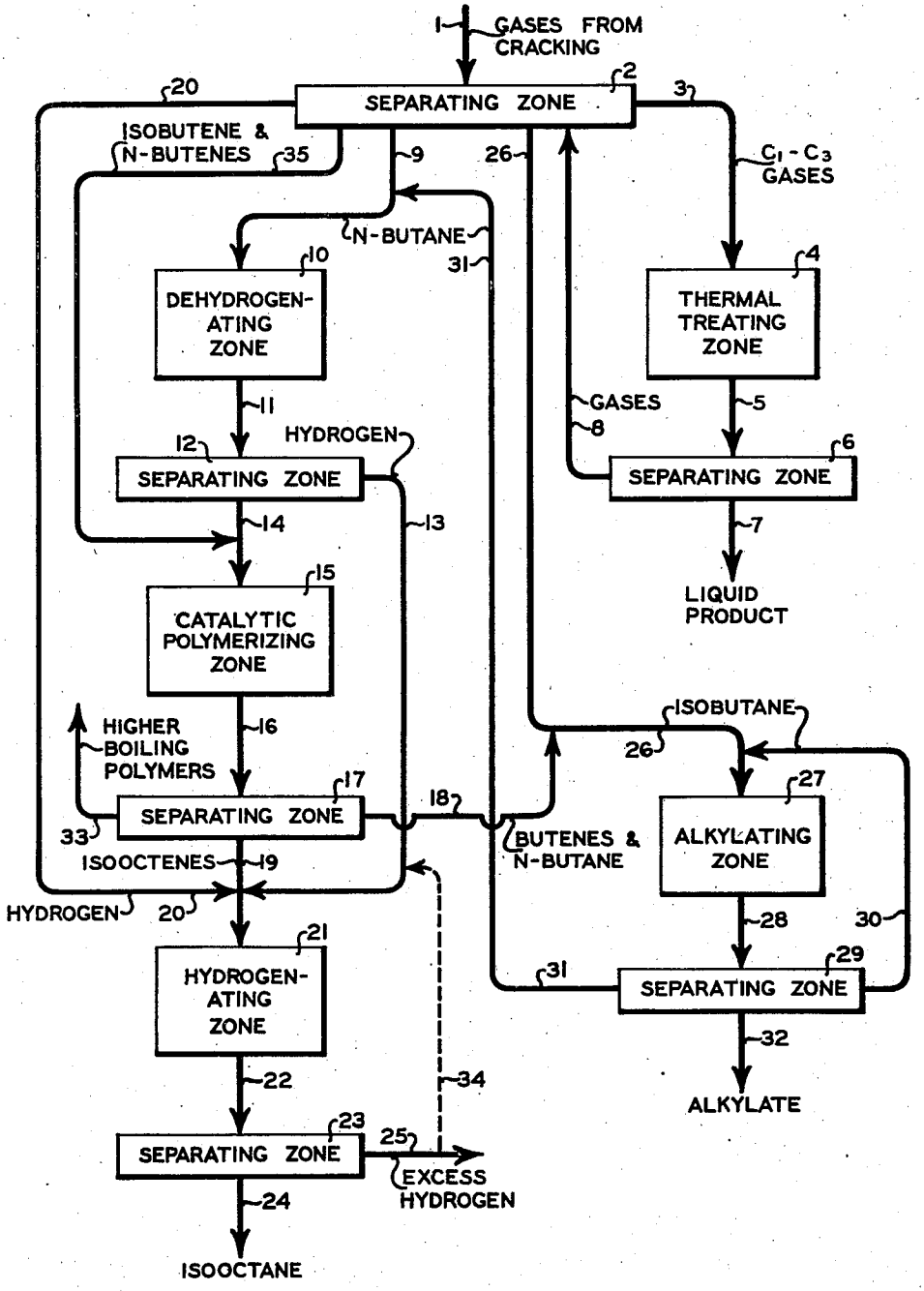
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the production of high quality gasoline from gases produced during the cracking of hydrocarbon oils such as crude petroleum, gas oil, topped crude oil, and oils produced from coal or from other sources. The invention involves a series of individual steps which are combined so as to cooperate in a novel and advantageous manner to produce the desired result.

In one specific embodiment the present invention comprises a process for producing substantial yields of motor fuel of high antiknock value from gases produced in the cracking of hydrocarbon oils which comprises separating said gases into hydrogen, a C_1—C_3 fraction, normal butane, isobutane, and an isobutene-normal butene mixture; thermally treating said C_1—C_3 fraction to form liquid products of gasoline boiling range and a residual gas containing C_4 hydrocarbons; returning said residual gas to the primary gas separating step; dehydrogenating normal butane to produce substantial proportions of butenes and hydrogen; commingling said butenes with said isobutene and normal butenes separated from the gas charged; selectively polymerizing said isobutene and normal butenes to form a product containing substantially no isobutene; separating said product into an iso-octene fraction, higher boiling polymers, and a mixture of unconverted butenes and normal butane; hydrogenating said iso-octene fraction with hydrogen separated from the original gas and from the normal butane dehydrogenation products to form a substantially iso-octane fraction; subjecting isobutane to alkylation by butenes contained in said mixture of unconverted butenes and normal butane to form a substantially saturated alkylation product; separating said alkylation product into unconverted isobutane, recovered normal butane, and a substantially saturated alkylate; recycling said unconverted isobutane to further alkylation treatment, and returning said recovered normal butane to dehydrogenation.

The principal steps of the process include thermal treatment of a C_1—C_3 fraction, dehydrogenation of normal butane to normal butenes, selective polymerization of isobutene and normal butenes separated from the gas charged and from the dehyrogenation products to form a polymer fraction containing a substantial proportion of iso-octenes, hydrogenation of iso-octenes by hydrogen recovered in the process, and alkylation of isobutane separated from the charge by n-butenes contained in the gases remaining after selective polymerization. Although the individual steps may be known to those skilled in the respective arts, the feature of the present invention is that they are combined in a novel and advantageous manner so that they cooperate to produce the desired result.

One essential feature of the invention is the thermal treatment applied to a C_1—C_3 fraction comprising methane, ethane, ethylene, propane, and propene to produce therefrom substantial yields of liquid products and of 4-carbon atom olefins and paraffins. Through the use of this step, additional quantities of butenes and butanes may be made available for subsequent use in the production of iso-octane by alkylation or by polymerization and hydrogenation reactions.

In the accompanying drawing, in order to illustrate the process of the invention without complicating it with unnecessary details of each specific step and since those skilled in the art are now generally familiar with the major steps of the process, the general practice of illustrating each specific step in detail has been departed from and a flow diagram has been used instead.

Referring to the accompanying diagram of a typical process flow, a gaseous charging stock obtained from cracking of a hydrocarbon oil is supplied through line 1 to separating zone 2 wherein are separated hydrogen, a C_1—C_3 hydrocarbon fraction, isobutane, normal butane, and a mixture of isobutene and normal butenes. Separating zone 2 may comprise absorbing, stripping, fractional distilling, solvent extracting or azeotropic distilling, etc. equipment of suitable design for effecting the aforementioned separations.

From separating zone 2 a C_1—C_3 fraction may be conducted through line 3 to thermal treating zone 4 which may comprise a reactor of suitable design operating at a temperature in the approximate range of 800–1100° F. and under a pressure of the order of 100–2000 pounds per square inch in order to form substantial yields of liquid products and a butene-containing fraction which may be conducted thence through line 5 to separating zone 6 in which reacted products may be withdrawn through line 7 to storage and a gas fraction containing substantial proportions of 4-carbon atom olefins and paraffins may be recycled through line 8 to separating zone 2.

Normal butane separated in separating zone 2 may be conducted therefrom through line 9 to dehydrogenating zone 10 which may comprise a tubular reactor or group of reactors main-

tained at a temperature in the approximate range of 750–1200° F. under a pressure of from substantially atmospheric to approximately 100 pounds per square inch and containing a granular material comprising a major proportion of a refractory carrier and a relatively smaller proportion of a compound of greater dehydrogenating activity than said carrier such as an oxide of an element selected from the members of the left-hand columns of groups IV, V, and VI of the periodic table. Although the dehydrogenating catalysts hereinabove set forth are the preferred catalysts, they are not to be considered as a limiting feature of the process for various other dehydrogenating catalysts known to those skilled in the art may be employed within the broad scope of this invention.

The conversion products from dehydrogenating zone 10, of which a substantial proportion are normal butenes, may be directed through line 11 to separating zone 12 wherein hydrogen resulting from the dehydrogenation of normal butane is separated from the heavier gaseous hydrocarbons comprising essentially normal butenes and unconverted normal butane. Separating zone 12 will ordinarily comprise an absorbing zone where hydrogen and light gaseous hydrocarbons such as methane are separated from higher molecular weight hydrocarbons and a distilling or stripping step wherein said higher molecular weight hydrocarbons are liberated from the absorption medium. However, other means for effecting separation may be employed in separating zone 12 obviating the necessity of absorbing and stripping steps such as, for example, a compressor all of which are within the broad concepts of this invention. The hydrogen or gas mixture containing a substantial proportion of hydrogen separated in separating zone 12 is directed, in the case here illustrated, through line 13 to line 19 for use as subsequently described. The normally gaseous hydrocarbons separated in separating zone 12 and comprising essentially normal butenes and unconverted normal butane may be directed through line 14 to catalytic polymerizing zone 15. A mixture comprising essentially isobutene and normal butenes separated in separating zone 2 by solvent extraction or by azeotropic distillation, for example, in the presence of sulfur dioxide, may be conducted thence through line 35 to line 14 and therein commingled with the butene-containing fraction being conducted to polymerization in catalytic polymerizing zone 15 in which isobutene and a portion of the normal butenes may be converted into substantial yields of isomeric octenes hydrogenatable to iso-octanes of high octane number.

A sulfuric or phosphoric acid catalyst may be employed in polymerizing zone 15 at a temperature so regulated in the presence of either of these catalysts as to effect conversion into polymers of substantially all of the isobutene and a portion of the normal butenes. When sulfuric acid of approximately 60–80% concentration is the polymerizing catalyst, temperatures of the order of 80–200° F. may be used under a pressure sufficient to force through the plant the mixture of acid and hydrocarbons. When a phosphoric acid is used as polymerizing catalyst, generally in the form of a calcined composite with a siliceous adsorbent as described in United States Patent No. 1,993,513 and others, polymerization may be effected at a temperature in the approximate range of 225–350° F. under a pressure in the approximate range of 500–1500 pounds per square inch.

The resulting polymerization products which consist of normally liquid polymers, containing iso-octenes, some higher boiling materials, and unconverted gases comprising essentially normal butenes and normal butane, are withdrawn from polymerizing zone 15 through line 16 to separating zone 17 which may comprise a fractional distilling column by which unconverted butenes and normal butane may be separated from the butene polymers. Separating zone 17 will ordinarily comprise a fractionating zone wherein liquid polymers boiling above the desired iso-octene fraction are separated and a debutanizing zone wherein residual gases consisting essentially of butenes and butane are separated from said iso-octene fraction. Although as described above the fractionating zone will ordinarily precede the debutanizing zone, this is not essential, and the individual zones may be used in reverse order. The mixture of unconverted butenes and normal butane is withdrawn from separating zone 17 through line 18 to line 26 for further treatment as will be described subsequently. Higher boiling polymers separated from iso-octenes in separating zone 17 may be conducted thence through line 33 to storage or to further use.

An iso-octene fraction is withdrawn from separating zone 17 through line 19 and therein commingled with hydrogen contained in the original charge and conducted from separating zone 2 through line 20 and with hydrogen separated from normal butane dehydrogenation products in separating zone 12, and conducted therefrom through line 13 as already mentioned. The commingled mixture of iso-octenes and hydrogen is then introduced to hydrogenating zone 21 wherein said iso-octene is hydrogenated to an iso-octane fraction of high antiknock value generally in the approximate range of 95–100 octane number. Hydrogenation in zone 21 is accomplished in the presence of a catalyst which preferably consists of nickel supported by a relatively porous siliceous carrier such as diatomaceous earth. This catalyst may be produced by precipitating nickel carbonate on diatomaceous earth and forming the composited material into pellets which are dried, calcined, and then reduced with hydrogen at a temperature of approximately 750° F. However, other hydrogenating catalysts well known in the art such as, for example, oxides of chromium, molybdenum, and tungsten may be employed when desired. Hydrogenation may be carried out preferably under a superatmospheric pressure ranging, for example, from 100 to 300 pounds or more per square inch and at a temperature in the approximate range of 200–500° F. The resulting products including the unused excess hydrogen are directed from zone 21 through line 22 to separating zone 23 wherein the iso-octane fraction is separated from any normally gaseous hydrocarbons and hydrogen. The iso-octane fraction is directed through line 24 to cooling and storage or elsewhere as desired, and the gases are removed from separating zone 23 through line 25 and discharged from the system to storage or elsewhere or may, when desired, be returned by well known means, as through alternative line 34, to the hydrogenating zone for reuse of the hydrogen.

Isobutane separated in separating zone 2 from other constituents of the gas charged may be conducted therefrom through line 26, and therein commingled with a mixture of unconverted bu-

tenes and normal butane separated from polymerization products in separating zone 17, and conducted thence through line 18 as aforementioned. The commingled mixture in line 26 comprising essentially isobutane, butenes, and normal butane is then introduced to alkylating zone 27 which may comprise a suitable reactor provided with adequate means for agitating, cooling, and/or heating to maintain a temperature in the approximate range of —15 to 200° F. generally required for alkylation in the presence of a chosen alkylating catalyst such as sulfuric acid, hydrogen fluoride, a mixture of boron fluoride and hydrogen fluoride, or aluminum chloride with hydrogen chloride. In the presence of an alkylating catalyst of the types mentioned, it is preferable to utilize a pressure sufficient to maintain in liquid phase a substantial proportion of the reacting hydrocarbons. In case a granular calcined composite of an acid of phosphorus and a siliceous adsorbent is employed as alkylating catalyst, the reactor may be a cylindrical chamber designed to operate at a temperature in the approximate range of 600–900° F. and under a pressure in the approximate range of 1000–3000 pounds per square inch.

Alkylation products and unconverted butanes may be withdrawn from alkylating zone 27 through line 28 to separating zone 29 which may comprise a fractional distilling column of suitable design for separating an unconverted isobutane fraction, a recovered normal butane fraction, and a substantially saturated alkylate containing a relatively high proportion of an aviation gasoline fraction of high antiknock value. The unconverted isobutane fraction may be recycled from separating zone 29 through lines 30 and 26 to further alkylation in alkylating zone 27. The recovered normal butane fraction may be directed from separating zone 29 through line 31 to line 9; already mentioned, through which normal butane is conducted to dehydrogenating zone 10. The substantially saturated alkylate which comprises one of the desired products of the process may be withdrawn from separating zone 29 through line 32 to cooling and storage or elsewhere as desired.

The operating conditions which may be employed in successfully conducting the process of the invention will vary considerably depending upon the specific type of catalyst employed in each of the zones, and since no novelty is claimed for any of the processes involved in the individual steps of the system nor for the catalysts which may be used therein, and since the regulation of the operating conditions in each of the individual steps to accomplish the object herein set forth, when using any of the known catalysts, is within the skill of those familiar with the arts involved, only those conditions which may be employed when using the preferred catalysts are herein disclosed.

The following example of one specific operation of the process will serve to illustrate satisfactory operating conditions as applied to specific catalysts but should not, however, be considered as a limitation of the generally broad scope of the invention:

A gas formed in the thermal cracking of a Trinidad gas oil may be separated into a hydrogen-containing fraction, a C_1—C_3 fraction, normal butane, isobutane, and an isobutene-normal butene mixture. A typical gas charged to the process may have the composition indicated in Table I.

TABLE I

Analysis of cracked gas

	Mole per cent
Nitrogen	1.9
Carbon monoxide	0.1
Hydrogen	4.0
Methane	17.3
Ethylene	2.0
Ethane	16.3
Propene	9.2
Propane	16.9
Isobutane	4.1
Isobutene	5.5
n-Butene	9.3
Butadiene	0.1
n-Butane	9.2
Pentane and higher	4.1

Pyrolysis of the C_1—C_3 fraction at approximately 1000° F. under a pressure of 200 pounds per square inch may yield a normally liquid product of gasoline boiling range and a gaseous fraction containing methane, ethane, propane, and some butanes. Dehydrogenation of the normal butane at 950° F. under substantially atmospheric pressure in the presence of a composite comprising essentially 8% by weight of chromium sesquioxide and 92% by weight of activated alumina may produce per pass approximately 25% of normal butenes which may be commingled with the isobutene and normal butenes separable by solvent extraction of the 4-carbon atom hydrocarbon fraction of the cracked gases charged, and the commingled mixture may then be subjected to contact with a calcined composite of pyrophosphoric acid and diatomaceous earth at approximately 325° F. under a pressure of 600 pounds per square inch to produce normally liquid polymers and unconverted gases comprising essentially normal butenes and normal butane.

Fractional distillation of the normally liquid polymers may be employed to separate iso-octene from relatively small amounts of higher boiling polymers after which the iso-octenes may be hydrogenated to isomeric octanes utilizing hydrogen formed in the dehydrogenating step of the process.

Isobutane contained in the gas charged may be alkylated by butenes contained in the unconverted gases recovered from the catalytic polymerizing step and utilizing as alkylating catalyst sulfuric acid of approximately 98% concentration at a temperature of 45° F. under a pressure of 300 pounds per square inch. The excess of isobutane and normal butane commingled with the substantially saturated alkylate may be separated therefrom as by fractional distillation and may then be recycled to further alkylating and dehydrogenating treatments.

The character of the invention and the type of results obtainable are evident from the preceding specification and example, although they are not to be considered as imposing undue limitations upon its generally broad scope.

I claim as my invention:

1. A process for producing more valuable products from a gaseous hydrocarbon mixture, which comprises separating said mixture into at least three fractions, an isobutane fraction, a normal butane fraction and a fraction comprising iso and normal butenes, subjecting said normal butane fraction to dehydrogenation to form butene and hydrogen, separating butene and unconverted normal butane from said hydrogen, combining said butene and unconverted normal

butane with the iso and normal butenes and subjecting the mixture to polymerization under conditions of temperature, pressure and contact time regulated to polymerize substantially all the isobutene and only a portion of the normal butenes to isooctenes leaving a quantity of normal butene unconverted which is approximately equivalent to the volume of isobutane in said mixture, separating said isooctenes from the normal butane and unconverted butenes, combining said unconverted butenes and the normal butane with said isobutane fraction and subjecting the mixture to alkylation to form a substantially saturated gasoline from the butene and isobutane, separating the uneacted normal butane from said gasoline and returning the former to the dehydrogenation step.

2. The process of claim 1 further characterized by the steps which comprise separating a hydrogen fraction from the first named mixture, combining said hydrogen fraction with the hydrogen fraction separated from the products of dehydrogenation, and hydrogenating said isooctenes in the presence of the combined hydrogen to form isooctane.

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