

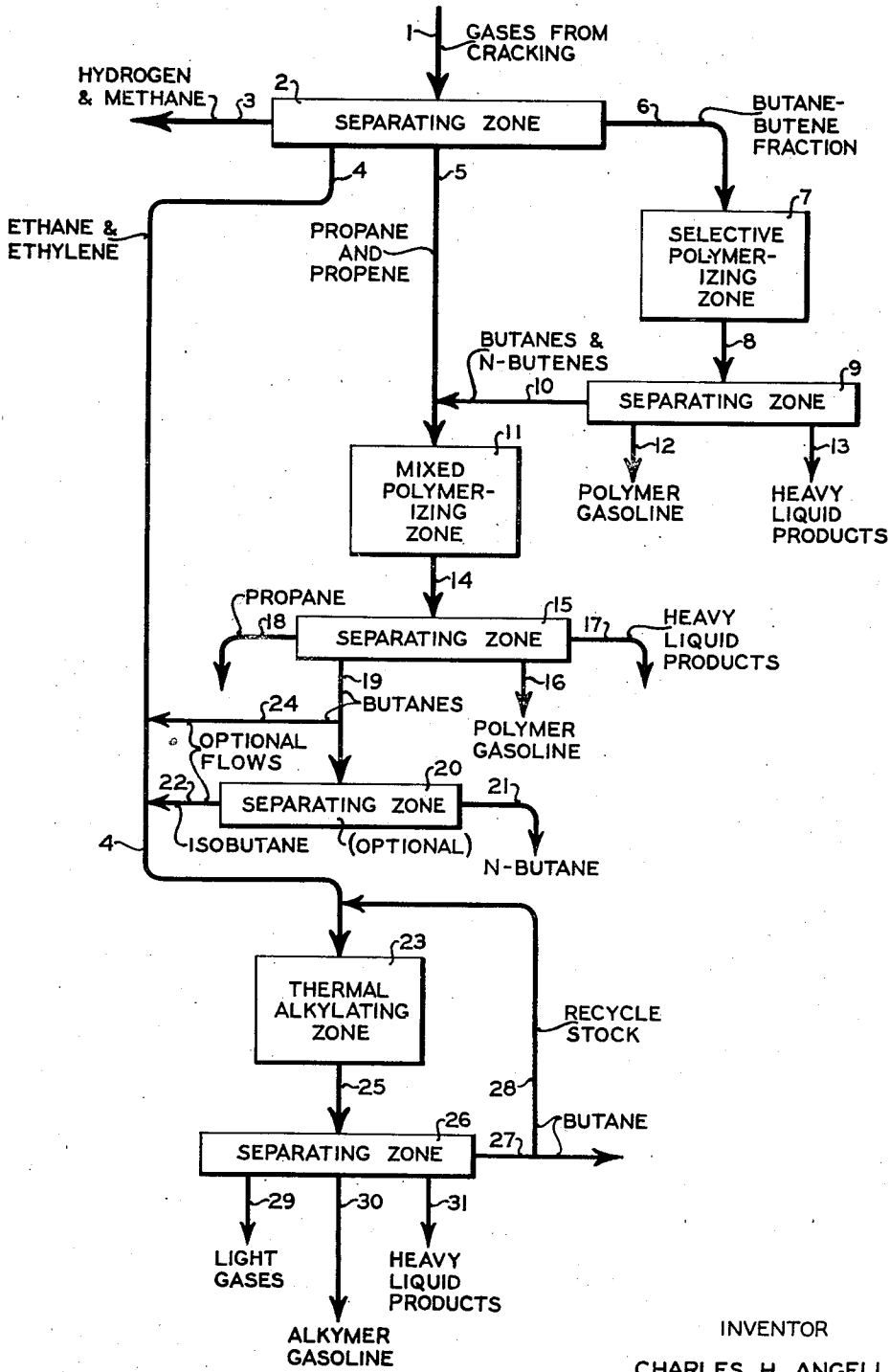
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the production of high quality gasoline from gases containing olefins and paraffins of 2, 3, and 4 carbon atoms per molecule such as are formed during cracking of hydrocarbon oils including crude petroleum, gas oil, topped crude oil, and oils produced from coal or from other sources. The invention involves a series of steps which are so combined as to cooperate in a novel and advantageous manner to produce an improved result.

In one specific embodiment the present invention comprises a process for producing motor fuel of high antiknock value which comprises separating cracked gases into a light fraction containing hydrogen and methane, an ethane-ethylene fraction, a propane-propene fraction, and a butane-butene fraction; subjecting said butane-butene fraction to selective polymerization to substantially convert isobutene into di-isobutene and form an unconverted gaseous fraction containing butanes and normal butenes; commingling said unconverted fraction containing butanes and normal butenes with said propane-propene fraction to form a commingled mixture; subjecting said commingled mixture to catalytic polymerization to form a product substantially free from normally gaseous olefins; fractionating said product into propane, butanes, polymer gasoline, and heavy liquid products; subjecting said butanes or optionally isobutane alone, to thermal alkylation by said ethane-ethylene fraction to form a substantially saturated product; separating said substantially saturated product into light gases, butane recycle stock, alkylmer gasoline, and heavy liquid products; and recycling at least a portion of said butane recycle stock to further thermal alkylation treatment.

An essential feature of the invention is the selective polymerization of isobutene in a primary polymerizing zone to form a substantial proportion of di-isobutene and mixed polymerization of residual normal butenes and propene in a secondary polymerizing zone to produce polymers of motor fuel boiling range followed by separation of the residual butanes which are thermally alkylated by ethylene to form a substantially saturated alkylmer gasoline of high antiknock value. With catalytic hydrogenation of the iso-butene polymers and also of the mixed polymers of propene and normal butenes, the 2, 3, and 4 carbon atom hydrocarbons charged are converted into a substantial yield of paraffinic motor fuel fractions of high antiknock value.

The invention resides not in any individual step of the process per se, but rather in the advantageous combination of steps which cooperate to produce the desired final result, namely, conversion of substantially all of the ethylene, propene, butenes, and isobutane contained in the cracked gas into relatively high yields of high antiknock

liquid hydrocarbons boiling within the range of gasoline.

The invention is of course not limited to the use of a charging stock consisting essentially of paraffins and olefins of 2, 3, and 4 carbon atoms per molecule, although the invention is primarily concerned with the treatment of such charging stock containing isobutane and the olefins, ethylene, propene, and butenes. Suitable charging stock may be separated within the scope of the invention from a mixture of normally gaseous and normally liquid hydrocarbons wherein these desired 2, 3, and 4 carbon atom hydrocarbons are included in substantial quantities with other components of the mixture.

It is also within the scope of the invention, when desired, to hydrogenate the polymer gasoline obtained from isobutene and from the mixed polymerization of normal butene and propene. In most instances it is preferable to separately hydrogenate the two polymer gasolines so that their respective products may be recovered separately without contaminating the hydrogenated product from the isobutene polymerizing step with the hydrogenated product from the propene-normal butene polymerizing step which has a lower octane number.

As previously indicated, no novelty is claimed herein for any of the individual conversion steps of the process per se. Various polymerizing and hydrogenating catalysts suitable for use in different catalytic conversion steps of the process as well as the operating conditions of temperature, pressure, and time of contact which may be employed successfully with each of the different catalysts and, in the thermal alkylating step of the process, to effect the desired predominating reactions are well known to those familiar with the art. It is therefore considered unnecessary to recite herein the various catalysts and/or specific operating conditions for conducting each of the steps of the process. Neither is the invention concerned with a specific method or methods whereby various satisfactory catalysts are produced. However, the following paragraphs will illustrate the operating conditions suitable in each of the process steps when utilizing the particular catalyst specified.

By the process of this invention, a gas comprising essentially paraffins and olefins is separated into ethane-ethylene, propane-propene, and butane-butene fractions. The resulting butane-butene fraction is subjected to catalytic polymerization in the presence of sulfuric acid of 60-70% concentration at a temperature between about 65° and 100° F. under a liquefying pressure to selectively absorb isobutene in the acid phase which is separated from the unconverted 4-carbon atom hydrocarbons comprising essentially butanes and normal butenes. The sulfuric acid

containing absorbed isobutene is then subjected to a temperature of about 210° F. to form isobutene polymers and regenerate sulfuric acid. The resulting isobutene polymers containing a substantial proportion of di-isobutene are hydrogenatable to iso-octane of 100 octane number.

The butane-butene fraction separated from the cracked gas may alternatively be subjected to contact with a so-called solid phosphoric acid catalyst as described in U. S. Patent No. 1,993,513 and others to effect substantially selective polymerization of isobutene. A catalyst temperature between about 75° and 200° F. is generally suitable for polymerizing isobutene with simultaneously no polymerization of normal butenes also contained in most butane-butene fractions. Suitable polymerizing pressure is within the approximate limits of 200 and 1500 pounds per square inch.

The 4-carbon atom hydrocarbons removed from the primary polymerizing step are commingled with a propane-propene fraction and the mixture is then subjected to further polymerizing treatment in the presence of solid phosphoric acid catalyst at a temperature between about 225° and about 550° F. under a pressure within the approximate limits of 100 and 1500 pounds per square inch to form a polymer gasoline which is separated from the unconverted isobutane, normal butane, and propane.

Branched chain polymers formed from isobutene and from mixtures of propene and normal butenes in the presence of sulfuric acid or of solid phosphoric acid catalyst are hydrogenated to substantially paraffinic products by means of hydrogen introduced from an outside source or separated from the gases charged to the process. Any suitable hydrogenating catalyst may be employed such as reduced nickel, nickel supported on a substantially inert carrier as diatomaceous earth, mixtures of nickel and copper, as well as oxides or sulfides of chromium, molybdenum, tungsten, and vanadium. Hydrogenation of olefin polymers in the presence of a mixture of nickel and diatomaceous earth is generally effected at a temperature of from about 150° to about 500° F. and under a pressure of from substantially atmospheric to approximately 2000 pounds per square inch although the use of higher pressure may occasionally be desirable.

The mixture of unconverted isobutane, normal butane, and propane remaining after the second polymerizing treatment is separated into propane and a mixture of butanes. When desired, said mixture of butanes is separated further into normal butane and isobutane and said isobutane is commingled with the ethane-ethylene fraction obtained from the gas mixture charged. The resulting commingled mixture containing isobutane and generally between about 1 and 10 mole per cent of ethylene is directed to a thermal alkylating treatment at a temperature of from about 750° to about 1000° F. under a pressure usually in excess of 1000 pounds per square inch but generally from about 1000 to about 4000 pounds per square inch to effect a substantial conversion of said isobutane and ethylene into substantially saturated liquid hydrocarbons of high antiknock value. As an alternative operation the mixture of butanes recovered from the products of the second polymerizing treatment may be commingled with the ethane-ethylene fraction and then subjected to thermal alkylation under substantially the same conditions set forth for the similar treatment of isobutane by said ethane-

ethylene fraction. The thermal alkylation products are separated into light gases, an unconverted butane fraction, alkylmer gasoline, and heavy liquid products. At least a portion of said unconverted butane fraction is recycled to further thermal alkylating treatment.

The accompanying drawing is a flow diagram illustrating one specific combination of steps by which the present invention may be carried out for producing gasoline of high octane number from normally gaseous hydrocarbons comprising essentially paraffins and olefins having 2, 3, and 4 carbon atoms per molecule.

Referring to the drawing, a gaseous charging stock containing 2-, 3-, and 4-carbon atom olefins and paraffins as well as methane and hydrogen is supplied through line 1 to separating zone 2 which comprises absorbing, stripping, and fractional distilling equipment of conventional form designed to substantially separate said gaseous charging stock into a light fraction containing hydrogen and methane, an ethane-ethylene mixture, a propane-propene fraction, and a butane-butene fraction. Said light fraction is discharged from separating zone 2 through line 3 to storage, to hydrogenation of polymers as hereinafter set forth, or to any other use desired. The ethane-ethylene mixture, propane-propene fraction, and butane-butene fraction are directed through lines 4, 5, and 6, respectively, to further use as hereinafter set forth.

The butane-butene fraction separated from lighter products in separating zone 2 and directed therefrom through line 6, is introduced to selective polymerizing zone 7 in which substantially all of the isobutene contained in said butane-butene fraction is polymerized to normally liquid polymers containing a substantial proportion of di-isobutene. Selective polymerizing zone 7 comprises a reactor in which said butane-butene fraction is subjected to contact with sulfuric acid of between about 60% and about 70% concentration at a temperature from about 65° to about 100° F. under a liquefying pressure to selectively absorb isobutene in the acid phase, after which said acid phase is separated from the unconverted 4-carbon atom hydrocarbons comprising essentially butanes and normal butenes. Said sulfuric acid phase containing absorbed isobutene possibly in the form of a sulfuric acid ester, is then heated in zone 7, by means not shown, to a temperature of about 210° F. to form isobutene polymers and to regenerate sulfuric acid which is used again in absorbing isobutene from the butane-butene fraction being charged to the selective polymerizing zone.

Substantially selective polymerization of isobutene is also effected at a temperature between about 75° and 200° F. under a liquefying pressure in the presence of solid phosphoric acid catalyst which comprises essentially a calcined composite of an acid of phosphorus and a siliceous carrier. Under these conditions a substantial proportion of the isobutene present is converted into diisobutene with relatively little simultaneous polymerisation of normal butenes.

The polymers formed in selective polymerizing zone 7, together with butanes and unconverted butenes, are directed therefrom through line 8 to separating zone 9 which comprises conventional fractional distilling equipment designed to separate a mixture of butanes and unconverted butenes from polymer gasoline consisting predominantly of di-isobutene and from relatively small amounts of heavy liquid products. Said mixture

of butanes and unconverted normal butenes is directed from separating zone 9 through line 10 and 5 to further polymerizing treatment in mixed polymerizing zone 11 hereinafter described. Polymer gasoline is withdrawn through line 12 to storage or directed to a hydrogenating treatment, not shown, to produce therefrom a substantially paraffinic motor fuel of high antiknock value containing a substantial proportion of isomeric octanes. Heavy liquid products boiling higher than octenes and generally higher than gasoline are withdrawn from separating zone 9 through line 13 to storage or to other use as desired.

The mixture of butanes and unconverted, substantially normal butenes separated from polymer gasoline and from heavy liquid products and directed from separating zone 9 through line 10 to line 5 is therein commingled with a propane-propene fraction and the commingled mixture is directed to mixed polymerizing zone 11 containing a solid phosphoric acid catalyst and maintained at a temperature between about 225° and 550° F. under a pressure within the approximate limits of 100 and 1500 pounds per square inch to convert said propene and butenes into polymers which are in admixture with unconverted propane and butanes. The polymerization products are directed from mixed polymerizing zone 11 through line 14 to separating zone 15 which comprises conventional fractionating equipment designed to separate propane, a mixture of isobutane and normal butane, a polymer gasoline, and heavy liquid products. Said polymer gasoline is withdrawn from separating zone 15 through line 16 to storage or to a subsequent hydrogenating treatment, not shown, in order to form a substantially paraffinic product of high anti-knock value suitable for use as aviation fuel. The heavy liquid products and propane are discharged from separating zone 15 through lines 17 and 18, respectively, to storage or to any use.

Optionally, the mixture of unconverted butanes separated from the polymerization products in zone 15 as hereinabove set forth, is directed through line 19 to optional separating zone 20 which comprises conventional fractionating equipment designed to substantially separate isobutane and normal butane. From zone 20 said normal butane is withdrawn through line 21 to storage or to other use while the isobutane fraction is directed through line 22 to line 4 through which said ethane-ethylene mixture separated from the gas charged is being directed to thermal alkylating zone 23. When desired, the mixture of butanes separated from the products of the second polymerizing treatment may be directed from line 19 through optional line 24 to line 4, therein commingled with said ethane-ethylene mixture, and thence directed to thermal alkylation in zone 23. Such treatment of the butane mixture is frequently advantageous as both isobutane and normal butane are convertible by thermal alkylation into normally liquid, substantially saturated hydrocarbons of high antiknock value.

The commingled mixture containing at least one butane and an ethane-ethylene mixture is introduced to thermal alkylation zone 23 which comprises a reactor or group of reactors of adequate design for operating at a temperature between about 750° and 1000° F. under a pressure within the approximate limits of 1000 and 4000 pounds per square inch. In order to promote alkylation and to prevent excessive olefin polymerization, it is preferable that not more than from about 1 to about 10 mole per cent of olefin be present

in the hydrocarbon mixture being charged to alkylation. The olefin-containing mixture may be commingled with the butane fraction prior to introduction to the alkylating zone, but to assist in diminishing olefin polymerization and in dissipating the heat liberated during alkylation, it is preferable that the olefinic hydrocarbon or hydrocarbon mixture containing olefins be added in relatively small increments throughout the length of the alkylation zone.

The products of thermal alkylation which contain substantial proportions of branched chain hexanes, as neohexane, and higher boiling paraffins are directed from zone 23 through line 25 to separating zone 26 which comprises fractional distilling equipment of conventional form designed for separately recovering from the products light gases, an unconverted butane fraction, alkylmer gasoline, and heavy liquid products. Said unconverted butane fraction is withdrawn from separating zone 26 through line 27, in part to storage, when desired, while at least a portion of said unconverted butane fraction is directed from line 27 through line 28 and recycled to line 4 through which the commingled mixture of butane, ethane, and ethylene is being directed to thermal alkylating zone 23 as hereinabove set forth. In zone 23 a relatively high concentration of butane, iso and/or normal, is necessary in order to suppress polymerization of the ethylene present. From separating zone 26 light gases, alkylmer gasoline, and heavy liquid products are withdrawn to storage or to other use through lines 29, 30, and 31, respectively.

The following example is introduced to show results which may be expected in one specific operation of the process although with no intention of unduly limiting the generally broad scope of the invention:

A gas formed during cracking of a crude oil and having the composition indicated in the following table, is separated into a butane-butene fraction, a propane-propene fraction, an ethane-ethylene fraction, and a mixture of methane and hydrogen.

TABLE
Analysis of gas from cracking

	Mole per cent
Hydrogen	3.2
Methane	9.5
Ethylene	13.2
Ethane	16.7
Propene	7.8
Propane	12.9
i-Butane	8.2
i-Butene	5.9
n-Butene	9.7
n-Butane	9.9
Pentane and higher	3.0

The butane-butene fraction separated from the cracked gas is subjected to contact with sulfuric acid of 66% concentration at 75° F. under a pressure of 200 pounds per square inch to selectively absorb isobutene in the sulfuric acid phase which is separated from unconverted butanes and normal butenes, and thereafter heated at 200-210° F. to form polymers containing a substantial proportion of di-isobutene and to regenerate sulfuric acid which is returned to absorb a further quantity of isobutene from the butane-butene fraction charged.

After selectively removing isobutene, the remaining mixture of unconverted normal butenes

and butanes is commingled with the propane-propene fraction of the gas charged and the resulting mixture of 3- and 4-carbon atom olefins and paraffins is contacted with a calcined composite of pyrophosphoric acid and diatomaceous earth at 425° F. under a pressure of 750 pounds per square inch to effect substantially complete conversion of propene and normal butenes into normally liquid polymers easily separable by fractional distillation from propane and a mixture of unconverted isobutane and normal butane. The ethane-ethylene fraction separated from the cracked gas is commingled with the butanes recovered from the products of the second polymerizing treatment, the ethane-ethylene fraction being added in sufficient amount so that the resulting mixture contains approximately 5 mole per cent of ethylene. Said mixture is subjected to thermal alkylation at 950° F. under a pressure of 4500 pounds per square inch to form isomeric hexanes and higher boiling paraffins admixed with unconverted butanes which are separated therefrom and recycled to further thermal alkylating treatment. By this process substantially all of the olefinic hydrocarbons, the butanes, and a portion of the propane contained in the cracked gas are converted into high antiknock gasoline suitable for use as aviation motor fuel.

Neither the foregoing example nor the drawing should, be interpreted as restricting the broader aspects of the invention as defined in the appended claims. Certain alternatives and refinements which are not illustrated in the drawing will be readily apparent to those familiar with the art, in view of the advantageous combination illustrated, and fall within the scope of the broad concepts of the invention. For example, the invention contemplates the elimination, when desired, of the selective polymerizing step of the system illustrated in case the production of a polymer gasoline which may be hydrogenated to produce a motor fuel meeting the requirements for aviation gasoline, is not an essential objective. In such instances the fraction supplied to the mixed polymerizing step will comprise substantially all of the iso and normal butenes, as well as the butanes, propane and propene and this step will be operated to form mixed polymers or inter-polymers of propene and butenes which have a good antiknock value and may be used in motor gasoline but are not susceptible to improvement in octane number upon hydrogenation. It is also within the scope of the invention, when desired, to effect polymerization of substantially all of the normal butenes, as well as substantially all of the isobutene in the polymerization step to which the butane-butene fraction is supplied. In such instances a polymer gasoline product of somewhat lower octane number will be produced as compared with that resulting from selective polymerization of the isobutene, but it may still be hydrogenated to improve its antiknock value and give a substantially saturated product. When this last mentioned method of operation is employed, only the propane-propene fraction will be supplied to polymerizing zone 11 and residual butanes from the butene polymerizing step will be supplied to separating zone 20 or directly to the thermal alkylating zone.

The invention also contemplates the removal of a portion of the ethane-ethylene fraction from the system without supplying it to the alkylating step or, alternatively, the introduction of normal

or isobutane, or both, from an external source to separating zone 20 or to the alkylating zone in order to maintain the desired relatively high ratio of butane to ethylene in the mixture subjected to alkylation.

I claim:

1. The process of converting normally gaseous olefins and paraffins into gasoline fractions of good antiknock value which comprises, separating from a mixture of hydrocarbons, which includes both olefinic and paraffinic fractions having 2, 3 and 4-carbon atoms in the molecule, a fraction consisting predominantly of butanes and butenes, a fraction consisting predominantly of propane and propene and a fraction consisting predominantly of ethane and ethylene, subjecting the butane-butene fraction to catalytic polymerization to convert substantially all of its iso-butene components into liquid polymers comprising gasoline fractions rich in iso-octenes and leave an unconverted normally gaseous fraction consisting predominantly of butanes and normal butenes, commingling the last named fraction with said propane-propene fraction, subjecting the mixture to catalytic polymerization in a second polymerizing step to convert substantially all of its normal butene components and at least a portion of its propene components to form mixed polymers of propane and normal butenes comprising another polymer gasoline of good antiknock value and leaving unconverted normally gaseous fractions consisting predominantly of propane and butanes, separating substantially pure butanes from the residual normally gaseous fractions of the second polymerization step, commingling said butanes with regulated quantities of the aforementioned ethane-ethylene fraction, subjecting the mixture to thermal alkylation to react substantially all of its ethylene components with a substantially equal molal proportion of its butane components and form a substantially saturated product comprising alkylmer gasoline of good antiknock value, separating substantially pure unconverted butane from the other products of the alkylating step and recycling regulated quantities thereof to the alkylating step.

2. The process of converting normally gaseous olefins and paraffins into gasoline fractions of good antiknock value which comprises, separating from a mixture of hydrocarbons, which contains both olefinic and paraffinic fractions having 2, 3 and 4-carbon atoms in the molecule, a fraction consisting predominantly of butanes and butenes, a fraction consisting predominantly of propane and propene and a fraction consisting predominantly of ethane and ethylene, subjecting the butane-butene fraction to catalytic polymerization to convert substantially all of its iso-butene components into liquid polymers comprising gasoline fractions rich in iso-octenes and leave an unconverted normally gaseous fraction consisting predominantly of butanes and normal butenes, commingling the last named fraction with said propane-propene fraction, subjecting the mixture to catalytic polymerization in a second polymerizing step to convert substantially all of its normal butene components and at least a portion of its propene components to form mixed polymers of propene and normal butenes comprising another polymer gasoline of good antiknock value and leaving unconverted normally gaseous fractions consisting predominantly of propane and butanes, separating substantially pure iso-butane from the residual normally gaseous fractions of the second polymerization step.

commingling said iso-butane with regulated quantities of the aforementioned ethane-ethylene fraction, subjecting the mixture to thermal alkylation to react substantially all of its ethylene components with a substantially equal molal proportion of its iso-butane components, forming a substantially saturated product comprising alkylmer gasoline of good antiknock value, separating substantially pure unconverted iso-butane from the other products of the alkylating step and recycling regulated quantities thereof to the alkylating step.

3. The process of converting normally gaseous olefinic and paraffinic hydrocarbons into good antiknock gasoline fractions which comprises, separating from a mixture of hydrocarbons, which includes both olefinic and paraffinic fractions having 2, 3 and 4-carbon atoms in the molecule, a fraction consisting predominantly of butanes and butenes, a fraction consisting predominantly of propane and propene and a fraction consisting predominantly of ethane and ethylene, subjecting the butane-butene fraction to catalytic polymerization to convert substantially all of its iso-butene components and not more than an equal molal proportion of its normal butene components into liquid polymers comprising gasoline fractions rich in iso-octenes, separating from the products of the polymerizing step said polymer gasoline, any heavier liquid fractions and an unconverted normally gaseous fraction consisting predominantly of butanes and normal butenes, commingling the last named fraction with said propane-propene fraction, subjecting the mixture to separate catalytic polymerization to convert substantially all of its normal butene components and at least a portion of its propene components into liquid polymers comprising another polymer gasoline of good antiknock value, separating from the products of the last named polymerizing step said polymer gasoline, any heavier liquid fractions, a fraction consisting predominantly of unconverted butanes and a fraction consisting predominantly of lighter gases, commingling unconverted butanes thus recovered from the products of the second polymerizing step with regulated quantities of the aforementioned ethane-ethylene fraction, subjecting the mixture to thermal alkylation, to react substantially all of its ethylene components with a substantially equal molal proportion of its butane components to form a substantially saturated product comprising alkylmer gasoline of good antiknock value, separating from the alkylation products said alkylmer gasoline, any heavier liquid fractions, a fraction consisting predominantly of unconverted butanes and a fraction consisting predominantly of lighter gases and recycling regulated quantities of said unconverted butane fraction to the alkylation step.

4. The process of converting normally gaseous olefinic and paraffinic hydrocarbons into good antiknock gasoline fractions which comprises, separating from a mixture of hydrocarbons, which includes both olefinic and paraffinic fractions having 2, 3 and 4-carbon atoms in the molecule, a fraction consisting predominantly of butanes and butenes, a fraction consisting predominantly of propane and propene and a fraction consisting predominantly of ethane and ethylene, subjecting the butane-butene fraction to catalytic polymerization to convert substantially all of its iso-butene components and not more than an equal molal proportion of its normal butene

components into liquid polymers comprising gasoline fractions rich in iso-octenes, separating from the products of the polymerizing step said polymer gasoline, any heavier liquid fractions and an unconverted normally gaseous fraction consisting predominantly of butanes and normal butenes, commingling the last named fraction with said propane-propene fraction, subjecting the mixture to separate catalytic polymerization to convert substantially all of its normal butene components and at least a portion of its propene components into liquid polymers comprising another polymer gasoline of good antiknock value, separating from the products of the last named polymerizing step said polymer gasoline, any heavier liquid fractions, a fraction consisting predominantly of unconverted normal butane, a fraction consisting predominantly of unconverted iso-butane and a fraction consisting predominantly of lighter gases, commingling said iso-butane fraction with regulated quantities of the aforementioned ethane-ethylene fraction, subjecting the mixture to thermal alkylation to react substantially all of its ethylene components with a substantially equal molal proportion of its iso-butane components to form liquid products comprising alkylmer gasoline of good antiknock value and leave unconverted iso-butane and lighter gases, separating from the products of the alkylation step said alkylmer gasoline, any heavier liquid fractions, a substantially pure iso-butane fraction and a lighter gaseous fraction which is predominantly ethane, and recycling the iso-butane fraction to the alkylating step in quantities regulated to maintain a high proportion of iso-butane to ethylene in the mixture supplied thereto.

5. A process for producing more valuable products from a hydrocarbon mixture containing olefins and paraffins of 2, 3 and 4 carbon atoms to the molecule, which comprises fractionating the mixture to separate therefrom a C₂ fraction, a C₃ fraction and a C₄ fraction, subjecting the C₄ fraction to selective polymerization to polymerize isobutene, commingling unpolymerized normal butenes and butanes from the last-mentioned step with said C₃ fraction and subjecting the resultant mixture to polymerization to polymerize normal butenes and propene, separating from the residual gaseous products of the last-named polymerization a C₄ fraction containing isobutane and commingling the same with said C₂ fraction, and subjecting the mixture thus formed to alkylation to react ethylene with isobutane.

6. A process for producing more valuable products from a hydrocarbon mixture containing olefins and paraffins of 2, 3 and 4 carbon atoms to the molecule, which comprises fractionating the mixture to separate therefrom a C₂ fraction, a C₃ fraction and a C₄ fraction, subjecting the C₄ fraction to selective polymerization to polymerize isobutene, commingling unpolymerized normal butenes and butanes from the last-mentioned step with said C₃ fraction and subjecting the resultant mixture to polymerization to polymerize normal butenes and propene, separating from the residual gaseous products of the last-named polymerization a substantially pure iso-butane fraction and commingling the same with said C₂ fraction, and subjecting the mixture thus formed to alkylation to react ethylene with isobutane.

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