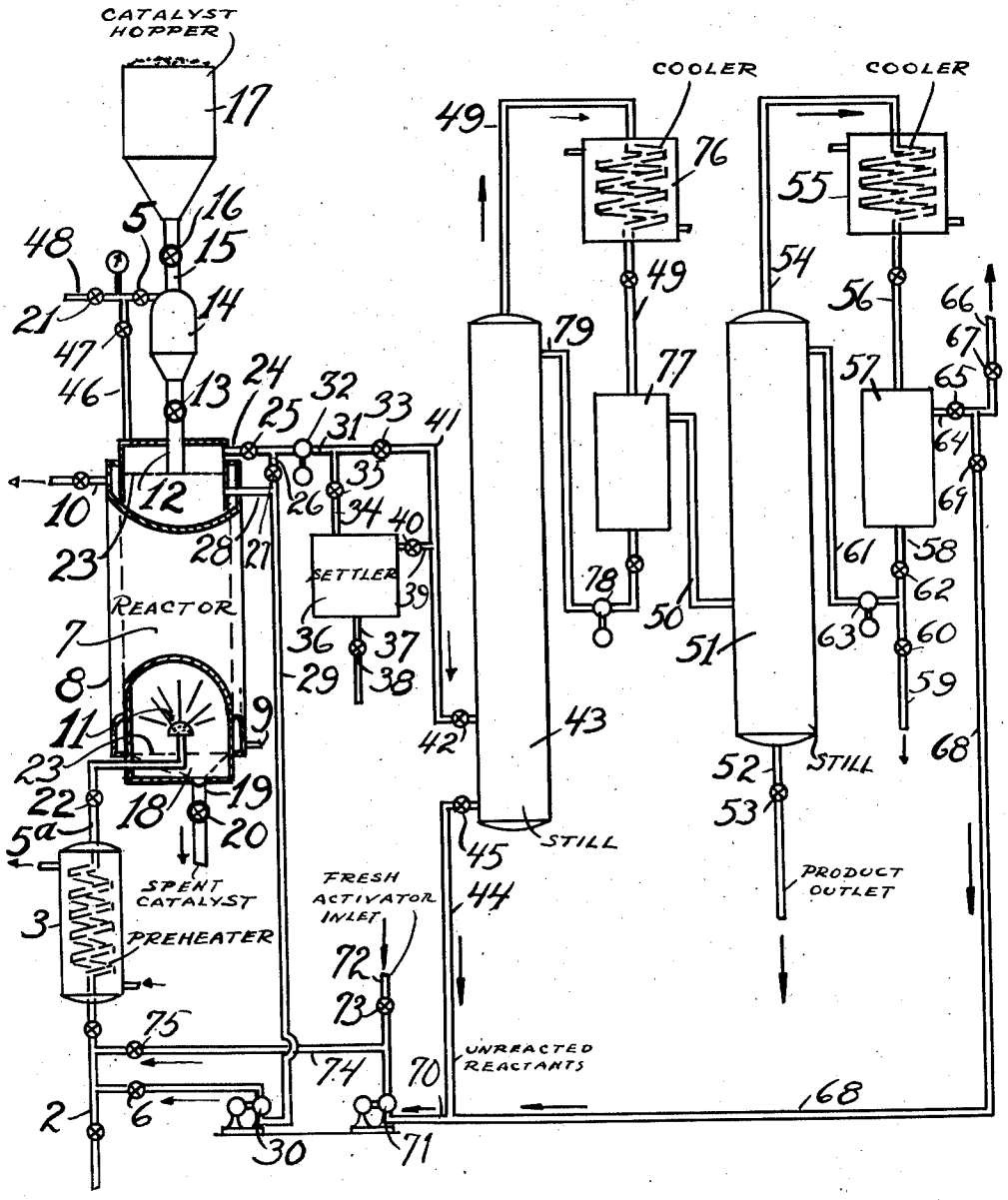
Dec. 23, 1947. J. M. WHITELEY, JR., ET AL 2,433,079

CATALYTIC ISOMERIZATION PROCESS

Filed Sept. 30, 1939 3 Sheets-Sheet 1

FIG.-1



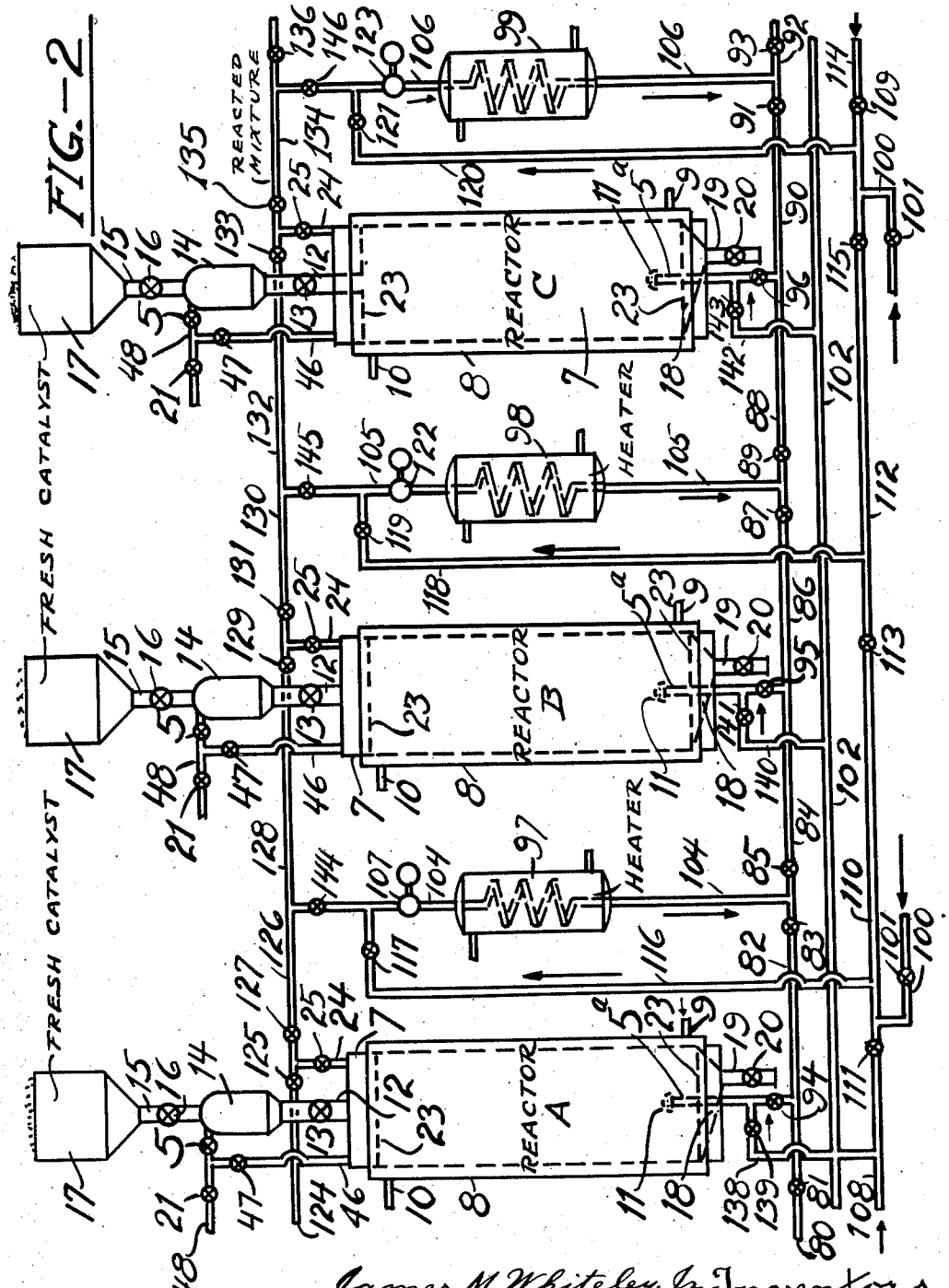
James M. Whiteley, Jr. Inventors
Charles S. Lynch
By R. L. Young Attorney

Dec. 23, 1947. J. M. WHITELEY, JR., ET AL 2,433,079

CATALYTIC ISOMERIZATION PROCESS

Filed Sept. 30, 1939 3 Sheets-Sheet 2

FIG. -2



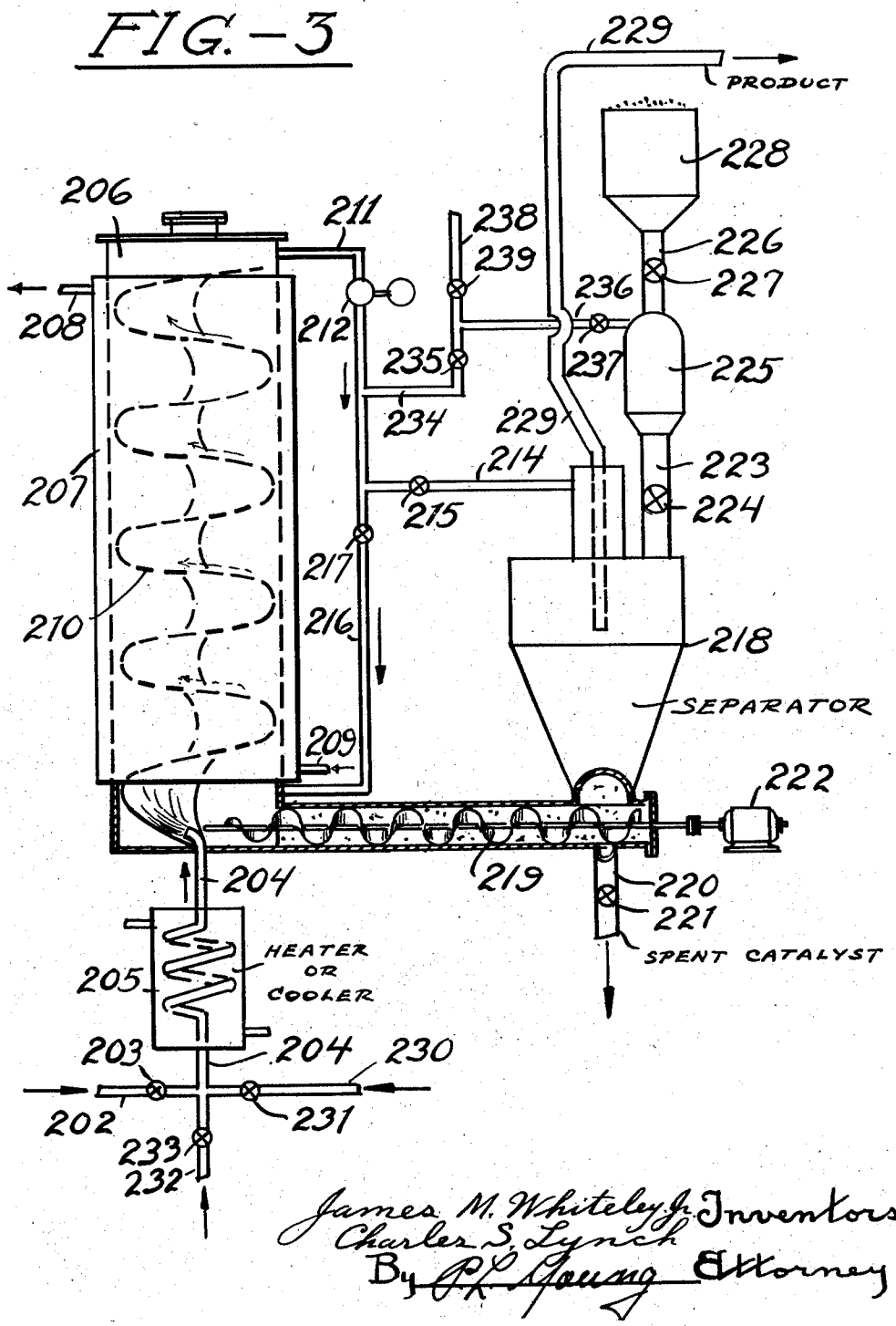
James M. Whiteley Jr. Inventors
Charles S. Lynch
By P. L. Young Attorney

Dec. 23, 1947. J. M. WHITELEY, JR., ET AL 2,433,079

CATALYTIC ISOMERIZATION PROCESS

Filed Sept. 30, 1939 3 Sheets-Sheet 3

FIG.-3



James M. Whiteley Jr. Inventors
Charles S. Lynch
By P. L. Young Attorney

Patented Dec. 23, 1947

2,433,079

UNITED STATES PATENT OFFICE

2,433,079

CATALYTIC ISOMERIZATION PROCESS

James M. Whiteley, Jr., Aruba, Curacao, Dutch West Indies, and Charles S. Lynch, Fanwood, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application September 30, 1939, Serial No. 297,198

9 Claims. (Cl. 260—683.5)

1

The process of the present invention relates to the isomerization of hydrocarbons, and, more particularly, to the conversion of normal or straight chain paraffinic hydrocarbons into iso- or branched chain paraffinic hydrocarbons by catalytic means. It is known that hydrocarbons, in particular the straight chain paraffins, may be isomerized into branched chain paraffins in the presence of various catalysts of the Friedel-Crafts type, such as aluminum chloride, aluminum bromide, molybdenum trisulfide, ferric chloride, zinc chloride, and the like, with or without the addition of promoters. The paraffinic hydrocarbon products possess different physical and chemical properties and are chiefly branched chain in character. Heretofore various difficulties have been encountered in attempting to place this operation upon a commercial scale. The Friedel-Crafts type catalysts are not easily controlled in their reaction. Furthermore, up to the present time a continuous liquid phase operation has presented certain inherent difficulties due, principally, to the problem of catalyst degradation and formation of undesirable by-products in major amounts. Furthermore, the ease of control of the operating conditions has not been perfected. As a result, truly continuous processes have not been operated on a commercial scale.

The success of the present invention lies in the fact that it has now been made possible to effect an economical continuous isomerization process upon a commercial scale employing a liquid phase operation. Troubles incident to the mechanical agitation which has heretofore been thought necessary have been substantially completely eliminated and the operating variables are now easily and readily controlled. It has been found that, for example, a moving bed type of catalyst in which the ratio of catalyst to hydrocarbon feed is maintained large and wherein a specified thruput is maintained under the operating conditions successfully accomplishes these advantages. By operating according to the process of the present invention, it has been found to be unnecessary to shut down the unit in order to effect a replacement of the spent catalyst.

It is an object of the present invention to effect an economical catalytic isomerization process, particularly with reference to the lower paraffinic hydrocarbons, and to carry out such a process while maintaining the catalyst mass in substantial excess to the quantity of hydrocarbon fed to the reaction. It is a further object of the

2

invention to provide a moving bed of isomerization catalyst and to continuously feed straight chain paraffins containing at least four carbon atoms per molecule under isomerization conditions in contact with said bed. Another object of the invention is to carry out a continuous liquid phase commercial isomerization process using a plurality of isomerization reactors connected in series or in parallel so as to make use of a large catalyst mass with a maximum efficiency and with a maximum production of branched chain paraffinic hydrocarbons which are known to be useful in various refinery operations and in some cases as gasoline constituents per se. Still another object of the invention is to produce branched chain paraffins from straight chain paraffins by isomerization while employing apparatus enabling operators to more accurately control the reaction conditions of the process.

In order to accomplish these objects, as well as other objects which will be apparent from a full understanding of the invention to be more fully hereinafter described, it has now been found that excellent yields of the desired isomeric hydrocarbons, in particular iso- or branched chain paraffins of four or more carbon atoms per molecule, may be obtained by employing a relatively large ratio of catalyst to straight chain hydrocarbons fed to a reactor at any one time. In other words, the objects of the invention may be accomplished by feeding hydrocarbons into stationary or moving bed type reactors substantially filled with a large mass of catalyst and allowing the feed stock to percolate thru the bed under the isomerization conditions desired.

The isomerization may be effected over a wide range of conditions of temperature, time of contact, catalyst form, concentration of promoter, etc., all of these factors being interrelated. In general, temperatures between about 30° F. and about 400° F. may be employed, although at temperatures above 300° F. there is apt to be some decomposition in the formation of lower hydrocarbons with a lower number of carbon atoms. However, the presence of hydrogen formed in situ or added from extraneous sources has a tendency to suppress such decomposition reactions. In cases where normal butane is employed, a temperature range between about room tmeperature and about 175° F. is advantageous. Good yields may be obtained within these ranges using a contact time of from about 10 seconds to about 15 or 20 hours depending upon the temperature and the form of catalyst

employed. In general, space velocities of from about 0.2 and about 5.0 volumes of straight chain paraffin per volume of catalyst per hour are employed.

Various promoters may be employed in the reaction, for example, hydrogen chloride, hydrogen bromide, and other hydrogen halides, lower alkyl halides, for example methyl chloride or bromide, ethyl chloride or bromide, butyl and amyl halides, and the like. In some instances it is even advantageous to add free halogen to the reaction. The promoter is aded in an amount equal to from about 0.5 to about 25%, preferably between about 2 and about 10%, based upon the paraffin feed stock.

As will be more fully hereinafter explained, the promoter, for example, hydrogen chloride, may be employed in excess amounts so that the reactor is not completely filled with liquid phase components but also contains a small gas phase above the liquid portion thereof. In this way, when employing the partial pressure of the hydrogen chloride, the concentration of the hydrogen chloride in the liquid phase is more readily controlled. At 200° F. an increase in pressure of 50 lbs. will result in a hydrogen chloride concentration of 2% in the liquid phase. An increase in pressure of 100 lbs./sq. in. corresponds, roughly, to about 5% hydrogen chloride in the liquid phase and an increase in pressure of 150 lbs. corresponds to about 8% of hydrogen chloride in the liquid phase. These data apply when employing normal butane as the reactant. Similar data on the solubility of hydrogen chloride in normal pentane at 75° F. show that the solubility is quite high and is proportional to the applied pressure of hydrogen chloride.

From the very nature of the process herein described the catalyst concentration is necessarily quite high. A concentration between about 100% and about 1000% and higher is usually employed. Fresh catalyst is added to the bed continuously or intermittently, depending upon the rate at which the catalyst becomes substantially completely degraded. The spent or partially spent catalyst is removed in like manner from the bottom of the bed in order to make room for the newly added catalyst.

The process is applicable to the treatment of normal butane, normal pentane, normal hexane, normal heptane, normal octane, and the corresponding higher homologues of the paraffin series. It is within the scope of the present invention to also employ mixtures of two or more of these paraffinic hydrocarbons. Likewise, the invention is applicable to the treatment of the straight run naphthas of relatively low octane number which are composed predominantly of normal paraffinic hydrocarbons. Such isomerization treatment as herein described materially increases the octane number of these naphthas. The invention is likewise applicable to the treatment of field butanes, paraffinic mixtures resulting from the removal of olefinic constituents of refinery C_4 and C_5 cuts, waste gases of paraffinic nature evolved from thermal and/or catalytic alkylation and polymerization units, and similar paraffinic hydrocarbons. In general, any hydrocarbon mixture composed predominantly of saturated straight chain compounds is suitable as a feed stock for the process herein outlined.

The process is chiefly directed to a continuous operation although it is to be distinctly understood that a batch type reaction is entirely feasible when employing a percolation process wherein normal paraffins are percolated thru a large bed of isomerization catalyst mass under isomerization conditions.

The process of the present invention contemplates the carrying out of the reaction in the liquid phase. Normal butane, when employed as a reactant, requires the use of superatmospheric pressures to maintain the reaction in liquid phase under the conditions of operation obtaining. Normal pentane may likewise often require the application of superatmospheric pressures in order to maintain liquid phase operation under the conditions obtaining.

In order to more fully understand the process of the present invention, reference may be had to the drawings which are more or less purely diagrammatic representations in sectional elevation of suitable flowplans showing some structural detail. The apparatus is capable of quite wide modification to suit the exigencies of any particular isomerization process. However, the drawings will be described with reference to the use of aluminum chloride as the catalyst, hydrogen chloride as the promoter, and normal butane as the feed stock.

Fig. 1 represents a single reactor and a series of stills and other conventional units for separating the reacted mixture from the catalyst and segregating the desired products from the undesired products and unreacted reactants. Fig. 2 is a more or less diagrammatic representation of a series of reactors similar to that disclosed in Fig. 1. Fig. 3 represents a diagrammatic presentation of still a second type of reactor applicable for carrying out the general process of the invention.

According to the process as carried out using a single reactor, fresh catalyst, for example aluminum chloride in lumps or granules or deposited on an inert carrier, such as pumice, bauxite, fuller's earth, kaolin, diatomaceous earth, Filtrol or impregnated on silica or alumina, is introduced into reactor 7 thru hopper 17 controlled by pipe 15 and valve 16 thru the intermediate pressure chamber 14 and from thence into reactor 7 by means of pipe 12 controlled by valve 13, thereby substantially filling reactor 7 between the two plates represented by numeral 23. Intermediate pressure chamber 14 is maintained at atmospheric pressure while being filled with fresh catalyst by closing pressure valve 47 in line 46 leading from the superatmospheric system and opening valves 21 and 5 in line 48. Upon being filled, chamber 14 is subjected to the pressure of the system by closing valves 16 and 21 and opening valves 5 and 47. Once the pressure is equalized, valve 13 is opened and the catalyst is introduced into reactor 7. Normal butane is introduced by means of pipe 2 into preheater 3 together with fresh activator, for example, hydrogen chloride, which is introduced into pipe 2 by means of lines 72 and 74 controlled by valves 73 and 75 respectively. Valve 22 is open and the mixture is conducted into reactor 7 by means of pipe 5A and a suitable dispersion device 11. Sufficient superatmospheric pressure is maintained in the system to insure that the normal butane remains in the liquid phase. As the liquid ascends and percolates thru the catalyst bed, the reactor is maintained at the desired reaction temperature by means of temperature jacket 8 into which steam or some other suitable heating medium is introduced by means of inlet 9 and withdrawn by means of outlet 10. As the reaction proceeds, the spent catalyst is withdrawn by means of incline

section 18 into outlet pipe 19 controlled by valve 20. The effluent from reactor 7 may be withdrawn thru either pipe 24 controlled by valve 25 or pipe 28, depending upon whether or not a partial pressure of hydrogen chloride is maintained in the upper portion of the reaction chamber. Valve 25 remains closed in this latter instance and the reactants are withdrawn thru pipe 28 and may be conducted by means of pipe 26 controlled by valve 27 into line 31 and introduced by means of pump 32 into a suitable settler or filter device 36 by means of line 34 thru open valve 35, valve 33 remaining closed. On the other hand, if the rate of conversion is not sufficiently rapid, the effluent from line 28 may be reconducted by means of line 29 thru pump 30 thru open valve 6 back to line 2 and reintroduced into the reactor for further conversion to the branched chain paraffin, namely, isobutane, valve 27 remaining closed. If the reactor is operated without a substantial partial pressure of the activator, for example, hydrogen chloride, the effluent from line 24 thru open valve 25 may be returned thru line 29 as described, or pump 32 may be placed in operation and the effluent introduced into the settler or filter unit 36 for the removal of the last traces of the catalyst which may be suspended in said effluent. The filtered or settled product is introduced into still 43 by means of pipes 39 and 41, valves 40 and 42 remaining open. On the other hand, if the effluent from reactor 7 is of sufficient clarity and contains very little catalyst in suspension, settler or filter unit 36 may be omitted by closing valves 35 and 40, and pipes 31 and 41 may be placed in operation by opening valve 33. The clear product introduced into still 43 is separated into unreacted reactants flowing from the still thru pipe 44 controlled by valve 45. The overhead product passing thru line 49, cooler 76, into receiving tank 77 may be either returned to still 43 to serve as reflux by means of pump 78 and line 79, or it may be conducted by means of line 50 into the secondary still or fractionating column 51 where the desired product, isobutane in the present instance, is withdrawn thru line 52 controlled by valve 53, and the lighter products, for example, any propane which may have been formed as well as hydrogen and hydrogen chloride, are conducted from still 51 thru line 54 into cooler 55. The condensate is conducted by means of pipe 56 to settling drum 57. A portion of the condensate in receiver 57 may be returned to still 51 to serve as reflux by means of lines 58 and 61, valve 60 remaining closed and valve 62 being opened. Pump 63 is employed to effect a flow of the condensate for reflux purposes. The remainder of the condensate may be either withdrawn thru line 59 controlled by valve 60 or line 66 controlled by valve 67. However, the greater portion of the hydrogen chloride and hydrogen will be evolved from receiver 57 thru line 64 controlled by valve 65. This may either be bled from the system or returned to the reactor 7 by means of lines 68, 70 and 74 controlled by valves 69 and 75 by means of pump 71. The unreacted reactants from still 43 are likewise returned to reactor 7 by means of lines 70 and 74 controlled by valve 75 by means of pump 71. The separated catalyst from the settler or filter unit 36 is withdrawn thru line 37 controlled by valve 38. This separated catalyst may either be discarded or if not entirely spent, may be returned to the catalyst zone in any suitable manner. Numerous details of construction have been purposely omitted from the drawing as represented by Fig. 1 for the purpose of simplicity in illustrating the process of the present invention. Obviously, valve 42 is in effect a pressure release valve. Numerous pressure recording instruments, flow regulators, and the like are required in actual operation but it is felt that those familiar with the details of operation are sufficiently skilled to know the correct placing of these instruments.

Fig. 2 discloses a series of three reactors, reactors A, B and C, so arranged as to provide a plurality of types of operation. The process of separating the desired product from these reactors is substantially identical with that disclosed in Fig. 1 wherein a single reactor has been described. With respect to reactors A, B and C, the elements are numbered so that the same element in the reactors is described by the same number as that given for that element in Fig. 1. No further details of the construction of the reactors is therefore deemed necessary. It should be distinctly understood in describing the operation of reactors A, B and C that more than three reactors are obviously included within the scope of the invention, it being sufficient, for the purposes of illustrating the invention, to describe in detail the inter operation of these three reactors.

The three reactors may be run in parallel so that each reactor operates as a unit unto itself similar in operation to the reactor described in Fig. 1. The feed stock enters the system thru pipe 100 controlled by valve 101. The feed stock then enters a series of pipes as represented by numerals 103, 110, 112 and 114 controlled by valves 111, 113, 115 and 109. For parallel operation of the reactors these valves are opened. The partially used activator, hydrogen chloride and/or the unreacted reactants, for example, normal butane, returned from the separation system and fresh activator are introduced into these same lines, thereby effecting the introduction of the mixture into pipes 116, 118 and 120 controlled by valves 117, 119 and 121 respectively. The fresh activator may be separately introduced by closing valve 111 and opening valves 139, 141 and 143, allowing lines 102, 138, 140 and 142 to carry the fresh activator to the reactors. The feed stock is then introduced by means of pumps 107, 122 and 123 and lines 104, 105 and 106 respectively into preheaters 97, 98 and 99, valves 144, 145 and 146 remaining closed. The effluent from the heaters is conducted by means of lines 104, 105 and 106 into lines 82, 86 and 90, valves 83, 87 and 91 remaining open and valves 85, 89 and 93 remaining closed. Valves 94, 95 and 96 are also opened, thereby permitting the preheated reaction mixture to enter the reactors A, B and C thru line 5 of each reactor, valves 139, 141 and 143 remaining closed. The effluent from reactors A, B and C is conducted by means of line 24 controlled by valve 25 in each reactor into lines 126, 130 and 134 from whence it may be conducted to the flashing tower of a separation system or to a settler or filter unit similar to that represented by numeral 36 in Fig. 1. On the other hand, if the rate of conversion has not been sufficiently great to effect a substantial maximum percentage yield of isobutane, valves 125, 129, 133 and 136 are closed, valves 144, 145 and 146 may then be opened, and by means of pumps 107, 122 and 123 the partially reacted mixture may be returned to the preheaters and reconducted to reactors A, B and C respectively as heretofore described. Although Fig. 2 does not disclose the operation, it is within the contemplation of the invention to provide each reactor with a draw-off line similar to line 28 of

Fig. 1 thereby permitting the operation of reactors A, B and C, using a partial pressure of hydrogen chloride sufficiently great to maintain a portion of the reaction in the gas phase.

Reactors A, B and C may also be operated in a series arrangement. This operation is conducted by permitting all of the fresh feed entering line 100 controlled by valve 101 to pass into line 116 controlled by valve 117. The recycled unreacted reactants and activator are conducted thru lines 114, 112 and 110 into line 116, valve 111 remaining closed unless it is desired to introduce fresh activator, in which case line 103 is employed and valve 111 is opened. Valves 83, 87 and 91 remain closed so that the effluent from heaters 97, 98 and 99 passes thru lines 104, 84, 105, 88, 106 and 92, valves 85, 95, 89, 96 and 93 remaining open. The effluent from the preheater preceding reactor A (not shown) enters reactor A thru line 80 controlled by valves 81 and 94. The effluent from the reactors enters lines 126, 130 and 134, valves 125, 128, 133 and 136 being closed, and valves 127, 131 and 135 being open. If reactor B is the initial reactor in the series arrangement, valve 144 remains closed. However, if a preheater is in operation ahead of reactor A, valves 144, 145 and 146 remain open and pumps 107, 122 and 123 are operated so as to permit the flow of reaction mixture thru the respective preheaters into the next succeeding reactor. The effluent from reactor D (not shown) or the effluent from any designated final reactor, for example reactor C (where heater 99 is omitted from operation), is permitted to pass to the conventional fractionation columns and settling zones as represented in Fig. 1 in order to separate the desired product, namely, isobutane, from the reacted mixture. This effluent flows thru line 134 controlled by valve 136, valve 146 in such an instance remaining closed.

This arrangement of a plurality of reactors in series for accomplishing the isomerization reaction may also be modified so as to attain a maximum catalyst efficiency during continuous operation of the process, for example, preheaters 97, 98 and 99, as well as the heat jackets 8 on reactors A, B and C, may be maintained at different temperature levels so as to accomplish a distinct temperature gradient between the several reactors and operated in accordance with the process outlined in the copending application of Charles S. Lynch entitled "Isomerization process," Serial No. 292,838 filed August 31, 1939, now Patent 2,280,710. Furthermore, it is possible to carry out the series operation of the plurality of reactors so as to employ a less reactive catalyst bed among the several reactors as a pretreatment reactor for the feed stock, thereby permitting the removal of impurities and undesirable constituents of the feed stock by polymerization methods. It is known that olefins, aromatics, and the like, are distinctly deleterious to the economical and smooth functioning of an isomerization process for paraffinic hydrocarbons. In the ordinary operation of the series process, reactors A, B and C will carry out the isomerization reactor in proportion to the activity of their catalytic contents, thus where a fresh feed is introduced into reactor A, a larger percentage of the conversion of normal butane to isobutane will be effected therein than in any subsequent isomerization reactor. Consequently, the catalyst in reactor A undergoes degradation and decomposition to a greater extent in reactor A than in the subsequent reactors. It is therefore within the contemplation of the present invention to permit the feed stock to continuously be introduced into reactor A and to then provide means for introducing the effluent from reactor A into some subsequent reactor in which the catalyst activity is substantially greater although it is not intended that this reactor be the next subsequent reactor. In other words, the effluent from reactor A would first be run thru reactor C prior to introducing the same into reactor B, or where a series of a large number of reactors were employed, the path of the feed stock might be so controlled as to run thru reactor A, then reactors E, D, C and B in that order. In other words, the isomerization conversion rate, by suitable manipulation of the feed stock, either unreacted or partially reacted, can be so controlled in its manipulations so as to accomplish a more or less uniform catalyst degradation in all of the reactors in series rather than having a major portion of the conversion effected in the initial reactor into which the unreacted feed stock is introduced. A more uniform catalyst degradation in each of the reactors is desirable for the reason that the introduction of fresh catalyst and the removal of spent catalyst from each reactor, if carried out on a more or less uniform continuous or semi-continuous basis, lends itself to greater ease of operation and supervision.

In some instances it may be desirable to effect a partial regeneration of the catalyst activity in any one or group of reactors. It so happens that it is sometimes advantageous, where a catalyst has dropped to a low efficiency yet has not been completely spent or degraded, to regenerate or revivify that catalyst. In such an instance, a reactor may be by-passed without interrupting the continuous operation of the other reactors either in parallel or in series operations. For example, if it is desired to shut down reactor B and yet continue the operation of reactors A and C, valves 95 and 25 are closed. In series operation the effluent from reactor A is conducted thru pump 107 by opening valves 127 and 144 thru preheater 97 into line 84 by means of open valve 85, valve 83 remaining closed. Valves 87 and 89 are opened and by means of lines 86 and 88 the effluent from reactor A, preheated by means of heater 97, is introduced into line 5A of reactor C by opened valve 96, valve 91 remaining closed. In parallel operation of reactors A and C with reactor B shut down, valves 85, 87, 89, 93, 119 and 145 are closed as well as valves 25 and 95. The effluent from reactor A enters line 126 by means of open valve 127, passes thru line 128 by means of open valve 129 and line 130 by means of open valve 131 into lines 132 and 134 by means of open valves 133, 135 and 136 and from there into the separation and settling tanks, the effluent from reactor C likewise joining the effluent from reactor A in line 134 and passing thru open valves 135 and 136.

In order to regenerate the partially spent aluminum chloride mass in reactor B, fresh activator, for example, hydrogen chloride, is introduced into line 102 and from there it is conducted by means of line 140 and open valve 141 into reactor B where it is allowed to contact the partially spent catalyst mass. The evolved hydrogen chloride may then be taken from the system thru the pressure equalizing system employed in introducing the fresh catalyst into the reactor, that is, lines 46 and 48 are employed by opening valves 47 and 21 and permitting valve 5 to remain closed.

It is sometimes feasible to permit the flow of reactants thru any specific reactor for longer periods of time than can be accomplished by once-thru operation in a given reactor. Fig. 2, there-

fore, discloses a provision for the recycling of the partially isomerized paraffinic hydrocarbon reactants by permitting the flow thru pipes 104, 105 and 106 to be partially diverted thru pipes 82, 86 and 90 respectively by valves 83, 87 and 91 being partially opened. In such an instance, valves 127, 131 and 135 are open and valves 125, 129 and 133 remain closed in a series type of operation. Valves 81, 85, 89 and 93 remain partially open to permit the passage of the reacted material into the next reactor. By operating in this manner it is possible to retain more of the feed stock introduced into any specific reactor for a longer length of time in that reactor or until the rate of conversion desired has been attained in that reactor. This is more or less a provision for a continuous recycle feature to the reactor to permit the desired length of time to effect the desired conversion to take place.

Fig. 3 presents a diagrammatic illustration of still another type of reactor suitable for carrying out the process of the present invention. The catalyst from catalyst hopper 228 is introduced into a pressure chamber 225 by means of pipe 226 controlled by valve 227. The pressure is then increased to that maintained in the reaction zone by opening valves 235 in line 234 and 237 in line 236, valve 239 in line 238 remaining closed. Once the pressure in the chamber 225 has reached that of the reaction zone, valve 237 is closed and valve 224 opened to permit the catalyst to pass thru line 223 into the cyclone separator 218. The catalyst, when operating the process according to the apparatus disclosed in Fig. 3, should preferably be a fairly finely divided powder of the order of 100 to 200 mesh. The catalyst in cyclone separator 218 is conveyed to reaction chamber 206 by means of a screw conveyer or slurry pump represented in the drawing as element 219. This screw or pump may be driven by any suitable mechanical means, for example, a motor 222. Fresh feed is introduced into the system thru line 202 controlled by valve 203. Fresh activator is introduced into the system thru line 232 controlled by valve 233. The two streams are united and enter a preheater 205 thru pipe 204 which in turn empties into the bottom of reactor 206. A pump (not shown) maintains a sufficient velocity of flow of the fresh feed, which is in the liquid phase, to create a swirling motion within the reactor 206 equipped with spiral baffle plates 210 so that the catalyst powder entering by means of screw conveyer or slurry pump 219 is taken up as a slurry in the liquid reactant and carried thru the series of baffles upwardly for the desired time. Reactor 206 is equipped with a heating jacket 207 provided with inlet 209 and outlet 208 whereby it is possible to maintain the desired reaction temperature during the residence of the catalyst and reactants in the reactor 206. Any suitable heating medium, such as heavy oil, steam or flue gases, and the like, may be employed as a heating medium in the jacket 207. The effluent from reactor 206, which consists of a slurry of small amounts of decomposition products, isoparaffins, catalyst and spent catalyst, together with small quantities of hydrogen, is then withdrawn by means of pump 212 and may then take one of two courses. If the reaction has not sufficiently progressed within the reactor 206, the partially reacted mixture may be returned to the reaction zone thru line 216 by opening valve 217. On the other hand, if the mixture is sufficiently isomerized, valve 217 remains closed and valve 215 is open thereby permitting the slurry to pass by means of pipe 214 into the catalyst separator 218. In practical operation it is desirable to partially open both valves 215 and 217. In catalyst separator 218 the slurry is broken, the catalyst mass settling to the bottom and substantially clear super-natant liquid is withdrawn by means of pipe 229 for further processing to isolate the desired product. The spent catalyst, having settled to the bottom of separator 218, may either be returned to the reactor 206 by means of screw conveyer or slurry pump 219, or if it has reached a point where it is no longer useful in the reaction because of degradation, it may be withdrawn from the system by means of pipe 220 controlled by valve 221. The product withdrawn thru pipe 229 may be subjected to a filtering operation or other suitable separating operation wherein the last traces of the catalyst are separated from the hydrocarbon product. Said hydrocarbon product may then be subjected to fractionation treatment to effect a separation of the desired isomers from the product. Unreacted reactants and activator may then be collected and returned to the reactor 206 thru line 230 controlled by valve 231. In operating pressure chamber 225, it is necessary, before refilling said chamber with fresh catalyst, to reduce the pressure to the pressure of the catalyst hopper 228. This is accomplished by closing valve 235 and opening valves 237 and 239. Valve 239 is then closed, valve 227 is opened, pressure chamber 225 is allowed to fill the catalyst, valve 227 is then closed and pressure from the system connecting the reactor is permitted to enter the chamber by means of valves 235 and 237 as heretofore described prior to introducing the catalyst in chamber 225 into the catalyst separator 218 by means of line 223 controlled by valve 224.

A single spiral baffle tower reactor has been described. However, it is within the contemplation of the invention to operate simultaneously and in inter-connection with each other a series of spiral baffle tower reactors, the operation of these being quite similar to the operation of the series of reactors described in Fig. 2 in connection with the single reactor described in Fig. 1. However, no difficulty is encountered in assembling a single reactor of the type disclosed in Fig. 3 into a series of inter-connected reactors capable of series and parallel operation as described with reference to the reactor of Fig. 1 in Fig. 2. It is to be realized, of course, that the actual catalyst concentration in a slurry is limited to amounts of the catalyst such that a slurry will be maintained. Those operating a process as described in Fig. 3 are well aware of the fact that a sufficient velocity of the feed entering the reactor must be maintained to pick up and carry in suspension the powdered catalyst entering the reactor by means of the screw conveyer or slurry pump. It is therefore not possible in this type of apparatus to maintain a catalyst concentration as high as may be maintained in connection with the bed type of operation. However, the results obtainable with the baffle tower slurry process are proportionately as excellent as those obtained with the bed type percolation method.

However, it should be distinctly understood that the process of the invention is not limited to any particular type of apparatus since it is only necessary, in carrying out the process of the present invention, to effect the isomerization reaction in the presence of extremely large quantities of catalyst per unit volume of paraffinic reactant.

Any apparatus, therefore, which is capable of accomplishing this type of operation, will be entirely suitable for carrying out the process of the present invention.

In order to more fully understand the exact nature of the present invention, the following examples are given:

Example 1

A reactor was filled with about 83 gms. of a commercial grade of $AlCl_3$ lumps. About 135 gms. of normal pentane, together with a small amount of HCl was percolated through this bed at a feed rate of about 0.9 v./v./hr. at a temperature of about 76° F. Isopentane was formed to the extent of about 6%. About 8% of the normal pentane was reacted.

Example 2

In a continuous unit, about 400 cc. of a commercial grade of $AlCl_3$ granules were charged to a reactor, the entire system being maintained under sufficient superatmospheric pressure to insure that the feed stock comprising essentially normal butane remained in the liquid phase throughout the reaction. For about 420 hours the feed stock of normal butane was continuously percolated upwardly through this catalyst bed maintained at from about 150 to about 175° F. at the rate of about 0.5 v./v./hr. About 20% of HCl was continuously added to the feed stock. Initially, the yield of isobutane was about 40%, after about 12 hours operation, about 60%, and after 400 hours operation, above 50%. In general, about 12 gallons of isobutane per pound of $AlCl_3$ charged was obtained. In this particular experiment, no additions of fresh $AlCl_3$ were made as the run progressed.

Example 3

About 2 liters of a commercial grade of $AlCl_3$ lumps were charged to a reactor. Normal pentane containing about 3% HCl was continuously percolated through the catalyst bed at a rate of about 0.3 v./v./hr. while maintaining the catalyst bed at about room temperature. After about 5 hours operation, the product produced yielded about 33% of isopentane. After about 3 hours additional at about 2.5 v./v./hr. the yield of isopentane obtained was about 30%.

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

1. A process of isomerizing normal paraffin of at least 4 carbon atoms per molecule to produce isoparaffin which comprises maintaining a continuous circulating stream of normal paraffin in liquid phase and containing hydrogen halide, maintaining a reaction zone within a portion of the said circulatory stream, said zone having therein a bed of aluminum chloride, percolating the normal paraffin through said bed under isomerization reaction conditions and recovering isoparaffin from the reacted mixture, the time of contact of the normal paraffin being sufficient to effect substantial isomerization.

2. A process as in claim 1 in which the fresh feed of normal paraffin is introduced into the stream ahead of the reaction zone and in which the reacted mixture is withdrawn from the stream behind the reaction zone and at a point remote from the point of introduction of the fresh feed, the total volume of liquid in the stream being maintained substantially constant.

3. An isomerization process which comprises percolating in liquid phase at least one normal paraffin containing at least 4 carbon atoms and a small amount of hydrogen chloride through a reaction zone substantially filled with granules of aluminum chloride at a temperature between about 40° F. and about 300° F., and recycling at least a portion of the reaction product without separation.

4. Process according to claim 3 in which the reaction zone comprises a moving bed of catalyst whereby during operation of the process spent catalyst is substantially continuously withdrawn from the end of the reaction zone into which the normal paraffin is fed, and fresh catalyst is substantially continuously fed into the reaction zone at the inlet end of the catalyst bed.

5. Isomerization process which comprises percolating in liquid phase at least one normal paraffin containing at least 4 carbon atoms and a small amount of hydrogen chloride through a reaction zone substantially filled with granules of aluminum chloride at a temperature between about 40° F. and about 300° F., the throughput velocity being sufficiently high for the particular temperature used that the extent of conversion of the normal paraffin into corresponding isoparaffin is substantially less than the maximum attainable, and recycling all of the reaction products without any separation until the desired extent of conversion is attained.

6. An isomerization process which comprises feeding fresh catalyst consisting essentially of aluminum chloride granules into the top of a vertical reaction tower through which said catalyst descends slowly, withdrawing spent catalyst at the bottom of said reaction tower at a rate corresponding approximately to the fresh catalyst feed rate, maintaining said reaction tower at a temperature between about 40° F. and about 300° F. by means of a surrounding temperature control jacket, feeding into the base of said reaction tower a liquid comprising a major proportion of normal paraffin containing at least 4 carbon atoms per molecule, whereby said normal paraffin feed passes upwardly through the descending catalyst bed at a throughput velocity high enough under the reaction temperature used that the extent of conversion of normal paraffin to isoparaffin is substantially less than the maximum attainable, withdrawing reaction products from the top of the reaction tower and recycling all of said reaction products through the reaction tower until the desired extent of conversion is attained, there being continuously maintained in said reaction tower a small gas phase above the liquid phase, and maintaining in said gas phase a sufficient partial pressure of hydrogen chloride to impart the desired concentration (between about 0.5% and 25%) of dissolved hydrogen chloride in the liquid phase for promoting the isomerization reaction.

7. Process according to claim 6 followed, after the desired conversion is attained, by removal of the reaction products from the top of the reaction tower into a still from which unreacted normal paraffin is removed as bottoms and recycled to the reaction tower, and from which still lighter products are taken overhead including isoparaffins formed by the reaction as well as hydrogen

halide promoter and reaction products lighter than the isoparaffin which may have been formed during the reaction, passing said overhead products into a second still from which the desired isoparaffins are withdrawn as bottoms and from which hydrogen halide and products lighter than the desired isoparaffins are taken overhead, and recycling at least a portion of said overhead products.

8. A process which comprises continuously percolating at least one normal paraffin containing at least four carbon atoms and a small amount of hydrogen chloride through a reaction zone substantially filled with granules of aluminum chloride, in the liquid phase, said zone being maintained at a temperature between about 40° F. and about 300° F., withdrawing the reaction mixture from said reaction zone, fractionating the desired branched chain paraffin from the reaction mixture and returning hydrogen chloride, low boiling degradation products of the reaction, unreacted reactants and at least a portion of the reaction product to the reaction zone together with the fresh feed.

9. A process which comprises continuously percolating normal butane and a small amount of hydrogen chloride through a reaction zone substantially filled with granules of aluminum chloride, in the liquid phase, said zone being maintained at a temperature between about 40° F. and about 300° F., withdrawing the reaction mixture from said reaction zone, fractionating the desired branched chain paraffin from the reaction mixture and returning hydrogen chloride, low boiling degradation products of the reaction, unreacted reactants and at least a portion of the reaction product to the reaction zone together with the fresh feed.

JAMES M. WHITELEY, JR.
CHARLES S. LYNCH.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,169,494	Ipatieff et al.	Aug. 15, 1939
1,647,446	Wolcott	Nov. 1, 1927
1,716,372	Downs	June 11, 1939
2,208,362	Engel	July 16, 1940
2,220,092	Evering et al.	Nov. 5, 1940
2,125,234	Atwell	July 26, 1938
1,882,000	Cross	Oct. 11, 1932
2,249,366	Van Peski et al.	July 15, 1941
2,265,548	Schuit	Dec. 9, 1941
1,825,270	Jenkins et al.	Sept. 29, 1931

FOREIGN PATENTS

Number	Country	Date
24,044	India	Aug. 23, 1937
193,071	Great Britain	Feb. 16, 1923
255,159	Great Britain	July 19, 1926
364,665	Great Britain	Jan. 4, 1932

OTHER REFERENCES

Petrov et al., Oil and Gas Jour., Feb. 2, 1939, pages 42 and 45. (Copy in Patent Office Library.)

Glasebrook et al., J. A. C. S. 58 (1936) 1944–1948. (Copy in Pat. Office Library.)