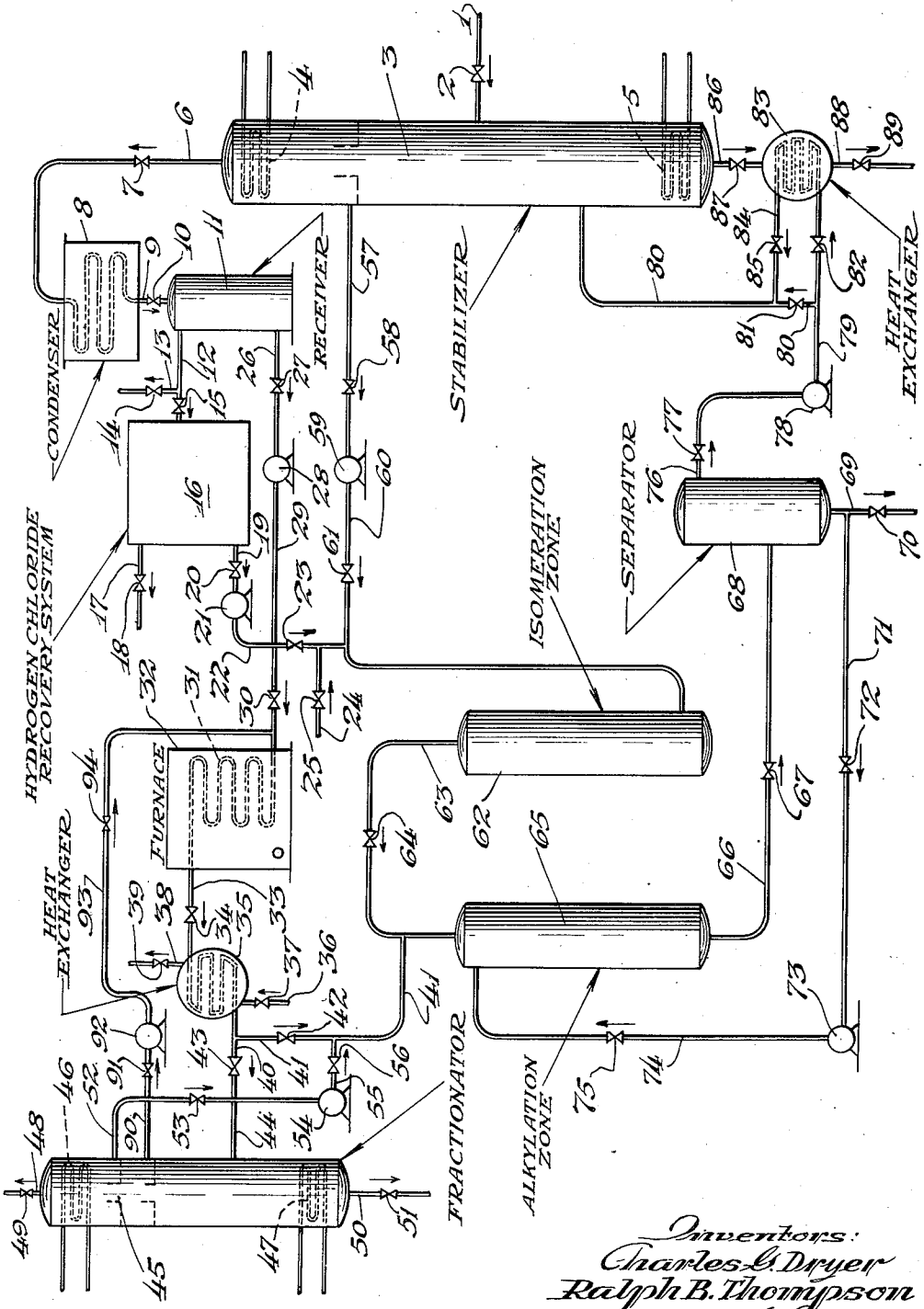
Sept. 28, 1943. C. G. DRYER ET AL 2,330,206

CONVERSION OF HYDROCARBONS

Filed July 30, 1941



Inventors:
Charles G. Dryer
Ralph B. Thompson
By Lee J. Gary
Attorney

Patented Sept. 28, 1943 2,330,206

UNITED STATES PATENT OFFICE

2,330,206

CONVERSION OF HYDROCARBONS

Charles G. Dryer and Ralph B. Thompson, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application July 30, 1941, Serial No. 404,604

14 Claims. (Cl. 260—683.4)

This invention relates to the conversion of hydrocarbons and more particularly to the treatment of natural gasoline or other substantially paraffinic hydrocarbon distillates.

One of the major problems confronting the petroleum industry at the present time is the marketing of the large quantity of natural gasoline available. The natural gasoline usually is of an acceptable octane value but is of such high vapor pressure that it cannot satisfactorily be used for motor fuel as originally recovered. When the natural gasoline is stabilized to reduce it to an acceptable vapor pressure, not only is a substantial portion of the gasoline discarded, but the gasoline is reduced to such a low octane value that it is not satisfactory for use as a motor fuel. It is, therefore, an object of this invention to provide suitable means of converting the large supply of natural gasoline into satisfactory motor fuel.

The present invention provides a method whereby the vapor pressure of natural gasoline or similar gasoline may be reduced to an acceptable value, while at the same time the octane value is either maintained or increased, while a minimum amount of the hydrocarbons is discarded from the gasoline. This is accomplished in accordance with the present invention by means of a series of cooperative and interdependent steps involving fractionation, thermal cracking, isomerization and alkylation.

In one specific embodiment the present invention comprises a process for improving the properties of natural gasoline by fractionating the same to separate a fraction containing the three carbon atom hydrocarbons and lower boiling constituents, a fraction containing the four carbon atom hydrocarbons, and higher boiling constituents, thermally cracking the three carbon atom hydrocarbons under controlled conditions to produce high yields of ethylene, isomerizing the fraction containing the four carbon atom hydrocarbons to produce isobutane, and alkylating the isobutane by said ethylene.

The following description and attached diagrammatic drawing illustrating one arrangement of apparatus for carrying out the process of our invention, are directed to the preferred type of operation, which preferred operation is not necessarily equivalent in results to be expected with other types of operation. Likewise, although in its broadest scope any suitable isomerization and alkylation catalysts may be employed, the preferred catalysts for both processes are metal halides and particularly aluminum chloride-containing catalysts which are utilized in conjunction with hydrogen halides and particularly with hydrogen chloride and which are utilized in a particular method of operation wherein the aluminum chloride and hydrogen chloride employed in the isomerization step are continuously carried over with the reactants into the alkylation zone, containing a granular packing material, and utilized therein to effect the akylation of the isobutane by the ethylene.

Referring to the drawing, the charging stock to the process, which comprises any natural gasoline or other substantially paraffinic gasoline, is introduced through line 1 and valve 2 to stabilizer 3. Since the natural gasolines available vary considerably with the method of their recovery, the exact operating conditions to be employed in stabilizer 3 will likewise vary considerably. In any event, fractionation of the natural gasoline introduced thereto is controlled by means of cooling coil 4 and internal reboiler 5 to separate, as an overhead fraction, the hydrocarbons containing 3 carbon atoms and lighter constituents, a fraction containing the 4 carbon atom hydrocarbons, and higher boiling constituents. In place of cooling coil 4, it is within the scope of the invention to employ any other suitable cooling and refluxing means, such as recycling a portion of the condensed overhead distillate. Likewise, in place of internal reboiler 5, any other suitable means of introducing the necessary heat may be employed, such as the use of an external reboiler. These means are well known in the art and there is no need for entering into a detailed description thereof in this application. It is also within the scope of the invention to employ two or three fractionating zones in place of the one stabilizing zone indicated in the drawing.

The gases released in stabilizer 3 are withdrawn from the upper portion thereof through line 6 and are directed through valve 7 into and through condenser 8, the resulting distillate and uncondensed gases passing through line 9 and valve 10 into receiver 11. Since some of the conversion products of the process are introduced to stabilizer 3, in a manner to be later described, the products collected in receiver 11 will contain some hydrogen chloride in addition to condensed 3 carbon atom hydrocarbons and other gases. The exact composition of the material collected in receiver 11 will vary considerably with the constituents of the natural gasoline charging stock and with the particular method of operation of the process. In any event, cooling of the overhead products from the stabilizer is preferably controlled to condense the three carbon atom hydrocarbons and to leave the hydrogen chloride and other light gases uncondensed. The uncondensed gases and hydrogen chloride are removed from receiver 11 through line 12 and may be withdrawn from the process through line 13 and valve 14 to any desired further treatment. Preferably all or a portion of this material is

directed through valve 15 into hydrogen chloride recovery system 16.

Any suitable hydrogen chloride recovery system may be employed. Since no novelty is claimed for the particular hydrogen chloride recovery system, there is no need to recite in detail the operation of this step. Regardless of the particular system employed, it is operated to separate the hydrogen chloride from the other constituents contained therein. The other constituents may be removed through line 17 and valve 18 to storage or further treatment as desired, while the hydrogen chloride is removed from zone 16 through line 19 and valve 20 to pump or compressor 21, by means of which it is directed through line 22 and valve 23 to the isomerization step of the process, which will be subsequently described. Additional hydrogen chloride from an extraneous source may be introduced into line 22 through line 24 and valve 25.

The distillate collected in receiver 11 consists essentially of 3 carbon atom hydrocarbons. Due to the limitations of close fractionation in practical operations, this distillate may contain a minor proportion of lower and higher boiling hydrocarbons. In any event, the distillate collected in receiver 11 is directed therefrom through line 26 and valve 27 to pump 28, by means of which it is directed through line 29 and valve 30 to heating coil 31 in furnace structure 32. The 3 carbon atom hydrocarbons are heated in coil 31 under conditions chosen to effect a high conversion thereof into ethylene. In general, these conditions comprise relatively high temperatures and relatively low pressures. Experiments conducted at 1292° F., 14 pounds per square inch, and a contact time of 35 seconds have yielded 25.5% of ethylene by the thermal conversion of propane. The temperatures employed in this zone will of course vary, and may range, for example, from 900° F. to 1400° F. at subatmospheric, atmospheric, and slightly superatmospheric pressures.

The products emerging from heating coil 31 are directed through line 33 and valve 34 and are cooled by any suitable means, such as heat exchanger 35, to which the cooling medium may be introduced through line 36 and valve 37 and withdrawn through line 38 and valve 39. In place of heat exchanger 35, the heated products may be cooled, for example, by direct quenching with a suitable cooling medium. The cooled products are withdrawn from heat exchanger 35 through line 40 and may be directed through line 41 and valve 42 into the alkylation step of the system.

The composition of these heat treated products will depend upon the characteristics of the distillate collected in receiver 11 and upon the exact operating conditions employed in coil 31. When the heated products contain an excessive amount of constituents other than ethylene, it may be desirable to direct the same through valve 43 and line 44 to fractionator 45, preferably equipped with cooling coil 46 and reboiler 47 or other suitable cooling and heating means, whereby to separate the products therein into lighter gases containing less than two carbon atoms per molecule, hydrocarbons containing two carbon atoms per molecule, unconverted propane, and any heavier products which may have been formed in the cracking operation. The lighter gases containing less than two carbon atoms per molecule including methane, hydrogen, and the like, may be removed from the process through line 48 and valve 49. The hydrocarbons containing two carbon atoms per molecule are withdrawn from fractionator 45 through line 52 and are directed through valve 53 to pump or compressor 54. The unconverted propane is withdrawn through line 90 and valve 91 to pump or compressor 92, by means of which it is recycled through line 93 and valve 94 to heating coil 31 for further conversion therein into ethylene. The products heavier than propane are withdrawn from fractionator 45 through line 50 and valve 51 to storage or elsewhere as desired. Alternatively, the hydrocarbons supplied to pump 54 may comprise those containing two carbon atoms per molecule as well as the unconverted propane, the latter eventually being recycled through lines 6, 26, and 29 to heating coil 31 for further conversion into ethylene. In either case, the products supplied to pump or compressor 54 are directed through line 55, valve 56 and line 41 to the alkylation step of the process. It is a particular feature of the present invention that the thermally cracked products will contain high percentages of ethylene which, when utilized in the alkylation of isobutane, as will be subsequently described, produces a final alkylate of high octane value.

The fraction containing the four-carbon atom hydrocarbons separated in stabilizer 3 will comprise essentially butane and may include minor proportions of lower and higher boiling fractions due to the limitations of close fractionation in practical operations. The amount of normal butane and isobutane contained in this fraction will depend upon the constituents present in the particular charging stock introduced to the process. However, the process of the present invention is equally applicable to either fractions containing substantially only normal butane or mixtures of normal butane and isobutane. This fraction is withdrawn from stabilizer 3 through line 57 and valve 58 to pump or compressor 59, by means of which it is introduced through line 60 and valve 61 to isomerization zone 62, together with the hydrogen chloride supplied thereto through lines 22 and/or 24, as previously described.

In case the charging stock contains olefinic or other constituents which may prove detrimental to the activity of the aluminum chloride-containing catalyst, it is also within the scope of the invention to pretreat this fraction prior to its introduction into isomerization zone 62. Any suitable means may be used for this purpose, among which may be mentioned the step of passing this fraction through a bed of aluminum chloride or other suitable reagent in a separate zone. Alternatively, the aluminum chloride sludge withdrawn through line 69, as hereinafter described, may be utilized for this purpose.

Isomerization zone 62 preferably contains aluminum chloride-containing catalyst and is operated under conditions whereby isomerization of the normal butane introduced thereto is effected and at the same time sufficient aluminum chloride to effect the subsequent alkylation reaction is carried along with the conversion products leaving this zone. In general, the temperatures employed in the isomerization zone when using aluminum chloride catalyst will range from about 160° to about 250° F. and preferably about 185° to about 195° F. The amount of hydrogen chloride commingled with the butane stream being introduced into the isomerization zone should be sufficient to promote the aluminum chloride catalyst in order to effect satisfactory isomerization of the normal butane. In general, this amount may range from about 1.5 to about 5.0

mol per cent or more. We have found that increased amounts of hydrogen chloride are not particularly harmful to the reaction, but that after a certain maximum the hydrogen chloride does not further assist in the reaction. The pressure employed in the isomerization zone is preferably sufficient to maintain liquid phase therein and, in general, will range from about 150 to about 500 pounds or more and preferably from about 210 to about 300 pounds.

The products from the isomerization zone which contain isobutane, aluminum chloride and hydrogen chloride, along with other constituents, pass from isomerization zone 62 through line 63 and valve 64 into alkylation zone 65. The conversion products from the thermal cracking step are then introduced to alkylation zone 65 by means of line 41, as previously described. Zone 65 preferably contains some sort of granular packing material such as for example crushed porcelain, preformed porcelain shapes such as berl saddles, pumic, fire brick, quartz, activated carbon, diatomaceous earth, raw and acid-treated clays, silica gel, alumina, magnesia, zirconia, titania, composites of silica and alumina and/or zirconia, metals possessing considerable surface such as spongy iron, etc.

The temperature in alkylation zone 65 is preferably controlled to effect alkylation of the isobutane by the ethylene. In general, this temperature may range from about 60° F. to about 200° F. or the temperature maintained in isomerization zone 62 and preferably within the ranges of about 90 to about 120° F. We have found that the presence of paraffinic hydrocarbons other than isobutane will not greatly affect the alkylation reaction in zone 65. However, if the total cracked products are directed through line 41 to the alkylation zone without intervening fractionation, these other paraffinic gases should be removed at some step in the process in order to avoid their accumulating within the system. One method of accomplishing this is by removing them in the hydrogen chloride recovery system previously described. The unconverted propane present in this stream eventually will be recycled by means of lines 26 and 29 to heating coil 31 for further conversion into ethylene. It is desirable to reduce to a minimum the amount of propylene present in the material supplied to the alkylation zone as some alkylation of the isobutane by the propylene will be effected in this zone and we have found that this tends to reduce the octane value of the final alkylated product.

It is essential to have an excess of isobutane present in the alkylation zone. Our experiments have indicated that it is preferable to maintain the percentage of olefins in the alkylation zone to between about 13 and about 14 percent of the hydrocarbon mixture present therein. Modified operations may permit satisfactory use of a broader range of olefins as, for example, from about 10 to about 15 percent or more. Increased amounts of olefins in the alkylation zone tend to undergo polymerization and other undesirable reactions with a concomitant reduction in the desired alkylation reaction.

Any suitable means of maintaining the desired temperatures in isomerization zone 62 and alkylation zone 65 may be employed. These means are well known in the art and have been omitted from the drawing in the interest of simplicity. Several obvious methods include the following: (1) Separately heating the butane stream prior to introduction into isomerization zone 62. (2) Direct heating of the isomerization and alkylation zones. (3) Surrounding the isomerization and alkylation zones with a bath of suitable heating or cooling medium, as the case may be. (4) Interposing a suitable heat exchanger between the isomerization zone and the alkylation zone to control the temperature. This method is not as desirable as some of the other methods as it is preferable to maintain the temperature of the mixture of the butanes and aluminum chloride until their introduction into the alkylation zone. (5) Controlling the temperature in the alkylation zone, all or in part, by regulating the temperature of the ethylene stream introduced thereto.

The products from alkylation zone 65 are directed therefrom through line 66 and valve 67 to separator 68, wherein the sludge formed in the alkylation reaction is separated from the hydrocarbons. The sludge is removed through line 69 and may be withdrawn from the process through valve 70 for any desired use. This sludge is believed to be an aluminum chloride-hydrocarbon complex and is usually fluid. It has been found that the sludge still retains some activity for inducing the alkylation reaction and it is within the scope of the invention to recycle all or a portion thereof by means of line 71, valve 72, pump 73, line 74, and valve 75 to alkylation zone 65.

The hydrocarbons separated from the sludge in separator 68 are removed therefrom through line 76 and valve 77 to pump 78, by means of which they are preferably supplied through line 79, line 80 and valve 81 to stabilizer 3, although they may be independently fractionated in accordance with an alternative but not necessarily equivalent embodiment of the invention. Provision is made in the case here illustrated for passing all or a portion of these hydrocarbons in indirect heat exchange with the final product of the process. This is accomplished by directing the hydrocarbons through valve 82 and through heat exchanger 83, wherefrom they are directed through line 84, valve 85 and line 80 to stabilizer 3. In stabilizer 3 the alkylated products are commingled with the higher boiling constituents of the charging stock introduced thereto and the commingled mixture is withdrawn therefrom through line 86, valve 87, heat exchanger 83, line 88 and valve 89.

The following example of one specific operation is given for the purpose of further illustrating the utility of the present invention, although not with the intention of unduly limiting it.

The charging stock comprises a California natural gasoline having an A. P. I. gravity of 74°, and end-boiling point of 325° F. and the following composition:

Constituents	Liquid volume percent
Methane	2.3
Ethane	7.7
Propane	23.5
Iso-butane	9.0
Normal butane	22.0
Pentane and heavier	35.3

The charging stock is fractionated to separate the propane and lighter constituents as an overhead fraction, the propane subsequently separated by condensation. The propane is cracked at a temperature of 1292° F. and a pressure of 14 pounds per square inch. The normal butane is isomerized

in the presence of aluminum chloride catalyst at a temperature of about 190° F. and under a pressure of about 250 pounds per square inch. Ethylene and unconverted propane from the thermal cracking step are commingled with the isobutane and the isobutane is alkylated by the ethylene at a temperature of about 105° F. under a pressure of 250 pounds. The ethylene introduced into the alkylation zone amounts to 14.1 percent of the total hydrocarbons therein. Approximately 1.8 mol percent of hydrogen chloride is commingled with the normal butane prior to isomerization and the hydrogen chloride included with the conversion products introduced to the alkylation zone amounts to 1.5 mol percent. The yield of hydrocarbons containing more than 4 carbon atoms per molecule obtained from the alkylation operation amounts to about 238 percent by weight, based on the olefins introduced into the alkylation zone. The alkylated product, when blended with the normally liquid constituents of the natural gasoline in separator 3, produces a final gasoline product of satisfactory vapor pressure and of high antiknock value.

We claim as our invention:

1. A process for treating a substantially paraffinic distillate containing propane and normal butane, which comprises separating said propane and normal butane from the higher boiling constituents, cracking said propane under temperature and pressure conditions adequate to produce substantial yields of ethylene, isomerizing said normal butane to isobutane under isomerizing conditions in the presence of a catalyst having isomerizing and alkylating properties, removing resultant products from the isomerizing step together with at least a portion of said catalyst and commingling therewith ethylene produced in the cracking step, and subjecting the resultant mixture to alkylating conditions to react isobutane with ethylene in the presence of said portion of the catalyst.

2. A process for the conversion of natural gasoline which comprises stabilizing said natural gasoline to separate a fraction containing propane, a fraction containing normal butane, and a fraction containing higher boiling constituents, cracking said propane under temperature and pressure conditions adequate to effect conversion thereof into substantial yields of ethylene, isomerizing said fraction containing normal butane in the presence of a catalyst having isomerizing and alkylating properties, removing resultant products from the isomerizing step together with at least a portion of said catalyst and commingling therewith ethylene produced in the cracking step, and subjecting the resultant mixture to alkylating conditions to react isobutane with ethylene in the presence of said portion of the catalyst.

3. A process for the conversion of natural gasoline containing propane and normal butane which comprises fractionating said natural gasoline in the presence of conversion products of the process, produced as hereinafter set forth, to separate a fraction containing said propane and lighter constituents, a fraction containing four carbon atoms per molecule including said normal butane, and a fraction containing the higher boiling constituents, withdrawing said fraction containing the propane and lighter constituents, cooling the same to condense said propane, separating the condensed propane from the lighter constituents, withdrawing the latter from the process, subjecting said propane to thermal cracking conditions to effect substantial conversion thereof into ethylene, withdrawing the last mentioned conversion products containing said ethylene, unconverted propane and higher and lower boiling constituents and cooling the same, introducing said fraction containing four carbon atoms per molecule, including said normal butane, into an isomerization zone containing an aluminum chloride-containing catalyst, maintaining said isomerization zone under isomerizing conditions, whereby to effect isomerization of said normal butane to isobutane and whereby to include a portion of said aluminum chloride with the conversion products withdrawn from said isomerization zone, introducing the last mentioned conversion products including isobutane and said portion of aluminum chloride into an alkylation zone containing a granular packing material, introducing into said alkylation zone said conversion products containing said ethylene, maintaining said alkylation zone under temperature and pressure conditions whereby to effect alkylation of said isobutane by said ethylene in the presence of said portion of aluminum chloride, withdrawing the products from said alkylation zone and introducing the same into a separating zone wherein the hydrocarbons are separated from aluminum chloride-containing products, withdrawing the latter from the process, and fractionating said last mentioned hydrocarbons in the presence of said natural gasoline as previously set forth.

4. A process such as defined in claim 3 wherein hydrogen chloride is commingled with said fraction containing four carbon atoms per molecule prior to the isomerization of said normal butane.

5. A process such as defined in claim 3 wherein hydrogen chloride is passed successively through said isomerization zone, said alkylation zone and said separating zone into said fractionation zone, to be withdrawn therefrom in commingled state with said fraction containing the propane and lighter constituents, and wherein said hydrogen chloride is recovered from said lighter constituents and the recovered hydrogen chloride is commingled with said fraction containing four carbon atoms per molecule prior to the isomerization of said normal butane.

6. A process such as defined in claim 3 wherein at least a portion of said aluminum chloride-containing products separated from the hydrocarbons is returned to said alkylation zone.

7. A process such as defined in claim 3 wherein said propane is cracked at a temperature of from about 900° to about 1400° F.

8. A process such as defined in claim 3 wherein said isomerization is effected at a temperature of from about 160° to about 250° F. under a pressure of from about 150 to about 500 pounds per square inch.

9. A process such as defined in claim 3 wherein said alkylation is effected at a temperature of from about 60° to about 200° F. under a pressure of from about 150 to about 500 pounds.

10. A process for the conversion of natural gasoline containing propane and normal butane which comprises fractionating said natural gasoline in the presence of the conversion products of the process, produced as hereinafter set forth, to separate a fraction containing said propane and lighter constituents, a fraction containing four carbon atoms per molecule including said normal butane, and a fraction containing the higher boiling constituents, withdrawing said fraction containing the propane and lighter constituents, cooling the same to condense the

propane, separating the condensed propane from the lighter constituents, withdrawing the latter from the process, heating said propane to a temperature of from about 900° to about 1400° F. whereby to effect substantial conversion thereof into ethylene, withdrawing the last mentioned conversion products containing said ethylene, unconverted propane and higher and lower boiling constituents and cooling the same, introducing said fraction containing four carbon atoms per molecule, including said normal butane, into an isomerization zone containing aluminum chloride-containing catalyst and maintained at a temperature of from about 185 to about 195° F. under a pressure of from about 210 to about 300 pounds per square inch, whereby to effect isomerization of said normal butane to isobutane and whereby to include a portion of said aluminum chloride with the conversion products withdrawn from said isomerization zone, introducing the last mentioned conversion products, including isobutane and said portion of aluminum chloride, into an alkylation zone containing a granular packing material, also introducing into said alkylation zone the conversion products containing said ethylene, maintaining said alkylation zone at a temperature of from about 90° to about 120° F. under a pressure of from about 210 to about 300 pounds per square inch, whereby to effect alkylation of said isobutane by said ethylene in the presence of the said portion of aluminum chloride, withdrawing the products from said alkylation zone and introducing the same into a separating zone wherein the hydrocarbons are separated from aluminum chloride-containing products, withdrawing the latter from the process, and fractionating said last mentioned hydrocarbons in the presence of said natural gasoline as previously set forth.

11. A process as defined in claim 10, wherein said conversion products containing said ethylene, unconverted propane and higher and lower boiling constituents are fractionated to separate said ethylene from said unconverted propane and said higher and lower boiling constituents, said ethylene being introduced to said alkylation zone, said unconverted propane being recycled to said heating for further conversion into ethylene, and said higher and lower boiling constituents being withdrawn from the process.

12. A process for treating paraffinic distillate containing propane and normal butane which comprises fractionating the distillate to separate therefrom a propane-containing fraction and a butane-containing fraction, cracking the first-named fraction to convert propane to ethylene, subjecting the second-mentioned fraction to isomerization in the presence of aluminum chloride to convert normal butane into isobutane, removing from the isomerizing step a reaction mixture containing isobutane and at least a portion of said aluminum chloride and commingling therewith ethylene produced in the cracking step, and subjecting the commingled materials to alkylating conditions to react isobutane with ethylene in the presence of said portion of the aluminum chloride.

13. The process as defined in claim 12 further characterized in that hydrogen chloride is supplied to the isomerizing step and transferred therefrom to the alkylating step.

14. The process as defined in claim 12 further characterized in that said distillate comprises natural gasoline.

CHARLES G. DRYER.
RALPH B. THOMPSON.