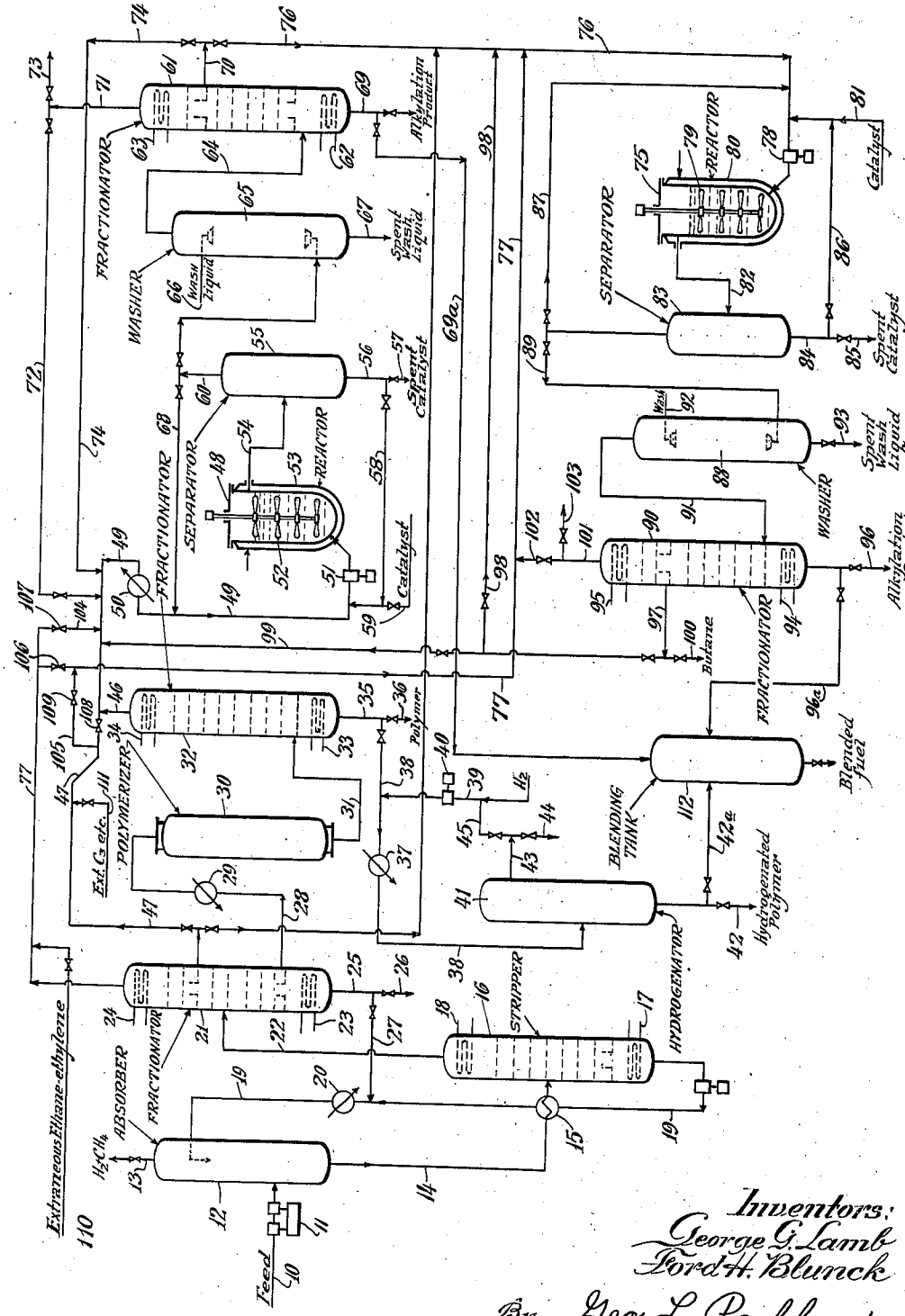
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HYDROCARBON CONVERSION

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Inventors:
George G. Lamb
Ford H. Blunck
By Geo. L. Parkhurst
Attorney.

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HYDROCARBON CONVERSION

George G. Lamb and Ford H. Blunck, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to an improved process for the conversion of normally gaseous hydrocarbons to normally liquid hydrocarbons suitable for use as motor fuel. More particularly, this invention relates to an improved process wherein normally gaseous hydrocarbons are converted catalytically to branched-chain hydrocarbons of high antiknock characteristics.

It has been recognized for some time that branched-chain paraffins are much more satisfactory for use as fuels in high compression automotive and airplane engines than straight-chain hydrocarbons. Many expedients are employed to convert straight-chain hydrocarbons, particularly those found in gasoline from refinery processes, to branched-chain or isomeric hydrocarbons in order to increase the utility of these hydrocarbons in high compression engines. These expedients include such processes as reforming, catalytic cracking, catalytic isomerization, etc.

It is also known that under suitable conditions olefins may be made to polymerize with other olefins or to alkylate paraffins thus forming hydrocarbons of higher molecular weight. If either or both of the reacting constituents is of the branched-chain type the product will also contain branched-chains.

An object of our invention is to provide an improved process for the conversion of normally gaseous hydrocarbons to hydrocarbons of high antiknock value. Another object of our invention is to provide an improved combination of polymerization and alkylation for converting normally gaseous hydrocarbons comprising both paraffins and olefins to normally liquid hydrocarbons. Further objects will become apparent as the description of our invention proceeds.

The invention will now be described in conjunction with the accompanying drawing which is a flow diagram of one preferred embodiment of our invention.

In brief, our invention contemplates the separation of normally gaseous paraffinic and olefinic hydrocarbons into fractions containing predominantly 2, 3, and 4 carbon atoms, selectively polymerizing the olefins from the 4 carbon atom fraction, alkylating a portion of the isobutane from the 4 carbon atom fraction with olefins from one of the other fractions, further alkylating the remainder of the isobutane with the olefins from the remaining fraction and returning unreacted gases to the conversion steps for further treatment.

Referring now to the drawing: feed stock enters through line 10. This feed stock may be any mixture of normally gaseous hydrocarbons containing ethane, propane and the butanes together with the corresponding olefins as well as methane and possibly hydrogen. The off gases from the cracking of petroleum oils to produce gasoline are particularly suitable as a feed for our process especially since in the past it has been customary to regard such gases as by-products and to utilize them chiefly as fuel. The gases are compressed in compressor 11 and forced into absorber 12 where they are contacted with a suitable absorber or scrubbing oil while under pressures of 50 to 350 pounds per square inch gauge. Unabsorbed gases consisting predominantly of hydrogen and methane are removed from the top of absorber 12 through line 13 and may be removed from the system. The absorbing medium used in absorber 12 will ordinarily be an oil of the character of light gas oil but lighter products may also be used, if advantageous. The enriched absorber oil is withdrawn from absorber 12 through line 14 passing through heat exchanger 15 into stripping tower 16 which is provided with suitable bottom heating means 17 and which may also be provided with top cooling means 18. The stripped absorber oil is removed from stripper 16 through line 19 and heat exchanger 15, cooled in cooler 20 and returned to absorber 12.

Uncondensed vapors and gases from stripper 16 are passed into fractionator 21 through line 22. Fractionator 21, having bottom heating means 23 and top cooling means 24 is of the super-fractionator type effecting the separation of the gases into fractions predominating in 2, 3, and 4 carbon atoms respectively. Hydrocarbons heavier than the butanes are withdrawn from the bottom of fractionator 21 through line 25 and may be discharged from the system through valved line 26 or returned for use as an absorber oil through line 27 which joins line 19. Other means for separating the gaseous hydrocarbons into the desired fractions will occur readily to one skilled in the art.

The butane fraction which will contain normal and isobutanes, the normal butenes and isobutylene is withdrawn through line 28, heated in heater 29 and sent to polymerizer 30 for the conversion of the olefins present.

In polymerizer 30 the polymerization of the olefins in the "butane" cut may be accomplished by any one of a number of methods, for example the gases heated to a temperature from about 300° F.

to about 325° F. may be passed over a catalyst consisting of phosphoric acid on kieselguhr at a pressure of about 650 pounds per square inch. In this event the gases will enter at the top of polymerizer 30 and pass down over the catalyst, being discharged near the bottom of the reactor 30 through line 31. Under these conditions the isobutylene is the predominate olefin undergoing reaction although a small amount of the normal butylenes will be converted by interpolymerization with the isobutylene. If the reaction is carried out at 325° F. to 350° F. at 650 pounds per square inch pressure additional interpolymerization of the normal olefins and iso-olefins will take place. The resulting product will be predominately iso-octene, with some trimers.

Another suitable catalyst comprises sulfuric acid of about 60 to 70% H_2SO_4 and preferably about 65% H_2SO_4 which is employed at above about 70° F. and below about 105° F. and preferably at about 85° F. and at approximately atmospheric pressure or a little above. Under these conditions only the isobutylene is absorbed in the sulfuric acid leaving the normal butylenes comparatively unreacted. Using this operation heater 29 may be replaced by a cooler to insure the proper temperature and polymerizer 30 in which contact is made by mechanical means to obtain an emulsion will be followed by separators to separate the polymer and gases from the sulfuric acid. A wash step may also be included to remove any entrained acid from the hydrocarbons.

Sulfuric acid may also be used as a catalyst at higher temperatures in order to obtain an interpolymerization between the isobutylene and the normal butylenes present. Temperatures above 140° F. and preferably at about 175° F., are employed using an acid of approximately the same concentration as in the previously described sulfuric acid polymerization. The product again is almost entirely octenes of the branched-chain type with some trimers present.

Another mode of converting the olefins present in the "butane" feed stock is to use boron fluoride as a catalyst. In order to obtain products of the gasoline boiling range it is desirable to maintain the polymerization reactor with a bottom temperature of about 250° to about 350° F. and preferably about 300° F. and the top of the tower at a suitably lower temperature usually within the range of about 150° to about 180° F. The reactor will be maintained at sufficient pressure so that the hydrocarbons containing 6 or more carbon atoms will be liquids at the temperature existing at the bottom of the tower. This type of catalytic polymerization removes the isobutylene almost exclusively with comparatively little effect on the normal butylenes.

Boron fluoride may also be used as catalyst for the production of polymers of higher molecular weight from the isobutylene present in the feed stock. If the temperature of the reactor is maintained at about 0° F. to about 40° F. and under sub-atmospheric pressure the resulting polymer will be in the nature of an oil, the viscosity of which will depend upon the particular temperature of operation, a lower temperature producing an oil of higher viscosity. If the reaction is carried out at from about −10° to about −100° F. a heavy polymer of resin-like tendencies and extremely high molecular weight is formed, the lower temperatures again producing the heavier polymer. This polymerization reaction will remove effectively the iso-olefins from the butane feed with the production of valuable hydrocarbon products. Since the demand for gasolines usually exceeds to a considerable extent the demand for oils and resins we prefer to operate our polymerization process to produce polymers of gasoline-like characteristics.

Another type of catalyst suitable for our purpose is the double salt type wherein aluminum chloride is one of the constituents. Specific examples include sodium chloroaluminate, lithium chloroaluminate, barium chloroaluminate, calcium chloroaluminate, etc. either as such or deposited on a suitable carrier such as pumice or kieselguhr. With catalysts of this type the preferred range of conditions to be maintained in catalyst chamber 30 are pressures of 200 to 1000 pounds per square inch and preferably of about 500 to 750 pounds per square inch and temperatures of 250 to 550° F. and preferably of 300 to 400° F. Again the product will be hydrocarbons of branched-chain structure within the gasoline boiling range.

The various details in reference to the polymerization procedure have not been illustrated and it should be understood that polymerization reactor 30 is intended to represent an integrated polymerization process having the necessary mixing, separating and discharge means with the accompanying cooling or heating means, etc., and means for regeneration if it is to be used, all of which will be well known to one skilled in the art. Other catalysts for the conversion of olefins to polymers are known and can be utilized in our process.

Polymerized olefins plus unreacted gases are led from polymerizer 30 by line 31 to fractionator 32 equipped with bottom heating means 33 and top cooling means 34. Within fractionator 32 the unreacted gases are separated from the polymer and the polymer withdrawn through line 35. This polymer may be discharged from the system through valved line 36 but since it will be an isomeric octene in most cases it is desirable to hydrogenate it to the paraffin. This is accomplished by directing it through heater 37 in line 38 together with hydrogen from line 39 which is forced into the system under high pressure by means of pump 40. The mixed olefin polymer is hydrogenated in hydrogenator 41 which may be any suitable reactor for this purpose. One method of accomplishing this result is by the use of a nickel catalyst using hydrogen pressures of about 15 pounds per square inch absolute and a temperature of 400° F. The hydrogenated polymer which will be chiefly "iso-octane" (trimethyl pentane) having an octane number of at least 90 is discharged through line 42, or sent to blending tank 112 through line 42a while the hydrogen is removed through line 43 and discharged from the system through line 44 or recycled to line 39 by line 45.

The gases from fractionator 32 now consist chiefly of normal and isobutanes together with any unreacted isobutylene and normal butylenes. If the polymerization reaction has been carried out to polymerize only the iso-olefins then the normal olefins will be present in considerable amount. These gases are discharged from fractionator 32 through line 46. The fraction from fractionator 21 comprising predominantly paraffins and olefins having 3 carbon atoms to the molecule is added to the gases from fractionator 32 by means of line 47 and directed to alkylation reactor 48 through line 49 having heating means 50 and pump 51. In alkylation reactor 48 the isobutane present from fractionator 32 is

alkylated by the propylene present in the fraction from line 47 to yield an alkylated product comprising predominantly branched-chain heptanes. This alkylation may be accomplished in various ways but preferably by the use of a catalyst.

As a catalyst may be used, for example, a salt of the double type of which one of the constituents is aluminum chloride. A preferred catalyst of this nature is sodium chloroaluminate although such salts as lithium chloroaluminate and calcium chloroaluminate may be used equally well. In this case the alkylation reactor 48 will be maintained at a temperature of approximately 400° F. and a pressure of about 500 to about 2000 pounds per square inch gauge.

Another suitable catalyst is sulfuric acid of from about 90 to about 101% H_2SO_4 and preferably about 96% to 97% H_2SO_4. The hydrocarbon gases and sulfuric acid are formed into an emulsion by mixing means 52. The temperature of the emulsion is maintained at from about 15° F. to about 95° F. and preferably between 40° F. and 60° F. This may be accomplished by a cooling jacket 53 about alkylation reactor 48 or by any other suitable means, such as cooling coils, etc. The hydrocarbon-acid emulsion is withdrawn from alkylation reactor 48 through line 54 and allowed to separate in separator 55. The acid is withdrawn from separator 55 through line 56 and discharged from the system for regeneration if necessary through line 57 or returned to the alkylation reactor through valved line 58 which joins line 59 through which fresh catalyst may be admitted. The hydrocarbons, consisting of alkylated isobutane and unreacted gases are withdrawn from separator 55 through line 60 and sent to fractionator 61 having bottom heating means 62 and top cooling means 63 by means of line 64. In order to remove traces of catalyst it may be desirable to wash the hydrocarbon stream in washer 65, the wash medium entering through line 66 and discharging through line 67. It may also be desirable to recycle a part of the alkylation product and gases to aid in forming the emulsion which may be accomplished by valved line 68 which joins line 49. The alkylation product is withdrawn through line 69, and sent to storage, or can be directed to blending tank 112 through line 69a.

The alkylation of the isobutane with propylene in reactor 48 may also be accomplished by using an aluminum chloride-paraffin complex as a catalyst. This operation is carried out in a manner very similar to that employed when using sulfuric acid as a catalyst, the temperature of the reaction being maintained at about 15° to 150° F. and preferably about 70° to 80° F., and 50 to 150 pounds per square inch pressure and preferably 75 pounds per square inch pressure gauge. In those reactions where a low temperature is desirable heater 50 will naturally be a cooling means. Other catalysts which promote the alkylation of paraffins with olefins are also contemplated in our invention.

In fractionator 61 the washed alkylated product and unreacted gases are fractionated to yield a product comprised essentially of branched-chain heptanes which, because of its saturated nature and high octane number, is suitable for use as a motor fuel in high compression engines. This is discharged from fractionator 61 through line 69 and sent to storage, or directed to tank 112 for blending through line 69a. The unreacted C_3 and C_4 carbon atoms are separated, the "butanes" being withdrawn through line 70 and the propane being discharged overhead through line 71. A part or all of the propane containing any unreacted propylene may be recycled to the alkylation reaction through valved line 72 which joins line 47 or may be discharged from the system through line 73 for use as a fuel or for such refinery processes as propane dewaxing, propane deasphalting, etc.

The butane from fractionator 61 may be recycled to the alkylation reactor 48 through valved line 74 which joins line 49 or a part may be recycled and a part further alkylated by ethylene from fractionator 21 or preferably all of it may be alkylated by ethylene. The "butane" which will contain normal butanes, the unreacted isobutane and any remaining unreacted isobutylene or normal butylene is directed to alkylation reactor 75 through valved line 76. The ethane-ethylene fraction from fractionator 21 is led through line 77 to join line 76 and the mixture forced into alkylation reactor 75 by means of pump 78. The remaining isobutane is alkylated by the ethylene present in the ethane-ethylene mixture using as catalysts many of those mentioned as suitable for use in alkylation reactor 48, namely, double salts, $AlCl_3$-paraffin complex, etc. In addition, it is possible to alkylate the isobutane with ethylene using phosphorus pentoxide operating at about 525° F. and employing a pressure of from 200 to about 800 pounds per square inch gauge. The primary product of this alkylation reaction will be branched-chain paraffin hydrocarbons of 6 or 8 carbon atoms of high antiknock value. As in the case of reactor 48 mixing means 79 and cooling jacket 80 are provided to aid in carrying out the reaction under the best conditions of contact and temperature. Catalyst may be injected by means of line 81. The hydrocarbon-catalyst mixture is withdrawn from alkylator 75 through a line 82 and separated in separator 83, the catalyst being withdrawn through line 84 and discharged from the system through valved line 85 or recycled for further use through line 86 which joins line 81. The separated hydrocarbons which will include the alkylated product and the unreacted gases pass overhead from separator 83 and while a part may be recycled to the alkylator by means of line 87, a larger portion is led to washer 88 by means of line 89 and directed to fractionator 90 through line 91. Wash medium may enter washer 88 through line 92 and discharge through line 93. From fractionator 90 having bottom heating means 94 and top cooling means 95 the alkylation product comprising essentially branched-chain hexanes is withdrawn through line 96 for storage, or sent through line 96a to blending tank 112. The gases are separated into two fractions, one predominating in 4 carbon atoms and one predominately ethane and ethylene. The butane is withdrawn from fractionator 90 by line 97 and may be recycled to the alkylation reactor 75 by valved line 98 which joins line 76 or to alkylation reactor 48 through line 99 which joins line 49.

If the "butane" is almost completely denuded of hydrocarbons other than normal butanes it may be discharged through line 100 and used for blending with commercial gasolines to increase the volatility, utilized as fuel, dehydrogenated or cracked to yield olefinic hydrocarbons, isomerized to yield isobutanes, etc. Generally speaking, the two-step alkylation process will remove the iso-paraffins from the "butane cut" so

that recycle is unnecessary. The ethane-ethylene fraction is taken overhead from fractionator 96 through line 101 and may be recycled to alkylation reactor 75 through valved line 102 which joins line 77 or may be discharged from the system through valved line 103 for use as fuel.

Although we have thus far described our invention as directing the 3 carbon atoms cut to one alkylation reactor and the 2 carbon atom cut to another alkylation reactor it is possible to utilize a mixture of the two in either or both alkylation reactions. If it is desired to send both the 2 carbon and 3 carbon atom fractions to alkylator 48 this may be done through line 104 which leads from line 77 to line 47. The ethylene-containing fraction and the propylene-containing fraction may be directed to alkylator 75 by means of line 105 which leads from line 47 to line 77. It is also possible to direct the ethylene-containing fraction to alkylator 48 and the propylene-containing fraction to alkylator 75 by a proper adjustment of the valves in lines 77, 104, 47 and 105. If it is desired, for example, to send ethylene to alkylator 48 and propylene to alkylator 75 valve 106 will be closed, valve 107 opened, valve 108 closed, and valve 109 opened. It may also be desirable to increase the olefin content of the gases for alkylation in which event extraneous ethylene or mixtures containing it may be introduced through line 110 while propylene-containing gases may be introduced through line 111.

The various reaction products from lines 42, 69 and 96 can be blended in tank 112 to yield a high octane number product of fairly wide boiling range, or they may be blended individually or in combination with ordinary gasoline to increase the octane number, with or without the addition of such agents as tetraethyl lead.

While we have described and illustrated certain specific embodiments of our invention, it is to be understood that these are not by way of limitation, and that various modifications and ramifications will occur to those skilled in the art.

We claim:

1. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes and at least one monoolefin having less than four carbon atoms per molecule which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes and a fraction rich in said at least one monoolefin having less than four carbon atoms per molecule, contacting said fraction rich in isobutane, isobutylene and normal butylenes with a catalyst under conditions adapted to polymerize a substantial portion of the olefins in said fraction, separating said polymerized olefins from unreacted isobutane, contacting said separated isobutane with said fraction rich in at least one olefin having less than four carbon atoms per molecule under conditions adapted to promote the alkylation of at least a substantial portion of said isobutane with said olefin, and separating said alkylated isobutane from unreacted hydrocarbons.

2. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes, propylene and ethylene which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes, a second fraction rich in said propylene, and a third fraction rich in said ethylene, contacting said fraction rich in isobutane, isobutylene and normal butylenes with a catalyst under conditions adapted to promote the polymerization of a substantial part of the olefins in said fraction, separating said polymerized olefins from unreacted hydrocarbons including said isobutane, contacting said separated isobutane with at least one of the remaining fractions under conditions adapted to promote the alkylation of at least a part of said separated isobutane with the olefin in said fraction, and separating alkylated isobutane from unreacted hydrocarbons.

3. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes, propylene and ethylene which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes, a fraction rich in propylene and a fraction rich in ethylene, contacting said fraction rich in isobutane, isobutylene and normal butylenes with a catalyst under conditions adapted to promote the polymerization of at least a substantial portion of the olefins in said fraction, separating said polymerized olefins from unreacted gases including said isobutane, contacting said separated isobutane with one of the remaining fractions in the presence of a catalyst under conditions adapted to promote the alkylation of a least a part of said separated isobutane with the olefin in said fraction, separating alkylated isobutane from unreacted hydrocarbons including unreacted isobutane, contacting said unreacted isobutane with the other of the remaining fractions in the presence of a catalyst under conditions adapted to promote the alkylation of at least a substantial part of said unreacted isobutane with the olefin in said remaining fraction, and separating said last-mentioned alkylated isobutane from unreacted hydrocarbons.

4. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes, propylene and ethylene which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes, a fraction rich in propylene and a fraction rich in ethylene, contacting said fraction rich in isibutane, isobutylene and normal butylenes with a catalyst under conditions adapted to promote the polymerization of at least a substantial portion of the olefins in said fraction, separating said polymerized olefins from unreacted gases including said isobutane, contacting said separated isobutane with said propylene-rich fraction in the presence of a catalyst under conditions adapted to promote the alkylation of at least a part of said isobutane with said propylene, separating alkylated isobutane from unreacted gases including unreacted isobutane, contacting said unreacted isobutane with said ethylene-rich fraction in the presence of a catalyst under conditions adapted to promote the alkylaiton of at least a substantial part of said unreacted isobutane with said ethylene, and separating said last-mentioned alkylated isobutane from unreacted hydrocarbons.

5. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes, propylene

and ethylene which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes, a fraction rich in propylene and a fraction rich in ethylene, contacting said fraction rich in isobutane, isobutylene and normal butylenes with a catalyst under conditions adapted to promote the polymerization of at least a substantial portion of the olefins in said fraction, separating said polymerized olefins from unreacted gases including said isobutane, contacting said separated isobutane with one of the remaining fractions in the presence of a catalyst under conditions adapted to promote the alkylation of at least a part of said separated isobutane with the olefin in said fraction, separating alkylated isobutane from unreacted hydrocarbons including unreacted isobutane, contacting said unreacted isobutane with the other of the remaining fractions in the presence of a catalyst under conditions adapted to promote the alkylation of at least a substantial part of said unreacted isobutane with the olefin in said remaining fraction, separating said last-mentioned alkylated isobutane from unreacted hydrocarbons, and blending said alkylated isobutane from each of the alkylation steps with gasoline to form an improved motor fuel.

6. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes, propylene and ethylene which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes, a fraction rich in propylene and a fraction rich in ethylene, contacting said fraction rich in isobutane, isobutylene and normal butylenes with a catalyst under conditions adapted to promote the polymerization of at least a substantial portion of the olefins in said fraction, separating said polymerized olefins from unreacted gases including said isobutane, hydrogenating said polymerized olefins to form saturated paraffinic hydrocarbons, contacting said separated isobutane with one of the remaining fractions in the presence of a catalyst under conditions adapted to promote the alkylation of at least a part of said separated isobutane with the olefin in said fraction, separating alkylated isobutane from unreacted hydrocarbons including unreacted isobutane, contacting said unreacted isobutane with the other of the remaining fractions in the presence of a catalyst under conditions adapted to promote the alkylation of at least a substantial part of said unreacted isobutane with the olefin in said remaining fraction, separating said last-mentioned alkylated isobutane from unreacted hydrocarbons, and blending said hydrogenated polymer and said alkylated isobutane from each of the alkylation steps to form an improved motor fuel.

7. A process for the production of a motor fuel from a mixture of normally gaseous hydrocarbons containing substantial amounts of isobutane, isobutylene, normal butylenes and ethylene which comprises separating said mixture into a fraction rich in said isobutane, isobutylene and normal butylenes and a fraction rich in said ethylene, contacting said fraction rich in isobutane, isobutylene and normal butylenes with a catalyst under conditions adapted to polymerize a substantial portion of the olefins in said fraction, separating said polymerized olefins from unreacted isobutane, contacting said separated isobutane with said fraction rich in ethylene under conditions adapted to promote the alkylation of at least a substantial portion of said isobutane with said ethylene, and separating said alkylated isobutane from unreacted hydrocarbons.

8. A process for the manufacture of high antiknock motor fuel which comprises separating from hydrocarbon mixtures containing normally gaseous components a C_3 hydrocarbon fraction containing propylene and a C_4 hydrocarbon fraction containing isobutane, isobutylene and normal butenes, contacting the C_4 hydrocarbon fraction with a treating agent for removing isobutylene from the remaining C_4 hydrocarbons including the isobutane and at least a part of the normal butenes, separately removing the remaining C_4 hydrocarbons including isobutane and normal butenes from the treating agent and products of the treating step, and subjecting said separately removed C_4 hydrocarbons including isobutane and normal butenes together with the C_3 hydrocarbon fraction containing propylene to the action of an alkylation catalyst under alkylation conditions in the presence of isoparaffins comprising isobutane whereby isobutane is alkylated by said propylene and normal butenes to produce high antiknock hydrocarbons within the gasoline boiling range.

9. The process of claim 8 wherein the treating agent is a polymerization catalyst and wherein the process includes the step of polymerizing removed isobutylene by means of said polymerization catalyst.

10. A process for the manufacture of high antiknock motor fuel which process comprises separating from hydrocarbon mixtures containing normally gaseous components a light hydrocarbon fraction rich in a mono-olefin of less than four carbon atoms and a C_4 hydrocarbon fraction containing isobutane, isobutylene and normal butenes, contacting the C_4 hydrocarbon fraction with a treating agent for removing isobutylene from the remaining C_4 hydrocarbons including the isobutane and at least a part of the normal butenes, separately removing the remaining C_4 hydrocarbons including isobutane and normal butenes from the treating agent and products of the treating step, and subjecting the separately removed C_4 hydrocarbons including isobutane and normal butenes together with the light hydrocarbon fraction rich in the monoolefin of less than four carbon atoms to the action of an alkylation catalyst under alkylation conditions whereby isobutane is alkylated by said monoolefin and normal butenes to produce high antiknock hydrocarbons within the gasoline boiling range.

11. The process of claim 10 wherein the alkylation catalyst is an aluminum halide hydrocarbon complex and wherein the light hydrocarbon fraction contains ethylene.

GEORGE G. LAMB.
FORD H. BLUNCK.