preferably those having relatively narrow
boiling ranges, may be isomerized according to
the process of the present invention to improve
their octane number and to bring about other
desirable changes in their characteristics. Like-
wise, normally gaseous paraffinic mixtures, such
as field butanes, paraffinic mixtures resulting
from the removal of olefinic constituents of re-
finery C₄ cuts, that is, waste gases from hot and
cold acid polymerization processes, waste gases
of paraffinic nature evolved from thermal or cata-
lytic alkylation processes and similar sources of
mixed paraffinic hydrocarbon nature, may be
utilized as suitable feed stocks for use in the pre-
sent process. In general, the process operates
more efficiently for the lower members of the
paraffin series. However, the presence of pro-
pane in the reactants is not objectionable since its
physical characteristics are not changed by treat-
ment according to the present process and its
presence serves to inhibit cracking to some extent.

Normal pentane and normal butane, however, are extremely desirable as constituents of the feed stocks employed.

The temperatures and pressures employed according to the process of the present invention vary widely depending upon the type of feed stock employed. Thus, where normal heptane is the feed stock, a temperature of 100° C. or even as low as 30° C. with an absolute reaction pressure of from two atmospheres to one-third of an atmosphere may be employed with highly satisfactory results. In general, the isomerization of straight chain paraffinic hydrocarbons in the presence of halides of the third group of the periodic system is advantageously performed at room temperature or below. However, the speed of reaction is sacrificed at these low temperatures whereas at higher temperatures appreciable cracking of the feed stock occurs which is undesirable for ultimate high yields of isomeric hydrocarbons. It is therefore necessary for those skilled in the art to determine according to their own needs whether to operate the process at low temperatures and slow conversion rates or at higher temperatures and quicker conversion rates but accompanied with a high percentage of cracking. In general, for best operating conditions, temperatures of around 25° C. up to as high as 200° C. may be employed depending, however, upon the type of catalyst used, the amount of catalyst used, the residence of the feed stock in the reactor (in the present case, the still pot) and the throughput of the feed stock in the system. Pressures ranging from a fraction of one atmosphere up to as high as 20 atmospheres may be employed, the upper limit in working temperature and pressure being the critical temperatures and pressure of the feed stock being isomerized. However, pressures even as high as 50 atmospheres may be used without seriously affecting the general expediency of the reaction.

The throughput most advantageous in operating the process of the present invention may be varied over quite wide ranges depending upon the correlation of the other reaction conditions and factors incident thereto. The capacity and size of the apparatus, in particular, the isomerization chambers and still towers, depends upon the relative purity of the product desired, i. e., the degree of isomerization required, the catalyst to hydrocarbon ratio in the still body which, in general, will be maintained between about 0.05 to 1.0 and about 1.0 to 1.5, preferably about 0.5 to 1.0, said ratios being employed when using the apparatus disclosed in either Figure 1 or Figure 2, and the temperature at which the isomerization is carried out. As heretofore explained, the temperature is correlated with the pressure applied to the system. In general, the throughput should be relatively low under mild isomerizing conditions and high under more drastic isomerizing conditions, low at high reflux ratios to make pure product and high at low reflux ratios to make a mixed product.

Aluminum chloride either of commercial grade or chemically pure may be used as the catalyst for the reaction. However, it is contemplated to also use aluminum bromide, both of these catalysts being extremely active as isomerization catalysts. Where possible, freshly prepared aluminum bromide should be used, and in the case of aluminum chloride, finely divided aluminum chloride materially increases the rate of reaction. Likewise, freshly prepared aluminum chloride appears to materially increase the rate

of reaction, all other conditions being equal. The reaction also proceeds at high conversion rates by intimately agitating and mixing the catalyst and reactants. Any suitable method may be employed, such as, for example, jets, whereby the liquid feed stock is forced through jets of restricted internal diameter into the catalyst chamber containing a relatively large amount of the catalyst. Likewise turbo mixers and other types of orifice mixers, centrifuges, mechanical stirrers, motor driven if desired, and the like, may be employed to accomplish this result. Other catalysts, such as molybdenum trisulfide, zinc chloride, etc., may be employed.

As above mentioned, the quantity of catalyst materially controls the rate of conversion of the reactant. In general, as large a body of catalyst should be maintained in the still pot or reboiler of a reflux tower as is consistent with practical and economical operation of the apparatus. As will be shown hereinafter, filters are necessary to separate the catalyst, either partially spent or otherwise, from the reacted hydrocarbons. The question of capacity of these filters is one of the factors limiting the quantity of catalyst maintained in the isomerization zone.

When using aluminum chloride as the isomerization catalyst, it is desirable to have present measured amounts of a catalyst promoter. In the present case it is desirable to employ as the catalyst promoter a hydrogen halide or substances equivalent thereto under the reaction conditions. Any hydrogen halide may be employed although it is desirable to use, in general, hydrogen chloride or hydrogen bromide. The hydrogen halide or its equivalent may be present in relatively small quantities, but, if desired, larger quantities may be employed. Specifically between about 0.01% and about 2.0% of H₂O based on the fresh feed, may be employed although it is preferred to use between about 0.05% and about 0.5%. With HCl as a promoter, the amount circulated may be between 0.5% and 50% on the hydrocarbon present in the system, but to obtain good still operation and lower costs, the quantity preferred is between 1% and 3%.

Referring to Fig. 1 of the drawings, a suitable feed stock, for example, normal butane or mixtures of normal paraffins containing normal butane, is introduced through feed inlet 2 into line 3 which in turn leads into a plurality of lines 4, 5, 6 and 7 controlled by valves 8, 9, 10 and 11 respectively. The plurality of inlets for the fresh feed stock into the fractionating column 12 is provided so as to enable the operator to introduce the feed stock through that inlet which leads to that portion of the reflux in the tower corresponding approximately to the composition of the feed stock. Thus, for example, a feed stock composed essentially of normal butane would be introduced through pipe 7 controlled by valve 11, valves 8, 9 and 10 remaining closed. On the other hand, a feed stock containing substantial amounts of isobutane as well as some normal butane would be introduced through pipe 4 controlled by valve 8, valves 9, 10 and 11 remaining closed. In practical operation, fractionating column 12 would contain some 50 or 60 plates where a bubble cap arrangement 13 was employed. It is to be distinctly understood, however, that any suitable equipment may be employed, such as, for example, a tower packed with some solid inert material such as carborundum, packing rings, jack chain, and the like, nor is it necessary that

the tower contain exactly 50 plates in the case of the bubble cap arrangement. For each particular type of feed stock those skilled in the art may readily determine the size of the tower to be employed. Where a feed of normal butane is introduced into fractionating tower 12, the temperature of the tower is maintained so as to allow substantially only isobutane to be drawn off from the uppermost portion of the tower. In such an instance, the normal butane, after absorbing some of the heat of the reflux, passes into the still pot 14 where it is contacted with an isomerization catalyst. The catalyst is introduced into the system from catalyst storage bin 24 connected to the catalyst hopper 27 by means of conduit 25 controlled by valve 26. The catalyst hopper 27 is intermittently emptied and filled with catalyst. The arrangement of the valves 26 and 29, together with valves 33 and 35, permits the introduction of catalyst at atmospheric pressure as it exists in storage bin 24 into the reactor or still pot 14 which may be maintained under considerable superatmospheric pressure, thus the contents of hopper 27 are conducted into reactor 14 through conduit 28 and open valve 29, valve 35 remaining closed and valve 33 open. When the hopper 27 has become exhausted of its supply of catalyst, valve 29 is closed, valve 33 is closed, valve 26 is closed and valve 35 is opened to allow the hopper 27 to return to atmospheric pressure. Valve 35 is then closed, valve 26 is opened and the hopper is filled with fresh catalyst from the storage chamber 24. Valve 26 is then closed and the operation repeated as above described. By means of pump 19 and open valve 17 the partially reacted hydrocarbon liquid is withdrawn through pipes 16 and 18 and recycled through a heating unit back to reactor 14 by closing valves 37, 39, 44 and 47 and opening valve 21, thereby allowing a partially isomerized hydrocarbon mixture to flow into heater 22 and from there through line 23 into reactor 14. The rate of circulation is adjusted so that there is intimate mixing of the catalyst and liquid hydrocarbon in the still pot. The heater supplies the heat required for distillation as well as maintaining the mixture at reaction temperature. As the reaction proceeds more nearly to equilibrium, there is a certain amount of heavier products formed, for example C₈ paraffins and heavier where normal butane is employed as the feed stock. Provision is therefore made for withdrawing from reactor 14 a portion of the reacted mixture through a suitable filter 15, for example, a rotary drum knife-edged type filter or, as illustrated in Fig. 1, a "Cuno" filter, in either case permitting the aluminum chloride catalyst to be retained in the isomerization zone without removing anything but liquid from the reaction zone. Provision is made by means 81 for continuously cleaning the filter. The filtered hydrocarbon liquid is then pumped through line 61 by means of pump 62 into a fractionating tower 70 provided with any suitable packing material or bubble cap trays 72 analogous to the contents of tower 12 as illustrated by numeral 13. This tower is provided with heating coils 73 in the bottom and cooling coils 74 in the top. The heavier products of the isomerization are withdrawn through line 74 controlled by valve 75. Here again a plurality of inlets is provided whereby the filtrate from reactor 14 is conducted by means of line 61 to line 63, which leads into a plurality of inlet lines to the fractionating tower 70, these lines 64, 66

and 68 being controlled by valves 65, 67 and 69 respectively. The operator is then able to introduce the filtrate into the fractionating tower at a point wherein the reflux of the tower corresponds most nearly to the composition of the feed stock. In cases where normal butane is used as the feed stock, normal and isobutane, together with lighter effluents, pass overhead through line 76 into either lines 77 controlled by valve 78 or lines 79 controlled by valve 80. If valve 80 is closed, valve 78 is opened and the overhead effluent from the tower passes through line 77 back to the original fractionating column 12 where it is reprocessed as heretofore described. It may be desirable, however, to permit the overhead effluent from fractionating tower 70 to be returned directly to the reaction medium, especially so in cases where the overhead effluent from fractionating tower 70 contains relatively little isobutane. In such a case, valve 78 is closed, valve 80 is opened and the overhead effluent passes through line 79 back into line 18 and through pump 19. As heretofore described, the contents of this line are passed through a heating zone and allowed to return to the reactor 14.

After some hours of continuous usage, the catalyst is allowed to proceed to a point where its ultimate use has become definitely diminished. In such a case, the catalyst may be withdrawn from the system as a batch operation or the spent catalyst may be withdrawn from the system continuously in small amounts together with fresh catalyst, catalyst activity being maintained at the desired level by withdrawal of catalyst and addition of fresh catalyst from hopper 27. In either case, when it is desired to remove catalyst from the reaction medium, valve 21 is closed either entirely or partially, and the catalyst slurry is conducted by means of pipe 38 through valve 39 into a filter 40 of any suitable design, for example, this filter may be of the ordinary press and frame type, a rotary drum filter with knife-edged plate, a centrifuge, a "Cuno" filter, or any other suitable commercial type of filtering apparatus may be employed. The spent catalyst is diagrammatically represented as being removed through line 41 controlled by valve 42, although it is realized that for a natural operation some means for specifically removing solids from the filter would necessarily be employed. The filtrate is then conducted by means of line 43 through open valve 44, through line 45 into heating zone 22 and from there back to reactor 14 by means of line 23. Valve 30, in such an instance, may remain closed, or if open, blower 49 may be employed to recirculate or introduce the gaseous promoter into line 45. Fresh feed inlet 36 is provided with a valve 37 by means of which the feed may be introduced directly into the recycle stream rather than into the fractionating column 12. In cases where the feed contains practically no isoparaffins, it may be desirable to introduce the feed through inlet 36 controlled by valve 37. However, it is more desirable to introduce the feed through inlet 2 in cases where the feed stock contains substantial amounts of the desired product.

Provision is made for the introduction of the necessary quantities of hydrogen halide, water, or the equivalent thereof, into the reaction by means of inlet 46 controlled by valve 47. It is only necessary to provide for the addition of fresh catalyst promoter to compensate for the

loss of catalyst promoter dissolved in the product being removed from the system since it is believed that the promoter functions as a true promoter and is not materially altered by the process of the invention. However, it may be desirable at times to vary the quantity of promoter in the reaction system, in which case line 46 controlled by valve 47 may be employed either as an inlet or an outlet as the occasion demands.

The overhead from fractionating tower 12, which consists mainly of isobutane, some small amounts of propane and hydrogen chloride, is conducted by means of line 52 into a condensing unit 53 having cooling coils 54. The condensate is conducted by means of line 55 into a receiving drum 56. From the upper portion of this drum the lighter products are withdrawn by means of line 48 and returned to the reaction zone 14 by means of blower 49 through lines 45 and 48 passing through heater 22 and thence through line 23 into reactor 14. Naturally, when adding catalyst through inlet 28 and valve 29 from hopper 27, the pressure is equalized through line 32 and some of the light constituents may find their way into reactor 14 by this means.

The condensate collected in receiving drum 56, and which is substantially isobutane in cases where normal butane is used as the feed stock, may be withdrawn from the system by means of line 50 and valve 51. On the other hand, provision is also made for the withdrawal of isobutane from the system through line 59 controlled by valve 60. In either case, it probably contains small amounts of lighter hydrocarbons and of hydrogen chloride. A separate and distinct fractionation under the required temperatures and pressures may be employed for obtaining substantially pure isobutane. The condensate from receiving drum 56 may be pumped back to the fractionating column 12 as reflux condensate by means of pump 58, line 57 and open valve 31.

Fig. 2 represents a diagrammatic view in side elevation of another type of apparatus suitable for the carrying out of the present invention. For purposes of illustration, normal butane will be described as the feed stock. Normal butane may be introduced through line 102 by means of open valve 103 into lines 104 and 105 from which, according to the desire of the operator, the feed is introduced into fractionating column 112 through one or more of lines 106, 108 and 110 through valves 107, 109 and 111 respectively. As is the case with Fig. 1, the composition of the feed stock determines the point of introduction of that feed stock into the fractionating column 112. In the case of substantially pure normal butane, it may be introduced in the system either through line 102 or through line 123 controlled by valve 144. In either case, the normal butane emerges from fractionating tower 112 which may contain bubble cap equipment 113 or packed inert material such as carborundum, packing rings, jack chain, pumice, etc., through line 147 controlled by valve 148, thereby permitting the liquid effluent from fractionating tower 112 to be returned by means of reflux line 147 to reactor 116 equipped with a heating coil or other suitable heating means 117 which is provided with mechanical agitating means 119 and stirrer 118. Vapors from reactor 116 are permitted to enter the fractionating column 112 by means of line 114 controlled by valve 115. The catalyst is conducted into reactor 116 in substantially the same manner as described in the

case of Fig. 1, the pressure equalizing line being line 127 controlled by valve 128 and having attached thereto bleed-off line 129 controlled by valve 130. Catalyst storage bin 120 is connected with the catalyst hopper 124 by means of conduit 121 controlled by valve 122. The catalyst hopper is connected with reactor 116 by means of conduit 125 controlled by valve 126. The effluent from reactor 116 is pumped through line 133 controlled by valve 182 by means of pump 134. In order to remove the spent or partially spent catalyst from reactor 116, the filter 136 may be of any suitable conventional design and may be of the same type as described for the filter in Fig. 1. Likewise, draw-off line 137 controlled by valve 138 is analogous to draw-off line 41 controlled by valve 42 previously described for Fig. 1. The filtrate is then returned to the reactor 116 by means of line 139.

When the reaction has proceeded sufficiently, there may be produced heavier compounds than that introduced in the feed stock, for example, the pentanes. At such times, it is preferred to conduct the filtrate either continuously or intermittently from filter 136 directly to bubble tower 159 by closing or partially closing valve 115 and opening or partially opening valves 150 and/or 182 in order to separate out the heavier constituents. In such a case, valves 135 and 144 are partially or completely closed, and pump 151 causes the filtrate to be conducted through line 149 to the bubble tower 159 provided with a plurality of fractionating devices diagrammatically represented as element 160 through one or more of lines 153, 155, and 157 controlled by valves 154, 156, and 158 respectively. This arrangement corresponds to tower 70 controlled by lines 64, 66 and 68 controlled by valves 65, 67 and 69 of Fig. 1 and operates in substantially the same way. As in the case of bubble tower 70 in Fig. 1, bubble tower 159 is provided with cooling coils 162 and heating coils 161, the heavier material being withdrawn from the tower through pipe 168 controlled by valve 169. The overhead from this tower is conducted by means of pipe 163 either directly to the feed lines 102 and 104 by means of line 164 controlled by valve 165, valve 167 being closed, or valve 165 may be closed and valve 167 opened, thereby permitting the overhead effluent to be conducted by means of line 166 to fractionating tower 112. This latter procedure is particularly desirable where very little, if any, isomers have been formed or in cases where the heavier products have been allowed to accumulate for considerable periods of time while the isomers of the feed have been substantially completely removed as formed.

It is advantageous, when expedient, to withdraw the hydrocarbons from reactor 116 by means of line 146 since this effluent contains relatively small amounts of catalyst therein and the efficient life of filter 136 is thereby greatly prolonged. When it is desired to introduce the feed stock directly into reactor 116, valves 135 and 144 may be opened, valves 154, 156, and 158 being closed, thereby permitting the feed stock to enter the system through lines 123 and 139.

The promoter, for example hydrogen chloride, hydrogen bromide or water in the required amounts, may be introduced into the system through line 140 controlled by valve 141, in which case it is introduced into reactor 116 by means of line 142 and blower 143. The desired product which may come overhead from column 112 may be withdrawn through line 170 controlled by valve

111 or, if desired the product present in the system may be taken overhead through line 172 and condensed in condenser 173 containing cooling coils 174. The condensate is then allowed to run to the settling drum 176 through line 175. The lighter constituents, which are usually in the vapor state under the conditions prevailing in settling drum 176, are withdrawn through line 179 controlled by valves 180 and 181 and returned to the reactor 116 by means of line 142 and blower 143. The condensate may be withdrawn through line 177 and pumped back by means of pump 178 and line 177 controlled by valve 145 into the top of the fractionating column 112 to serve as reflux condensate. If desired, however, a portion or substantially all of this draw-off from settling drum 176 may be removed from the system by closing valve 145, opening valve 132 and permitting the product to flow through line 131.

Various modifications as to the design and size of the equipment may be made to fit the exigencies of the particular case. It is not intended that the invention should be limited by the type of equipment described, it being sufficient for the successful operation of this invention to provide for a semi-continuous or batch operation wherein the conditions are so maintained that normal paraffins entering the bottom of a still column either in a reboiling equipment or in a still column provided for the purpose may be isomerized in the presence of an isomerization catalyst under suitable reaction conditions, thereby simultaneously removing from the system as overhead from the fractionating column the desired isomeric hydrocarbons. Any means within the skill of those working in the art by which this result may be accomplished are entirely suitable and are considered to be within the scope of the invention herein described. Those parts of the apparatus coming in contact with the catalyst and/or promoters preferably should be lined with or constructed of corrosion-resistant materials such as stainless steel, ceramic materials, or other types of corrosion-resistant materials commonly employed in chemical plants for such purposes.

The following examples illustrate the process of the invention, although it is to be distinctly understood that the invention is not limited thereto.

Example 1

500 cc. of normal heptane was charged into the distilling flask of a 5 ft. column packed with carborundum. This column was equivalent to 30 theoretical plates and was equipped for operation under reduced pressure. Aluminum chloride was charged into the distilling flask with the normal heptane. The normal heptane was boiled and refluxed in the column. Products were taken overhead when the temperature at the top of the column was below the boiling point of normal heptane. The aluminum chloride was charged to the extent of 10% by weight of the feed. The reaction temperature automatically remained at about 98° C. The experiment was conducted under atmospheric pressure and there resulted a 33.7% by volume yield of isomeric products which had an octane blending value of about 96. The isomerized product contained .4% by volume of propane, 37% by volume of isobutane, about 21.1% by volume of isopentane, 7.8% of isohexane and 27.5% of isoheptane. The remainder of the isomerized product was made up of normal paraffins of 4 to 6 carbon atoms. The average reac-

tion time was about 2½ hours with continuous reflux.

Example 2

In a similar run conducted at about 33° C. in volving the use of 10% by weight of aluminum chloride and about 1% by weight of water based on the feed, a reaction time of about 8 hours and an absolute reaction pressure of about 1.45 lbs./sq. in., a 40.4% by volume yield of isomerized products were obtained. An analysis of the product showed that it contained about 24.9% by volume of isobutane with only about .6% by volume of normal butane, about 23.5% by volume of isopentane with no detectable amounts of normal pentane present, about 16% by volume of isohexane with about 2.4% of normal hexane and 32.6% by volume of isoheptane. The blending value of the isomerized product was about 74.5 in this particular instance.

Example 3

As exemplary of the continuous operation on normal butane, the still pot was maintained at a temperature of about 200° F., the pressure on the still being about 260 lbs./sq. in. gauge, approximately 40 lbs./sq. in. of this pressure being due to HCl being recirculated through the gas system. A reflux ratio of about 10 to 1 was maintained on the top of the still which was equivalent to about 50 theoretical plates. The butane product drawn off overhead consisted of about 85% isobutane, about 15% normal butane and contained a trace of propane.

The normal butane was fed to the still in the still pot rather than in the side of the still column and contained a trace of olefins and between about 7 and about 10% isobutane. The aluminum chloride in the still was equivalent to about 25% of the weight of the hydrocarbon in the still pot and had a volume of approximately 10% of the volume of the still pot. Additional aluminum chloride equivalent to about 2.0% by weight of the normal butane in the feed was added. Spent catalyst was withdrawn intermittently and was found to be still quite active so that the catalyst consumption was actually less than the 2.0% by weight on the fresh feed. The spent catalyst withdrawn, which was equivalent to that in the still, was a brown finely divided solid which, when dumped into water, reacted violently.

The hourly rate of addition of normal butane was such that the time of residence in the still was about 2 hours, that is, it was equivalent to about one-half the volume of the hydrocarbon in the still pot and column.

Example 4

In a small laboratory run in a ½ inch diameter column of a height equivalent to about 50 plates, the still pot was charged with a mixture of about 110 gms. normal pentane and about 110 gms. AlCl₃. A small amount of HCl was added slowly while the run was in progress. Operating the still at atmospheric pressure with a still temperature of about 96° F., isopentane practically pure was produced at the rate of about 4 gms. per hour. No butane or other lower boiling hydrocarbons could be detected in the product although they may have been present in small amounts.

Example 5

In another experiment run according to the conditions specified in Example 1 except that the reaction temperature was about 67° C., the catalyst was activated by the addition of 1% of water

based on the feed, and the length of catalyst contact was about 6 hours, the pressure being about 5.15 lbs./sq. in. absolute. Isomers were obtained to the extent of about 21% by volume of which about 34.8% by volume was isobutane, about 1.3% normal butane, about 23.2% isopentane, about 4.1% normal pentane, about 6.8% isohexane, about 6.3% normal hexane and about 23.3% isoheptane were produced.

The present invention is not intended to be limited to any theory or mechanism of the reaction but only to the following claims in which it is desired to claim all novelty inherent in the invention. The nature and objects of the present invention having been thus fully described and illustrated, what is new and useful and is desired to be secured by Letters Patent is:

1. A continuous process which comprises reacting a refinery C₄ cut substantially free of olefins and containing substantial amounts of normal butane in a combination isomerization-fractionation operation under isomerization reaction conditions in the presence of an aluminum halide and a hydrogen halide, directly, simultaneously and continuously removing overhead from the boiling liquid reaction mixture as distillate substantially only products of the reaction boiling below normal butane, removing at least a portion of the undistilled boiling liquid reaction mixture substantially free of aluminum halide from the reaction zone, and separately and independently fractionally distilling the said undistilled boiling liquid reaction mixture to obtain at least two fractions, one of which is higher boiling than the normal butane and the other of

which boils at substantially the boiling point of normal butane, continuously returning to the isomerization reaction zone the second-mentioned fraction and removing from the isomerization system the first-mentioned fraction.

2. A continuous process which comprises isomerizing normal paraffin containing at least four carbon atoms per molecule in the presence of an isomerization catalyst under isomerization reaction conditions in a combination isomerization-fractionation operation, directly, simultaneously and continuously removing overhead from the boiling liquid reaction mixture as distillate substantially only products of the reaction boiling below the boiling point of the normal paraffin feed stock, removing at least a portion of the undistilled boiling liquid reaction mixture substantially free of isomerization catalyst from the reaction zone and separately and independently fractionally distilling the said undistilled boiling liquid reaction mixture to obtain at least two fractions, one of which is higher boiling than the normal paraffin feed stock and at least one other of which boils at substantially the boiling point of the normal paraffin feed stock, continuously returning to the isomerization reaction zone the last-mentioned fraction and removing from the isomerization system the first-mentioned fraction.

3. A process as in claim 2 wherein the feed stock comprises essentially normal butane.

4. A process as in claim 2 wherein the feed stock comprises essentially normal pentane.

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