



Nov. 28, 1972

R. E. DIXON ET AL

3,704,334

HYDROCARBON CONVERSION

Filed March 2, 1970

4 Sheets-Sheet 2

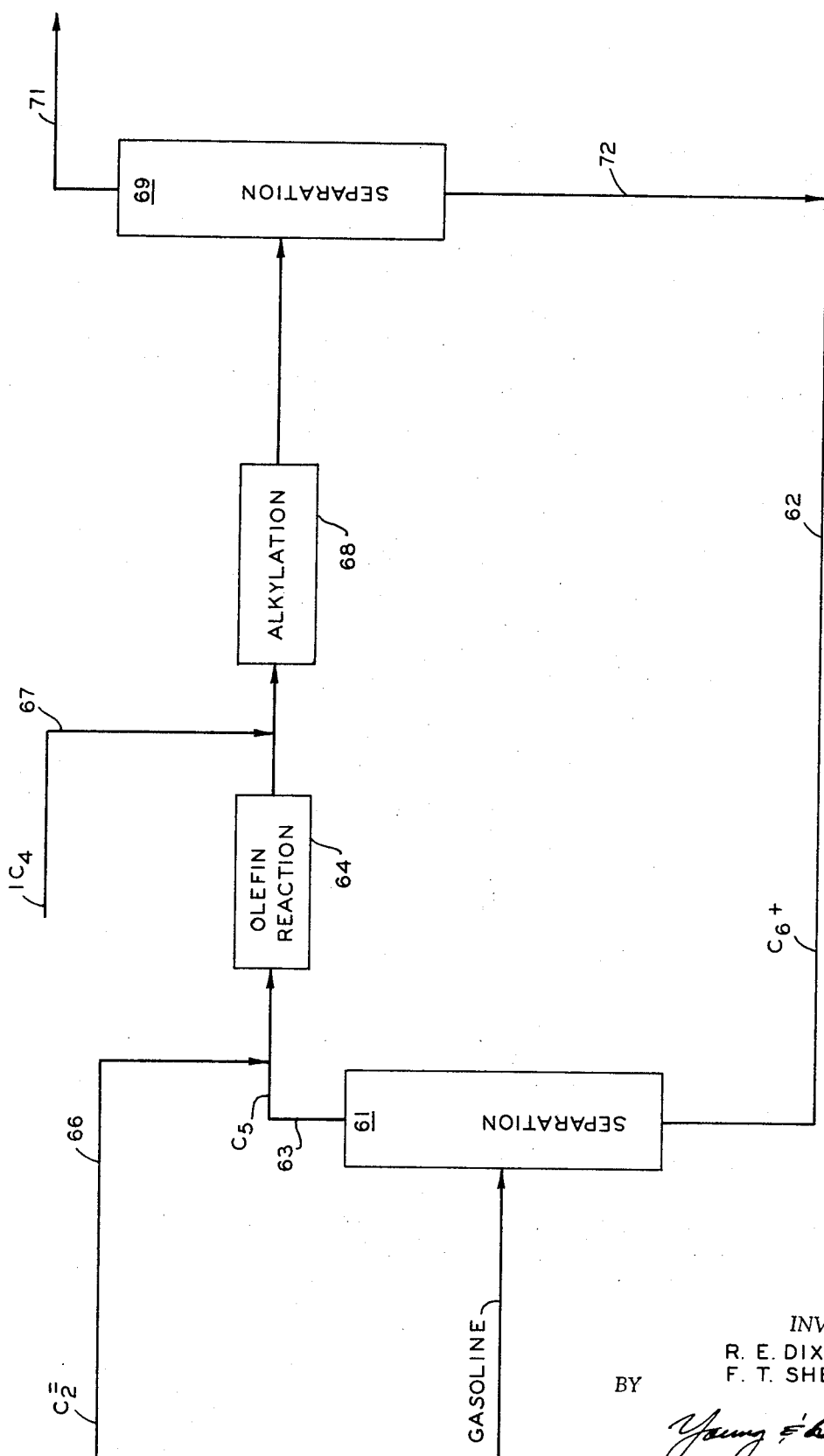


FIG. 2

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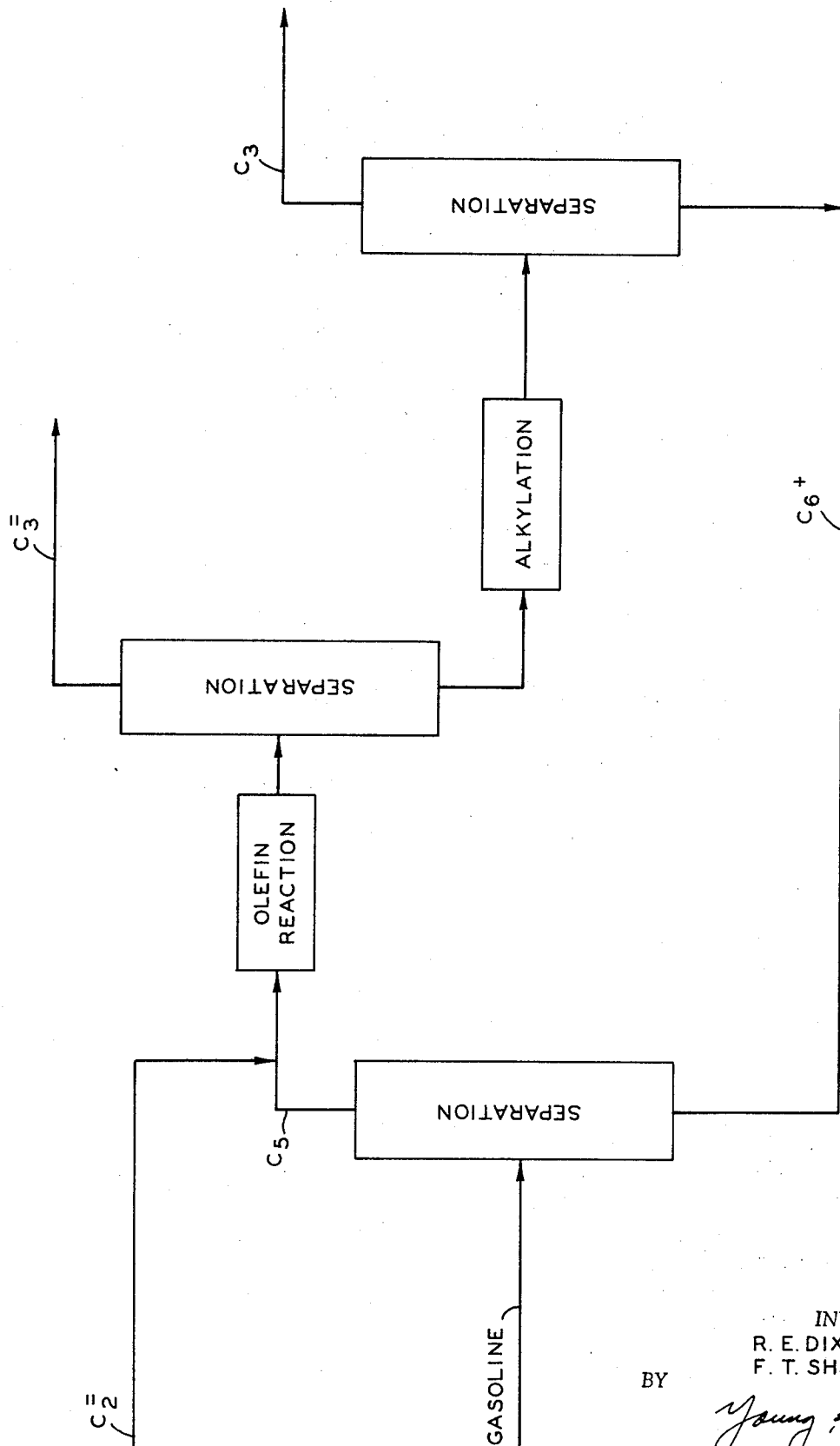


FIG. 3

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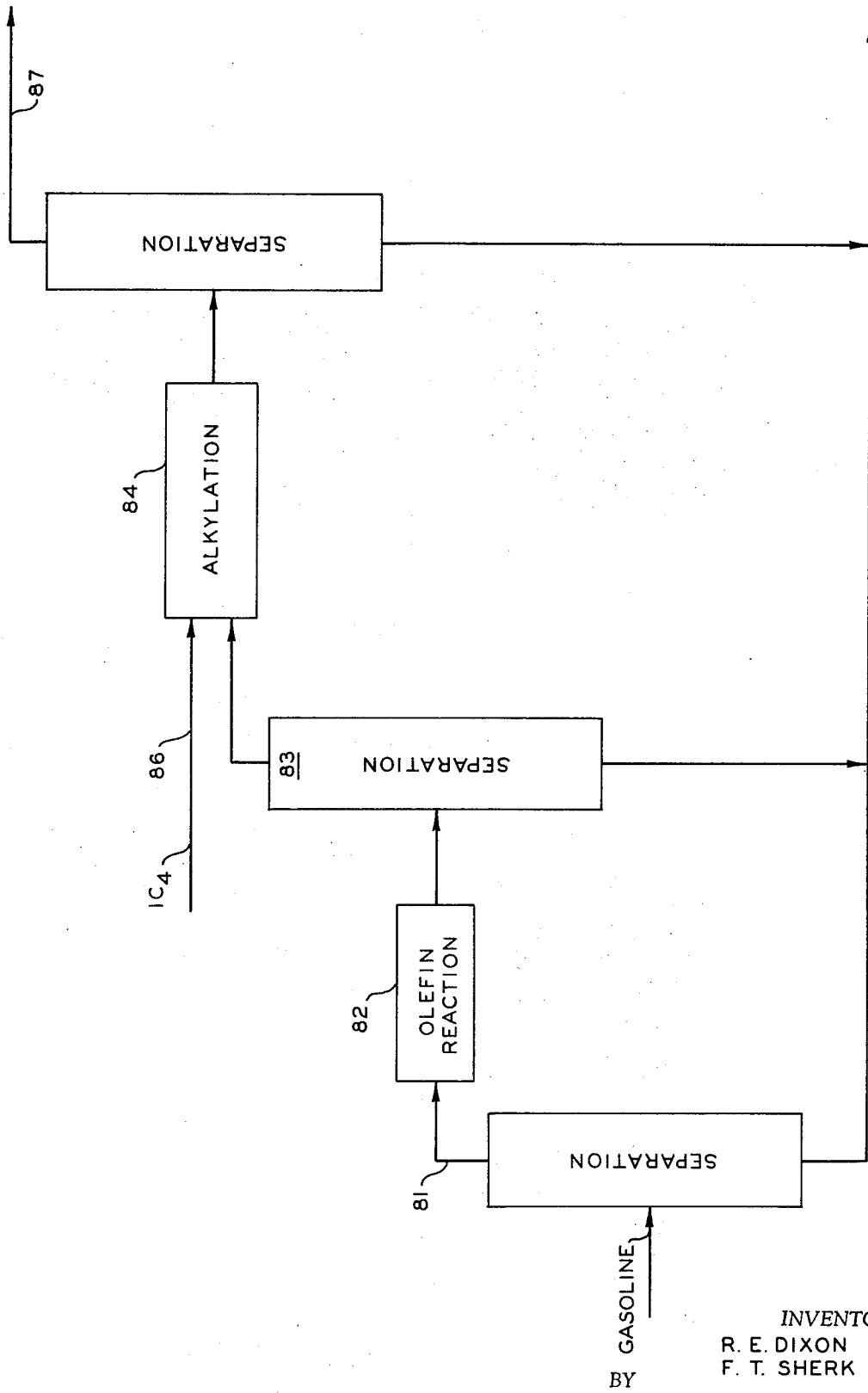


FIG. 4

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1

2

3,704,334

## HYDROCARBON CONVERSION

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assignors to Phillips Petroleum Company  
Continuation-in-part of application Ser. No. 683,354,  
Nov. 15, 1967. This application Mar. 2, 1970,  
Ser. No. 15,347

Int. Cl. C07c 3/00, 3/50

U.S. Cl. 260—683.43

6 Claims

## ABSTRACT OF THE DISCLOSURE

Pentene and/or hexene are converted by the olefin reaction to produce butene. In one embodiment C<sub>5</sub> and/or C<sub>6</sub> olefins are separated from a gasoline stream, converted according to the olefin reaction, and lighter olefins produced thereby are alkylated, thereby removing from the gasoline components which are objectionable from the standpoint of motor vehicle hydrocarbon emissions and producing high octane lower volatility components which reduce or eliminate the need for lead-containing antiknock additive and reduce olefinic hydrocarbon emission due to vaporization loss.

This is a continuation in part of application Ser. No. 683,354, filed Nov. 15, 1967, now abandoned.

This invention relates to hydrocarbon conversion. In one aspect, it relates to converting propylene and at least one of pentene or hexene by the olefin reaction to produce butenes. In another aspect, it relates to improving the quality of a gasoline by removing C<sub>5</sub> and/or C<sub>6</sub> olefins from a gasoline stream and converting such olefins to produce an alkylate suitable for blending back into the gasoline. In another aspect, it relates to improving the quality of the gasoline stream by converting ethylene and/or propylene and C<sub>5</sub> and/or C<sub>6</sub> olefins to butenes which are useful in producing an alkylate suitable for blending back into the gasoline. In still another aspect it relates to cleaving a C<sub>5</sub> and/or C<sub>6</sub> olefin with ethylene to produce both an olefin stream suitable for alkylation and a pure propylene stream suitable for polymerization or other chemical use.

In the production of gasoline, it is desirable to produce high octane products. One useful method in producing high octane gasoline is alkylation by which butenes are reacted with isobutane to form high octane components. By the practice of the present invention and its application to the production of gasoline, additional butenes are alkylated and, therefore, additional alkylate can be produced resulting in a reduction in or the complete elimination of the need for a lead containing antiknock additive.

Further, it is desirable to remove C<sub>5</sub> and/or C<sub>6</sub> olefins from gasoline which is to be used as motor fuel to reduce the tendency to produce undesirable emissions which are unwanted in the atmosphere. It has been found that the removal of C<sub>5</sub> olefins from gasoline greatly reduces the smog forming potential of emissions from gasoline powered motor vehicles. Very large quantities of these C<sub>5</sub> olefins are available in the total amount of gasoline produced by thermal or catalytic cracking. By the practice of the present invention a substantial reduction in the potential pollutants in gasoline can be made, resulting in a substantial lowering of the smog forming emissions when the gasoline is burned in an internal combustion engine.

An object of the invention is to reduce the smog forming potential of a gasoline. Another object of the invention is to reduce the amount of lead additive necessary to produce a gasoline having a given octane rating. Another object of this invention is to convert propylene and pen-

tene and/or hexene to butene. Another object of this invention is to increase the amount of high octane alkylate available in a stream of a cracked gasoline.

Other aspects, objects and advantages of our invention are apparent in the written description, drawings, and the claims.

According to the invention, C<sub>5</sub> and/or C<sub>6</sub> olefins are converted according to the olefin reaction as defined herein to produce butenes and the butenes are alkylated to produce high octane number low smog potential gasoline components. Further, according to the invention the butenes are produced by disproportionation of the C<sub>5</sub> and/or C<sub>6</sub> olefins. Further, according to the invention the butenes are produced by cleaving the C<sub>5</sub> and/or C<sub>6</sub> olefins with ethylene and/or propylene.

Further according to the invention, a feed stream containing propylene and pentene and/or hexene is converted by the olefin reaction to produce butene. Further according to the invention, the propylene and pentene and/or hexene for the above conversions are obtained from a gasoline stream and the butene produced thereby is fed to an alkylation zone to produce additional gasoline.

In the drawings, FIG. 1 illustrates the invention applied to the treatment of a catalytic cracker effluent. FIG. 2 illustrates the practice of the invention utilizing ethylene cleavage of the C<sub>5</sub> olefin fraction of a gasoline stream. FIG. 3 illustrates ethylene cleavage and providing a product propylene stream. FIG. 4 illustrates the practice of the invention with the olefin reaction of C<sub>5</sub> olefins without a separate cleavage olefin.

In FIG. 1 the effluent from a catalytic cracker is fed through pipe 11 into a fractionation zone indicated generally at 12 wherein a C<sub>2</sub> and lighter stream is removed from pipe 13, a C<sub>3</sub> stream is passed through pipe 14, a C<sub>4</sub> stream through pipe 16, a cracked gasoline stream through pipe 17, a cycle oil stream through pipe 18, and a residue stream through pipe 19. The cracked gasoline stream in pipe 17 is fed into dehexanizer 21, the bottoms product of which is removed through pipe 22 and is a C<sub>7</sub>+ stream suitable for use as gasoline or for gasoline blending. The overhead from dehexanizer 21 comprising a C<sub>5</sub>-C<sub>6</sub> stream is blended with the C<sub>3</sub> stream from fractionation zone 12 and fed through pipe 23 to pipe 24 to heater 26 and to olefin reaction zone 27.

The C<sub>3</sub> stream separated from a cat. cracked gasoline normally contains propane and propylene; the C<sub>4</sub> stream normally contains butanes and butenes, both normal and isomeric; the C<sub>5</sub>-C<sub>6</sub> stream contains pentanes, pentenes, hexanes and hexenes, normal and isomeric.

The effluent from olefin reaction zone 27 contains butene produced therein. In the embodiment illustrated in the drawing, the effluent from olefin reaction zone 27 is cooled in heat exchanger 29 and passed to vapor liquid separation zone 30. The overhead from zone 30 is compressed in compressor 32 and recycled through pipe 33 to pipe 24. The liquid product from vapor liquid separation zone 30 passes through pump 35 and pipe 34 to a depropanizer 36. The bottoms product from depropanizer 36 is passed through pipe 38 to debutanizer 39. The overhead from debutanizer 39 is passed through pipe 40 to pipe 16 which feeds alkylation zone 41. The effluent from alkylation zone 41 is passed to fractionation zone 42 from which an alkylate stream is removed through pipe 43, a normal butane stream through pipe 44 and a recycle isobutane stream through pipe 46. Fresh isobutane is added as needed through pipe 47. The combined isobutane streams are fed through pipe 48 to pipe 16. Pump 50 provides the necessary pressure.

The overhead from depropanizer 36 is passed through pipe 37 and condenser 37a to overhead accumulator 37b. C<sub>3</sub> and lighter hydrocarbons from accumulator 37b are

recycled through pipe 51 to pipe 32 and thence to pipe 24. A first portion of the liquid from accumulator 37b is passed to depropanizer 36 as reflux. To prevent the build-up of propane, a second portion of the liquid from accumulator 37b is passed to C<sub>3</sub> stripper 53 from which the overhead is combined with the overhead from depropanizer 36 and the bottoms product, comprising propane, is removed.

Some C<sub>5</sub>'s and C<sub>6</sub>'s from the bottoms product of debutanizer 39 are removed through pipe 56 as a product stream to prevent the build-up of heavier hydrocarbons while the remainder of this stream is recycled through pipe 57 to pipe 24.

The streams from pipes 22, 43 and 56, comprising the C<sub>7</sub>+ gasoline stream, alkylate and C<sub>5</sub>'s and C<sub>6</sub>'s and heavier, are available as product streams for use directly as gasoline or for blending to produce gasoline of specific desired characteristics.

Although FIG. 1 illustrates the processing of both C<sub>5</sub> and C<sub>6</sub> olefins from the gasoline cut, either one or the other can be processed as desired in a particular operation. In many instances it is desirable to process a C<sub>5</sub> cut since that includes a major source of smog forming components. Any C<sub>4</sub> components remaining in the gasoline can also be removed and processed with the C<sub>5</sub> components.

By operating as illustrated, that is by removing C<sub>2</sub> and lighter products through pipe 13, the light olefin for cleavage of C<sub>5</sub> and/or C<sub>6</sub> olefins are provided by feeding propylene from pipe 14 and recycling ethylene and propylene from pipes 31 and 51. To prevent build-up of propane, it is removed through pipe 54. By feeding propylene and not ethylene to olefin reaction zone 27, the ethylene which is produced can be separated substantially free of ethane. That is, for example, a substantially pure ethylene stream can be removed from separator 30 or other separator means and made available for polymerization or for producing other high quality gasoline products, for example diisopropyl.

On the other hand, if ethylene is fed into zone 27, and not propylene, propylene is produced substantially free of propane and can be separated to provide substantially pure propylene for other petrochemical use, polypropylene manufacture, for example. In the latter instance it would not be necessary to provide the C<sub>3</sub> stripper shown, but it probably would be necessary to provide means to prevent the build-up of ethane.

Of course, if substantially pure ethylene and/or propylene are fed into zone 27 as the cleaving olefin, the need for means to prevent the build-up of ethane or propane are substantially reduced or eliminated.

Where desired, propylene can be fed to alkylation either together with the butylenes or in a separate alkylation zone, depending upon the need for light cleavage olefin, the required octane number of the gasoline being made, etc. Where a sufficiently large amount of ethylene and/or propylene is available it can be used without recycle, whereupon the presence of reasonable amounts of ethane or propane is of little importance since they can readily be removed from the system along with the ethylene or propylene.

Although recycle of a portion of the C<sub>5</sub>-C<sub>6</sub> stream is shown, this may not be necessary or desirable when a large enough amount of ethylene or propylene is available in olefin reaction zone 27. When a sufficient amount of the cleaving olefin is present substantially all of the convertible C<sub>5</sub>-C<sub>6</sub> olefin will be converted in a single pass. To attain maximum conversion of the C<sub>5</sub>-C<sub>6</sub> olefins it is preferred to provide for double bond isomerization of these reactants, preferably through the use of a bi-component olefin reaction and isomerization catalyst as described below. However, passing the C<sub>5</sub>-C<sub>6</sub> stream over a double bond isomerization catalyst prior to contact with the olefin reaction catalyst also is helpful. In some instances passing the reactants sequentially through a plu-

rality of olefin reaction catalyst beds separated by beds of isomerization catalysts is beneficial.

In FIG. 2, ethylene is provided as the light olefin for cleavage. The gasoline stream is separated in separator 61 and the C<sub>6</sub> and heavier portion of the stream removed through pipe 62. The C<sub>5</sub> portion, containing C<sub>5</sub> hydrocarbons and any lighter components and which may contain some small amount of C<sub>6</sub>, is removed through pipe 63 and passed to olefin reaction zone 64 along with ethylene from pipe 66. This results in the conversion of the bulk of the pentenes and any hexenes in the stream to propylene and butenes. The propylene and butenes are charged to the alkylation zone 68 along with unconverted pentene and hexenes and with isobutane from pipe 67. Of course, if desired, other isoparaffins, for example isopentane can be fed together with or in place of the isobutane. By additional fractionation the unconverted pentenes and/or hexenes can be recycled to the olefin reaction unit 64 prior to alkylation, but in many instances a once through operation is desired. If desired the effluent of alkylation zone 68 can be separated in separator 69 to remove components not wanted in the gasoline stream, such as propane for example, which can be removed through pipe 71, and the remainder returned to the gasoline stream through pipe 72. Ethylene can be separated from the effluent of olefin reactor 64 and recycled thereto, or removed from the system either ahead of or downstream of alkylation zone 68. Also, if desired, the C<sub>5</sub> and heavier components can be removed prior to alkylation to allow flexibility in gasoline product blending and alkylation unit loading.

In FIG. 3, the operation is very similar to that of FIG. 2 except that propylene is removed as a product from the effluent of the olefin reaction zone. As noted above, when the cleaving olefin is ethylene, high purity propylene is produced in the olefin reaction zone.

In FIG. 4, the C<sub>5</sub> portion of a gasoline stream is reacted according to the olefin reaction without the addition of a light olefin. The C<sub>5</sub> cut is fed through pipe 81 to olefin reaction zone 82. The effluent of zone 82 is separated in separator 83 with the C<sub>5</sub> and lighter fraction being fed to alkylation reactor 84 along with isobutane from pipe 86. The C<sub>6</sub> and heavier portion of the effluent from separator 83 is returned to the gasoline stream. The effluent of alkylation zone 84 is separated, propane or other light hydrocarbons being removed through pipe 87 and the remainder being returned to the gasoline.

The olefin reaction is defined as a process for the catalytic conversion over a catalyst of a feed comprising one or more ethylenically unsaturated compounds to produce a resulting product which contains at least ten percent by weight of product compounds, which product compounds can be visualized as resulting from at least one primary reaction, as defined below, or the combination of at least one primary reaction and at least one unsaturated bond isomerization reaction, and wherein the sum of the compounds contained in said resulting product consisting of hydrogen, saturated hydrocarbons, and compounds which can be visualized as formed by skeletal isomerization but which cannot be visualized as formed by one or more of the above-noted reactions, comprises less than twenty-five percent by weight of the total of said resulting product. Feed components and unsaturated bond isomers thereof are not included in the resulting product for the purpose of determining the above-noted percentages.

In the olefin reaction, as defined above, the primary reaction is a reaction which can be visualized as comprising the breaking of two existing unsaturated bonds between first and second carbon atoms and between third and fourth carbon atoms, respectively, and the formation of two new unsaturated bonds between said first and third and between said second and fourth carbon atoms. Said first and second carbon atoms and said third and

fourth carbon atoms can be in the same or different molecules.

The olefin reaction has been illustrated by the following reactions:

(1) The disproportionation of an acyclic mono- or polyene having at least three carbon atoms into other acyclic mono- or polyenes of both higher and lower number of carbon atoms; for example, the disproportionation of propylene yields ethylene and butenes; the disproportionation of 1,5-hexadiene yields ethylene and 1,5,9-decatriene;

(2) The conversion of an acyclic mono- or polyene having three or more carbon atoms and a different acyclic mono- or polyene having three or more carbon atoms to produce different acyclic olefins; for example, the conversion of propylene and isobutylene yields ethylene and isopentene;

(3) The conversion of ethylene and an internal acyclic mono- or polyene having four or more carbon atoms to produce other olefins having a lower number of carbon atoms than that of the acyclic mono- or polyenes; for example, the conversion of ethylene and 4-methylpentene-2 yields 3-methylbutene-1 and propylene;

(4) The conversion of ethylene or an acyclic mono- or polyene having three or more carbon atoms and a cyclic mono- or cyclic polyene to produce an acyclic polyene having a higher number of carbon atoms than that of any of the starting materials; for example, the conversion of cyclohexene and 2-butene yields 2,8-decadiene; the conversion of 1,5-cyclooctadiene and ethylene yields 1,5,9-decatriene;

(5) The conversion of one or more cyclic mono- or cyclic polyenes to produce a cyclic polyene having a higher number of carbon atoms than any of the starting materials; for example, the conversion of cyclopentene yields 1,6-cyclodecadiene;

(6) The conversion of an acyclic polyene having at least seven carbon atoms and having at least five carbon atoms between any two double bonds to produce acyclic and cyclic mono- and polyenes having a lower number of carbon atoms than that of the feed; for example, the conversion of 1,7-octadiene yields cyclohexene and ethylene; or

(7) The conversion of one or more acyclic polyenes having at least three carbon atoms between any two double bonds to produce acyclic and acyclic mono- and polyenes generally having both a higher and lower number of carbon atoms than that of the feed material; for example, the conversion of 1,4-pentadiene yields 1,4-cyclohexadiene and ethylene.

Reactions believed particularly useful in the practice of the present invention include the reactions numbered 1, 2, 3 and 4 above.

The catalysts which are useful for the present invention are those which have activity for the disproportionation of propylene into ethylene and butenes. Some examples of such catalysts are:

(1) silica or thoria promoted by an oxide or a compound convertible to the oxide by calcination or sulfide of tungsten or molybdenum or by an oxide or a compound convertible to the oxide by calcination of rhenium, vanadium, niobium, tellurium or tantalum;

(2) Alumina promoted with an oxide or compound convertible to an oxide by calcination of molybdenum, tungsten, or rhenium; a sulfide of tungsten or molybdenum; or an alkali metal salt, ammonium salt, alkaline earth metal salt, or bismuth salt of phosphomolybdic acid;

(3) One or more of the group zirconia, aluminum phosphate, zirconium phosphate, calcium phosphate, magnesium phosphate, or titanium phosphate promoted by one or more of a sulfide of molybdenum or tungsten, or an oxide or a compound convertible to the oxide by calcination of molybdenum, tungsten, vanadium, niobium,

tantalum or rhenium or magnesium tungstate or beryllium phosphotungstate; and

(4) Silica, alumina, zirconia, aluminum phosphate, zirconium phosphate, calcium phosphate, magnesium phosphate, or titanium phosphate promoted by a hexacarbonyl of molybdenum or tungsten.

The catalysts of (1) can be prepared and activated by conventional techniques such as by combining a catalyst grade silica with suitable tungsten, molybdenum, rhenium, vanadium, niobium, tellurium, or tantalum compounds by a conventional method such as, for example, impregnation, dry mixing, or coprecipitation. Suitable tungsten and molybdenum compounds include tungsten oxide and molybdenum oxide and compounds convertible to these oxides. The supported oxides are activated by calcining in air and the supported sulfides are activated by heating in an inert atmosphere.

The catalysts of (2) can be prepared and activated by conventional techniques such as by combining catalyst grade alumina with an oxide or a compound convertible to an oxide by calcination of molybdenum, tungsten or rhenium and calcining the resulting mixture after removal of any solvent used in the impregnation. The sulfides of tungsten or molybdenum or the salts of phosphomolybdic acid can be utilized to impregnate a catalyst grade alumina by solution in a proper solvent after which the solvent is evaporated and the resulting mixture dried to prepare the catalyst.

The catalyst compositions of (3) can be prepared and activated by conventional techniques. For example, molybdenum oxides can be coprecipitated with aluminum phosphate followed by calcination in air to reduce an activated catalyst. Alternatively, the support material, such as zirconia, can be impregnated with a compound of the promoter convertible to the oxide, such as ammonium tungstate, followed by calcination in air. In the preparation of a sulfide-containing catalyst, a sulfide of the promoter can be ball-milled with a support, such as zirconium phosphate, followed by heating in an inert atmosphere such as nitrogen. Magnesium tungstate and beryllium phosphotungstate can be dry mixed with titanium phosphate, for example, and activated by calcination in the air at elevated temperatures.

The catalyst compositions of (4) can be prepared and activated by impregnating a previously calcined support material, such as calcium phosphate, with a solution of the hexacarbonyl of the promoter in an organic solvent such as benzene, followed by drying in a vacuum or in an inert atmosphere at about 50 to 700° F.

The catalytic agent is considered to be the reaction product resulting from the admixture of the support material and the promoter material which is subjected to activation treatment.

The operating temperature for the process of this invention when using catalysts of (1) is in the range of about 400 to 1100° F. The process of this invention when using the catalysts of (2) will be operated at a temperature in the range of about 150 to 500° F. The process using the catalysts of (3) will be carried out at a temperature of about 600 to 1200° F. The process using the catalysts of (4) will be carried out at a temperature of about 0 to 600° F. In the process of the invention, pressures are not important but will be in the range of about 0 to 2,000 p.s.i.g.

Other catalysts include those disclosed in Ser. No. 412,343, filed Nov. 9, 1964, U.S. 3,395,196; Ser. No. 517,918, filed Jan. 3, 1966; Ser. No. 517,905, filed Jan. 3, 1966; Ser. No. 421,692, filed Dec. 28, 1964, U.S. 3,418,390; Ser. No. 529,230, filed Feb. 23, 1966; Ser. No. 516,673, filed Dec. 27, 1965; and U.S. Pat. 3,261,879, issued July 19, 1966.

The finished catalyst can be in the form of powder, or granules as well as in other shapes such as agglomerates, pellets, spheres, extrudates, beads, and depending upon

the type of contacting technique which utilizes the catalyst.

It is frequently advantageous to associated double bond isomerization with the olefin reaction. This can be done by providing a combined catalyst system which contains both an olefin reaction catalyst and a double bond isomerization catalyst. In one such system, the olefin feed sequentially contacts an isomerization catalyst and an olefin reaction catalyst. In sequential operation a plurality of beds of olefin reaction catalysts and isomerization catalysts can be used. In another such system, the feed contacts a compatible mixture of such catalysts. A convenient combined catalyst system of this type is a fixed bed system containing an intimate physical mixture of a particulate olefin reaction catalyst and a particulate iso-

stream in pipe 51 is at a temperature of 100° F. and a pressure of 350 p.s.i.a. The bottoms product from depropanizer 36 is fed to debutanizer 39 which is operated at a pressure of 175 p.s.i.a. The overhead from the debutanizer 39 is fed in pipe 40 along with the C<sub>4</sub> stream in pipe 16 and the isobutane in pipe 48 is fed to alkylation zone at a temperature of 100° F. and a pressure of 150 p.s.i.a. Fractionation zone 42 is operated at a pressure of 120 p.s.i.a.

The compositions of the streams in pipes 14, 23, 24, 28, 31, 32, 34, 37, 40, 51, 54, 56 and 57 are shown in the following table. It will be seen that 302.10 mols of butylene are made available in stream 40 for use in alkylation zone 41. This is produced from streams 14 and 23 which contain substantially no butenes.

TABLE  
[Composition in mols]

Components:	Stream number												
	14	23	24	28	31	32	34	37	40	51	54	56	57
Ethylene.....	0.80	0	680.22	679.42	369.95	679.42	309.48	0	0	309.48	0	0	0
Ethane.....	0	0	0	0	0	0	0	0	0	0	0	0	0
Propylene.....	167.16	0	1,365.42	1,212.91	336.68	1,198.26	876.23	8.76	8.76	861.59	5.88	0	0
Propane.....	77.58	0	1,267.95	1,267.95	328.78	1,190.37	939.16	18.78	18.78	861.59	58.79	0	0
Butenes.....	0	0	52.65	361.23	49.85	52.34	311.38	305.15	302.10	2.49	3.74	2.75	0.31
Butanes.....	0	0	0	0	0	0	0	0	0	0	0	0	0
Pentenes.....	0	192.0	198.68	42.27	2.81	2.81	39.45	39.45	0.79	0	0	34.80	3.87
Pentanes.....	0	76.0	89.75	89.75	5.40	5.40	84.35	84.35	0.84	0	0	75.16	8.35
Hexenes.....	0	0	0.17	1.31	0.04	0.04	1.27	1.27	0	0	0	1.15	0.13
Hexanes.....	0	0	0	0	0	0	0	0	0	0	0	0	0
Total.....	254.54	268.0	3,654.84	3,654.84	1,093.52	3,128.66	2,561.33	457.78	331.28	2,035.41	68.41	113.85	12.65

merization catalyst. Such mixtures are sometimes called bifunctional olefin reaction catalysts. A wide variety of isomerization catalysts can be used. Preferred catalysts are those which have little or no polymerization or cracking activity and which are active for isomerization at conditions suitable for obtaining an olefin reaction product with the selected olefin reaction catalyst. When air activated refractory oxide olefin reaction catalysts are used, metal oxide isomerization catalysts such as MgO, ZnO, etc., are particularly appropriate.

Paraffin alkylation combines an isoparaffin with an olefin to form a higher boiling paraffin or excellent motor fuel properties. Catalytic alkylation is preferred using such catalysts as hydrogen fluoride, sulfuric acid, and Friedel-Crafts-type halide catalysts. Usually alkylation is effected at a pressure to maintain liquid phase alkylation and at a temperature to produce the highest octane alkylate from the olefin or olefins used.

When alkylating isobutane with a mixture of propylene and butylenes using HF, the catalyst is usually at least about 90 percent hydrogen fluoride. Water content ranges from about zero to about 3 percent. The pressure usually is about 100 to about 160 p.s.i.g., depending upon the components, and sufficient to maintain liquid phase alkylation. The temperature is usually 80° F. to about 120° F. The isobutane/olefin mol ratio usually is between 4 to 1 to 15 to 1, preferably above about 8 to 1. HF catalyst to total hydrocarbon volume ratio is usually about 0.3 to 1 to 10 to 1.

In an illustration according to the invention as shown in FIG. 1, a cracked gasoline stream is separated in fractionation zone 12 to produce the streams in pipes 14, 16, 17, 18 and 19. The heater 26, the feed to olefin reaction zone 27 is heated to a temperature of about 800° F. The pressure at the inlet of reaction zone 27 is about 340 p.s.i.a. and the pressure at the outlet about 300 p.s.i.a. The effluent stream from reaction zone 27 is cooled in color 29 to a temperature of 100° F. and is fed to liquid-vapor separator 30 operating at 280 p.s.i.a. Compressor 32 raises the pressure on the vapor in pipe 31 to 350 p.s.i.a. for return to heater 26. Pump 35 pumps the liquid into depropanizer 36 which is operated at 375 p.s.i.a. pressure. Stripper 53 is also operated at 375 p.s.i.a. pressure. The

In an illustration according to the invention as shown in FIG. 2, a catalyst system comprising one part by weight of 8 percent tungsten oxide supported on silica and 6 parts by weight of magnesium oxide is used and the temperature is 750° F. and the pressure is 400 p.s.i.g. 21,500 b.p.d. (barrels per day) of debutanized catalytic gasoline from a Mid-Continent refinery is fed to the system. The gasoline is fractionated to produce the C<sub>5</sub> and C<sub>6</sub>+ cuts. Characteristics of the gasoline and the C<sub>5</sub> and C<sub>6</sub>+ portions are given in the following table:

TABLE.—CHARACTERISTICS OF CAT. GASOLINE FRACTIONS

	Cat. gasoline	C <sub>5</sub> cut	C <sub>6</sub> + cut
API gravity at 60° F.....	54.7	85.3	49.8
RVP (Reid vapor pressure).....	5.35	16.8	2.4
RON (research octane No.).....	90.2	96.3	89.3
RON plus (research octane No. plus 3 cc. TEL/gal.).....	96.7	102.0	95.8
MON (motor octane No.).....	79.0	82.2	78.6
MON plus 3 (motor octane No. plus 3 cc. TEL/gal.).....	84.4	88.2	83.8
ASTM distillation ° F.:			
IBP.....	118	93	160
5.....	139	94	182
10.....	148	95	191
20.....	166	96	203
30.....	184	98	219
50.....	237	98	264
70.....	304	100	323
90.....	383	104	391
95.....	409	106	415
EP.....	441	148	445

The pentenes content is approximately 10 volume percent of the gasoline. The C<sub>5</sub> cut is about 15 volume percent of the gasoline and contains nearly all of the pentenes. Equal quantities of hexene and hexanes are assumed to constitute the small C<sub>6</sub> content of the C<sub>5</sub> portion.

In the olefin reaction zone, the bulk of the pentenes and hexenes are converted to propylene and butenes while the saturates do not react. The propylenes and butenes are fed to the alkylation zone 68 together with unconverted pentenes, hexenes and saturates in the C<sub>5</sub> feed. In the alkylation zone, the catalyst is hydrogen fluoride, the temperature is 120° F. and the pressure is 115 p.s.i.g. Here, the olefins fed are substantially all converted to motor fuel alkylate which is blended with the C<sub>6</sub>+ gasoline fraction.

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Gasoline yield is increased from 21,500 b.p.d. to 25,490 b.p.d., RON+3 from 96.7 to 98.1 and RVP is decreased from 5.4 to 4.0. Ethylene required for the olefin reaction is 174,000 lbs./day and the isobutane fed to the alkylation zone is 4,091 b.p.d. 441 b.p.d. of propane are recovered.

In an illustration according to the invention as shown in FIG. 4 a tungsten oxide on silica olefin reaction catalyst as in the illustration of FIG. 2. However 1,800 b.p.d. of high purity propylene is removed from the olefin reaction effluent. Gasoline yield is increased from 21,500 b.p.d. to 22,131 b.p.d., RON+3 from 96.7 to 97.2 and RVP decreased from 5.4 to 4.0. The same amount of ethylene (174,000 lbs./day) is required as for FIG. 2 but only 1,710 b.p.d. of isobutane are required since the propylene is not alkylated. 343 b.p.d. of propane are produced.

In an illustration according to the invention as shown in FIG. 4 a tungsten oxide on silica olefin reaction catalyst is used (without an isomerization component) and the temperature is 750° F. and the pressure 400 p.s.i.g. The same feed as in the illustration for FIG. 2 is used. The pentenes are converted to propylene, butenes and C<sub>6</sub>+olefins. The same catalyst and conditions of temperature and pressure are used in the alkylation zone 84 as in alkylation zone 68 of FIG. 2. Gasoline yield is increased from 21,500 b.p.d. to 22,753 b.p.d., RON+3 from 96.7 to 96.9 and RVP decreased from 5.4 to 4.1. 1,646 b.p.d. of isobutane are used and 69 b.p.d. of propane produced.

What is claimed is:

1. A hydrocarbon conversion method comprising the steps of:

separating a hydrocarbon stream to produce a C<sub>3</sub> stream containing propylene, a C<sub>4</sub> stream containing butene and isobutane, and a gasoline stream;

separating said gasoline stream to produce a stream comprising at least one of pentene and hexene and to remove a C<sub>7</sub> and heavier stream;

converting said propylene and said at least one of pentene and hexene in an olefin reaction zone by the olefin reaction which, as defined herein, can be visualized as comprising the reaction between two first pairs of carbon atoms, the two carbon atoms of each first pair being connected by an olefinic double bond, to form two new pairs from the carbon atoms of said first pairs, the two carbon atoms of each said new pairs being connected by an olefinic double bond, to produce butene;

separating produced butene from the product stream of the olefin reaction;

feeding the C<sub>4</sub> stream from the hydrocarbon stream and said produced butene to an alkylation zone and alkylating isobutene and butene therein to produce alkylate; and

combining said alkylate with said C<sub>7</sub> and heavier stream.

2. A method of reducing the smog forming potential and increasing the octane rating of an olefin containing gasoline, comprising the steps of:

separating said gasoline in a first separation zone to provide a first separated olefin stream containing at least one olefin selected from pentenes and hexenes and a remainder stream;

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converting said olefin together with at least one light olefin selected from ethylene and propylene according to the olefin reaction which, as defined herein, can be visualized as comprising the reaction between two first pairs of carbon atoms, the two carbon atoms of each first pair being connected by an olefinic double bond, to form two new pairs from the carbon atoms of said pairs, the two carbon atoms of each of said new pairs being connected by an olefinic double bond, in an olefin reaction zone to produce butene;

feeding said butene from said olefin reaction zone together with isobutane to an alkylation zone and alkylating isobutane and butene therein to produce alkylate; and

combining said alkylate with said remainder stream.

3. The method of claim 2 wherein said light olefin is ethylene, propylene is produced in said olefin reaction zone, and the effluent of the olefin reaction zone is separated in a second separation zone to produce a high purity propylene product.

4. The method of claim 2 wherein said light olefin is ethylene, propylene is produced in said olefin reaction zone, and propylene and butene produced in said olefin reaction zone are both fed to said alkylation zone.

5. The method according to claim 2 wherein said light olefin is ethylene.

6. A method of reducing the smog forming potential of an olefin-containing gasoline and producing additional gasoline component of low smog forming potential comprising the steps of:

separating said gasoline in a first separation zone to provide a first separated olefin stream containing at least one olefin selected from pentenes and hexenes;

converting said olefin according to the olefin reaction which, as defined herein, can be visualized as comprising the reaction between two first pairs of carbon atoms, the two carbon atoms of each first pair being connected by an olefinic double bond, to form two new pairs from the carbon atoms of said first pairs, the two carbon atoms of each of said new pairs being connected by an olefinic double bond, in an olefin reaction zone to produce butene;

feeding said butene from said olefin reaction zone together with isobutene to an alkylation zone and alkylating isobutane and butene therein to produce alkylate; and

combining said alkylate and said gasoline after said gasoline is separated in said first separation zone.

#### References Cited

##### UNITED STATES PATENTS

3,236,912	2/1966	Phillips	260—683.45
3,365,513	1/1968	Heckelsberg	260—683 D
2,340,007	1/1944	Mattox	208—117
3,296,330	1/1967	Sherk	260—683 D
2,387,309	10/1945	Sweeney	260—683.47

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