Dec. 8, 1953 M. P. MATUSZAK 2,662,103

PRODUCTION OF PARAFFINS

Filed Dec. 18, 1945 2 Sheets-Sheet 1

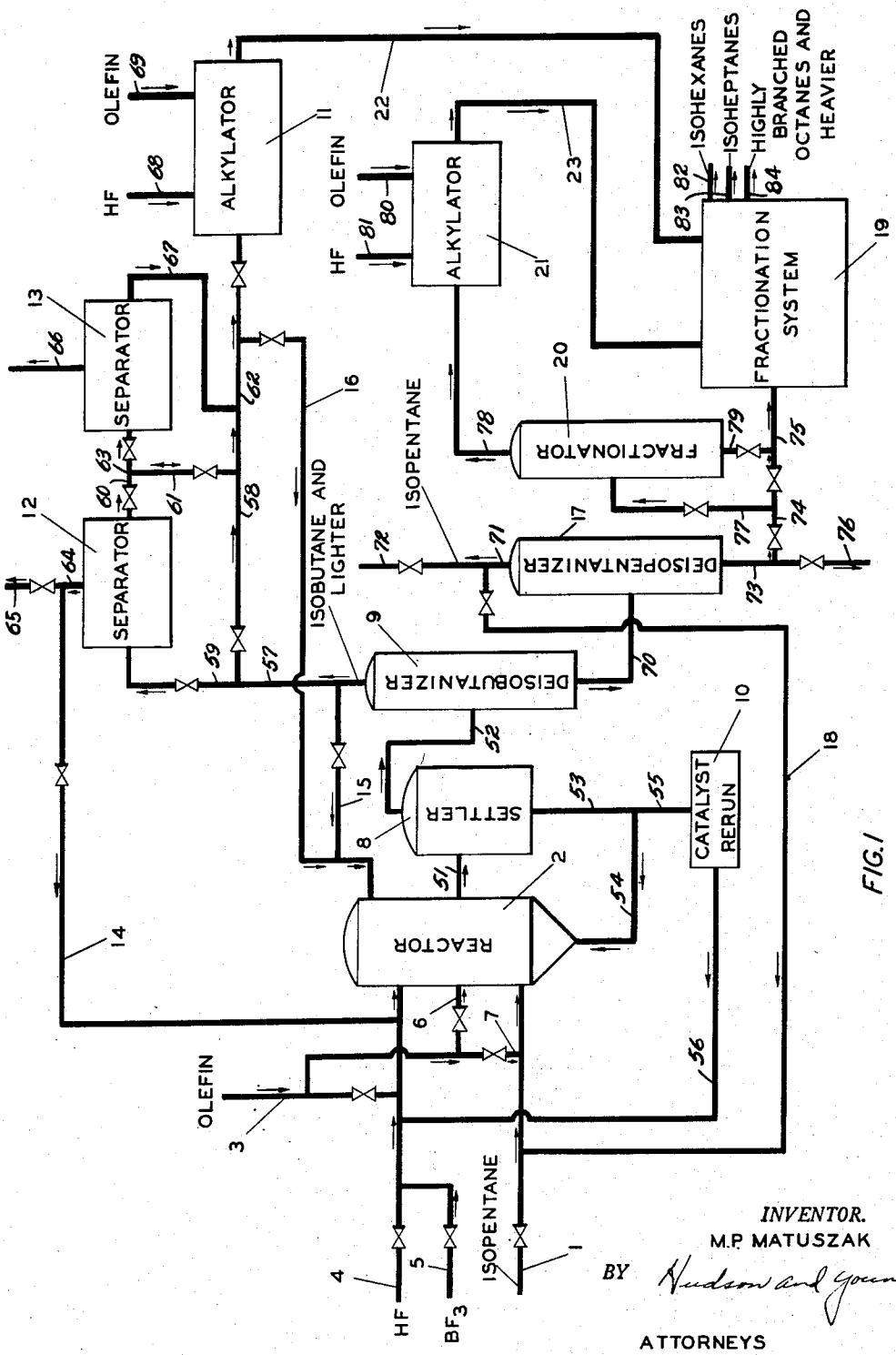


FIG. 1

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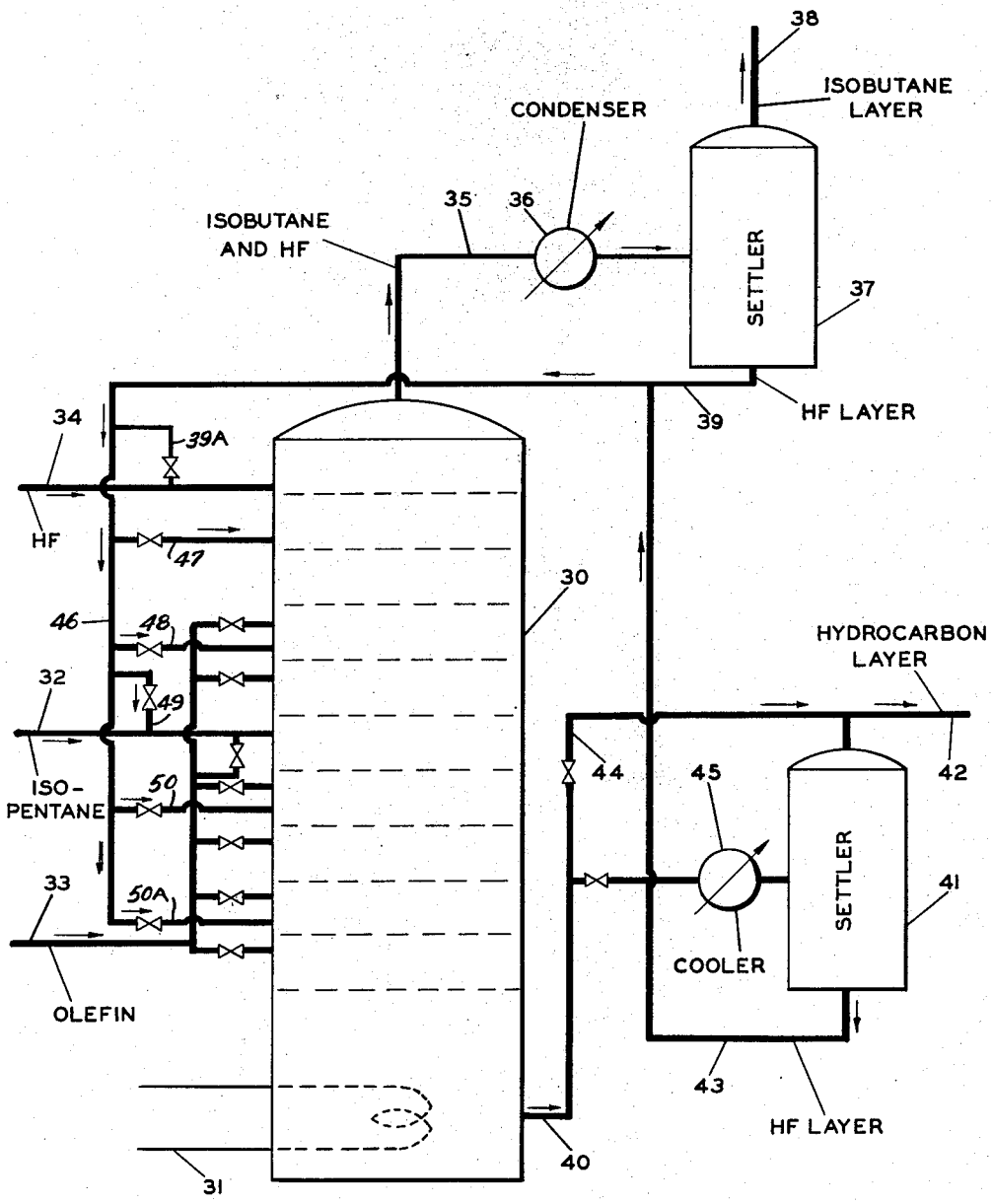


FIG. 2

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2,662,103

PRODUCTION OF PARAFFINS

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4 Claims. (Cl. 260—683.4)

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This invention relates to the production of paraffins from isopentane and more particularly to the production of isobutane and paraffins heavier than isopentane from isopentane. Still more particularly, it relates to production of isobutane and paraffins heavier than isopentane from isopentane by a process involving simultaneous disproportionation and alkylation of isopentane with a low-boiling aliphatic olefin having at least 3 carbon atoms per molecule and with a catalyst consisting of liquid substantially anhydrous hydrofluoric acid either alone or promoted with up to 10 per cent of boron fluoride based on the total weight of catalyst.

This application is a continuation in part of my co-pending application, Serial No. 467,872, filed December 4, 1942, now Patent 2,399,368 issued April 30, 1946.

The principal object of this invention is to increase the total yield of higher-boiling and normally liquid or gasoline-range paraffins produced from a given weight of an olefinic reactant in hydrofluoric acid-catalyzed conversion of isopentane to heavier paraffins.

Another object is to produce high yields of isobutane and isohexanes from isopentane and an olefin in the presence of liquid substantially anhydrous hydrofluoric acid alkylation catalyst.

Another object is to provide a process of the foregoing type wherein isoparaffins heavier than isopentane and having high octane rating are produced in greater overall yield from given quantities of isopentane and aliphatic olefin.

Numerous other objects of the present invention will be apparent to those skilled in the art from a consideration of this specification taken in conjunction with the accompanying drawings wherein

Fig. 1 portrays diagrammatically one arrangement of equipment which may very advantageously be employed in carrying out the present invention, and

Fig. 2 portrays a modification of the reaction vessel wherein the reaction is carried out in a combined reaction-fractional distillation column.

I have now found that by the employment of suitable proportions of reactants and of suitable reaction conditions which are fully detailed hereinafter, a highly desirable side reaction which normally occurs not at all or only to a very minor extent in the conventional alkylation of isopentane with olefins may be selectively encouraged. This side reaction results in disproportionation of isopentane to isobutane and isohexanes (primarily the methyl pentanes). For example,

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under certain conditions a surprisingly large proportion of the isopentane is converted to isobutane and isohexanes concurrently with primary alkylation of a minor proportion of the isopentane, so that yields of hexanes and higher-boiling gasoline hydrocarbons of at least 400 and even as high as 500 or more per cent by weight of the olefin charged are obtained.

The isobutane produced by the disproportionation may be used as feed stock for other processes, as for a process in which it itself is alkylated. I have found that in the interest of an increased yield of higher-boiling or gasoline hydrocarbons (C_5 and heavier) from the disproportionation-alkylation, it is preferable to remove the isobutane from the reaction mixture as soon as possible after its formation, and that it is preferable not to recycle the isobutane to this particular process. On the contrary, better yields of higher octane hydrocarbons are obtained if the isobutane is alkylated with an olefin in a separate zone.

Substantially immediate removal of the isobutane as soon as it is formed may be accomplished in any suitable manner. For example charging and withdrawal rates and residence time in a continuous process may be so adjusted that the reaction mixture is promptly withdrawn from the reaction zone and passed to suitable steps for the rapid removal of isobutane. It is desirable to avoid alkylation of isobutane in the disproportionation-reaction zone. Removal of isobutane from the reaction zone is additionally desirable because it facilitates the desired reaction, namely, disproportionation. In many cases it will be found desirable to effect substantially immediate removal of isobutane from the seat or center of reaction by conducting the reaction in a fractional distillation column.

The molar ratio of isopentane to olefin charged to the reaction zone should be at least 5:1 and preferably is at least 7:1. It may range as high as 10:1 or even higher, up to 20:1. This ratio has reference to the external feed, i. e., to the total isopentane and olefin introduced to the reaction zone. This is to be distinguished from the internal molar ratio, i. e., the molar ratio of isoparaffin to olefin in the reaction zone itself. As will be obvious to those skilled in the art, because of very rapid consumption of olefin, the internal molar ratio of isoparaffin to olefin may be exceedingly high, for example as high as 100:1 or even 1000:1. In the case of continuous operation, the external molar ratio of isopentane to olefin may be determined from the relative amounts of

isopentane and olefin charged at any instant. In a batch type operation, where the olefin is usually added over an extended period of time to the reaction zone containing the isopentane and the hydrofluoric acid catalyst, the molar ratio referred to above is that of the total isopentane charged to the total olefin charge.

The amount of hydrofluoric acid employed as catalyst may vary within wide limits. Ordinarily it will be such that the volume of hydrofluoric acid is at least equal to that of the hydrocarbons present in the reaction zone. Usually the hydrofluoric acid will be present in such amount that it will form a separate acid phase, thereby requiring provision of suitable means for agitating and securing intimate contact between the hydrocarbon phase and the catalyst phase. The volume ratio of hydrofluoric acid to hydrocarbons may range from 1:10 up to 2:1.

The reaction temperature may range from 40 to 300° F. Temperatures below 40° F. are disadvantageous and are seldom employed. The preferred temperature range is from 100 to 200° F. Employment of temperatures within this range gives considerably higher yields and is preferred.

The pressure in the reaction zone should be sufficient to maintain the hydrocarbons and the hydrofluoric acid in liquid phase.

Ordinarily I employ a catalyst consisting of substantially anhydrous hydrofluoric acid. This catalyst should preferably not contain more than a few per cent of water, say not over 5 per cent. If the hydrocarbons available contain entrained or dissolved water to any substantial extent, appropriate measures should be taken to remove such water prior to charging the hydrocarbons to the reaction zone, so that the hydrocarbons charged are essentially anhydrous. This prevents the accumulation of water in the hydrofluoric acid which has a very great affinity for water. Accumulation of water in the catalyst is undesirable because it destroys its activity and requires that an objectionably large proportion of the catalyst be continuously rejected from the system since hydrofluoric acid and water form an azeotrope which cannot be resolved economically in any way now known to the art.

In some cases, it may be desirable to employ a catalyst consisting of substantially anhydrous hydrofluoric acid promoted with a minor proportion of boron fluoride. For example, the amount of boron fluoride employed may range from a trace up to but not exceeding 10 weight per cent of the total catalyst. Boron fluoride promotes the action of hydrofluoric acid and causes the reaction to proceed somewhat more expeditiously. However, the expense connected with the use of boron fluoride and recovery thereof may make its employment unwarranted.

As the olefin I may use any low-boiling aliphatic olefin having at least 3 carbon atoms per molecule. Thus I may use any of the C_3 to C_5 olefins including propylene, any of the butylenes and any of the amylenes. Mixtures of any two or more of the C_3 to C_5 olefins may be used.

The reaction time may vary within quite wide limits depending upon the conditions under which the reaction is carried out. Normally the reaction time will not be less than 5 minutes nor greater than 1 hour. The hydrocarbons should be held in the reaction zone long enough to accomplish substantially complete consumption of the olefin and formation of the desired products to the desired extent. It is believed that the olefin is consumed substantially entirely by alkylation of a minor proportion of the isopentane. The reaction is characterized by the formation of isobutane from isopentane in an amount equal to at least 150 and occasionally as high as 250 weight per cent of the olefin charged. It is further characterized by the formation of C_6 and higher paraffins from isopentane to the extent of at least 400 and occasionally as high as 500 or more weight per cent of the olefin. The yield of pentane-free liquid hydrocarbons produced by the process of the present invention is at least 130 weight per cent and often as high as 200 or even 230 weight per cent of the theoretical alkylation yield. In most cases at least 30 volume per cent of the C_6 and higher paraffins produced by the process are hexanes (isohexanes) which are very valuable. In addition my process yields substantial percentages of each of higher branched chain paraffins, namely, heptanes, octanes, nonanes and decanes and heavier.

The major reaction occurring in the process of the present invention is disproportionation of the isopentane to isobutane and to isoparaffins heavier than isopentane. A minor reaction is the alkylation of a portion of the isopentane with the olefin employed. The olefin acts to alkylate a minor proportion only of the isopentane. The disproportionation of the isopentane takes place very expeditiously in the presence of the reactants and catalyst and under the conditions employed in the alkylation of the isopentane. My invention is based on the discovery that alkylation of a minor proportion of the isopentane with the olefin in the presence of hydrofluoric acid promotes the disproportionation of the remainder of the isopentane to a very pronounced degree.

The process of my invention may very advantageously be carried out in a combination reaction-fractional distillation column to which the isopentane and the olefin in the proper external molar ratio may be charged continuously. Liquid substantially anhydrous hydrofluoric acid may be injected continuously at a point or several points of the column. This hydrofluoric acid may serve as the reflux for the column. The bottom of the column is reboiled in the usual way. The olefin may be introduced with the isopentane or at another point in the column. It may be introduced at a multiplicity of points along the column. Since the olefin is substantially immediately consumed by reaction none goes out in the overhead vapors. The overhead from the column is an azeotrope of isobutane and hydrogen fluoride. This mode of operation is especially advantageous because the isobutane formed by disproportionation is immediately removed from the zone of reaction by fractional distillation. The overhead vapors of isobutane and hydrofluoric acid may be condensed and the resulting liquid condensate subjected to layer formation. The isobutane layer is withdrawn from the system and may be passed to a separate alkylation step wherein it is alkylated with an olefin. The acid layer is recycled to one or more points of the column as a source of hydrofluoric acid for the reaction and as a reflux for the column. The column may be operated under any suitable low superatmospheric pressure which is sufficient to hold the temperatures in the column at the desired level. The zone of the bulk of the reaction should be between 40 and 300° F. and preferably between 100 and 200° F. The top temperature of the column will be the boiling point of the isobutane-hydrofluoric acid azeotrope under the

column pressure. The bottom temperature should be at least sufficiently high to insure substantially complete removal of isopentane from the withdrawn kettle product so that the isopentane charged to the column is not allowed to escape therefrom but is held therein until it is converted to higher and lower isoparaffins.

Where the reaction is conducted in a fractional distillation column in the manner just described, the amount of hydrofluoric acid present must be sufficient to form a separate liquid acid phase in the major reaction zone in the column. Although at times it may be desirable to provide special means for attaining intimate contact between the acid phase and the hydrocarbon phase wherever they are present in the column, ordinarily the bubble trays or column packing will provide the necessary intimacy of contact. However, if desired, additional provision may be made for obtaining such contact. The selection of suitable means for accomplishing this result will be obvious to those skilled in the art.

The bottoms product from the reactor-fractionator is treated in any suitable manner to recover the valuable products contained therein, namely, the paraffins boiling above isopentane. If an acid phase is present, this bottoms product is passed to the usual settler where the hydrocarbon is drawn off separately from the acid phase, which is recycled to the column.

In Fig. 1 of the drawings, isopentane is charged via line 1 to reactor 2. Olefin enters the system via line 3; hydrofluoric acid enters by line 4. If it is desired to use a small amount of boron fluoride as a promoter, it may be fed in via line 5. The olefin may be admixed with the hydrofluoric acid prior to entry into 2; but preferably it may be fed in separately as via line 6 or it may be fed in admixture with the isopentane as via line 7. Reactor 2 is provided with the usual means for maintaining the desired temperature therein and for obtaining the desired degree of contact between the acid phase and the hydrocarbon phase. The reaction effluent is passed via line 51 to settler 8 from which the hydrocarbon layer is fed via line 52 to deisobutanizing column 9. The acid layer is withdrawn via line 53 and recycled via line 54 to reactor 2. Ordinarily a suitable portion of the acid layer is continuously rerun as in unit 10 prior to recycling. The portion to be rerun is passed via line 55 to rerun unit 10 (which is of known type) and the rerun HF is returned via line 56 to line 4 and reactor 2.

The overhead fraction from deisobutanizing column 9 may be passed directly via lines 57, 58 and 62 to a separate alkylation unit 11 wherein it is alkylated with an olefin using hydrofluoric acid as the catalyst. Ordinarily this overhead fraction will contain substantial proportions of hydrofluoric acid. Removal of such hydrofluoric acid is not necessary prior to alkylation in unit 11. If desired, however, the overhead from column 9 may be fed to unit 12 and/or unit 13 for removal of hydrofluoric acid and light gases such as propane and lighter, respectively. Hydrofluoric acid separated in unit 12 may be recycled via line 14. The thus purified isobutane may be fed to alkylation unit 11. While it is distinctly disadvantageous to do so, there may be occasions when it will be desired to recycle the isobutane derived from the overhead of column 9 to the reactor 2. This may be done by means of lines 15 or 16.

The isobutane overhead fraction from column 9 may be passed via lines 57 and 59 to unit 12 wherein hydrofluoric acid may be removed in known manner. The thus purified isobutane may be fed to alkylation unit 11 by means of lines 60, 61 and 62. The separated HF is discharged from unit 12 via line 64 whence it may be discharged from the system via line 65 and/or recycled to reactor 2 via line 14. Alternatively the isobutane leaving unit 12 via line 60 may be fed via line 63 into separation unit 13 wherein light gases namely propane and lighter are separated in known manner. The light gases are discharged from unit 13 and the system via line 66. The so purified isobutane leaves unit 13 via line 67 and is fed thereby and by line 62 to alkylation unit 11.

If desired the isobutane overhead fraction from column 9 may be passed via lines 58, 61 and 63 to unit 13 for the separation of light gases only, the resulting isobutane free from such gases as propane and lighter thence being passed via lines 67 and 62 as before.

Extraneous HF is fed to alkylation unit 11 via line 68 and olefin is fed thereto via line 69.

The bottoms product from column 9 is fed via line 70 to deisopentanizing column 17 which removes overhead the unreacted isopentane. This isopentane is withdrawn via line 71 and may be recycled to unit 2 via line 18. If desired a portion of the overhead from column 17 may be discharged from the system via line 72. The bottoms product from column 17 consists of paraffins heavier than isopentane and contains not only the alkylate formed in unit 2 but also the C_6 and heavier paraffins formed by disproportionation of isopentane therein. This product may be treated in any suitable manner to recover its components, for example, it may be passed via lines 73, 74 and 75 to fractionation system 19 for separation into several high octane fractions as indicated. If desired, a portion or all of the C_6 and heavier bottoms fraction withdrawn from column 17 via line 73 may be withdrawn from the system via line 76. In many cases it may be desirable to pass the bottoms product from line 73 through lines 74 and 77 to a column 20 wherein the isohexanes are separated overhead via line 78 from the heavier material which is withdrawn as bottoms product via line 79. This bottoms product may conveniently be fed from line 79 through line 75 to the fractionation system 19 for further resolution into the desired fractions thereof.

If desired, the isohexanes fraction separated as overhead in column 20 may be fed via line 78 to an alkylation unit 21 wherein it is alkylated with olefin introduced via line 80 using HF introduced via line 81 as the catalyst.

The alkylate-containing hydrocarbon mixture formed in units 11 and 21 may if desired be fed via lines 22 and 23 respectively to the common fractionation system 19.

Fractionation system 19 is of a type well known to the art and may conveniently comprise a series of fractional distillation columns. If the isohexanes were not previously removed by the use of column 20 they are separated in system 19 as a fraction withdrawn via line 82. The isoheptanes may similarly be withdrawn as a separate fraction via line 83. The octanes and heavier may be withdrawn via line 84.

In Fig. 2 of the drawings, there is portrayed equipment for carrying out the reaction of the present invention in a fractional distillation column 30. Column 30 is equipped with the usual bubble trays as indicated by the dotted lines and with the usual reboiler 31. The isopentane either

by itself or in admixture with the olefin is introduced at an intermediate point in the column, usually around the midpoint, by means of line 32. Optionally the olefin may be separately introduced at one or a plurality of points which may be below the point of isopentane entry as shown in the drawing, or which might in certain cases be above the point of isopentane entry. For this purpose line 33 and associated injection lines may be provided. The hydrofluoric acid in liquid form is introduced via line 34. The overhead vapors consisting essentially of isobutane and hydrofluoric acid are removed via line 35, cooled in condenser 36 to liquefy them, and the resulting liquid condensate subjected to layer separation in settler 37. The isobutane layer is withdrawn from settler 37 by line 38. The acid layer is drawn off by line 39 and is recycled via line 39A for admixture with incoming fresh hydrofluoric acid in line 34. The reboiled bottoms product, consisting essentially of paraffins boiling above isopentane, is fed via line 40 to settler 41 when a separate acid phase is present. The hydrocarbon layer is withdrawn via line 42 and fed to a recovery system which may be similar to that shown in Fig. 1 or any other fractionation system. The acid layer is withdrawn by line 43 and recycled via lines 39 and 39A to line 34 and to column 30. If the bottoms product in line 40 does not contain a separate phase of hydrofluoric acid, it may be passed directly via line 44 to the recovery system. It is often desirable to cool the bottoms product flowing in line 40 in order to get a better separation in settler 41. For this purpose cooler 45 may be provided.

While it is generally preferred to re-introduce the hydrofluoric acid flowing in line 39 to the top of column 30 by means of lines 39A and 34, I may, as is indicated by Fig. 2 of the drawings, introduce a portion of this recycle at other points in column 6. For this purpose line 46 and associated inlet lines 47, 48, 49, 50 and 50A may be employed.

The following examples are illustrative of some of the many aspects of the invention but are not necessarily limitative.

Examples I to VI

Data for several batch-type runs for the conversion of isopentane in the presence of hydrofluoric acid, using various olefins, are presented together, for the sake of brevity and conciseness, in the following tabulation.

In the run with propylene, Example I, the amount of isobutane formed was not determined, but it was probably approximately molecularly equivalent to the hexanes (isohexanes), which constituted over 30 per cent of the liquid product. This run was made at an insufficiently high temperature for optimum results, but it is clear that a high extent of disproportionation occurred in spite of this fact.

Among other things, it may be noted from these data that the yield of depentanized liquid product was much higher than that to be expected from ordinary alkylation, being as high as over twice the theoretical alkylation yield computed on the basis of one molecule of olefin reacting with one molecule of isopentane. Yields even higher than those shown are obtained at relatively higher temperatures, such as temperatures in the preferred range of 100 to 200° F. With respect to the two runs made with isobutylene, the yield was highest in the run that was made at the relatively higher temperature. In all these runs, more than one molecule of isopentane reacted per molecule of olefin to give higher-boiling paraffins; indeed, in the higher-temperature run with isobutylene over five molecules of isopentane reacted per molecule of olefin. Since olefins, because of their relatively greater readiness to react chemically, are in general more valuable than the corresponding paraffins, a major advantage of the disproportionation-alkylation here exemplified is obvious.

Disproportionation-alkylation of isopentane

Example	I	II	III	IV	V	VI
Olefin	C_3H_6	i-C_4H_8	i-C_4H_8	1-C_4H_8	2-C_4H_8	C_5H_{10}
Temperature, ° F.	65–79	64–86	33–61	66–100	68–102	73–100
Reaction time, min.	35–70	10–30	10–30	10–30	10–30	9–31
Isopentane/olefin (mol.) (feed)	7.25	8.75	7.62	8.31	7.5	10.2
Hydrocarbons/HF (vol.)	7.6	1	1	1	1	
Isobutane formed, weight percent of olefin	------	261	200	155	187	165
Pentane-free liquid product:						
Yield—						
Weight percent of olefin	406	535	443	405	445	437
Weight percent of theoretical alkylation yield	136	234	194	177	195	216
Composition, vol. percent:						
Hexanes	30.7	45.2	42.3	37.7	41.4	49.5
Heptanes	8.8	10.2	9.0	5.1	6.7	7.5
Octanes	41.7	5.8	11.6	6.4	7.7	3.4
Nonanes	6.3	27.3	22.6	37.0	32.2	21.9
Decanes	9.1	9.5	10.2	13.8	12.0	15.4
Heavier	3.4	2.0	4.3			2.3
Total	100.0	100.0	100.0	100.0	100.0	100.0
Aviation-gasoline fraction:						
Cut point, ° F.	338	289	289	284	293	295
Yield, vol. percent	95.1	81.4	76.2	80.7	84.3	78.0
Reid vapor pressure, lb.	3.2	4.65	4.60	4.45	4.10	5.15
Gravity, ° API	71.2	75.6	75.2	74.6	73.7	76.4
ASTM distillation, ° F.—						
First drop	138	143	143	142	145	140
10% evap.	173	153	155	155	161	150
50% evap.	213	175	177	183	191	166
90% evap.	274	264	273	271	268	284
End point	344	334	328	321	336	332
ASTM octane No.—						
0 cc. TEL	75.0	75.0	76.2	74.6	79.2	72.2
1 cc. TEL	86.3	88.7	90.1	87.7	89.3	86.3
Total products, weight percent of olefin	------	796	643	560	632	602

In the above tabulation two figures are given for temperature. The first figure is the temperature at the start of the reaction, and the second figure is the temperature at the end of the reaction which is exothermic. Likewise, two numbers are given for reaction time. These figures give the shortest and the longest times that the olefin was in the reaction zone. These were batch-type runs in which the olefin was added gradually over an extended period of time.

A major advantage of the present invention is provided by the exceedingly high yield of concomitantly formed isobutane, which is of the order of twice the original olefin by weight. This isobutane is of particular value because present sources of this hydrocarbon are inadequate to meet the demand for isobutane as a feed for the manufacture of high-octaine aviation gasoline by alkylation. Therefore, this concomitantly formed isobutane may be advantageously separated, preferably as soon as possible after formation, and it may be alkylated with an olefin to aviation-gasoline paraffins in a separate alkyla-

tion unit such as unit 11 in Fig. 1, preferably in the presence of hydrofluoric acid as catalyst. This procedure is much more advantageous than recycling the isobutane together with unreacted isopentane back to the first unit 2, for the over-all yield of gasoline-range liquid paraffins for the two-stage operation is considerably larger than for the one-stage operation. Furthermore, the liquid product from the alkylation of isobutane is considerably higher in octane rating than the liquid product from the disproportionation-alkylation of isopentane with the same olefin; for example, the aviation-gasoline alkylate from hydrofluoric acid alkylation of isobutane with isobutylene has an octane number of about 95—96, which is 20 units higher than the values given in the foregoing tabulation for the aviation-range fraction of the product from the conversion of isopentane. Hence, because of the present demand for high-octane aviation gasoline, the two-stage operation yielding two gasoline-range products is relatively more advantageous than the one-stage operation having combined recycling of isobutane and unreacted isopentane. However, this one-stage operation is not outside the broadest scope of this invention.

The isohexanes produced by the disproportionation may be similarly advantageously separated from the product, as by fractional distillation and may be used as such for blending in motor fuels or may be alkylated with an olefin as in unit 21 of Fig. 1, preferably in the presence of hydrofluoric acid to give paraffins of different volatility.

It should be observed that the reactions promoted in accordance with this invention do not comprise secondary reactions such as for example that of cracking subsequent to ordinary alkylation. In such "cracking-alkylation," the reactant isoparaffin is alkylated with an olefin as in ordinary alkylation and the resulting alkylate is allowed to crack into smaller compounds. Obviously, such cracking-alkylation results in little or no improvement in the over-all yield of paraffins heavier than the original paraffin, whereas by the present invention the over-all yield of such heavier paraffins is markedly increased, and to a surprisingly and quite unexpectedly high degree in the light of past knowledge. Briefly, instead of promoting reactions following alkylation, the present process promotes reactions preceding or accompanying alkylation.

In accordance with this invention, certain desirable reactions are selectively promoted that ordinarily occur to only relatively minor extents in alkylations of paraffins with olefins in the presence of liquid acid-type alkylation catalyst. Because the invention may be practised otherwise than as specifically described or illustrated, and because many modifications and variations within the spirit and scope of it will be obvious to those skilled in the art of hydrocarbon conversion, the invention should not be unduly restricted by the foregoing specification and examples.

I claim:

1. An improved process for converting isopentane to higher-boiling isoparaffins boiling in the gasoline range, which comprises charging isopentane and a low-boiling aliphatic olefin having at least three carbon atoms per molecule, in a molar ratio of isopentane charged to olefin charged of at least 7:1, to an intermediate portion of combined reaction-fractional distillation zone, introducing a liquid hydrofluoric acid alkylation catalyst to the upper portion of said zone as a liquid reflux for said distillation, maintaining in an intermediate reaction portion of said zone a reaction temperature between 100 and 200° F., a ratio of liquid hydrofluoric acid catalyst to liquid hydrocarbons from 1:10 to 2:1, and a reaction time between 5 and 60 minutes and sufficient to effect complete reaction of charged olefin and formation of isobutane to the extent of at least 150 weight per cent of said olefin and of C_6 and higher isoparaffins to the extent of at least 400 weight per cent of said olefin and to the extent of at least 130 weight per cent of the theoretical alkylation yield, at least 30 volume per cent of said C_6 and higher paraffins being isohexane, removing as an overhead distillate from said zone a mixture comprising hydrogen fluoride and isobutane and lighter hydrocarbons, cooling and condensing said mixture and separating a liquid hydrocarbon material from liquid hydrofluoric acid, returning at least a portion of said liquid hydrofluoric acid to said zone as said reflux, separately alkylating isobutane contained in said liquid hydrocarbon material to produce normally liquid isoparaffins boiling in the gasoline range, passing a resulting crude alkylate to a separating means, removing from the aforesaid reaction-fractional distillation zone as a high-boiling product a liquid hydrocarbon material free from hydrogen fluoride and comprising C_6-and-higher hydrocarbons produced in said zone, passing the last said liquid hydrocarbon material to the aforesaid separating means, and removing from said separating means as a product of the process an isoparaffinic hydrocarbon material comprising isoparaffins boiling in the gasoline range produced from isopentane in said zone, and produced from said isobutane alkylation.

2. An improved process for converting isopentane to higher-boiling isoparaffins boiling in the gasoline range, which comprises charging isopentane and a low-boiling aliphatic olefin having at least three carbon atoms per molecule, in a molar ratio of isopentane charged to olefin charged of at least 7:1, to an intermediate portion of combined reaction-fractional distillation zone, introducing a liquid hydrofluoric acid alkylation catalyst to the upper portion of said zone as a liquid reflux for said distillation, maintaining in an intermediate reaction portion of said zone a reaction temperature, a ratio of liquid hydrofluoric acid catalyst to liquid hydrocarbons from 1:10 to 2:1, and a reaction time between 5 and 60 minutes and sufficient to effect complete reaction of charged olefin and formation of isobutane to the extent of at least 150 weight per cent of said olefin and of C_6 and higher isoparaffins to the extent of at least 400 weight per cent of said olefin and to the extent of at least 130 weight per cent of the theoretical alkylation yield, at least 30 volume per cent of said C_6 and higher paraffins being isohexane, removing as an overhead distillate from said zone a mixture comprising hydrogen fluoride and isobutane and lighter hydrocarbons, cooling and condensing said mixture and separating a liquid hydrocarbon material from liquid hydrofluoric acid, returning at least a portion of said liquid hydrofluoric acid to said zone as said reflux, removing from the aforesaid reaction-fractional distillation zone as a high-boiling product a liquid hydrocarbon material free from hydrogen fluoride and comprising C_6-and-higher hydrocarbons produced in said zone, passing the last said liquid hydrocarbon material to separating means, and removing from said separating

means as a product of the process an isoparaffinic hydrocarbon material comprising isoparaffins boiling in the gasoline range produced from isopentane in said zone.

3. An alkylation process which comprises reacting isobutane with an olefin under alkylating conditions, separately alkylating isopentane with propylene in the presence of hydrogen fluoride at a temperature of from about 75° F. to about 150° F. while maintaining a molar ratio of isopentane to propylene of about 7.25:1, whereby to produce a substantial amount of isobutane concurrently with the alkylated isopentane, and supplying the isobutane thus produced to the first-mentioned alkylating step.

4. An alkylation process which comprises reacting isobutane with an olefin under alkylating conditions, separately batchwise alkylating isopentane with propylene in the presence of hydrogen fluoride at a temperature of from about 75° F. to about 150° F. while maintaining a molar ratio of isopentane to propylene of about 7.25:1, whereby to produce a substantial amount of isobutane concurrently with the alkylated isopentane, and supplying the isobutane thus produced to the first-mentioned alkylating step.

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