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MOTOR FUEL

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This invention relates to a process of producing motor fuels and particularly motor fuels of the type of gasoline from hydrocarbon gases, more particularly the butanes and butylenes. In the cracking of petroleum oils to produce gasoline there is produced a mixture of hydrocarbon gases from which may be conveniently separated a propane fraction and a butane fraction. The butane fraction contains a mixture of the normal and isobutane and the three butylenes, i. e., 1-butene, 2-butene and isobutylene. The object of the present invention is to convert this gas fraction hereinafter referred to as the C₄ hydrocarbons into valuable motor fuel. Another object of the invention is to produce a high octane motor fuel from the C₄ hydrocarbons in higher yield than heretofore has been produced from this material. Still another object of the invention is to process a mixture of the C₄ hydrocarbons in a novel manner whereby they are converted into certain polymerization products with a chemical structure which confers upon them high anti-detonating properties instead of the products heretofore produced having undesirable chemical structure giving low anti-detonating characteristics. Other objects of the invention will be apparent from the following description.

It has been known heretofore that a mixture of butylenes can be polymerized by catalysts under various conditions of heating to yield a motor fuel having an antiknock value of about 80 octane number. It has also been known that isobutylene can be polymerized to produce diisobutylene or so-called iso-octene having a high antiknock value and that the iso-octene can be hydrogenated to produce iso-octane having an anti-knock value of about 100 octane number.

Referring to the drawing, a stream of C₄ hydrocarbons is introduced under pressure by line 10 to heater 11 where the temperature is raised to about 250 to 350° F. The hydrocarbon stream is then passed into catalyst chamber 12 containing a suitable polymerization catalyst where the pressure is suitably maintained at about 250–750 lb./sq. in., preferably at about 500 lb./sq. in. For this purpose I prefer to employ phosphoric acid on silica or on various silicates such as infusorial earth. Before introducing the feed into the polymerizer 12, however, I may add an additional amount of isobutylene by line 13 to make the concentration of isobutylene equal to or greater than the concentration of 2-butene in the C₄ fraction in case there is a deficiency of isobutylene. I may also add a small carefully regulated amount of steam to the hydrocarbons be-

fore introducing them into polymerizer 12 in order to increase the life of the catalyst and to improve the quality of the product. The conditions maintained in polymerizer 12 are such with respect to catalyst, temperature and time of reaction as to permit the 1-butene to pass through substantially unchanged.

In ordinary commercially available C₄ hydrocarbon mixtures, the concentration of 2-butene will usually be about 5 to 20%. I have found that if isobutylene is present in an equi-molecular amount with the 2-butene, these hydrocarbons polymerize together under the conditions described, to produce a co-polymer or octene which, on later hydrogenation, is characterized by a high knock rating only slightly less than that of iso-octane derived entirely from isobutylene. By this method of copolymerization of the 2-butene I am therefore enabled to produce a motor fuel of outstanding knock rating, whereas the polymerization of the 2-butene alone produces a motor fuel of only intermediate value with respect to antiknock characteristics.

The reaction mixture from 12 is conducted by line 14 to fractionator 15 wherein C₄ hydrocarbons are removed as a vapor and the polymerization products, comprised principally of dibutylenes are withdrawn by line 16. The C₄ hydrocarbons are conducted by line 17 to fractionator 18 where they are further fractionated to separate them into an isobutane fraction (containing most of the 1-butene) which is withdrawn as a vapor by line 19, and a normal butane fraction, withdrawn by line 20. Higher boiling hydrocarbons which may be present are removed by line 21. Normal butane, which may be contaminated with a small amount of 1-butene is conducted by line 20 to scrubber 20a where the 1-butene is absorbed by a suitable reagent such as sulfuric acid. The absorption product may be utilized in a sulfuric acid polymerization process or, by hydrolysis, may be converted into secondary butyl alcohol. Where the amount of contaminating 1-butene is very small, I may bypass scrubber 20a by line 20b. The normal butane stream is then led by line 20c to isomerizer 22 where it is held in contact in liquefied form with a suitable isomerizing catalyst at a mild temperature, for example about 150 to 200° F. The catalyst may be anhydrous aluminum chloride, aluminum bromide, aluminum chloride promoted with boron chloride, or aluminum chloride activated by a trace of moisture, by HCl or by other activating halides, e. g., CCl₄, ethylene dichloride, etc. Under the action of these catalysts

and under these mild temperature conditions, for example 100–300° F., the normal butane is converted into isobutane to a large extent, for example 50–80%. Any 1-butene which may be present is partly polymerized and partly converted into 2-butene under these conditions. After treating to remove the catalyst, for example, by filtration or by distillation and/or by washing with water, the reaction product is returned by line 23 to tower 18 whereby isobutane formed in isomerizer 22 is separated and any unchanged normal butane is recycled to the isomerizer 22.

The isobutane withdrawn by line 19 is conducted through heater 24 wherein it is heated to a relatively high temperature, for example about 800–1000° F., and treated with a suitable dehydrogenating catalyst in dehydrogenator 25. If chromium oxide is employed as the catalyst the temperature may be maintained at about 900 to 925° F. The products, consisting principally of isobutylene and hydrogen with some unchanged isobutane and some degradation products, are withdrawn by line 26 leading to fractionator 27 where hydrogen is separated by line 28 and liquid isobutylene is removed by line 13. Isobutylene which tends to be carried away in line 28 with the hydrogen and degradation products such as ethane and propane may be recovered by introducing an absorber oil in the top of tower 27. In the event that an absorber oil is used, the absorbed product is subsequently separated from the rich absorbent oil, fractionated by suitable means (not shown) and the isobutylene recovered therefrom is returned to feed line 13.

Isobutylene may be conducted by line 13 back to heater 11 as previously described, the amount introduced being sufficient to increase the concentration of isobutylene in line 10 above that of the 2-butene concentration therein. Excess isobutylene may be withdrawn by valved line 29 for various other uses; for example, it may be polymerized with a suitable catalyst to produce pure iso-octene which may then be hydrogenated to produce iso-octane motor fuel, especially valuable for aviation engines. The isobutylene may also be employed for the manufacture of resins, for example by treatment in the liquid phase with boron fluoride at low temperatures of the order of 0 to –100° F. If desired, isobutylene from other sources, such as the dehydration of isobutyl alcohol, may be introduced into the system by line 30 in any amount. Similarly, in the case where isobutane is available from other sources, such as from the treatment of petroleum naphthas with aluminum chloride, it may be introduced into the system by valved line 31.

Hydrogen which is derived from the fractionator 27 and may contain substantial amounts of lower hydrocarbons is conducted by line 28 to heater 32 wherein it is mixed with the polymers from lines 16 and/or 21. The polymers are hydrogenated by suitable means in hydrogenator 33—for example, in heater 32 the temperature of the polymers and hydrogen may be raised to about 300–500° F. and the heated products introduced into hydrogenation catalyst chamber 33 where they are brought into contact with a suitable catalyst such as metallic nickel or nickel oxide. The products are then conducted by line 34 into fractionator 35 where the hydrogenated products, consisting primarily of octanes, are withdrawn by line 36 as a high knock rating motor fuel having a knock rating of about 90–97 octane number. Any excess hydrogen and un-

condensed gases, including propane and lighter hydrocarbon gases, are withdrawn by line 37. Heavier products undesired in the motor fuel are withdrawn by line 38 and may be employed as charging stock for a cranking process or refined to produce lubricating oil and other petroleum products.

As a modification of the foregoing process I may remove the 1-butene from the gases withdrawn at the top of fractionator 15 by conducting them through valved line 40 to isomerizer 41 wherein the gases are contacted with an acid catalyst, such as a phosphoric acid-silicate catalyst in the presence of a small amount of steam if desired, at a temperature of about 500–600° F., for example 550° F. Under these conditions the 1-butene is converted substantially into 2-butene and some isobutylene. The isomerized mixture is then conducted by line 42 to polymerizer 43, additional isobutylene being introduced by line 44 to bring the concentration of isobutylene in the mixture up to that of the 2-butene. Co-polymerization is effected in polymerizer 43, employing a suitable catalyst, for example phosphoric acid at about 250 to 350° F., the conditions being substantially the same as in polymerizer 12. Polymerization products are then conducted by lines 45 and 17 leading to fractionator 18 where the polymers are separated and removed by line 21 as hereinbefore described. In this modification of my process, I am able to obtain a higher ultimate yield of polymers. Furthermore the amount of 1-butene introduced into fractionator 18 is reduced to a minimum and the fractionation is thereby simplified.

In another modification of my process I may eliminate fractionator 18 and isomerizer 22 by closing valves 46 and 47 and opening valve 48 in line 49, thus diverting the gases from fractionator 15 to line 49 from whence they are conducted to condenser 49a and thence to scrubber 49b to remove olefins as previously described with scrubber 20a. The hydrocarbon stream is then led to isomerizer 50 which is operated under substantially the same conditions, with the same catalysts as described for use in isomerizer 22. Normal butane is converted to an appreciable extent into isobutane by the catalyst in 50 and the resulting products are conducted by line 51 to heater 24 and thence to dehydrogenator 25, as hereinbefore described. With this modification some simplification of the process and apparatus is effected, but at the cost of having to process a mixture of butanes in dehydrogenator 25 with resulting lower efficiency and with the production of a butylene gas containing a mixture of butylenes less valuable for special process such as lubricating oil synthesis and for the production of isobutene of high purity.

Although I have described my process with regard to specific examples thereof I contemplate various other obvious combinations with operations well known in the art. Thus I may precede fractionator 18 with a scrubber, for example a sulfuric acid scrubber, and remove from the gasses introduced through line 17 all olefins, thereby simplifying the fractionating operation in tower 18. Instead of a scrubber I may also use polymerization catalysts for converting substantially all olefins in the gas introduced through line 17 into high boiling polymers which may be withdrawn from the base of fractionator 18 by line 21. As examples of such vigorous polymerizing catalysts I may mention aluminum chloride, sodium aluminum chloride (NaAlCl₄),

BF₃, etc. and I may also use phosphoric acid under conditions where sufficient time is provided for complete olefin polymerization. In some cases I may also combine fractionators 15 and 18 into a single fractionating stage to simplify the apparatus.

Heat exchange equipment, coolers, valves, compressors, etc. may be supplied where desired. Also, it should be understood that where the C₄ hydrocarbons are treated in the liquid phase, pumps may be supplied to provide sufficient pressure for the purpose, pressures of about 50 to 500 lbs. being sometimes required, depending on the temperature. The process has been described in simplified form for clarity, but it should be understood that various details may be supplied without departing from the spirit of my invention.

Having thus described my process, what I claim is:

1. The process of converting a gas mixture of C₄ hydrocarbons containing 1-butene, 2-butene, and normal butane into higher boiling hydrocarbons suitable for motor fuel and characterized by a high knock rating, which comprises adjusting the butylene composition of said C₄ hydrocarbon mixture to provide a concentration of isobutylene equal to or greater than the concentration of 2-butene in the mixture, subjecting the adjusted mixture of C₄ hydrocarbons to the action of a polymerizing catalyst under conditions whereat isobutylene and 2-butene are substantially co-polymerized and 1-butene present in the mixture is substantially unaffected, separating the resulting polymers from the gas mixture, treating the unreacted gas mixture in the liquid phase with an isomerizing catalyst under mild temperature conditions and thereby substantially converting normal butane to isobutane, subjecting the isomerized gas mixture to the action of a dehydrogenating catalyst at elevated temperature whereby isobutane contained therein is substantially converted to isobutylene and hydrogen and recycling the isobutylene thus obtained to the original C₄ hydrocarbon mixture to adjust the ratio of isobutylene to 2-butene contained therein.

2. The process of claim 1 wherein hydrogen obtained from the dehydrogenation of isobutane is combined with the polymer resulting from the co-polymerization of isobutylene and 2-butene to produce a substantially saturated motor fuel of high knock rating.

3. The process of converting a gas mixture containing normal butane and the three butenes into motor fuel of high knock rating which comprises selectively co-polymerizing, by means of a catalyst, the isobutylene and 2-butene in said mixture substantially without polymerizing the 1-butene, said polymerization of isobutylene and 2-butene being regulated to produce principally octenes, subjecting the unpolymerized hydrocarbons, including 1-butene, to the action of an olefin isomerizing catalyst whereby said 1-butene is substantially converted to 2-butene and isobutylene, adding an additional amount of isobutylene sufficient to make the concentration substantially equal the amount of 2-butene in said isomerized hydrocarbon mixture and subjecting the gases to a second selective polymerizing operation whereby the isobutylene and 2-butene are co-polymerized principally to octenes, subjecting the remaining substantially saturated unpolymerized hydrocarbons to the action of a paraffin isomerizing catalyst whereby a substantial amount of the normal butane is converted to

isobutane, dehydrogenating the resulting isobutane and unconverted normal butane whereby a substantial amount of isobutylene is produced and recycling said isobutylene to one of said polymerizing operations previously described.

4. The process of claim 3 wherein octenes produced in said polymerization operations are converted to octanes by subsequent hydrogenation.

5. The process of claim 3 wherein the polymerization catalyst is phosphoric acid maintained at about 250 to 350° F., the olefin isomerizing catalyst is also phosphoric acid maintained at a temperature of about 500 to 600° F. and the paraffin isomerizing catalyst is a Friedel-Crafts catalyst such as aluminum chloride.

6. The process of converting a gas mixture containing normal and isobutane and the three butenes into motor fuel of high knock rating which comprises selectively co-polymerizing, by means of a catalyst, the isobutylene and 2-butene in said mixture substantially without polymerizing the 1-butene, said polymerization of isobutylene and 2-butene being regulated to produce principally octenes, subjecting the unpolymerized hydrocarbons, including 1-butene, to the action of an olefin isomerizing catalyst whereby said 1-butene is substantially converted to 2-butene, adding an amount of isobutylene to increase the concentration to substantially that of the 2-butene in said isomerized hydrocarbon mixture and subjecting the gases to a second selective polymerizing operation whereby the butenes are converted principally to octenes, subjecting the remaining unpolymerized hydrocarbons, consisting principally of normal butane and isobutane, to fractionation, removing the isobutane as a distillate, withdrawing the normal butane as a reflux liquid and subjecting it to the action of a paraffin isomerizing catalyst whereby it is converted substantially to isobutane, returning the converted butane-isobutane mixture to said fractionating operation whence isobutane is removed and unconverted normal butane is recycled to said paraffin isomerizing operation, dehydrogenating said isobutane fraction to produce isobutylene and recycling said isobutylene to one of said polymerizing operations previously described.

7. The process of claim 6 wherein octenes produced in said polymerizing operations are converted to octanes by the action of hydrogen withdrawn from said dehydrogenating operation.

8. The process of converting a gas mixture of C₄ hydrocarbons containing butanes and butenes into higher boiling hydrocarbons suitable for motor fuel and characterized by a high knock rating, which comprises adjusting the butylene composition of said C₄ hydrocarbon mixture to provide a concentration of isobutylene equal to or greater than the concentration of 2-butene in the mixture, subjecting the adjusted mixture of C₄ hydrocarbons to the action of a polymerizing catalyst under conditions whereat isobutylene and 2-butene are substantially co-polymerized and 1-butene present in the mixture is substantially unaffected, separating the resulting polymers from the gas mixture, treating the gas mixture in the presence of an acid acting catalyst whereby the 1-butene contained therein is substantially isomerized to 2-butene and iso-butylene copolymerizing the 2-butene in the mixture with an equal or greater amount of isobutylene added thereto, separating the resulting polymers from the gas mixture, treating the gas mixture in the liquid phase with an isomerizing catalyst under mild temperature conditions and thereby sub-

- stantially converting n-butane to isobutane, subjecting the isomerized gas mixture to the action of a dehydrogenating catalyst at elevated temperature whereby isobutane contained therein is substantially converted to isobutylene and hydrogen and recycling the isobutylene thus obtained to said hydrocarbon gas mixtures to be polymerized in order to adjust the ratio of isobutylene to 2-butene contained therein.
- 10 9. In the conversion of an unsaturated C₄ fraction of hydrocarbons containing all three butenes in substantial amounts, into high knock rating motor fuels within the gasoline boiling range, the improvement comprising adjusting the olefin composition of said hydrocarbon fraction to obtain an isobutylene concentration at least equal to the concentration of normal 2-butene in said C₄ hydrocarbon fraction and subsequently subjecting said olefin mixture to polymerization in the presence of an acid acting catalyst at a temperature above 250° F. whereby isobutylene and 2-butene are copolymerized to produce motor fuel octenes substantially without affecting 1-butene present in said unsaturated C₄ fraction and separating said octenes from unpolymerized C₄ hydrocarbons.
- 10 10. The process of claim 9 wherein the catalyst is phosphoric acid disposed on a suitable solid supporting material.
- 15 11. The process of claim 9 wherein the said C₄ fraction contains an excess of 2-butene over isobutylene and the concentration of isobutylene in said unsaturated C₄ hydrocarbon fraction is adjusted by adding extraneous isobutylene thereto.

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