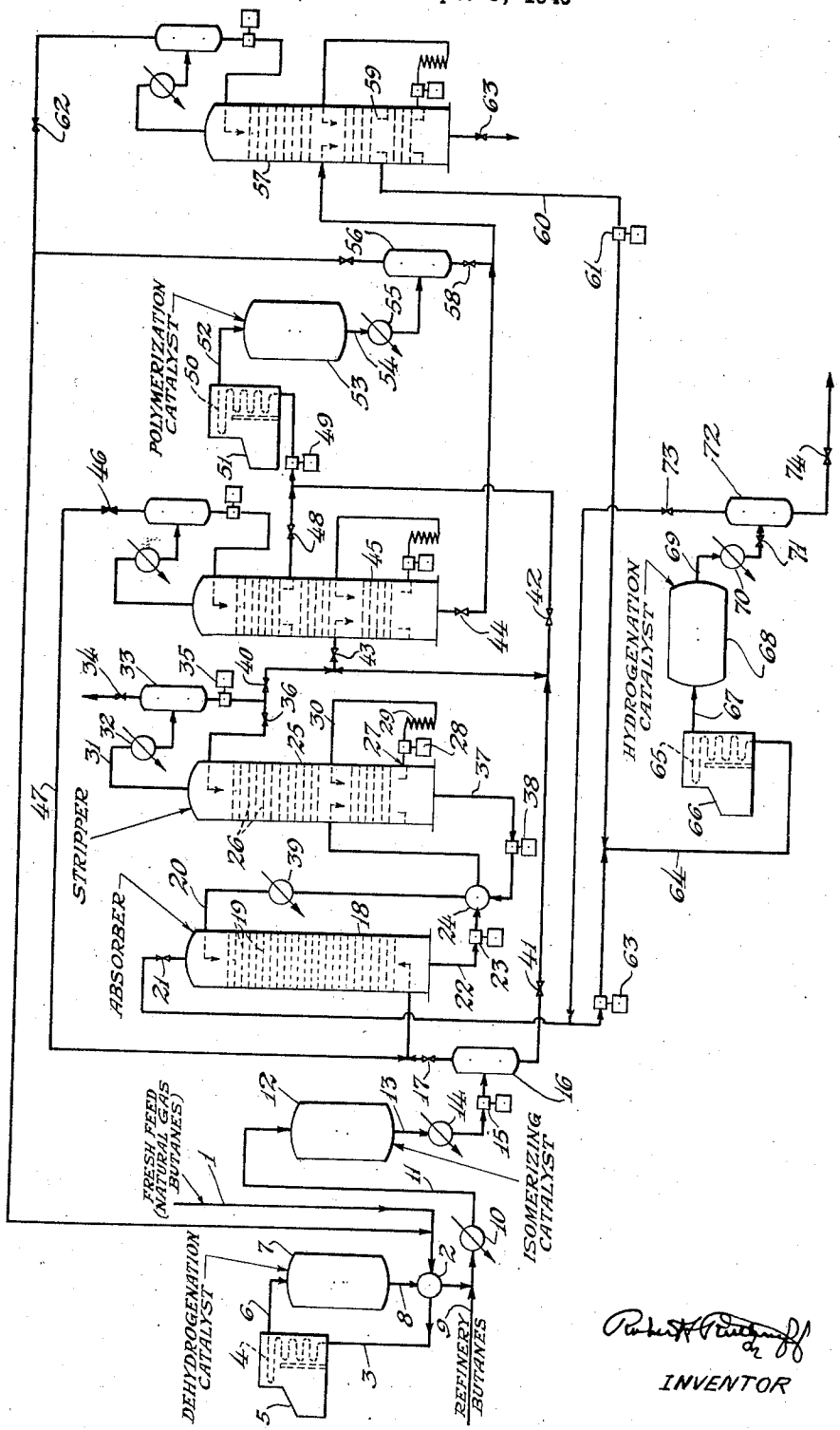
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ISOMERIZATION OF OLEFINS

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ISOMERIZATION OF OLEFINS

Robert F. Ruthruff, Chicago, Ill.

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16 Claims. (Cl. 260—683)

This invention relates to the catalytic conversion of paraffinic and olefinic hydrocarbons containing four carbon atoms to the molecule into liquid hydrocarbons of high octane number boiling within the usual motor fuel range. More particularly, this invention relates to the catalytic conversion of paraffinic and olefinic hydrocarbons containing four carbon atoms to the molecule into liquid hydrocarbons boiling within the usual motor fuel range by a unitary combination process whereby the yield and octane number of said liquid hydrocarbons are higher than have been previously obtainable when operating in conformity with the teachings of the art. In a more restricted sense, this invention relates to the catalytic conversion of less reactive olefins containing four carbon atoms to the molecule into other olefins of the same molecular weight but greater reactivity. Specifically, in its more restricted sense, this invention relates to the catalytic conversion of butene-1 into butene-2 and to the catalytic conversion of butene-2 into isobutene.

Briefly, one embodiment of my invention embraces the catalytic dehydrogenation of paraffinic hydrocarbons containing four carbon atoms to the molecule, subjecting the resulting products to catalytic isomerization whereby the less reactive olefins therein are converted to more reactive olefins, subjecting the resulting products to catalytic polymerization whereby olefins are converted to liquids and hydrogenating the resulting liquids to produce a material of high octane number.

It is a principal object of this invention to provide a catalytic unitary combination process for the conversion of paraffinc and olefinic hydrocarbons containing four carbon atoms to the molecule into a high yield of high octane number liquid hydrocarbons boiling within the usual motor fuel range. In a more restricted sense, it is a principal object of this invention to provide a catalytic process for the conversion of less reactive olefins containing four carbon atoms to the molecule into other olefins of the same molecular weight but of greater reactivity. Specifically, in a more restricted sense, it is a principal object of this invention to provide a catalytic process for the conversion of butene-1 into butene-2 and for the catalytic conversion of butene-2 into isobutene. Other objects of this invention will become apparent as the description thereof proceeds.

For the more complete understanding of my invention, reference may be had to the drawing forming a part of this specification and wherein a diagrammatic representation of one form of apparatus suitable for carrying out the process of the instant invention will be found.

Turning now to a more complete description of the drawing, fresh charge to the unit, comprising paraffinic hydrocarbons containing four atoms of carbon to the molecule and representing, for example, a fraction of the proper boiling range obtained from natural gas, is introduced through line 1. The fresh charge may be preheated if desired, for example, by being brought into indirect heat exchange relationship with a hot stream from a source hereinafter to be described in exchanger 2, the thus preheated charge then passing through line 3 to coil 4 disposed in furnace setting 5. The charge, during passage through coil 4 is brought to the proper reaction temperature and is then discharged, via line 6, to reactor 7 containing a suitable catalyst. Any one of a number of contact agents may be used in reactor 7. Among such materials may be mentioned alumina, especially the material known as activated alumina; chromium oxide gel, for example, chromium oxide gel prepared in conformity with the method described and claimed in U. S. Patent 2,211,302, issued August 13, 1940, to John Turkevich and the present applicant; alumina, especially the material known as activated alumina, bearing a relatively minor proportion of an oxide of an element of the left hand subgroups of groups IV, V and VI of the periodic table and particularly activated alumina bearing a relatively minor proportion of chromium oxide or molybdenum oxide.

The exact operating conditions with respect to temperature and time in catalytic reactor 7 depend largely upon the catalyst selected although, as will be understood by those skilled in the art, temperature and time are, in a sense and within limits, more or less interchangeable. In other words, within limits, similar or even identical results are obtained by exposing the charge at a relatively high temperature for a relatively short time or by exposing the charge for a relatively long time at a relatively low temperature. In general, when employing some of the more active dehydrogenation catalysts, for example, activated alumina plus 4 to 8% chromium oxide, temperatures of from about 500° to 650° C. may be employed with space velocities of about 200 to 7500. Satisfactory results are obtained when operating at 600° C. and a space velocity of 2500. Preferably, moderate to low pressures are employed, for example, 50 pounds per square inch gage or less.

While a single catalytic dehydrogenation reactor is shown, it is to be understood that all catalysts employed gradually lose activity when on stream and accordingly require periodic regeneration. Accordingly, for continuous operation, provision must be made for the regeneration of one part of the total catalyst while another portion is dehydrogenating the charge. This may be accomplished, for example, by using a pair of

reactors, each similar to 7, the catalyst in one being regenerated by burning accumulated carbonaceous deposits therefrom by a stream of air or dilute air while the catalyst in the other is simultaneously exercising its dehydrogenating action on the charge, the functions of the two reactors being reversed periodically. Also, for this type of operation, the moving catalyst technique is especially suitable or the suspended catalyst technique may be employed. For a more complete exposition of the various methods of employing catalysts mentioned briefly in the instant paragraph, reference may be had to my copending application, Serial Number 334,741, filed May 13, 1940.

Also, it should be pointed out that the dehydrogenating reaction is highly endothermic and accordingly it is advisable to provide means for supplying the required heat. This may be accomplished, for example, by having the catalyst disposed in tubes surrounded by a heated fluid, for example, by having the catalyst heated by hot combustion gases surrounding the tubes, said heated gases being obtained during the regeneration of another portion of the catalyst.

Reaction products from dehydrogenation reactor 7 leave by line 8 and are partially cooled in indirect heat exchanger 2 with fresh charge.

If desired, but not necessarily, hydrogen may now be removed from the reaction products. However, leaving hydrogen in the reaction products until after the olefin isomerization reaction to follow results in certain advantages as will hereinafter become apparent. If the hydrogen is not removed from the catalytic dehydrogenation reaction products, hydrocarbons containing four carbon atoms to the molecule and obtained, for example, from the gases produced during cracking and/or reforming operations may be introduced via line 9. As will hereinafter become apparent, the refinery gas cut may form the sole fresh feed to the process, no natural gas butanes being introduced through line 1.

The resulting gas stream, consisting essentially of hydrogen and hydrocarbons containing four carbon atoms to the molecule is further cooled as necessary by passage through cooler 10 following which it passes through line 11 to isomerization reactor 12 which contains a suitable isomerization catalyst. Certain metal pyrophosphates, particularly stabilized metal pyrophosphates, for example, pyrophosphates of copper, mercury, zinc, magnesium, cobalt, iron or aluminum especially when in a stabilized form are employed for the purpose. I have found that copper pyrophosphate, especially stabilized copper pyrophosphate, to be particularly efficacious. Specific examples of the preparation of such catalysts will be given hereinafter.

Reaction conditions to be maintained in isomerization reactor 12 depend to a large extent upon the exact catalyst employed. However, as a guide, when using stabilized copper pyrophosphate prepared in accordance with Example 1, below, a low to moderate superatmospheric pressure, preferably in the neighborhood of 100 pounds per square inch or less is used at a temperature in the approximate range 250°–450° C., the time of contact being in the neighborhood of 5 to 100 seconds more or less. Particularly good results are obtained when operating at 25 pounds per square inch, a temperature of 325° C. and a contact time of 20 seconds.

It is obvious that the above outlined conditions are within the catalytic polymerization range and during isomerization it is highly desirable to avoid polymerization as much as possible. To this end, the operating pressure during isomerization should be as low as feasible. Also, preferably, the charge to the isomerization reactor is diluted with an inert gas, steam for example, to cut down the olefin concentration and accordingly polymerization. In the embodiment being described, the hydrogen produced during catalytic dehydrogenation is so employed but it is to be understood that steam or other similar inert gases may be used, either alone or in conjunction with hydrogen.

The reaction products leaving isomerization reactor 12 through line 13 consist essentially of hydrogen, butanes that escaped catalytic dehydrogenation and the two olefines, butene-2 and isobutene. Under proper catalytic isomerization conditions as outlined above the butene-1 content of the gas stream is practically nil and the isobutene-butene-2 ratio is unity or more.

Hydrogen is now removed from the gas stream. Any suitable means may be employed for the purpose, for example, absorption. To this end, the reaction products are cooled in cooler 14, are compressed to a moderate superatmospheric pressure, for example, 50 to 300 pounds per square inch depending upon the temperature of the cooling water and other considerations, in compressor 15, the resulting material being sent to separator 16. Uncondensed components of the reaction products are sent by valved line 17 to absorber 18. Absorber 18 is provided with means for facilitating liquid-vapor contact therein such as bubble trays 19 although other suitable devices for the purpose, for example, Raschig ring packing or Berl saddles may be used if desired. Cold absorber oil is introduced into absorber 18 by line 20 and is contacted with the ascending gas stream in said absorber. Unabsorbed gas, consisting essentially of hydrogen, is discharged through valved line 21 while rich absorber oil leaves through line 22, is moved by pump 23 through indirect heat exchanger 24 where it is heated by a hot stream from a source hereinafter to be described, following which it enters stripper 25. Stripper 25 is preferably provided with means for facilitating liquid-vapor contact, top cooling means and bottom heating means. Means for facilitating liquid-vapor contact may take the form of bubble trays 26, although other suitable means, such as Raschig ring packing or Berl saddles may be employed. For bottom heating, liquid may be removed from trap out tray 27 positioned near the bottom of stripper 25, moved by pump 28 through suitable heater 29 and thence by line 30 for discharge into the mid-portion of stripper 25. Other suitable heating means may be employed, either alone or in combination with the device described or other devices, for example, an open steam coil positioned near the bottom of the tower or a similarly positioned closed coil through which heated fluid may be circulated. For top cooling, gaseous products from stripper 25 may be removed through line 31, cooled in cooler 32 and discharged into separator 33. Any uncondensed material may be removed continuously or intermittently at frequent intervals through valved line 34 while liquids may be moved by pump 35, a portion of these being passed via valved line 36 back to the upper portion of stripper 25 to provide reflux therein. Other suitable cooling means may be employed, either alone or in combination with the device described or other devices, for example, an upper positioned closed coil through

which cold fluid is circulated, or cold fluid of suitable properties from an outside source may be added to the upper portion of stripper 25 to provide open reflux therein.

Absorbed materials are removed from the rich absorber oil in stripper 25. Stripped absorber oil leaves by line 37, is moved by pump 38 through exchanger 24 wherein it is partially cooled by rich absorber oil, thence through cooler 39 and finally back to absorber 18 via line 20. Absorbed materials eliminated in stripper 25 leave through line 31. The recirculation of part of these back to the stripper to provide open reflux therein has already been described. Liquid material not used to provide reflux passes through valved line 40 and joins with liquids from separator 16 which leave this element through valved line 41. The resulting composite stream may be processed without further rectification if desired by passing it through valved line 42, the valves in valved lines 43 and 48 being closed. Preferably however the small amount of components boiling lower than hydrocarbons having four carbons in the molecule and small amounts of polymers formed during isomerization are removed by fractionation in tower 45. In such a case the composite feed stream is sent to tower 45 through valved line 43; valved line 48 also being open while valved line 42 is closed. Tower 45 is provided with means for facilitating liquid-vapor contact, bottom heating means and upper disposed cooling means as described in connection with stripper 25. Light components originally present in the composite feed stream are removed through valved line 46 and are preferably sent to absorber 18 via line 47. By operating in this way gas consisting essentially of hydrogen is eliminated through valved line 21 while gases consisting essentially of hydrocarbons of less than four carbon atoms to the molecule are eliminated through valved line 34. Material consisting essentially of hydrocarbons containing four carbon atoms to the molecule are removed through valved line 48. The small amount of polymers formed during isomerization are removed through valved line 44.

Hydrocarbons containing four carbon atoms to the molecule which are removed through valved line 48 from tower 45 are preferably compressed to a high superatmospheric pressure by pump 49 and are passed through coil 50 in furnace setting 51 wherein the materials are heated to the desired catalytic polymerization reaction temperature. The thus heated polymerization charge passes through line 52 to catalytic polymerization reactor 53. A wide variety of catalysts may be employed in polymerization reactor 53. Among these may be mentioned clays, especially acid activated clays, sodium aluminum chloride, lithium aluminum chloride, alumina hydrolytically absorbed on silica gel, synthetic silica-alumina complexes, calcined phosphoric acid-kieselguhr mixtures, phosphoric acid on charcoal, phosphoric acid on silica and the like. Especially good results are obtained using certain metal pyrophosphates, specifically, pyrophosphates of copper, mercury, zinc, magnesium, cobalt, iron or aluminum, particularly such metal pyrophosphates in the unstabilized or even promoted condition. Specific examples of the preparation of such catalysts will hereinafter appear. The exact operating conditions to be employed depend to a great extent upon the exact composition of the gas being treated, the catalyst selected and many other factors. As an example of suitable operating conditions when using unstabilized copper pyrophosphate catalyst, the hydrocarbon charge was passed over this contact agent at a temperature of 160 to 180° C., a pressure of 1500 pounds per square inch and a rate of 40 cubic feet of charge measured as a gas at standard conditions per hour per pound of catalyst. Under these operating conditions olefin polymerization was practically quantitative.

In contradistinction to the catalytic dehydrogenation reaction previously described, the catalytic polymerization reaction is decidedly exothermic and accordingly it is advisable to provide cooling means within reaction vessel 53. This cooling may be accomplished, for example, by bypassing a portion of the feed to furnace coil 50 around said coil by a line (not shown) and introducing said cold feed into reactor 53 at one or more points. As usual, the polymerization catalyst sooner or later becomes more or less inactive and must then be replaced or regenerated. When copper pyrophosphate is employed, while it can be regenerated, the active life of the catalyst is so long that, when exhausted, it can be replaced rather than being regenerated without sacrifice in economic advantage. Whether the catalyst is regenerated or replaced it is advisable to use a plurality of reactors so that operations are continuous. It is common practice to employ three or more reactors, the catalyst in one being regenerated or replaced while the remaining ones are on stream. Flow in the on stream reactors is commonly countercurrent, that is, fresh feed is contacted with the most nearly exhausted catalyst. When two or more reactors are employed on stream simultaneously it is common practice to install intercoolers between successive reactors to remove part or all of the heat generated by the polymerization reaction.

Products from catalytic reactor 53 leave through line 54, the products may be cooled in exchanger 55 prior to passage to separator 56. Liquids from separator 56 pass to tower 57 via valved line 58. Tower 57 is provided with means to facilitate liquid-vapor contact, with lower disposed heating means and upper disposed cooling means as described in detail in connection with stripper 25. Liquid polymer of the desired boiling range is separated from gaseous products and heavier liquids in fractionating tower 57, polymer being removed through line 60 from trap out tray 59 by means of pump 61 while gas, consisting essentially of the butanes passes through valved line 62 back to the catalytic dehydrogenation zone. Liquid polymers of higher boiling range than desired may be discharged from tower 57 by valved line 63. It will be noted that the small quantity of polymers formed during isomerization and removed from tower 45 by valved line 44 are also charged to tower 57 for fractionation.

The liquid polymer discharged through line 60 from tower 57 is hydrogenated by suitable well known methods and means to produce a saturated naphtha of high octane rating. To accomplish this hydrogenation, hydrogen eliminated from absorber 18 through valved line 21 is preferably employed. This hydrogen is compressed by pump 63 and is mixed with polymer of the desired boiling range from pump 61, the resulting composite feed passing by line 64 to coil 65 in furnace setting 66. On passage through coil 65 the mixture is brought to reaction temperature and is discharged via transfer line 67 to hydrogenation reactor 68. A number of contact agents may be employed in reactor 68 but most of these

may be roughly divided into two groups (*a*) nickel, especially nickel on a suitable support and (*b*) oxides and/or sulfides of sixth group metals, for example, molybdenum and tungsten, particularly such compounds on suitable supports. The exact reaction conditions to be employed in reactor **68** depend largely on the type of catalyst employed. Catalysts of type (*a*) operate under comparatively mild conditions but are prone to become poisoned. Catalysts of type (*b*) are less active but are extremely stable. With type (*b*) catalysts pressures of from 500 to 3000 pounds per square inch may be employed at 260 to 370° C. With type (*a*) catalysts pressure may be 50 to 500 pounds per square inch at a temperature of say 150 to 300° C. With both types of catalysts it is preferable to use a large excess of hydrogen, for example, 5 or more moles of hydrogen per mole of polymer charged to the reactor.

The choice of catalyst to be employed in the hydrogenation zone is largely governed by the sulfur content of the feed thereto. When a sulfur free feed or a feed of low sulfur content is employed, it is preferable to employ the more active type catalyst. The sulfur content of the feed to the hydrogenation zone is usually quite low since most of the isomerization catalysts have the ability to remove and hold sulfur compounds present in the material being processed. The same is true when pyrophosphates are employed in the polymerization zone. As a result, after passing over, for example, stabilized copper pyrophosphate in the isomerization zone and unstabilized or promoted copper pyrophosphate in the polymerization zone the charge to the hydrogenation zone is sulfur free or nearly so and hence the more active type of hydrogenation catalysts may be used. With high sulfur feeds the isomerization catalysts and polymerization catalysts usually become exhausted more rapidly than when sulfur free or low sulfur charging stocks are employed. The regeneration of the polymerization catalyst has already been described. The isomerization catalyst zone may be arranged similarly for similar ends. Provision should likewise preferably be made to allow regeneration of the active type of hydrogenation catalyst and still maintain continuity of operation. The life of the less active type of hydrogenation catalyst is so long usually that provisions for regeneration while maintaining continuity of operation are usually unnecessary. When such catalysts, after use for weeks or months, finally become exhausted the whole unit can be shut down and the catalyst replaced. Obviously, if desired, the charge to the dehydrogenation zone may be caustic washed or otherwise treated by methods well known to those skilled in the art to remove sulfur and the same may be done prior to any or any combination of the succeeding catalytic zones.

Reaction products from hydrogenation reactor **68** leave through line **69**, are cooled in exchanger **70** and after partial or complete pressure reduction across valve **71** are discharged into separator **72**. Excess hydrogen is eliminated through valved line **73** and is sent back to valved line **21** for recycling. If desired, part or all of this stream may be introduced into absorber **18** by suitable means (not shown). Hydrogenated high octane ultimate product is eliminated through valved line **74**. This material may be further processed if desired, for example, by fractionation in a suitable tower (not shown).

It is evident that if necessary the exclusive fresh feed to the system may consist of either natural gas butanes or the C_4 cut from refinery gas. With either charging stock or with a mixture of the two, the hydrocarbon gases are largely converted into liquid hydrocarbons of high octane number.

The advantages that follow allowing the hydrogen produced during catalytic dehydrogenation to remain in the gas stream until after the olefins have been catalytically isomerized have already been mentioned. It should be understood however that, if desired, the hydrogen may be removed immediately after the catalytic dehydrogenation step. This is easily accomplished by passing (after cooling) the gas mixture produced in catalytic dehydrogenation reactor **7** to separator **16**, the light gas eliminated therefrom going to absorber **18**. This gas is treated in a manner identical with that previously described and the hydrogen free gas consisting essentially of hydrocarbons of four carbon atoms to the molecule are eliminated from stripper **25** via valved line **41**. This mixture, after preliminary stabilization is desired in a tower similar to **45**, is then passed through a heater and thence to isomerizer **12**. Isomerized products then pass to polymerizer **53** and the remaining course is identical to that already described. As will be apparent to those skilled in the art, by a simple group of manifolds (not shown) the unit of the drawing can be made to operate with hydrogen removal after isomerization and prior to polymerization (as shown) or after dehydrogenation and prior to isomerization (not shown).

It will be evident that by practicing the process just described a higher yield of higher octane number liquid hydrocarbons is obtained than has hitherto been believed possible. As is well known to those skilled in the art, by the hydrogenation of catalytic polymer obtained from isobutene a product is obtained of about 98 octane number. Likewise, by the copolymerization of butene-2 and isobutene under such conditions that not more than one molecule of butene-2 reacts per molecule of isobutene reacting a product is obtained which, on hydrogenation, has an octane number about as high as that from straight isobutene, for example, 92 to 96. However, if more than one molecule of butene-2 reacts per molecule of isobutene reacting or if appreciable amounts of butene-1 react, the resulting polymer, after hydrogenation is of comparatively low octane number. The isobutane-butane ratio in most natural gases is very low, averaging say 0.25. Accordingly, on catalytic dehydrogenation of such a mixture, the isobutene normal butenes ratio in the products is also low, again being in the neighborhood of 0.25. Also, the isobutene-normal butenes ratio in cracking or reforming unit gases is low, averaging perhaps 0.35. Obviously, if dehydrogenated natural gas or cracking or reforming unit gases or mixtures thereof is subjected to catalytic polymerization, if polymerization is complete or nearly so the polymer product, after hydrogenation, will have a very low antiknock value. If, on the other hand, the extent of polymerization is deliberately restricted so that for each mole of isobutene reacting not more than one mole of normal butenes react (butene-2 polymerizes at a faster rate than butene-1), the resulting product, after hydrogenation, will have a high octane number but the yield of such a product will be low.

By the practice of the present invention, wherein the butenes available are isomerized

prior to polymerization, complete olefin cleanup during polymerization results in the production of a polymer which, after hydrogenation, has a high octane number. During the isomerization reaction, all or practically all of the butene-1 forms butene-2 while a large proportion of butene-2 is converted to isobutene. With the isobutene originally present in the charge to the isomerizer, plus that resulting from isomerization it is easily possible to obtain a product exhibiting an isobutene-butene-2 ratio of one or more. When such a mixture is catalytically polymerized, complete or practically complete olefin cleanup may be obtained with the production of a product which, after hydrogenation, has a high octane number.

Suitable catalysts for use in the dehydrogenation reactor and the hydrogenation reactor have already been described briefly and methods for the preparation of these are well known to those skilled in the art. The preferred isomerization and polymerization catalysts are less familiar and accordingly their preparation will be described.

The pyrophosphate catalysts employed in the practice of the instant invention may be prepared by any appropriate method. All of them may be made by metathesis, for example, by the addition of a solution of a soluble pyrophosphate, for example, sodium pyrophosphate, to a solution of a salt of the metal in question, the precipitated metal pyrophosphate being removed from the mother liquor by filtration or otherwise following which it is washed and dried. Or, if desired, the pyrophosphate catalysts of the instant invention may be prepared by first forming the metal monohydrogen orthophosphate of the general formula $MHPO_4$ (where M represents a divalent metal) or $N_2(HPO_4)_3$ (where N represents a trivalent metal), removing the metal monohydrogen orthophosphate from the mother liquor by filtration or otherwise following which the compound is washed and ignited to form the desired pyrophosphate in conformity with the following reactions: $2MHPO_4=M_2P_2O_7+H_2O$ and $2N_2(HPO_4)_3=N_4(P_2O_7)_3+3H_2O$. Or, if desired, as a modification of the method just described, certain of the pyrophosphates exhibiting catalytic activity may be prepared by first forming the metal monoammonium orthophosphate of the general formula MNH_4PO_4 (where M represents a divalent metal), removing a metal monoammonium orthophosphate from the mother liquor by filtration or otherwise, washing following which the compound is ignited to form the desired pyrophosphate in accordance with the following equation: $2MNH_4PO_4=M_2P_2O_7+2NH_3+H_2O$.

For the better understanding of methods that may be employed to form the pyrophosphate catalysts of the instant invention a few specific examples of a few suitable procedures will be given.

Example 1

A 0.2 molar solution of sodium pyrophosphate is added to a 0.2 molar solution of a copper salt such as copper sulfate, the sodium pyrophosphate being added in an amount about 10% in excess of that stoichiometrically equivalent to the copper sulfate. The addition is carried out gradually and the reaction mixture is stirred during the process. The precipitate is removed by filtration, washed thoroughly with water, partially dried and then extruded into spaghetti which is cut to form cylinders of the desired length. These cylinders are dried to form the final catalyst. If desired, prior to extrusion, about 33% of finely divided carbon based on the final dried catalyst may be added. This material aids in binding the catalyst particles together and has other beneficial effects.

The catalyst formed in accordance with Example 1 is eminently suitable for use in the catalytic isomerization of olefins as previously described. By some mechanism, as yet imperfectly understood, the excess sodium pyrophosphate stabilizes the resulting copper pyrophosphate against reduction at low temperatures.

Example 2

Exactly similar to Example 1, except that instead of using 10% excess of sodium pyrophosphate, an amount about 5% less than that stoichiometrically equivalent to the copper sulfate is employed. The catalyst of this example is eminently suitable for use in the catalytic polymerization of olefins as previously described. Such a catalyst, made without an excess of sodium pyrophosphate is unstabilized. If desired, an even more active catalyst may be prepared by incorporating promoters, such as finely divided metals, especially finely divided metals in the activated state, in the catalyst. For example, from 0.5 to 5% zinc dust (based on the copper employed) may be suspended in the sodium pyrophosphate solution used in the preparation of the catalyst or the zinc dust may be suspended in the copper salt solution or it may be distributed between the two.

Example 3

A dilute solution of magnesium sulfate is made decidedly acid with hydrochloric acid, using about 2 to 3 cc. concentrated acid per gram of magnesium salt. Following this about 5 g. diammonium hydrogen phosphate is added per gram of magnesium salt and there is then added slowly, with stirring, 5% ammonia solution until the reaction mixture is distinctly alkaline. The resulting reaction mixture is allowed to stand several hours (with stirring if desired) following which the magnesium ammonium orthophosphate is removed by filtration, washed with 5% ammonia and then ignited to give the desired catalyst which is especially useful in olefin isomerization but may be used as a polymerization catalyst if desired.

Example 4

A dilute solution of zinc sulfate is carefully neutralized using methyl red (or orange) indicator. The resulting solution is brought to the boil, is agitated and treated with a large excess of a 15% solution of diammonium hydrogen orthophosphate. After addition is complete the solution is kept hot for an hour and is then allowed to cool following which the precipitate is removed by filtration, is washed with cold water and ignited to give zinc pyrophosphate. Cobalt pyrophosphate can be made in an analogous manner. Both of these catalysts are most suitable for use in olefin isomerization but may be used in olefin polymerization if desired.

While my invention has been described with respect to certain specific embodiments thereof it is to be understood that other modes of applying the principles of the invention may be employed in lieu of those explained and accordingly the specific embodiments presented are not intended to limit my invention except insofar as

these may be set forth in the following claims.

I claim:

1. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with a pyrophosphate of a metal selected from the group consisting of copper, mercury, zinc, iron, aluminum, cobalt and magnesium at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

2. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with a stabilized pyrophosphate of a metal selected from the group consisting of copper, mercury, zinc, iron, aluminum, cobalt and magnesium at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

3. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with mercury pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

4. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with stabilized mercury pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

5. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with zinc pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

6. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with stabilized zinc pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

7. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with copper pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

8. In a process for the conversion of a hydrocarbon fraction comprising straight chain butenes, the step including contacting said hydrocarbon fraction with stabilized copper pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of said straight chain butenes to isobutene proceeds at a substantially higher rate than butene polymerization.

9. In the process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with a pyrophosphate of a metal selected from the group consisting of copper, mercury, zinc, iron, aluminum, cobalt and magnesium at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

10. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with a stabilized pyrophosphate of a metal selected from the group consisting of copper, mercury, zinc, iron, aluminum, cobalt and magnesium at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

11. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with mercury pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of normal butene proceeds at a substantially higher rate than butene polymerization.

12. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with stabilized mercury pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

13. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with zinc pyrophosphate at a temperature from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

14. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with stabilized zinc pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

15. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with copper pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

16. In a process for the conversion of a normal butene to isobutene, the step including contacting said normal butene with stabilized copper pyrophosphate at a temperature of from about 250° C. to 450° C. for a time period and under a pressure such that isomerization of the normal butene proceeds at a substantially higher rate than butene polymerization.

ROBERT F. RUTHRUFF.