

UNITED STATES PATENT OFFICE

2,060,871

MANUFACTURE OF HYDROCARBONS

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No Drawing. Application June 22, 1933, Serial No. 677,079

8 Claims. (Cl. 196-10)

This invention relates more particularly to the treatment of olefinic hydrocarbons which are normally gaseous at ordinary temperatures and pressures.

Olefinic hydrocarbons with which the present invention is concerned occur along with corresponding paraffinic or saturated hydrocarbons in commercial hydrocarbon mixtures such as those encountered in the cracking of petroleum, in gas making processes and as by-products in various chemical industries. In general they are more chemically active than other classes of hydrocarbons, particularly if they contain more than one double bond or triple bonds between carbon atoms. Even when under mild catalytic influence they exhibit this reactivity in their pronounced tendency to polymerize and form substances of higher molecular weight. In some instances this instability may be a disadvantage, particularly in the case of cracked hydrocarbon oil distillates which are of suitable boiling range to permit their use in internal combustion engines, since the polymers which develop on storage are of a gummy character and impart color to the oil.

The present process provides for more effectively utilizing the olefinic constituents of commercial hydrocarbon mixtures particularly those occurring in the gases from oil cracking processes to produce valuable derivatives therefrom and it may also be applied to individual olefins produced by special chemical methods or by fractionation of mixtures.

In one specific embodiment the invention comprises the treatment of normally gaseous olefinic hydrocarbons with phosphoric acid containing metal salts as promoter catalysts to controllably produce polymers therefrom which are utilisable as constituents of motor fuel. Salts of zinc are preferred.

To assist in developing the exact character of the invention the following table is introduced, which gives the formulas and boiling points of some of the lower molecular weight olefins:

Compounds	Formula	Boiling point °C.
Ethylene.....	CH ₂ =CH ₂	-105
Propylene.....	CH ₃ CH=CH ₂	-43
Ethyl ethylene.....	CH ₃ CH ₂ CH=CH ₂	-5
Plane-sym. } dimethyl ethylene	CH ₃ .CH=CH.CH ₃	+1
Axial-sym. }		+2.5
Unsym. dimethyl ethylene.....	(CH ₃) ₂ C=CH ₂	-6
n-Propyl ethylene.....	CH ₃ CH ₂ CH ₂ CH=CH ₂	+39
α-amylenes.....		
Isopropyl ethylene.....	(CH ₃) ₂ CH.CH=CH ₂	+21
α-isoamylenes.....		

Compounds	Formula	Boiling point °C.
Sym. methyl ethyl ethylene	CH ₃ .CH ₂ .CH=CH.CH ₃	+36
β-amylenes.....		
Unsym. methylethylethylene	CH ₃ .CH ₂ .CH ₂ .CH=CH ₂	+31
γ-amylenes.....		
Trimethyl ethylene	(CH ₃) ₂ C=CH.CH ₃	+36
β-isoamylenes.....	(CH ₃) ₂ C=C(CH ₃) ₂	+73
Tetramethyl ethylene.....		

The boiling points given in the table indicate that the four carbon atom members are gaseous at ordinary temperatures and that the five carbon atom members may readily exist in minor proportions in commercial gas mixtures, such as the cracked hydrocarbon mixtures with which the present invention is specially concerned.

The present process is particularly directed to the production of dimers and trimers from mono-olefins, particularly such olefins whose dimers and trimers boil between the approximate range of commercial motor fuel, say, for example, from 100 to 400° F. It has been found that the dimers and some of the trimers of propylene, the butylenes and amylenes boil within this range and furthermore, that these compounds have unusually high anti-knock characteristics. The following table shows the approximate boiling points of the dimers of propylene, butylenes, amylenes and hexylenes which all occur in appreciable quantities in the gases from oil cracking processes:

Boiling points of olefin dimers

	°F.
Hexylene	155
Octylene	255
Decylene	323
Dodecylene	417

Ethylene is as a rule the most resistant to the action of the preferred catalyst mixtures but by a suitable choice of promoter catalysts and conditions of operation it may be caused to polymerize itself and also to combine with other olefin molecules.

Polymers of higher molecular weight than the di- or tri-molecular polymers of gaseous olefins are of too high boiling point to be used in commercial gasolines and the end products of too extensive polymerization are resinous pitchy solids which are entirely unsuitable. By using phosphoric acid containing selected promoter catalysts according to the present process and choosing properly interrelated temperatures and pressures the polymerizing reactions may be held in the

- desired direction without the formation of the higher molecular weight substances mentioned. Concentrated phosphoric acid of commercial grade may be employed and in some instances, particularly where the concentration of olefins is low in the gas mixture, the temperature may be raised considerably, sometimes as high as 200° C. so that the desired reactions are accelerated and yet there is no undue formation of undesirably heavy polymers. Any desired pressure may be employed, the influence of this factor being principally to increase the capacity of apparatus though pressure may also accelerate the reactions of polymerization. When low or moderate temperatures are employed liquefaction of some olefins will occur if the pressure employed is above the critical pressure, this further assisting in increasing capacity of equipment and intimacy of contact.
- The compounds which may be employed as promoter catalysts in phosphoric acid comprise various salts of metals such as, for example, phosphates, chlorides or sulphates of aluminum, zinc, cadmium, mercury, iron, nickel, cobalt, copper, magnesium, etc. The use of any particular metal salt will be limited by its solubility in phosphoric acid of any particular strength. Concentrations of salts as high as 20% of the phosphoric acid may be used when the salts are sufficiently soluble though as a rule amounts of from 2 to 10% are sufficient for accomplishing the desired acceleration of the catalytic effect of the acid. The additional catalytic effect observed in these cases may be due either to the basic or the acid radicals, or both. It is obvious that metal oxides or metals themselves may be dissolved in phosphoric acid to an extent depending upon the solubility of the phosphates formed.
- The salts which may be thus employed to accelerate and modify the catalyzing effect of phosphoric acid upon olefins comprise a number of classes which differ from each other in many of their physical and chemical characteristics. It is to be understood that the different salts which may be used are not exact equivalents in their action but that each exerts its own peculiar influence upon the catalyzing power of the base material, to-wit: the phosphoric acid. The field of catalysis is to a large extent still in an experimental state even though many substances have been found by empirical methods to have special value in certain reactions. Thus, nickel is generally the best catalyst for hydrogenating fatty oils and the oxides of vanadium are generally the best for catalyzing the production of sulphur trioxide from sulphur dioxide-oxygen mixtures. In the present instance different salts may be chosen which will produce decidedly better results than others when working with olefin gas mixtures of varying composition. Particular instances of metal salts which have positive accelerating action and others which have a neutral or a negative effect will be developed in subsequent examples.
- Ordinary ortho-phosphoric acid, H_3PO_4 , is generally the preferred acid of phosphorus for use in connection with reactions of the present character. However, it is within the scope of the invention to employ other acids of phosphorus insofar as they possess sufficient catalyzing activity either alone or after the addition of promoter catalysts.

Below is given a tabulation of the known acids of phosphorus along with their melting points and temperatures of decomposition:

Acids of phosphorus

			M. P. ° C.	Dec. ° C.
Hypophosphorous	H_3PO_2		26.5	Above 5
Orthophosphorous	H_3PO_3	$P_2O_3 \cdot 3H_2O$	70.0	200
Pyrophosphorous	$H_4P_2O_5$	$P_2O_5 \cdot 2H_2O$	38.0	130
Hypophosphoric	$H_4P_2O_6$		55.0	70
Metaphosphoric	HPO_3	$P_2O_5 \cdot H_2O$	Sublimes	
Pyrophosphoric	$H_4P_2O_7$	$P_2O_5 \cdot 2H_2O$	61	Looses $\frac{1}{2}$ H_2O at 213
Orthophosphoric	H_3PO_4	$P_2O_5 \cdot 3H_2O$	38.6	

In producing low boiling polymers from gaseous olefins or mixtures thereof such as are encountered in commercial hydrocarbon gases, the simplest mode of operation consists in bubbling the gas mixture through a stationary body of acid catalyst mixture of regulated strength and composition containing a selected promoter catalyst, using cooling coils or precooled gases to keep down the temperature rise if this is shown to be necessary. Atmospheric temperatures and pressures are frequently sufficient to produce good treating effects but, as previously stated, temperatures as high as 200° C. may be employed and superatmospheric pressures of the order of 10 to 20 atmospheres may be used with safety if the time of contact and the amount of catalyst are properly chosen. When operating with more or less pure olefins or gas mixtures of high olefin content, a control is offered in blending the mixture with some inert gas such as hydrogen or nitrogen to assist in controlling the rate of reaction. Batch treatments may be conducted in autoclaves, or, if desired, continuous counterflow treatments may be employed as these are known in the art, and in such cases the gas mixture may be passed upwardly counter-current to descending streams of acid catalyst mixture in towers containing filling or packing material or regularly spaced trays to assist in subdividing the stream of catalyst. The polymerized olefins will appear as a layer upon the surface of the acid in the case of the first mentioned batch method of treatment, from which they may be removed continuously or intermittently. When employing the counter-current tower operation, liquid will be recovered from above the acid after settling in intermediate accumulators.

A marked advantage in the use of phosphoric acid catalysts containing metal salt promoters resides in the fact that very little solution of original olefins or their polymers occurs therein. The consumption of acid is small and a given amount may be used repeatedly without the necessity for purification steps which must ordinarily be employed in removing sludge products from such powerful polymerizing and condensing agents as sulphuric acid, aluminum chloride, etcetera. Neither phosphoric nor phosphorous acid has any pronounced oxidizing action under suitable conditions of treatment so that condensation reactions due to removal of hydrogen or abstraction of water are substantially absent.

The present type of catalyst comprising phosphoric acid as a base and containing minor amounts of metal salts as promoters possess the advantage of maintaining their activity over long periods of time and producing high yields of relatively low boiling liquid hydrocarbon polymers per unit weight of catalyst material. Use of the invention indicates that there is some ester formation with the phosphoric acid, which reaction, however, does not lower but frequently enhances the catalytic power of the mixture. Extensive formation of esters after a certain concentration is reached may result in the formation of small yields of

alcohols such as, for example, isopropyl alcohol, but this production is seldom of serious consequence. Such alcohols as may be formed, if not desired as a constituent of the liquid hydrocarbon polymers, are removable by solution in water.

In carrying out the invention the apparatus used and the conditions of operation chosen in respect to temperature, pressure, proportioning of reacting constituents, choice of acid and promoter catalyst, etcetera, will be varied to suit individual cases. When the process is used to polymerize individual olefins or mixtures of known composition, it is possible to so regulate the treatments that compounds or mixtures of compounds of very definite composition may be produced. For example, any one of the olefins given in the first table (with the possible exception of ethylene) may be polymerized to form a corresponding polymer with a minimum production of undesirable by-products from side reactions.

The following examples are selected to show the results obtainable when using catalysts of the present character. In all the experiments which furnish the data commercial propylene of 95% purity was used, since the efficiency of treatments is much more readily calculated when dealing with a single compound. However, comparable results have been obtained on mixtures of olefins such as those present in cracking hydrocarbon gases. In Table I following are shown some results obtained when polymerizing commercial propylene with 89% phosphoric acid alone and with promoter salts at atmospheric pressure, the gas being merely bubbled through the catalyst mixture:

TABLE I

Polymerization of propylene with 89% phosphoric acid at atmospheric pressure

Catalyst	Temperature ° C.	Per cent liquid yield
89% H_3PO_4 -----	155-160	3.6
89% H_3PO_4 +5% Zn-----	150-180	7.7
89% H_3PO_4 +5% $ZnCl_2$ -----	150-155	15.2
89% H_3PO_4 +5% $MgCl_2$ -----	155-160	16.0

This data shows that the presence of zinc phosphate (resulting from the solution of zinc in phosphoric acid) doubled the liquid yield under a given set of experimental conditions, while the presence of zinc chloride in approximately the same percentage increased the yield four times over that obtainable with the acid alone.

The following data shown in Table II shows the results of two comparative experiments run at atmospheric pressure using 100% phosphoric acid with and without the addition of 5% anhydrous copper sulfate:

Table II

Catalyst	Temperature ° C.	Percent liquid yield
100% H_3PO_4 -----	150-140	8.7
100% H_3PO_4 -5% $CuSO_4$ -----	150-155	19.6

The effect of the promoter in this case was to double the yield of liquid products, even when employing a higher rate of gas flow in the apparatus. Owing to the use of the anhydrous salt there may have been some effect due to the dehydration of the acid.

In Table III data is introduced to show that

certain salts may have a neutral or negative effect:

Table III

Polymerization of propylene heating in a rotating autoclave in the presence of H_3PO_4 containing promoter as shown. Initial pressure 150 pounds per square inch

Part 1				
Catalyst	Temp. ° C.	Max. pres. kg./cm. ²	Final pres. kg./cm. ²	Percent liquid yield
89% H_3PO_4 -----	150	39	25	41.8
89% H_3PO_4 + $Cd_3(PO_4)_2$ -----	150	40	25	43.0
89% H_3PO_4 + $Cd(C_2H_3O_2)_2$ -----	150	41	31.5	29.0
89% H_3PO_4 + $CuCl_2$ -----	150	43	37	21.4
89% H_3PO_4 + KBF_4 -----	150	35	28	22.2
Part 2				
100% H_3PO_4 + $CuCl_2$ -----	125	39	36	6.0
100% H_3PO_4 + $CuSO_4$ -----	125	38	24	32.8

The data shows that cadmium phosphate (produced by dissolving metallic cadmium in the acid) had a very slight positive catalytic action while cadmium acetate, cuprous chloride and potassium borofluoride slowed up the catalytic activity of the acid, and therefore in the present instance were not desirable. Such salts, however, in the case of more readily polymerizable olefins, may have value in preventing over-polymerization with concurrent production of high boiling polymers of a tarry character which are unsuitable as constituents of motor fuel.

The comparative data shown in Part 2 of the table between cupric chloride and cupric sulfate indicate some of the variations to be expected when using different salts. The copper sulfate is again of outstanding value in accelerating the action under the conditions of the experiment which it will be noted differ from the conditions in Part 1 in the use of a lower temperature.

The character of the invention is sufficiently described in the preceding specification and its value is brought out by the experimental data introduced, but neither is to be construed as imposing undue limitations thereon except as hereinbefore specified.

I claim as my invention:

1. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of a catalytic acid of phosphorus and a metallic salt which promotes the catalytic activity of the acid and selected from the group consisting of the phosphates, chlorides, and sulphates of aluminum, zinc, cadmium, mercury, iron, nickel, cobalt, copper, and magnesium.

2. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of a phosphoric acid and a metallic salt which promotes the catalytic activity of the acid and selected from the group consisting of the phosphates, chlorides, and sulphates of aluminum, zinc, cadmium, mercury, iron, nickel, cobalt, copper, and magnesium.

3. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of pyrophosphoric acid and a metallic salt which promotes the catalytic activity of the acid and selected from the group consisting of the phosphates, chlorides, and sulphates of aluminum,

zinc, cadmium, mercury, iron, nickel, cobalt, copper, and magnesium.

4. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of a phosphoric acid solution having dissolved therein a metallic salt which promotes the catalytic activity of the acid and selected from the group consisting of the phosphates, chlorides, and sulphates of aluminum, zinc, cadmium, mercury, iron, nickel, cobalt, copper, and magnesium.
5. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of a phosphoric acid and a zinc salt.

6. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of pyrophosphoric acid and a zinc salt.

7. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of a phosphoric acid solution having a zinc salt dissolved therein.

8. A process for converting normally gaseous olefins into hydrocarbon liquids which comprises polymerizing the olefins in the presence of a catalytic acid of phosphorus and a zinc salt.

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