

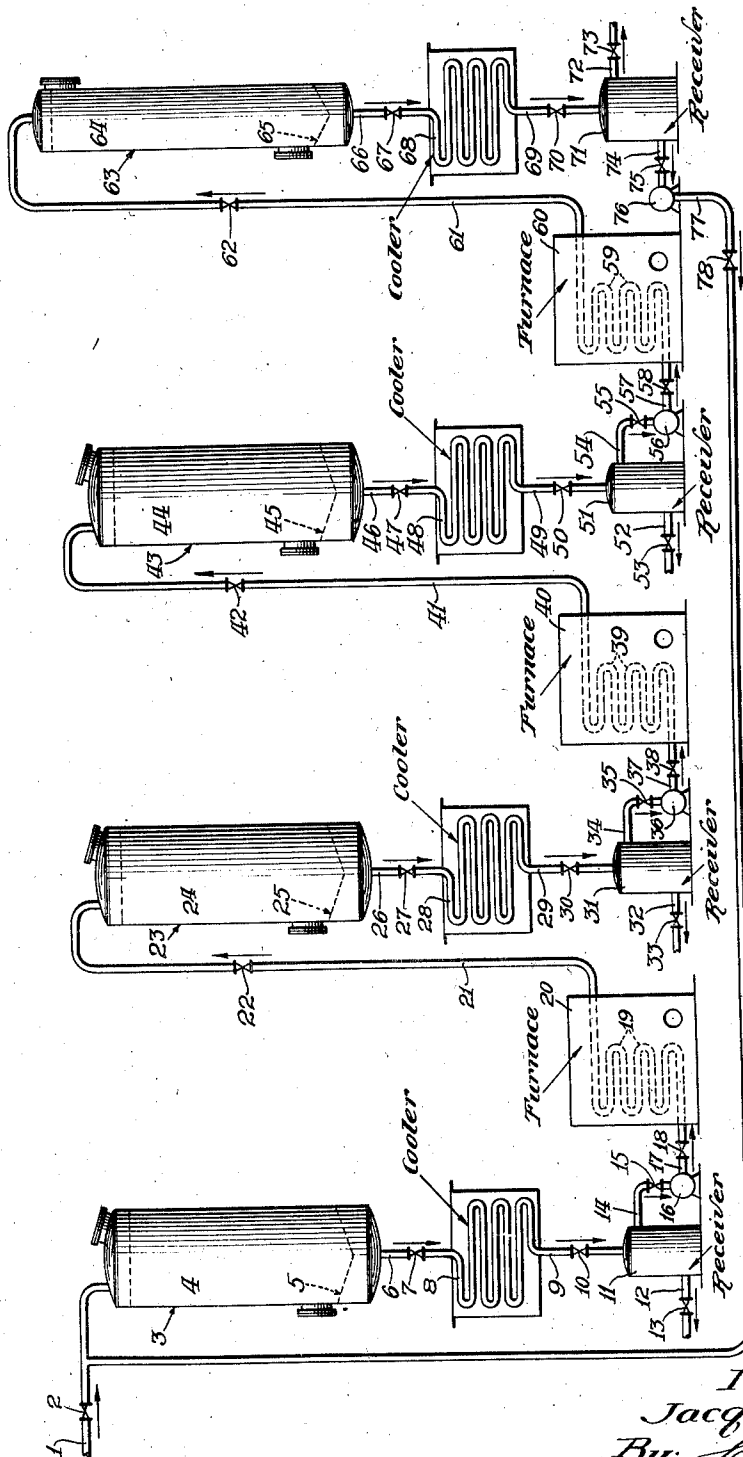
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MANUFACTURE OF MOTOR FUELS

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MANUFACTURE OF MOTOR FUELS

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This invention relates particularly to the treatment of hydrocarbons of an unsaturated character, such as the mono-olefins.

In a more specific sense, the invention is concerned with the selective treatment of the mono-olefins which are normally gaseous to produce particular compounds which are of a superior value as anti-knock blending fluids for gasolines inferior in this respect.

Oil cracking processes are productive of considerable quantities of fixed gases and heavy residual products, both liquid and solid. The fixed gases produced, for example, in cracking a topped crude with the primary object of producing gasoline may run as high as 10% by weight of the charging oil under intensive cracking conditions. The composition of these gases will vary with the severity of the cracking operation, the nature of the charging stock, the phase prevalent during the operation, and other factors. The following table shows a list of the hydrocarbon compounds which have been found in the fixed gases from oil cracking plants: Hydrogen H_2 , methane CH_4 , ethane C_2H_6 , ethylene C_2H_4 , propane C_3H_8 , propylene C_3H_6 , butanes (normal and iso) C_4H_{10} , and butenes (normal and iso) C_4H_8 .

The above tabulation omits mention of minor constituents such as hydrogen sulphide, low boiling mercaptans, and more highly unsaturated hydrocarbons than the mono-olefins, such as, for example, butadienes, but it will serve to indicate the general character of some of the gas mixtures which may be treated by the present process.

Intensive researches have been conducted to find a practical method for augmenting the supply of cracked gasoline by forming liquid polymers from the gaseous olefins present in cracked hydrocarbon gas mixtures. Fortunately, all of the dimers and many of the trimers and mixed polymers of the normally gaseous mono-olefins boil within the range of commercial motor fuel and are characterized by a satisfactory stability and particularly by a good antiknock value, which generally exceeds that of any of the components of cracked gasoline. For purposes of reference the following table is introduced to show the boiling ranges of the dimers of the lower boiling mono-olefins:

Boiling points of olefin dimers

	°F.
Hexylene.....	155
Octylene.....	255
Decylene.....	323
Dodecylene.....	417

The tendency of the gaseous mono-olefins to polymerize varies considerably when using different catalysts and also with the same catalyst.

The present process is an adaptation of a particular type of catalysts to selectively polymerize normally gaseous olefins, and particularly those present in the gases from oil cracking operations. In addition the invention contemplates the further utilization of the saturated paraffinic counterparts of normally gaseous olefins to produce further quantities of polymerizable gases so that substantially complete utilization of hydrocarbons of 3 and 4 carbon atoms in the production of liquid motor fuel fractions is accomplished.

In one specific embodiment, the invention comprises the treatment of hydrocarbon gas mixtures comprising both paraffin and olefin hydrocarbons with solid phosphoric acid catalysts in stages characterized by variable temperature, e. g. of the order of 75° F. to 500° F. and pressure and catalytic relationships to selectively and successively polymerize and separate the olefins in the order of their reactivity, following which the residual paraffinic hydrocarbons are catalytically dehydrogenated, the hydrogen separated and the olefins recycled to catalytic polymerization.

In a preferred embodiment, the process is directed to the treatment of the hydrocarbon gas mixtures produced incidental to oil cracking operations, particularly those containing relatively high percentages of 3 and 4 carbon atom hydrocarbons such as stabilizer refluxes. The gases treated may also contain 2 carbon atom hydrocarbons.

I have found that by utilizing certain types of solid phosphoric acid catalysts which will be later described more in detail that the olefins present in hydrocarbon gas mixtures can be selectively and successively polymerized and have particularly determined that this separation is best effected while varying the temperatures at which the olefins are contacted with the solid catalysts over a considerable range. I have further found it to be both possible and practical to catalytically dehydrogenate residual paraffinic gases which remain after the polymerization of the olefins in cracked gas mixtures so that substantially all of the 3 and 4 carbon atom hydrocarbons are utilized as a source of good motor fuel stock.

The polymerizing catalysts which are used in the present connection are of a special and unique character and warrant detailed description, as they are evidently peculiar in their action. They are made generally by mixing an acid of phosphorus, preferably a phosphoric acid such as the ortho and the pyro acid, with a substantially unreactive and generally siliceous adsorbent until a paste is obtained, this paste being then calcined to produce a solid cake, which is ground and sized to produce catalyst granules. It has been found in the case of highly adsorbent materials, such as kieselguhr, that primary composites may be made in which the acid of phos-

phorus is the major constituent by weight. Thus a stiff paste is produced when 80 parts of commercial ortho-phosphoric acid is mixed at ordinary temperatures with 20 parts of kieselguhr. Conversely, relatively dry mixes result when about 30 parts of this acid is mixed with 70 parts by weight of the adsorbent. By incorporating varying quantities of phosphoric acid with these adsorbents, catalyst masses are produced which have varying polymerizing effectiveness which may be due to the variation in the actual contact surface of the acid which is exposed during service.

By controlling the proportions of adsorbent and acid and also the temperature employed in the drying or calcining step, granular catalyst composites may be produced which vary both in the percentage of the acidic component and in the strength of said component. Thus for the polymerization of such readily polymerizable compounds as iso-butylene catalysts may be utilized which have been produced by merely mixing commercial orthophosphoric acid of approximately 90% concentration with a siliceous and finely divided adsorbent material and drying at temperatures of approximately 250° F. to 300° F., which operation if conducted for periods of time which vary somewhat with the amount of acid present in the mix, ultimately yields solid catalysts which contain 100% orthophosphoric acid as their essential constituent.

When a catalyst composite comprising an acid approximating the pyro acid in composition as the essential active ingredient is desired, and the ortho acid has been used in the primary mixtures, the most effective catalysts are produced when the pasty mixtures are heated at temperatures from approximately 400 to 600° F. for a considerable period of time, usually from 40 to 60 hours. During this heating water is evolved and analysis shows that the remaining acid has a composition closely approaching that of the pyro acid. Advantages are frequently gained in utilizing the higher temperatures and also in starting with the pyro acid. When using this acid in primary mixes temperatures of from approximately 310 to 360° F. are used to insure proper fluidity. With efficient mixing devices the time required for producing uniform distribution is lowered considerably, frequently only 5 minutes being required. If dehydration is found to have taken place to too great an extent so that the polymerizing effectiveness is reduced (as shown by small scale tests) the particles may be contacted with superheated steam at temperatures within the approximate range of 400 to 600° F. to produce the catalytic acid of optimum composition.

A feature of the present invention resides in the employment of ordinarily liquid phosphoric acids as polymerizing catalysts in substantially solid form, this being accomplished by the alternative use of a number of different adsorbent carrying materials which vary somewhat in their adsorptive capacity and also in their chemical and physical properties and their influence upon the catalytic effect of the mixtures. The materials which may be employed are divisible roughly into two classes. The first class comprises materials of a predominately siliceous character and includes diatomaceous earth, kieselguhr and artificially prepared porous silicas such as, for example, "Sil-O-Cel". In the case of naturally occurring diatoms it is believed that they sometimes contain minor amounts of highly active aluminum oxide which in some instances seems to con-

tribute to the total catalytic effect of the solid catalyst. This active material is not present in the artificially prepared forms of silica.

The second class of materials which may be employed either alone or in conjunction with the first class (and with certain other optional ingredients to be later described) comprises generally certain members of the class of aluminum silicates and includes such naturally occurring substances as the various fuller's earths and clays such as bentonite, montmorillonite, etc. The class also includes certain artificially prepared aluminum silicates of which the product known as "Tonsil" is representative, this substance being in a sense a purified aluminum silicate made by treating certain selected clays with hydrochloric or other mineral acid and washing out the soluble reaction products. Both the naturally occurring and acid-treated substances in this general class are characterized by a high adsorptive capacity which is particularly in evidence in making up the present type of phosphoric acid catalysts, and they may also contain traces of active ingredients which assist in producing the desired polymerizing effects. Again each substance which may be used alternatively will exert its own specific influence which will not necessarily be identical with that of the other members of the class.

To assist in developing the character of the present invention the attached drawing has been provided which shows diagrammatically in general side elevation and by the use of conventional figures an arrangement of apparatus in which the process may be conducted.

Referring to the drawing olefin-containing hydrocarbon gas mixtures such as, for example, those produced as an overhead product in the stabilization of cracked naphthas may be introduced under moderate superatmospheric pressure of the order of 100-300 lbs. per square inch by way of line 1 containing control valve 2. A primary heater has not been indicated in the drawing though in practical operation this will usually be necessary to control the temperature of the gases entering the first catalytic treater. The gas mixtures thus admitted are passed in series through a number of catalytic treaters in which conditions of time, temperature and catalytic activity may be separately or collectively increased to produce progressively increasing severity of treating conditions so that the more readily polymerizable olefins are first polymerized and those more resistant to polymerizing influences are converted to liquids in the succeeding stages. Preferably there is intermediate cooling and condensation of polymers between stages followed by reheating of the gases and their further contacting with the preferred catalysts.

Treater 3 is indicated as the first member of a series and contains a mass of granular catalyst 4 supported upon a perforated false bottom 5, the gas mixture passing downwardly there-through. I have determined that isobutylene which is one of the heavier constituents of olefin-containing gas mixtures is rapidly polymerized at temperatures as low as 70° F. so that it may be removed from mixtures without affecting propylene at all, while the normal butenes are affected to a lesser degree depending upon the actual temperature employed which may vary somewhat with the composition of the gas mixture treated and particularly with the relative proportions of the different olefins therein contained. A factor

influencing the greater rate of polymerization of the four-carbon atom olefins at low temperatures of the order of 70-200° F. is probably that they may be partly in liquid phase when sufficient pressure is used and are therefore in contact with the catalyst for a period of time much greater than that corresponding to a vapor phase operation at temperatures above their critical temperatures. Later examples will indicate the relative rates of polymerization of isobutylene and the normal butylenes under temperature conditions at which propylene is substantially unaffected.

Under the normally low temperatures employed in the first treater of a series of the present character substantially all of the liquid polymers produced will condense in the lower portion of the treater below the catalyst mass and may be passed along with incondensable gases through a line 6 containing a control valve 7 through a cooler 8 and thence through a line 9 containing a control valve 10 to a receiver 11. The liquid polymers formed in this primary stage will consist principally of the dimer of isobutylene which has been found to be hydrogenatable to isooctane or 2,2,4-trimethylpentane. Some mixed polymerization of isobutylene with α - and β -butylenes will occur but to a lesser extent. These polymers may be drawn off through a line 12 containing a control valve 13.

The residual gases in receiver 11 which comprise the majority of the n-butenes, propylene and ethylene along with their paraffinic counterparts are passed through line 14 containing control valve 15 to a pump or compressor 16 which discharges them through line 17 containing control valve 18 and through an intermediate heating element 19 disposed to receive heat from a furnace 20.

We have found that it is possible and practical by utilizing temperatures below a given point to first cause the polymerization of the isobutylene present in olefin-containing mixtures so that a large amount of the polymer di-isobutylene which hydrogenates to 2,2,4-trimethyl pentane is formed and further that at slightly elevated temperature above this point and after the removal of a considerable portion of the isobutylene by this direct type of polymerization, the next stage in the polymerization reactions is represented by the condensation of residual isobutylene molecules with molecules of normal butenes, the mixed polymers formed in this manner yielding 2,2,3-trimethylpentane on hydrogenation. Since the mechanism of the reactions leading ultimately to polymer formation when employing phosphoric acid as a catalyst is evidently the primary formation of esters, the minimum temperature utilisable to form polymers from a given olefin will be in general that corresponding to the stability of the ester.

The average conditions for causing further mixed polymerization reactions between iso and n-butylenes in the second stage of a process of the present character are generally temperatures within the approximate range of 150-250° F. when employing the preferred type of solid phosphoric acid catalyst. Obviously if the amount of isobutylene remaining unpolymersized after the first stage of the operation is not enough to undergo mixed polymerization with the n-butylenes, the subsequent reactions in the second stage will be concerned only with the polymerization of α and β -butylenes among themselves. The exact temperatures used in this stage will there-

fore depend somewhat upon the relative proportions of iso and n-butylenes. When there is considerable isobutylene left the lower temperature may be used while if the n-butylenes predominate, temperatures approximating the higher limit are best employed.

When three stages of polymerizing treatment are employed as a practical treatment the temperature in the first stage may be approximately 70-200° F., in the second stage 200 to 400° F. and in the final stage above 400° F. These stages may, however, overlap.

Thus a gas mixture after the polymerization of a substantial portion of the original isobutylene content may be brought to a point within this temperature range and passed by way of line 21 containing control valve 22 through a second stationary mass of granular catalyst 24 supported on a perforated plate 25 in a secondary treater 23, and the polymers formed then liquefied by cooling and condensation. In this intermediate stage the liquid polymers may condense as in the first stage if they are present in sufficient concentration and they will then pass through a line 26 containing control valve 27, through a cooler 28 and thence through a line 29 containing control valve 30 to a receiver 31. The liquid polymers from the second stage which will contain a high percentage of mixed octylenes which are hydrogenatable to 2,2,3-trimethylpentane will be removed by way of draw line 32 containing control valve 33 to suitable storage. The residual gases which will be substantially free from 4-carbon atom olefins and contain only propylene and ethylene as representatives of this series will pass through line 34 containing control valve 35 to a second gas pump 36 and be discharged through line 37 containing control valve 38 through a heating element 39 arranged in a furnace setting 40.

The temperatures employed in the final catalytic treater which functions to polymerize residual propylene after removal of the 4-carbon atom olefins will be within the approximate range of 400-500° F. and as before the entering gases are heated to a suitable temperature within this range and passed through line 41 containing control valve 42 downwardly through a granular catalytic mass 44 supported upon a perforated false bottom 45 in a treater 43.

After the final stage of polymerization for the removal of propylene as a mixture of dimers and trimers thereof and possibly some mixed polymers with ethylene and any residual butylenes, the total gas mixture is passed by way of a line 46 containing control valve 47 to a cooler 48 to condense the polymers and the total products are then passed by way of line 49 containing control valve 50 to a receiver 51 which has a liquid draw line 52 containing a control valve 53. The gas mixture remaining at this point will contain substantially no olefins other than ethylene and relatively large percentages of 3 and 4 carbon atom paraffin hydrocarbons. In order to produce more olefins for polymerization this gas mixture is passed from the receiver by way of line 54 containing control valve 55 to a gas pump 56 and is discharged by way of line 57 containing control valve 58 through a heating element 59 disposed to receive heat from a furnace 60. The optimum temperature for catalytically dehydrogenating the 3 and 4-carbon atom paraffin hydrocarbons comprising propane, isobutane and n-butane is commonly within the range of 900-950° F. depending upon the concentration of

these hydrocarbons in the gas mixture and the particular catalyst employed. The pressure is substantially atmospheric or at most only sufficiently superatmospheric to cause flow through the dehydrogenator and the cooler following.

The heated gas mixture passes through line 61 containing control valve 62 and enters a chamber 63 containing a mass of dehydrogenating catalyst 64 supported upon a perforated plate 65. The catalysts which have been found most suitable for selectively dehydrogenating normally paraffinic gases to produce their olefinic counterparts are those which comprise refractory oxides and certain silicates as base material supporting minor additions of alkali and heavy metal salts. The preferred oxides are those of magnesium produced by calcining the normal magnesite at temperatures of approximately 1600° F. and aluminum oxide produced by a similar calcination of aluminum ores or precipitated aluminum hydroxide. The silicates which function in the best manner are principally the clays of the montmorillonite group which includes varieties of this mineral and particularly the crude montmorillonite known as bentonite which is found in numerous localities in the western portion of the United States.

The promoters which are used along with the base catalysts according to the concepts of the present invention include several classes of materials, principally salts of the alkali metals and heavy metals although the invention may also employ compounds of the alkaline earth metals. Active catalytic masses have been prepared by properly adding salts of the following acids as promoters: chromic, boric, carbonic, molybdic, pertitanic, permanganic, aluminic, phosphoric, etc. The method of addition of any given salt or its residue resulting from calcination, such as an oxide or a sulfide, will vary with the physical and chemical properties of the material, particularly with its solubility in water. The numerous alternative catalysts which may be thus prepared have distinct and peculiar activity when employed in dehydrogenating paraffinic gases and are not exactly equivalent in their action although substantially all possess sufficient catalyzing power to warrant their use in practice. The selection of any particular alternative catalyst will be determined by cost considerations and the efficiency of the selected catalyst upon the dehydrogenating reaction being dealt with.

According to one alternative mode of operation the gas mixture from the catalytic dehydrogenator which will contain considerable percentages of hydrogen, methane, ethane and ethylene is cooled sufficiently so that there is a separation as liquid of the hydrocarbons containing three or more carbon atoms while the fixed gases mentioned are withdrawn and their diluent effect upon subsequent treatment of the olefins is eliminated. Thus the hot gas mixture from dehydrogenating element 63 may pass through a line 66 containing control valve 67 through a cooler 68, the cooled products comprising both liquids and gases following line 69 containing control valve 70 to receiver 71, and the fixed gases mentioned being then withdrawn by way of vent line 72 containing control valve 73.

3 and 4-carbon atom olefins and such portions of their corresponding paraffins which have not been dehydrogenated will then be passed in liquid phase through line 74 containing control valve 75 to recirculating pump 76 which discharges the highly olefinic liquids through a line 77 contain-

ing control valve 78 back to line 1. These products may need some further heating to bring them to the proper temperature for the primary step of polymerization and this heat may be picked up from the gases in line 1 by direct heat exchange.

It will be obvious from the foregoing general description that the present process permits the practically complete utilization of all 3 and 4-carbon atom hydrocarbons present in hydrocarbon gas mixtures such as those released from the receivers of oil cracking plants or as stabilizer reflux formed from the primary gasoline-containing distillates. These hydrocarbons are treated in such a way that three separate polymer products are produced which in general will have a decreasing antiknock value in the order of their production. The process thus permits a control in the production of different types of blending material for improving the antiknock value of inferior motor fuel fractions.

The following example is given to illustrate the general character of the results obtainable by the present process though it is not given with the intent of correspondingly limiting the scope of the invention.

A cracked stabilizer reflux was treated which had the following approximate composition: Ethylene 4%, ethane 5%, propylene 20%, propane 30%, isobutylene 8%, n-butylenes 12%, and butanes 21%.

An efficient polymerizing catalyst was employed which had been manufactured by adding approximately 65% by weight of pyrophosphoric acid to kieselguhr followed by thorough mixing at a temperature of 320° F., further heating at 608° F. to produce a cake and grinding and sizing to produce catalyst granules of approximately 6-20 mesh. A mass of these granules was used as a filler in vertical treating towers which were employed in series to remove first the major portion of the isobutylene, then the butenes and lastly the propylene.

For the selective polymerization of the isobutylene content the stabilizer reflux which was substantially in liquid phase was passed downwardly through the first treating tower at normal atmospheric temperatures of approximately 70° F. at a pressure of about 200 pounds per square inch. The liquid resulting was stabilized by heating to approximately 150° F. which vaporized substantially all of the residual unpolymerized three and four-carbon atom olefins and left principally diisobutylene polymer. The gases were passed through a second treater at the temperature at which they were produced and this second catalyst contact polymerized substantially all of the residual four-carbon atom olefins to make a mixture of octenes.

Following the second stage the liquid polymers were separated and the gas mixture which then contained substantially only propylene as its olefinic constituent was heated to a temperature of 450° F. and passed through a third bed of catalyst to polymerize the propylene to dimeric and trimeric forms.

The residual gases from the stabilization of the propylene polymers were subjected to dehydrogenation at a temperature of 932° F. and substantially atmospheric pressure using as a catalyst a granular magnesium oxide supporting successive deposits of lead chromate and zinc sulfate, the total weight of the promoting substances being about 5% of the total weight of the composite. The dehydrogenated paraffins

were collected as liquids by appropriate cooling and compression while the lighter fixed gases were removed.

By the foregoing procedure substantially all of the 3- and 4-carbon atom hydrocarbons both paraffinic and olefinic were converted into liquids boiling within the gasoline range since the propane and butanes were each converted to a substantial degree into their corresponding olefins in the catalytic dehydrogenating step. The following table shows the average yields and octane numbers of the olefinic polymers produced continuously in the three stages.

Stage No.	Gals. M. cu. ft. of gas	O. N., motor method
1	2.0	85
2	6.0	82
3	10.0	80

These polymer fractions all boil within the approximate range of 122 to 437° F., the initial boiling point being due principally to the absorption of low boiling paraffin hydrocarbons originally present in the gas mixture and partly formed by secondary reactions involving release of hydrogen and hydrogenation of a certain portion of the low boiling olefins. The exact character of these reactions is difficult to follow on an analytical basis.

The novelty and utility of the present invention can be seen from the foregoing specification and example although neither section is to be construed as unduly limiting its generally broad scope.

I claim as my invention:

1. A process for the conversion of hydrocarbon gases comprising paraffin hydrocarbons and substantial amounts of propylene and butylenes into liquid hydrocarbons, which comprises subjecting the hydrocarbon gas to the action of a polymerizing catalyst at temperatures of the order of 70 to 200° F. under sufficient pressure to maintain a substantial portion thereof in liquid phase to polymerize and convert the butylenes into liquid olefinic hydrocarbons, separating the resulting liquid olefins from the unconverted gaseous hydrocarbons, subjecting the latter to the action of a polymerizing catalyst at a temperature of from 200 to 500° F. to polymerize and convert the propylene into liquid olefins, separating the resulting olefins from the unconverted residual gases, subjecting the latter containing the paraffin hydrocarbons to the action of a dehydrogenating catalyst at a dehydrogenating temperature to convert the paraffin hydrocarbons into gaseous olefins, separating resultant 3 and 4 carbon atom olefins as liquid from the gaseous dehydrogenation products of less than 3 carbon atoms returning the thus separated olefins in liquid form to the first-mentioned polymerizing stage for further polymerizing treatment, and recovering the polymerized liquid hydrocarbons produced in each polymerizing stage.

2. A process such as claimed in claim 1 wherein the polymerizing catalysts used comprise essentially a phosphoric acid.

3. A process such as claimed in claim 1 wherein the polymerizing catalysts used comprise essentially an acid of phosphorus.

4. A process such as claimed in claim 1 wherein the dehydrogenating catalyst comprises essentially aluminum oxide and a promoter catalyst.

5. A process for the conversion of hydrocarbon

gases comprising paraffin hydrocarbons and substantial amounts of propylene and butylenes into liquid hydrocarbons, which comprises subjecting the hydrocarbon gas to the action of a polymerizing catalyst comprising essentially a phosphoric acid at temperatures of the order of 70 to 200° F. and under sufficient superatmospheric pressure to maintain a substantial portion thereof in liquid phase to polymerize and convert the butylenes into liquid olefins, separating the resulting liquid olefins from the gaseous hydrocarbons, subjecting the latter to the action of a polymerizing catalyst comprising essentially a phosphoric acid at temperatures of the order of 200 to 500° F. under superatmospheric pressure to polymerize and convert the propylene into liquid olefins, separating the resulting liquid olefins from the residual gases, subjecting the latter containing the paraffin hydrocarbons to the action of a dehydrogenating catalyst comprising essentially aluminum oxide and a promoter, at a dehydrogenating temperature, to convert the paraffin hydrocarbons into gaseous olefins, separating resultant 3 and 4 carbon atom olefins as liquid from the gaseous dehydrogenation products of less than 3 carbon atoms and returning the thus separated olefins in liquid form to the first-mentioned polymerizing stage for further polymerizing treatment.

6. A process for the treatment of hydrocarbon gases to convert the same into liquid hydrocarbons which comprises, subjecting the hydrocarbon gases in several stages to the action of a polymerizing agent to selectively polymerize the 4-, 3- and 2-carbon atom olefins contained therein by subjecting the hydrocarbon gases under sufficient pressure to maintain a substantial portion thereof in liquid phase to the action of a polymerizing catalyst comprising essentially an acid of phosphorus at a temperature of from 70 to 200° F. in the first stage of the process, separating the liquid and gaseous hydrocarbons, subjecting the gaseous hydrocarbons to the action of a polymerizing catalyst comprising essentially an acid of phosphorus in the second stage of the process at a temperature of from 200 to 400° F., separating the liquid hydrocarbons from the gaseous hydrocarbons, subjecting the resulting gaseous hydrocarbons to the action of a polymerizing catalyst comprising essentially an acid of phosphorus at a temperature above 400° F., separating the liquid hydrocarbons from the residual gases comprising essentially paraffin hydrocarbons, subjecting the residual gases to the action of a dehydrogenating catalyst at a dehydrogenating temperature to convert the paraffin hydrocarbons into olefin hydrocarbons, separating resultant 3 and 4 carbon atom olefins as liquid from the gaseous dehydrogenation products of less than 3 carbon atoms returning thus separated olefin hydrocarbons in liquid form to the first-mentioned polymerizing stage for further polymerizing treatment, and recovering the polymerized liquid hydrocarbons produced in each of the polymerizing stages.

7. A process such as claimed in claim 6 wherein the dehydrogenating catalyst comprises essentially aluminum oxide and a promoter.

8. A process for the treatment of hydrocarbon gases to convert the same into liquid hydrocarbons which comprises, subjecting the hydrocarbon gases in several stages to the action of a polymerizing agent to selectively polymerize the 4-, 3- and 2-carbon atom olefins contained therein by subjecting the hydrocarbon gases under

sufficient pressure to maintain a substantial portion thereof in liquid phase to the action of a polymerizing catalyst comprising essentially a solid phosphoric acid at a temperature of from 5 70 to 200° F. in the first stage of the process, separating the liquid and gaseous hydrocarbons, subjecting the gaseous hydrocarbons to the action of a polymerizing catalyst comprising essentially a solid phosphoric acid in the second stage of the 10 process at a temperature of from 200 to 400° F., separating the liquid hydrocarbons from the gaseous hydrocarbons, subjecting the resulting gaseous hydrocarbons to the action of a polymerizing catalyst comprising essentially a solid phosphoric acid at a temperature above 400° F., separating the liquid hydrocarbons from the residual 15 gases comprising essentially paraffin hydrocarbons, subjecting the residual gases to the action of a dehydrogenating catalyst at a dehydrogenating temperature to convert the paraffin hydrocarbons into olefin hydrocarbons, separating resultant 3 and 4 carbon atom olefins as liquid 20 from the gaseous dehydrogenation products of less than 3 carbon atoms, returning the thus separated olefin hydrocarbons in liquid form to the first-mentioned polymerizing stage for further polymerizing treatment, and recovering the polymerized liquid hydrocarbons produced in each of the polymerizing stages.

30 9. A process for producing normally liquid

hydrocarbons from a mixture of 3 and 4 carbon atom olefins and paraffins which comprises subjecting the mixture to catalytic polymerization under sufficient pressure to maintain a substantial portion thereof in liquid phase, separating 5 resulting olefin polymers from the unconverted paraffins, dehydrogenating the separated paraffins to produce 3 and 4 carbon atom olefins therefrom, separating the latter as liquid from the gaseous dehydrogenation products of less than 3 10 carbon atoms, and supplying the 3 and 4 carbon atom olefins in liquid form to the polymerizing step.

10. A process for producing normally liquid hydrocarbons from a normally gaseous mixture 15 of more than 2 carbon atom hydrocarbons, including 4 carbon atom olefins and paraffins, which comprises subjecting the mixture to catalytic polymerization under sufficient pressure to maintain a substantial portion of the 4 carbon atom 20 hydrocarbons in liquid phase, separating resultant olefin polymers from the unconverted paraffins, dehydrogenating the separated paraffins to produce 4 carbon atom olefins therefrom, separating the latter as liquid from gaseous dehydrogenation products of less than 3 carbon atoms 25 and supplying the 4 carbon atom olefins in liquid form to the polymerizing step.

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