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TREATMENT OF HYDROCARBONS

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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 superior value as antiknock blending fluids for gasolines inferior in this respect.

Oil cracking processes which are in use as a means of supplementing the supply of gasoline obtainable by straight run distillation from crudes, and also for producing higher antiknock value material than the so-called "natural" gasolines i. e. gasolines which are produced by straight distillation of crude oils, are also productive of considerable quantities of fixed gases and heavy residual products, both liquid and solid, which are in a sense waste products of the process in that very little utilization of them has been made other than as fuels. 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}
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

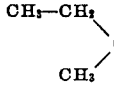
The tendency to polymerize of the gaseous mono-olefins varies considerably when using different catalysts and also with the same catalyst. The present process is an adaptation of a particular type of catalyst to selectively polymerize the olefins in hydrocarbon gas mixtures, and particularly those present in the gases from oil cracking operations.

In one specific embodiment the present invention comprises the treatment of olefin-containing hydrocarbon gas mixtures with solid phosphoric acid catalysts in two or more stages to selectively and successively remove and separate the olefins in the order of their reactivity. As a feature of the invention, the concentration of phosphoric acid is increased from stage to stage. As an illustration, the solid catalyst in the first stage may contain less than 50%, for example, between 30% and 40% of a phosphoric acid, and that in the second stage in excess of 50% acid, for example, between 60% and 70%. The temperature of treatment may also be increased from stage to stage. Thus a temperature of from 125° F. to 175° F. may be used in the first stage and a temperature of from 175° F. to 500° F. in the second stage. Suitable conditions for a three-stage operation are 30% to 40% phosphoric acid and a temperature of 125° to 175° F. in the first stage, about 50% acid and a temperature of 225° to 275° F. in the second stage, and more than 60% acid and a temperature of 350 to 500° F. in the third stage.

In a preferred embodiment the process is directed to the treatment of the fixed hydrocarbon gas mixtures produced incidental to oil cracking operations.

The following table shows in greater detail the structural formulas and boiling points of the

normal and iso-olefins which may be present in varying proportions in gas mixtures treated by the present process:

Compounds	Formula	Boiling point ° C.
Ethylene	$CH_2=CH_2$	−105
Propylene	$CH_3CH=CH_2$	−48
Ethyl ethylene	$CH_3CH_2CH=CH_2$	−5
Plane-sym. dimethyl ethyl-ene (butenes)	$CH_3\cdot CH=CH\cdot CH_3$	+1
Axial-sym. dimethyl ethyl-ene (butenes)	$CH_3\cdot CH=CH\cdot CH_3$	+2.5
Unsym. dimethyl ethylene (iso-butylene)	$(CH_3)_2C=CH_2$	−6
n-Propyl ethylene α-amylene	$CH_3CH_2CH_2CH=CH_2$	+39
Isopropyl ethylene α-isoamylene	$(CH_3)_2CH\cdot CH=CH_2$	+21
Sym. methyl ethyl ethylene β-amylene	$CH_3\cdot CH_2\cdot CH=CH\cdot CH_3$	+36
Unsym. methyl ethyl ethylene γ-amylene	CH_3-CH_2 	+31
Trimethyl ethylene β-isoamylene	$(CH_3)_2C=CH\cdot CH_3$	+36
Tetramethyl ethylene	$(CH_3)_2C=C(CH_3)_2$	+73

It has been found that by utilizing solid composite catalysts containing increasing amounts of phosphoric acids the olefins present in hydrocarbon gas mixtures can be more or less selectively polymerized. In general, the compounds of higher molecular weight and condensed or iso-structure are removed first. As a rule the amount of five carbon atom hydrocarbons in cracked gas mixtures is small and not a considerable item either in the matter of direct recovery by absorption processes or indirect recovery by polymerization by processes of the present character. In this sense iso-butylene may be considered as the most reactive and readily polymerizable of the compounds normally encountered and in the following description of the operation of the process it will be so considered.

The 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 or 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 phosphorus is the major constituent by weight. Thus a stiff paste is produced when 80 parts of commercial orthophosphoric acid are mixed at ordinary temperatures with 20 parts of kieselguhr. Conversely, relatively dry mixes result when about 30 parts of this acid are 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. To produce catalysts useful for selectively polymerizing alpha and beta butenes after iso-butylene has been selectively removed it is preferable to employ conditions which ultimately produce an acid somewhere between 100% ortho and 100% pyro acid in composition, and in this operation the temperature of calcining will vary from approximately 300° F. to 400° F., depending again upon the exact amount of acid by weight of the mixture and the type of the adsorbent.

When a catalyst composite comprising the pyro acid 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. 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 500° F. to produce the catalytic acid of optimum composition. When utilizing pyro acid in the initial mixes it is preferable to use somewhat elevated temperatures in the mixing step, usually between 250 and 350° F., to increase the fluidity of the acid and insure rapid and uniform distribution throughout the adsorbent.

The main 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 absorptive 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 contribute 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 earth 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.

In some cases the structure of the solid phosphoric acid catalyst may be improved by the primary incorporation of organic materials which yield a carbonaceus residue on heating. Substances which may be used in this manner include such materials as cellulose, starches, sugars, glue, gelatin, flour, molasses, agar-agar, etc. They evidently function as binders to some extent to prevent the breakdown of the catalyst structure when subjected to elevated temperatures and the action of hydrocarbon vapors or liquids in service.

In carrying out the process on a mixture of olefin-containing hydrocarbon gases the general procedure is to contact the gas mixture successively with contact masses containing increasing quantities of a phosphoric acid in admixture with an adsorbent. Thus, iso-butylene is selectively removed from a gas mixture by first contacting the mixture with a solid catalyst mass which is relatively weak in its polymerizing action and which may contain ordinarily about 30% by weight of either orthophosphoric acid or mixtures varying in strength between 100% ortho acid and the pure pyro acid, and 70% by weight of a siliceous carrier, usually kieselguhr. By suitably varying the temperature and time of contact it is possible to use catalyst composites containing the pyro acid at this point, although somewhat greater selectivity may be obtained with masses containing ortho acid as the essential ingredient. Under temperature conditions of from 220° F. to 625° F. with a catalyst of this character and even pressures as high as 200 lbs., there is substantially no action upon olefins other than iso-butylene, which is converted principally into its dimer, iso-octene. In a simple two-stage operation the next step consists in contacting the residual gases after separation of liquid polymers with solid phosphoric acid catalysts containing approximately 70% of pyro-phosphoric acid and 30% of adsorbent by weight at temperatures of approximately 400° to 500° F. and moderately superatmospheric pressures of the order of 100 to 200 lbs. per square inch, or higher, which obtain in the receivers of cracking plants or in stabilizers operating on primary cracked distillates. In this second stage, residual butenes, propylene, and to some extent ethylene, are polymerized to form gasoline boiling range liquids. By grading the amount of phosphoric acid in the catalyst masses, selective polymerization of the butenes may also be made with little or no effect upon propylene and ethylene, although for most practical purposes a two-stage operation is sufficient.

Where separation and selective polymerizing of iso-butylene, normal butenes and propylene, is required or desirable, the operation may be conducted in three stages. In the first stage the conditions will be the same as those recited in the preceding paragraph. In the second stage, wherein alpha and beta butenes are polymerized, catalyst composites containing about 50% by weight of phosphoric acid varying in composition between 100% ortho acid and 100% pyro acid may be used, and temperatures of from approximately 225° F. to 275° F. After the removal of the butenes in this stage the severity of treatment in respect to amount and type of acid and the temperatures employed is then increased to correspond to those of the second stage of the two-stage operation just described above. In this third stage the polymers will be produced entirely from propylene.

The invention may employ as a preliminary treatment any suitable method for the removal of hydrogen sulphide, low boiling mercaptans, dienes and other gases which may interfere with the normal functioning of the catalysts or the production of polymers of sufficient purity for ready incorporation with refined gasolines. On the other hand, the liquid products may be subjected to any of the ordinary chemical treatments commonly employed on cracked distillates, such as a limited amount of sulphuric acid, caustic soda, sweetening reagents and the addition of small amounts of inhibitors.

The catalysts are best employed in vertical cylindrical towers and best results are commonly obtained by passing olefin-containing gas mixtures downwardly therethrough after preheating the gases to some temperature found to be most suitable for the selective removal of the olefins. The down flow keeps any liquid condensates washed from the catalyst particles and prevents contamination of their surfaces by the gradual deposition of high boiling polymers, which eventually carbonize and make regeneration of the catalyst particles necessary. The regeneration steps commonly comprise: (1) removal of distillable materials by the use of superheated steam at temperatures of approximately 600° to 700° F.; (2) the use of oxidizing gas mixtures of graded oxygen content to burn out the carbonaceous material; and (3) the rehydration of the acid by steam at temperatures of 400° to 500° F. In the burning step it is most advantageous in commercial units to employ primarily instead of air a flue gas mixture produced by using only a very slight excess of air in the combustion of the fuel, so that the total oxygen content is below 1%. If air is used at first too high temperatures are likely to develop and portions of the catalyst will be over-burned, causing a loss of the volatile meta acid, which is formed as a result of too extensive dehydration. In the burning step the temperature of 950° F. should not be exceeded.

The reactions of polymerization of olefins are exothermic and consequently the temperature of a gas mixture on passage through a bed of preferred catalysts tends to rise in proportion to the percentage of olefins present, the strength of the catalyst and the rate of passage of the gas, and advantages are sometimes gained by intermediate cooling between towers connected in series. This may be extended not only to the removal of the initially formed liquid polymers by partial cooling but also to the complete liquefaction of liquid polymers and intermediate stabilization to per-

mit only the residual gases to contact with further quantities of the catalyst.

In lieu of catalysts of varying acid content in successive towers, catalysts which are either fresh or partially spent may be employed to arrive at the desired selective polymerizing effects.

Solid phosphoric acid catalysts are characterized by their ability to polymerize olefins to produce relatively low boiling hydrocarbon polymers rather than heavy tars or pitches and by their long life due to the absence of such highly carbonaceous reaction products and also due to lack of oxidizing tendency in the phosphoric acid which constitutes the major portion thereof. In contrast to this it is notable that when employing sulphuric acid as a polymerizing agent, caution is necessary to prevent oxidation and undesirable side reactions such as ester formation and that, when employing metal halides such as aluminum chloride or zinc chloride, the tendency toward the formation of heavy polymers is very pronounced, so that it is not possible to produce more than minor amounts of desired low boiling hydrocarbons without the concurrent production of large quantities of heavy materials. Furthermore, such catalysts are readily regenerated after they have been contaminated by surface carbon deposits after long periods of service by merely burning off the deposits with air or other oxidizing gas at moderate temperatures. A still further advantage resides in the fact that they are substantially of a non-corrosive character as compared with the decided corrosive action of liquid phosphoric acid and other liquid polymerizing agents. The peculiar structural strength of catalyst masses of the present type should be noted in connection with the general advantages which they possess, this being of special commercial value.

The following examples are given to indicate the character of the results obtainable by the use of the present process, although not with the intention of correspondingly limiting the scope of the invention:

Example 1

A gas mixture consisting of 89% by volume of propylene and 11% by volume of iso-butylene was passed at 140 pounds pressure and a temperature of 305° F. over a catalyst prepared by incorporating 30 parts by weight of 89% ortho-phosphoric acid and 70 parts by weight of diatomaceous earth and calcining the mixture according to the general methods described in preceding paragraphs. By controlling the space velocity it was possible to selectively polymerize 85% of the iso-butylene present in the mixture without affecting the propylene. By contacting the gas mixture further with a catalyst made by mixing 60 parts by weight of pyro-phosphoric acid and 40 parts by weight of diatomaceous earth and calcining according to the preferred procedure the complete polymerization of the remaining olefins was effected.

Example 2

This example is given to illustrate the possibility in accordance with the present process of selectively polymerizing iso-butylene in the presence of its closely related isomer, 1-butene.

A gas mixture comprising 88% by volume of 1-butene and 12% by volume of iso-butylene was passed at 100 pounds pressure and at a temperature of 212° F. through a bed of catalyst comprising initially 30% of ortho-phosphoric acid as in Example 1. At the optimum rate of flow consistent with plant capacity it was found possible to selectively remove 70% of the iso-butylene as polymer under these conditions. At a temperature of 350° F. at a slightly increased space velocity over the catalyst 80% of the iso-butylene could be removed with a slight effect upon the 1-butene. Increasing the temperature still further, that is up to 617° F., indicated that the optimum had been exceeded, so that only 20% of the iso-butylene appeared as polymer even when employing varying gas rates. This was probably due to the shortened time of contact. Even at the highest temperature employed, however, substantially none of the 1-butene was polymerized, though some was isomerized into 2-butene.

Example 3

This illustrates the applicability of the process to the treatment of cracked hydrocarbon gas mixtures. The idea of selective and successive polymerization was applied to a light hydrocarbon reflux produced in stabilizing a primary cracked naphtha to a given vapor pressure. The following table shows the olefin content of the mixture treated:

	Percent
Ethylene	5
Propylene	25
n-Butenes	15
Isobutylene	5

The gas mixture was passed successively through three treating towers containing solid phosphoric acid catalysts. The first tower contained a granular catalyst bed in which the active phosphoric acid constituent was approximately 40% by weight of the total material. At a temperature of 175° F. the isobutylene was selectively polymerized and removed as liquid polymers. This liquid material had a blending octane number of approximately 120.

Prior to their admission to the second tower, the gases were heated to a temperature of 270° F. and passed downwardly through a bed of catalyst which consisted of 60% by weight of a phosphoric acid approximating the pyro acid in composition and 40% by weight of kieselguhr and some silico-phosphoric acid complexes. In this step residual 4-carbon atom olefins were polymerized to form a liquid polymer having a blending octane number of 105–110.

In the final stage of the process the gases were heated to a temperature of 450° F. and passed through a bed of catalyst similar in composition to that employed in the second stage of treatment. This removed about 85% of the residual propylene and furnished a yield of liquid polymers having a blending octane number of about 90. In this stage some of the ethylene was removed by condensation with the propylene as shown by the presence of some pentenes and heptenes in the polymers. The major portion, however, of the ethylene was unaffected.

The character of the invention is evident from the preceding specification and the results obtainable are illustrated by the three preceding examples although neither the descriptive material nor the numerical data are given with the intention of unduly limiting its scope.

We claim as our invention:

1. A process for the treatment of a mixture of 3 and 4 carbon atom olefin hydrocarbons to produce liquid polymers therefrom which comprises, subjecting said mixture of olefin hydrocarbons in stages to the action of a polymerizing agent com-

prising an earthy adsorbent and phosphoric acid containing less than 40% and more than 30% of phosphoric acid at a temperature of less than 175° F. and more than 125° F., and then to the action of a polymerizing agent comprising phosphoric acid and an earthy adsorbent containing more than 60% of phosphoric acid and less than 70% at a temperature higher than 175° F. and less than 500° F.

2. A process for the treatment of a mixture of 3 and 4 carbon atom olefin hydrocarbons to produce liquid polymers therefrom which comprises, subjecting said mixture of olefin hydrocarbons in stages to the action of a polymerizing agent comprising an earthy adsorbent and phosphoric acid containing less than 40% and more than 30% of phosphoric acid at a temperature of less than 175° F. and more than 125° F., then to the action of a polymerizing agent comprising phosphoric acid and an earthy adsorbent containing about 50% by weight of phosphoric acid at a temperature greater than 225° F. and less than 275° F., and then to the action of a polymerizing agent comprising phosphoric acid and an earthy adsorbent containing between 60% and 70% of phosphoric acid at a temperature higher than 350° F. and less than 500° F.

3. A process for producing liquid hydrocarbons from a hydrocarbon mixture containing isobutene, normal butenes and propylene which comprises contacting the mixture with solid phosphoric acid catalyst in a first polymerizing stage wherein the phosphoric acid concentration of the catalyst and the polymerizing temperature are controlled and correlated to selectively polymerize isobutene from the mixture, then contacting the remaining unpolymerized portion of the mixture with additional solid phosphoric acid catalyst in a second polymerizing stage wherein the phosphoric acid concentration of the catalyst and the polymerizing temperature are controlled and correlated to selectively polymerize normal butenes, and finally contacting the remaining propylene content of the mixture with still additional solid phosphoric acid catalyst in a third polymerizing stage wherein the phosphoric acid concentration of the catalyst and the polymerizing temperature are controlled and correlated for optimum polymerization of propylene.

4. A process for producing liquid hydrocarbons from a hydrocarbon mixture containing butenes and propylene which comprises contacting the mixture with solid phosphoric acid catalyst at polymerizing temperature, the phosphoric acid concentration of the catalyst and the temperature being controlled and correlated to selectively polymerize butenes from the mixture, and then contacting the remaining portion of the mixture with additional solid phosphoric acid catalyst under conditions of temperature and phosphoric acid concentration which are controlled and correlated for optimum polymerization of propylene.

5. A process for producing liquid hydrocarbons from a hydrocarbon mixture containing isobutene and normal butenes which comprises contacting the mixture at polymerizing temperature with solid phosphoric acid catalyst, the phosphoric acid concentration of the catalyst and the temperature being controlled and correlated to selectively polymerize isobutene from the mixture, and then contacting the remaining portion of the mixture with additional solid phosphoric acid catalyst under conditions of temperature and phosphoric acid concentration which are controlled and correlated for optimum polymerization of normal butenes.

6. A process for producing liquid hydrocarbons from a hydrocarbon mixture containing isobutene, normal butenes and propylene which comprises contacting the mixture with solid phosphoric acid catalyst in a first polymerizing stage wherein the phosphoric acid concentration of the catalyst and the polymerizing temperature are controlled and correlated to selectively polymerize isobutene from the mixture, then selectively polymerizing normal butenes from the remaining portion of the mixture by contacting the latter with additional solid phosphoric acid catalyst in a second polymerizing stage of higher phosphoric acid concentration and higher temperature than the first stage, and finally polymerizing the propylene content of the mixture by contacting the same with still additional solid phosphoric acid catalyst in a third polymerizing stage of higher phosphoric acid concentration and higher temperature than the second stage.

7. A process for producing liquid hydrocarbons from a hydrocarbon mixture containing butenes and propylene which comprises contacting the mixture with solid phosphoric acid catalyst in a polymerizing stage wherein the phosphoric acid concentration of the catalyst and the polymerizing temperature are controlled and correlated to selectively polymerize butenes from the mixture, and then polymerizing the propylene content of the mixture by contacting the same with additional solid phosphoric acid catalyst in a separate polymerizing stage of higher phosphoric acid concentration and higher temperature than the first-mentioned stage.

8. A process for producing liquid hydrocarbons from a hydrocarbon mixture containing isobutene and normal butenes which comprises contacting the mixture with solid phosphoric acid catalyst in a polymerizing stage wherein the phosphoric acid concentration of the catalyst and the polymerizing temperature are controlled and correlated to selectively polymerize isobutene from the mixture, and then polymerizing the normal butene content of the mixture by contacting the same with additional solid phosphoric acid catalyst in a separate polymerizing stage of higher phosphoric acid concentration and higher temperature than the first-mentioned stage.

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