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PROCESS FOR PRODUCING MOTOR FUELS

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This invention pertains to a process for the production of motor fuels from normally gaseous olefines and more particularly fuels that exert superior resistance to detonation when employed in internal combustion motors of high compression ratio operated at relatively high temperatures.

Specifically, the process employed comprises the steps of directing the catalytic polymerization of gaseous olefines by means of special catalysts and carefully controlled conditions and of subsequently hydrogenating the liquid polymer product.

The polymerization of gaseous olefines containing from 2 to 5 carbon atoms per molecule, such for instance as result from the cracking of petroleum oils, has already been demonstrated as practical on a commercial scale for materially augmenting the available supply of motor fuel and particularly of fuel having higher than average non-detonating or "octane" value. Both thermal and catalytic means have been demonstrated for effecting such polymerization.

While such polymer fuels alone and in blends with lower "octane" fuels admirably meet the present operating requirements in automotive service they all fail in two essential respects of meeting the more drastic requirements for aviation use. These two respects: low "lead susceptiblity" and "octane instability" at high engine temperatures, which will be discussed at greater length hereinafter, are apparently both due to the inherent chemical structure of the polymer molecules and hence cannot be avoided though it is still possible that they may be overcome by appropriate subsequent changes in that structure. With the true polymers produced by catalytic means, substantially 100% olefines, the most obvious possible change in structure is of course by hydrogenation to the corresponding paraffines. The paraffines, however, as a class have long been recognized to be very substantially inferior to olefines in "octane" value. Only the specific highly branched chain paraffines such as 2,2,4-trimethyl pentane and tetramethyl butane, which have for some time been known to possess the three essential characteristics of high "octane number", adequate "octane stability" and satisfactory "lead susceptibility", have justified any hope whatever that the hydrogenation of polymer olefines generally might lead to fuels superior in these respects to the olefines themselves.

However, only in the single instance in which isobutene has been segregated in quantity and polymerization has been catalytically effected under conditions to yield substantially pure diisobutylene, which on hydrogenation gives 2,2,4-trimethyl pentane, has the commercial polymerization of a petroluem gas hitherto yielded a base stock from which an ideal aviation fuel could be produced. When the entire cracking gas containing ethylene, propylene and the three butenes has been employed in hitherto known catalytic polymerization processes the product on hydrogenation has invariably suffered a very material reduction in "octane value" and has in other ways fallen short of the ideal aviation fuel.

Since isobutene constitutes only about one third of the butenes available from the widely employed methods of petroleum cracking and a still smaller proportion of the total olefines available it is obvious that any method which would reliably utilize a substantial proportion of the total olefines or even of the 1- and 2-butene available and produce polymer olefines of such structure that when hydrogenated they gave branched chain paraffines comparable in properties to the classic 2,2,4-trimethyl pentane would not only constitute a material contribution to the petroleum industry but to the national defense as well.

It is the broad object of this invention to provide a process which will convert gaseous olefines other than isobutene into a satisfactory base stock for the manufacture of aviation motor fuels.

It is a more specific object of this invention to provide a process for the catalytic polymerization of mixed butenes to polymer olefines which on hydrogenation suffer no appreciable reduction in "octane number".

It is another specific object of this invention to provide a process for the polymerization of mixed butenes by means of a catalyst which is capable of more exact control than hitherto known to produce both a maximum of polymers boiling in the range of aviation gasolines and a type of polymer which may be hydrogenated to high octane stable lead susceptible fuels.

Still other and more specific objects of the invention will be apparent from the description and discussion which follows:

Since the production of polymer liquids which may be hydrogenated to high octane fuels appears to require that such polymers shall have a very definite structure and since such structure is not inherent in all possible polymers of the proper boiling range producible from the normally gaseous olefines available in quantity it follows that

any process for the production of the desirable type of polymer must be capable of definite control to a high degree. Purely thermal means are seldom capable of effecting but a single one of several possible reactions to the exclusion of all others. Especially is this true of hydrocarbon reactions and still more especially of olefine polymerization. The efficient production of polymers suitable for subsequent conversion by hydrogenation to superior fuels must consequently be realized entirely by catalytic means.

Of the various materials known to possess olefine polymerizing ability the strong inorganic acids, their salts and certain of their specific derivatives constitute the group which appears to be most suitable for the production of low boiling motor fuels. Of this group the oxy-acids of phosphorus have not only yielded the most generally satisfactory catalysts but at the same time at least three specific types of catalyst which are more or less suited to the process of the present invention.

The "solid phosphoric acid" catalysts disclosed in U. S. Patent #1,993,513, such metal phosphates as calcium and cadmium and the phosphoric "acid-film" catalyst, disclosed and claimed in application Serial No. 67,917 copending herewith, are representative of these types. In the first, liquid orthophosphoric or phosphorous acid is absorbed in a highly porous silicious material such as diatomaceous earth or kieselguhr and calcined either with or without the inclusion of various binders, promoters or other ingredients. In the second the solid salt per se or appropriately supported on an inert carrier constitutes the contact agent. In the third, the pure liquid acid is adsorbed in a thin film on the surface of a non-porous inert supporting material such as broken glassy quartz. All are capable of effecting the "directed" polymerization of olefines, an essential feature of this invention, though the third is possessed of additional points of advantage which appear to make it the more desirable and the more practical choice. The subsequent description of the process of this invention is accordingly limited substantially to the acid-film type of catalyst.

In such a catalyst a thin uniform film of acid is caused to be adsorbed on the surface of a non-porous inert solid support of such dimensions as will provide a practical maximum surface area per unit of volume and still permit of free gas passage at space velocities up to about 3.0–5.0 (volume of gas/volume of catalyst/minute). Orthophosphoric acid on broken 10–20 mesh glassy quartz has been found highly satisfactory. The non-porosity of the support and the thin acid film combine to make the catalyst both uniformly active throughout and uniformly accessible to reactants, which features make possible a more exact control of the polymerization reaction with a very substantial reduction in the amount of over-polymerization. The small amount of acid required to form the film, equivalent on the average to about 3.5 pounds of P_2O_5 per cubic foot of catalyst, permits of ready and rapid adjustment of the acid concentration through control of the humidity of the gas passing and permits an exceptionally low catalyst first cost and regeneration cost. The practical indestructibility of the support contributes materially to long catalyst life.

The catalyst may simply and conveniently be prepared in place in the catalyst chamber by lodging the supporting material therein, flowing dilute aqueous acid over it and bringing the acid to polymerizing concentration in a current of gas of controlled humidity as described and claimed in copending application Serial No. 67,921.

In general phosphoric acid-film catalysts in which the acid is from about 95 to 115% H_3PO_4, corresponding to 68.5 to 83% P_2O_5, have substantial activity in polymerizing the normally gaseous olefines with a rather flat maximum activity between about 100 and 110% H_3PO_4, 72.5 to 79.8% P_2O_5. The extremes of operating temperature are at about 50° F. on the low side, due to slowness of reaction, and at about 500° F. on the high side due to carbonization of hydrocarbons by the strong acid. Pressures as high as economically practical are usually preferable.

When the rate of passage of a gas containing olefines of from 2 to 5 carbon atoms per molecule over a phosphoric acid-film catalyst is controlled so that a liquid polymer product of any given boiling range is produced its properties as a motor fuel are substantially the same irrespective of the identity or proportions of individual olefines present or of the temperature, within the practical range, at which polymerization is effected. The product is entirely olefinic, has a relatively high octane value under moderate engine conditions, is but little improved in octane value by the addition of tetraethyl lead in considerable quantity and exhibits considerable loss in octane value in operation under more severe engine conditions.

This general similarity of the polymer olefines is apparent from the following table in which data are presented for a comprehensive range of such fuels tested under several conditions.

Polymer fuels; preparation and test data

Fuel	Composition			Conditions of polymerization			Octane number—M. M.						
							cc. T. E. L.				Series 30		
	C_3H_6	1 and 2-C_4H_8	Iso-C_4H_8	Temp.	Press.	Catalyst	0	1	2	3	212°	300°	375°
				° F.	*Lbs./sq. in.*								
1	8	51	41	300	200	Film	82.3				100+	92.6	74
2	5	27	68	377	200	do	85.1	87.2	87.1	87.1			
3*	45	22	17	325–475	150	Solid	82						
4	10	79	11	300–380	210	Film	83.8						
5		50	50	375–400	100	$Ca(PO_3)_2$ (solid)					90+	94	79
6	6	54	40	230–270	200	Film	84						
7	16	54	30	410–470	210	Solid	82						
8		10	90	220	Atm.	H_2SO_4 (liquid)	84.5	87.8	88.1	88.2			
9**	75	15		1000	500	Thermal					82	77	69

* 11% butane, 5% pentane.
** 10% C_2H_4; all percent approximate.

Fuels 1–9 inclusive all correspond to light motor gasoline though their boiling ranges were not identical. Under "Composition" is indicated, except for fuel #9, the proportions by weight of propylene, normal butenes and isobutene which were used up in forming the polymer liquid. In fuel #9 ethylene corresponding to about 10% by weight of the fuel went into its formation. Octane numbers by both the A. S. T. M. "motor method" and the "Series 30 motor" test method, the former with 0, 1, 2 and 3 cubic centimeters of tetraethyl lead per gallon, are recorded.

Polymerization temperatures covering the wide range from approximately 200° to 500° F., widely different catalysts and olefines from nearly pure isobutene to largely propylene are thus seen to give polymer liquids differing by only about 3.0 octane numbers, susceptible of improvement by only about 3.0 octane numbers when treated with 3 cc. per gallon of tetraethyl lead and suffering a drastic reduction in octane value at the higher engine temperatures.

The fundamental dissimilarity in such olefinic fuels becomes apparent only after they have been hydrogenated. This is clearly illustrated by the following data:

Octane values (motor method) of polymer fuels, before and after hydrogenation

Fuel number	Before hydrogenation	After hydrogenation
1	82.3	89.2
2	85.1	94.5
3	82.0	61.0
4	83.8	82.2
6	84.0	88.0
7	82.0	62.0
8	84.5	97.0

While the 100% olefinic fuels of this group vary by only about 3.0 octane numbers, on complete hydrogenation they are changed in octane value by from +12.5 to −21 units with a maximum variation of 36 octane numbers in the hydrogenated product.

Starting from this decidedly confused picture of the hydrogenated polymers the two major factors in securing a desirable polymer for hydrogenation were discovered to be, first, that propylene is usually undesirable in the polymerization reaction, and second, that the reaction with a phosphoric acid or phosphate catalyst must be effected within rather narrow temperature limits. By so operating a polymer product may be produced which on hydrogenation shows an invariable increase in octane number, so long as the boiling range of the fuel is unchanged, shows an entirely normal improvement in octane number on the addition of tetraethyl lead and is only slightly, if at all, depreciated by severe engine operating conditions. Careful control of other conditions than temperature, such for instance as the removal of the products of the reaction at the proper point in their passage through the catalyst, were also found to contribute materially to this desirable result. Certain corollary facts were also discovered with contribute largely to the success of practical operation. For instance, these catalysts were found to be extremely selective in polymerizing isobutene at temperatures of about 100° F. and below while they exhibit an entire lack of selectivity between propylene and the normal butenes at any practical temperature.

In bringing these several discoveries together into a practical process for the production of fuel especially adapted for aviation use the amount of olefine containing gas available and the proportions of individual olefines contained must be given first consideration. When sufficient isobutene is available to satisfy requirements for such a fuel the gas need not be fractionated and may after proper purification be polymerized directly at a temperature of about 100° F. wherupon substantially only isobutene will be removed and di-isobutylene formed. Since a small amount of propylene polymers may be permissible as indicated by fuels 1, 2 and 6 above, the following data obtained on a gas in which isobutene constituted 52% of the olefines present will serve to indicate how much the temperature of polymerization may be permitted to vary when olefines other than isobutene are present:

Selectivity in polymerization of isobutene

Temp., °F.	Percent isobutene in olefine polymers
100	100
150	92
200	85
250	76
300	70
350	62
400	57
450	56
500	55

It will be noted that the selectivity for isobutene decreases in substantially a straight line with increasing temperature from 100 to 400° F. and that at 400° and above the ratio of olefines polymerized is substantially the same as the ratio in which they are present.

In such selective isobutene polymerizing step atmospheric or higher pressure may be employed as convenient. A rate of passage of the gas over the catalyst such that about 80% of the isobutene is removed will insure against over-polymerization resulting in any very considerable amount of polymers being produced which boil above the range of aviation gasoline. In case it is desirable to secure a higher recovery of isobutene it will usually be found advantageous to divide the catalyst into two series units and remove both heat of reaction and already formed polymer product between them. By such method up to 98–99% of the available isobutene may be utilized without danger of over-polymerization. In arriving at the proper division of catalyst to be made it will be found that a length of catalyst path which will give 80% conversion at a given gas rate should be divided into a first 10% and a final 90% and the heat and product removal stage interposed, whereupon the rate of gas passage may be safely reduced the small amount necessary to give 98–99% removal of isobutene.

Having removed such of the isobutene as is necessary to provide aviation fuel requirements the remainder of the gas, containing normal butenes, propylene and ethylene, may be subjected to further polymerization at a higher temperature which will depend almost entirely upon the use to which the secondary polymer product is to be put. If it is merely for blending with fuels of poor octane value to produce an improved automotive fuel no hydrogenation will be required and polymerization temperatures up to the practical limit of 450–475° F. may be employed. Interstage heat and product removal may still however be useful in permitting a maximum recovery of olefines without an undue

amount of too high boiling polymers being formed.

If on the other hand it be desirable to produce a fuel of between about 80 and 85 octane number, as measured by the A. S. T. M. Motor Method, which at the same time is normally responsive to the addition of tetraethyl lead and has good octane stability under severe engine conditions it will be possible to do so by effecting polymerization of the isobutene free gas at an intermediate temperature, not above 400° F. and preferably not above an average of 350° F. Fuel #4 recorded in the foregoing tables may be taken as typical of such a product.

When the isobutene available is insufficient to provide the amount of aviation quality fuel required an entirely different procedure must be followed. A fairly close cut butane-butene fraction is prepared from the cracking still gas and polymerization is effected at a temperature only moderately above that at which the catalyst begins to lose its extreme selectivity for isobutene, as for instance between 200° and 300° F. Other factors being equal it will be found that the lower the temperature of polymerization of the mixed butenes the greater the assurance that the octene polymer product when hydrogenated will show a substantial increase rather than a decrease in octane number and be otherwise suitable as an aviation fuel.

In the following table fuels 13–18 inclusive, prepared from synthetic mixtures, are indicative of the results to be obtained by the polymerization and hydrogenation of a butane-butene cut. Fuel #10 indicates the normal effect of tetraethyl lead on a hydrogenated polymer as contrasted to unhydrogenated fuels #2 and #8. Fuels 11 and 12 indicate the octane stability of hydrogenated fuels as contrasted to unhydrogenated fuels #1 and #5.

Butene polymer fuels

Fuel number	Composition				Temp. of polym., °F.	Polymer	Octane number—M. M.						
							Hydrogenated polymers						
							cc. T. E. L.				Series 30		
	Iso-C_4H_8	1-C_4H_8	2-C_4H_8	C_3H_6			0	1	2	3	212°	300°	375°
10	33	48*		19	380	82	86	92	96.5	99.5			
11	30	54*		16	350	81.4	86.4	----	------	------	86.5	88.7	84.8
12	41	51*		8	300	82.7	92.4	----	------	------	95.2	95.3	91.3
13	----------	88	12	--------	400	80–83	80	----	------	------	------	------	------
14	40	--------	60	--------	400	80–83	85	----	------	------	------	------	------
15	40	--------	60	--------	230	80–83	93	----	------	------	------	------	------
16	44	--------	56	--------	300	80–83	93	----	------	------	------	------	------
17	46	--------	54	--------	250	80–83	96	----	------	------	------	------	------
18	----------	--------	100	--------	200	80–83	93	----	------	------	------	------	------

*Total 1- and 2-butenes.

While fuels 2, 8, 12, 15, 16 and 17 of the foregoing tables indicate the quality of fuels possible through the directed polymerization of mixed butenes followed by hydrogenation of the polymer product one further example will serve to indicate the quantity of such superior fuels resulting and at the same time also to illustrate a specific modification of the invention.

A fuel derived from 8% proplyene, 42% isobutene and 50% of normal butenes was prepared by polymerization with a phosphoric acid catalyst at 200–210° F. It had an octane number (Motor Method) of 84.6 before hydrogenation and 94.2 after 95% saturation. On redistillation through an efficient fractionating column, equivalent to 13 theoretical plates, to a vapor line temperature of 224° F. 60% of a distillate which contained nothing higher than the dimer of butene was obtained which on hydrogenation was found to have an octane number (M. M.) of 97 as compared to 98–100 for the hydrogenated di-isobutylene, prepared by selectively polymerizing isobutene by hitherto known methods. It is thus thus seen that by means of directed mixed butene polymerization and fractionation 60/42 or 1.43 times as much fuel of substantially the same octane value resulted as could have been prepared from the isobutene consumed. The fuel must, therefore, contain a substantial proportion of iso-octanes other than the 2,2,4-trimethyl pentane which would have resulted from the isobutene alone. Obviously the fractionation step might, so far as the quality of the hydrogenated dimer fuel is concerned, either precede or follow hydrogenation.

When the olefine containing gas available for polymerization has resulted from the pyrolytic decomposition or cracking of a mineral hydrocarbon many substances are present other than pure hydrocarbons which may poison the catalyst or contaminate the product, or both: It has for instance been found that most gases from petroleum cracking contain a very small proportion of an alkaline reacting body which if not removed acts as a powerful poison to a phosphoric acid film catalyst. The gas must therefore usually be given a dilute acid wash prior to any polymerization treatment with this catalyst. On the other hand the numerous sulfur containing substances present appear to have substantially no effect on the catalyst. Those of acidic nature, such as hydrogen sulfide and the mercaptans, if not removed, are apparently condensed with an olefine double bond during the polymerization and appear as very difficulty removable sulfur bodies in the product. Washing the gas with an alkaline solution prior to passage over the catalyst is accordingly usually desirable.

After proper purification, the water vapor content of the gas is adjusted to correspond to the water vapor pressure of the concentration of acid desired in the catalyst at the temperature to be employed in the polymerization. This step is of the utmost importance with the film type catalyst because of the small bulk of acid contained and the rapidity with which water vapor equilibrium is established.

The polymerization catalyst chamber may take any convenient form such as a series of elongated vertical cylinders which may be arranged in parallel or series as occasion demands. Provision for

removal of the heat of reaction is essential since it would be sufficient, if not dissipated, to raise the temperature of the reaction mixture by more than 200° F. Removal of polymer product part-way through the polymerization stage is, as already pointed out, often desirable to prevent over-polymerization and should be comprehended in the plant design.

For hydrogenation of the polymer product at least two widely different processes are available which appear to give identical results so far as the essential fuel characteristics of the product are concerned.

When the polymer liquid is low in sulfur a more or less conventional low-pressure liquid phase process employing a sulfur-sensitive catalyst such as active nickel may be employed. The catalyst may be prepared by the reduction of nickel nitrate, oxide or formate with hydrogen at about 600° F. or by dissolving the aluminum from a nickel-aluminum alloy with caustic solution. When a reduced nickel is employed it is often preferable to support it on an inert carrier such as kieselguhr, pumice or alumina.

Since substantially no polymer from a petroleum gas will ever be entirely sulfur free the proportion of catalyst to polymer will vary somewhat with the sulfur content. With a very low sulfur polymer from 1 to 2% by weight of catalyst is ample to effect rapid and complete hydrogenation. With more sulfur in the polymer an appreciable amount of nickel is rendered inactive and a higher proportion of catalyst is necessary.

The catalyst is suspended in the polymer liquid and charged to an apparatus equipped for efficient mechanical agitation and capable of withstanding moderate pressures. Hydrogen, free from carbon monoxide, is then supplied at a temperature of about 300° F. and to a total pressure of about 200 pounds per square inch. Under such conditions hydrogenation is substantially complete in 30 minutes. Hydrogen consumption is about 20 cubic feet (N. T. P.) per gallon of polymer and the volume yield of hydrogenated product is approximately 104%. The boiling range is practically identical with that of the polymer charged.

In the alternative method of hydrogenation, which is particularly adapted for use with high sulfur polymers, hydrogen at a presure of 3000–3500 pounds per square inch and a sulfur insensitive catalyst such as molybdenum sulfide is employed. The catalyst may be in any convenient form such as cylindrical pellets of about 0.5 x 0.5 centimeter. The operation is preferably continuous and employs about one volume of liquid polymer per volume of catalyst per hour. A suitable temperature of reaction is 460–480° F. The consumption of hydrogen is about 35 cubic feet (N. T. P.) per gallon of polymer and the volume yield of hydrogenated product is from 90 to 95%.

The improvement in octane number, in octane stability and in lead susceptibility effected through hydrogenation by either method is directly proportional to the extent to which the olefines are converted to paraffines. While it might thus occasionally be sufficient to discontinue hydrogenation at some lower percentage, the maximum saturation (95–99%) readily effected will usually be found preferable.

After hydrogenation by either process the product will usually require to be redistilled to produce a fuel of the exact boiling range desired but will seldom require other treatment.

While certain modes of operation have been described as desirable for meeting certain specific demands, there are many other ways in which the principles taught might be applied to meet both changes in the olefine containing raw material available and the particular balance of products desired.

Having now disclosed the essential steps in a process for the production of high octane stable liquid motor fuels from normally gaseous olefines and especially from the mixed butenes and having described how the process may be operated to yield the desired useful result;

We claim:

1. A process for producing iso-octanes from a normally gaseous hydrocarbon mixture containing isobutene and the normal butenes which comprises subjecting said mixture to the action of a catalyst consisting of a thin film of phosphoric acid adsorbed on a non-porous, inert, solid support at a temperature between 50° and about 400° F. for a time and at a pressure effective to produce octenes, separating the resultant liquid polymers from unpolymerized material, and saturating the former by hydrogenation.

2. A process for producing 2,2,4-trimethyl pentane from a normally gaseous hydrocarbon mixture containing butenes and propylene, which comprises subjecting said mixture to the action of a catalyst consisting of a thin film of phosphoric acid adsorbed on a non-porous, inert, solid support at a temperature of from 50° to about 100° F. for a time and at a presure effective to selectively polymerize the isobutene contained in the mixture, separating the resulting octenes from the unpolymerized material, and saturating said octenes by hydrogenation.

3. A process for producing iso-octanes having an octane number above about 80 from a normally gaseous hydrocarbon mixture containing olefines consisting substantially of the isomeric butenes, which comprises subjecting said mixture to the action of a catalyst consisting of a thin film of phosphoric acid adsorbed on a non-porous, inert, solid suport at a temperature between about 100° and 400° F. to effect the mixed polymerization of isobutene and the normal butenes, separating the resulting polymers from the unpolymerized material, and saturating the former by hydrogenation.

4. The process as defined in claim 3 further characterized in that said temperature is substantially within the range of from 150° to 300° F.

5. A process for producing iso-octanes having an octane number above about 80 from a normally gaseous hydrocarbon mixture containing olefines consisting substantially of the isomeric butenes, which comprises subjecting said mixture to the action of a catalyst consisting of a thin film of phosphoric acid adsorbed on a non-porous, inert, solid support at a temperature between about 100° and 400° F. to effect the mixed polymerization of normal butenes and isobutene to an extent such that the weight of polymer produced is substantially in excess of the weight of isobutene consumed, separating the polymer liquid from the unpolymerized material, and saturating the former by hydrogenation.

6. The process as defined in claim 5 further characterized in that the weight of total octanes produced is at least 1.4 times the isobutene consumed.

7. A process for producing iso-octanes which have an octane number of at least 90, are normally responsive to further improvement in oc-

tane number on the addition of tetraethyl lead, and are not substantially depreciated by high engine temperatures encountered in aviation service, from a normally gaseous hydrocarbon mixture containing olefines consisting substantially of isobutene and the normal butenes, which comprises subjecting such mixture to the action of a catalyst consisting of a thin film of phosphoric acid adsorbed on a non-porous, inert, solid support at a temperature between about 150° and 300° F. to effect the mixed polymerization of normal and isobutene to an extent such that the weight of polymer produced is at least 1.4 times the weight of isobutene consumed, separating the resulting polymer liquid from unpolymerized material, and substantially saturating the former by hydrogenation.

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