UNITED STATES PATENT OFFICE

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MANUFACTURE OF HYDROCARBONS

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2 Claims. (Cl. 260—683)

This invention relates particularly to the manufacture of hydrocarbons suitable for use in motor fuel blends.

Still more specifically the invention relates to the manufacture of liquid olefinic hydrocarbons of an isomeric or branched chain structure which have the high antiknock characteristics of hydrocarbons of such condensed structure both before and after their hydrogenation to produce the corresponding paraffins.

The demands for motor fuels of continually increasing antiknock value due to the use of higher compression ratios in automobile and airplane engines have been met principally by cracking the relatively heavy portions of petroleum to produce low boiling distillates of a more unsaturated character than those producible directly from crude petroleums furnishing the original charging stock owing to the presence of higher percentages of olefins, naphthenes, and aromatics. However, the production by cracking of fuels having octane numbers above a certain point which is in the neighborhood of 70 is attended with increasing losses both as gas and heavy carbonaceous residues so that in practice the production of fuels having higher octane numbers than 70 is a very costly proceeding. In order to conserve the values lost in the gases recourse has been had to polymerizing their olefinic constituents either by thermal or catalytic processes with some success and this art is in the development stage at the present time.

The procedure most commonly followed in producing liquid hydrocarbon fractions from the gases from cracking operations has been principally along the line of employing the overhead distillates from the cracking plant stabilizers in which the three- and four-carbon atom hydrocarbons are more or less concentrated. In these overhead products commonly known as "stabilizer refluxes" the percentage of so-called higher olefins consisting of propene and the butenes may run from approximately 15 to as high as 40–50% depending upon the type of cracking process from which they were produced. A further development has been the separation by improved fractionation methods of the so-called butane-butene or "B—B" fractions which contain principally four carbon atom olefins and paraffins. Applying polymerization process either thermally or catalytically to stabilizer refluxes commonly gives a liquid product having an extended boiling range which contains polymers (principally dimers and trimers) of propene and the butenes along with some products of mixed polymerization. In the case of the "B—B" fractions a large percentage of the polymer products are dimers and trimers of the butenes which comprise various octenes and dodecenes respectively.

It has been further determined that at least when employing suitable catalysts the olefins in cuts in which they are concentrated may be more or less selectively and successively polymerized to make individual fractions having progressively changing characteristics. For example, isobutene may be first selectively polymerized under moderately severe conditions after which the n-butenes are polymerized under more severe conditions of time, temperature, etc. and lastly the propene is caused to undergo polymerization. The polymers of the butenes are principally octenes and in the case of isobutene the principal product is apparently a compound which readily hydrogenates to the well known 2,2,4-trimethyl pentane which is used as a standard representing 100 octane number in the motor testing of fuels. The octenes produced by the polymerization of n-butenes have somewhat lower octane numbers.

Specifications for aviation fuels are particularly stringent as regards antiknock value, saturation, and volatility, and can usually be met only by mixtures of isomeric paraffins boiling within the approximate range of from atmospheric to 400° F., and it is the purpose of the present invention to make possible the production of considerably increased yields of isoparaffin hydrocarbons boiling generally lower than the iso-octanes which constitute the principal products resulting from the polymerization of the olefins in the "B—B" fractions already mentioned.

In one specific embodiment the present invention comprises the manufacture of iso-heptenes by the mixed polymerization of isobutene and propene in the presence of solid phosphoric acid catalysts.

According to the present invention mixed polymerization is brought about between two normally gaseous olefins which are not adjacent in order of their reactivity in polymerization reactions. As already shown the order in which the normally gaseous olefins are polymerized as conditions of increasing severity are employed are isobutene, n-butenes, and propene, with a certain amount of intermediate products of mixed polymerization when going from one stage to another. It has now been determined, however, that the heptenes produced by the mixed polymerization of n-butenes and propene are considerably less valuable as sources of low boiling antiknock material than those resulting from the mixed polymerization of isobutene and propene. It may therefore be safely inferred that according to the rules governing the relation between

antiknock value and structure in hydrocarbons, the heptenes from the isobutene-propene polymerization are largely of isomeric structure while those produced from the n-butene-propene polymerization probably contain higher percentages of straight chain compounds. Owing to the difficulty of positively identifying the isomeric heptenes, no extensive efforts have been made to separate individual compounds but reliance has been placed principally upon the boiling range and octane numbers of the hydrogenated fractions.

To obtain the isobutene and propene necessary for reaction according to the present process, several methods may be employed. In one method isobutene may be selectively polymerized at relatively low temperatures of the order of normal atmospheric to 150° F. in the presence of the catalysts to be later described and then may be separately depolymerized at higher temperatures in the presence of the same type of catalyst. The isobutene may also be removed by treatment with relatively weak sulfuric acid of the order of 65–75% concentration after which the ter-butyl alcohol is produced by distillation of the ester and the alcohol then dehydrated by passage over such catalysts as aluminum oxide to reform isobutene. Another method of preparing isobutene consists in catalytically dehydrogenating isobutane which may be removed as a primary product in the stabilization of gasoline since this compound normally boils at 13° F. while the n-butane boils at 33° F. and there is a sufficient spread in the boiling points to enable a practical separation. The separation of isobutene from admixture with n-butenes is hardly practical since the iso compound boils at 22° F. while 1-butene boils at 24° F. and the 2-butenes boil from 34 to 36.5° F. As economic conditions warrant based on the increased yields of isoheptenes and the increased octane numbers made available, any method of preparing isobutene may be employed.

The preparation of propene is a simple matter since this compound boils at —56° F. and is readily fractionated from admixture with residual n-butenes in gaseous mixtures.

The preferred catalysts for effecting the manufacture of isoheptenes comprise the so-called "solid phosphoric acid" catalysts which are prepared by incorporating an equal or a major proportion by weight of an acid of phosphorus with a relatively inert and generally a siliceous carrier to form a paste and then calcining to produce a solid cake at temperatures of the order of 300° C. followed by grinding and sizing of the cake to produce solid catalyst granules. This procedure may be varied somewhat by first extruding and cutting the paste to make small particles of regular form and size which are then calcined to drive off moisture and produce as an active catalyst phosphoric acid of the required composition. It has been determined that the best solid phosphoric acid catalysts contain an acid approaching the pyro acid in composition as their active ingredient along with a variable amount of silico-phosphoric acid complexes when a highly siliceous carrier such as kieselguhr has been employed in the primary mixes.

The catalysts preferred for use in the present invention are characterized by the fact that they are precalcined before use both to fix the composition of the acid and to form particles of a more or less solid character capable of withstanding the conditions of service to which they are put. When these catalysts become coated with carbonaceous deposits they can be regenerated by air oxidation at temperatures of the order of 500° C. followed by contacting with superheated steam at about 250–300° C. to rehydrate the acid to the most desirable composition.

The preferred conditions of operation for producing isoheptenes from isobutene and propene with solid phosphoric acid catalysts are temperatures of the order of 200–325° F. and pressures of 550 lbs. per square inch which are maintained while passing the gas mixture downwardly through a bed of the granular catalyst at a rate consistent with the maximum production and antiknock quality of the isoheptene products. Following the polymerizing step the products are fractionated to recover gasoline boiling range liquids while the unreacted gases are separated and returned for further contacting with the catalyst after an examination of the relative proportions of the isobutene and propene which may be altered by the addition of either compound to the mixture as desired.

While the invention is particularly applicable to the treatment of gaseous mixtures containing equimolecular proportions of isobutene and propene it is also applicable to mixtures in which these reactants are present in nonequivalent proportions or in which they are mixed with paraffinic hydrocarbons. The principal requirement is the presence of only a minimum percentage of n-butenes which on the one hand would react with isobutene to form iso-octenes under polymerizing conditions of moderate severity or with the propene under more severe conditions to form heptenes of more or less normal structure.

The efficiency of the present process in common with other polymerizations with solid phosphoric acid catalysts, depends to a definite extent on maintaining the composition of the phosphoric acid catalyst in respect to its degree of hydration and for this reason best results in respect to life of the catalyst are obtained when a definite amount of steam is present in admixture with the hydrocarbons undergoing reaction. The absolute amount will vary considerably with the conditions of operation but usually are comprised within the range of 1–5%. This partial pressure effect serves to prevent loss of water from the catalyst particles with the formation of the relatively inactive metaphosphoric acid.

To show the advantages of the present invention as contrasted with other modes of operation to recover liquid hydrocarbon fractions from normally gaseous olefins by polymerization, the following numerical data is introduced though not with the intention of unduly limiting the proper scope of the invention.

Using the solid phosphoric acid catalysts described above on stabilizer reflux and similar mixtures at 450–550° F. and 100–200 lbs. pressure, gasoline boiling range polymer products are producible which are hydrogenatable to form aviation gasolines having octane numbers from 70–75.

Utilizing the "B—B" fractions and the conditions most favorable to the formation of isooctenes, the gasoline boiling range products may be hydrogenated to produce octane fractions having 95–96 octane number, although there is a lack of low boiling fractions required for proper volatility in aviation fuels.

To make low boiling hydrocarbon fractions from isobutene and propene, a gas mixture was

prepared which had the following composition by volume:

Composition of gas mixture treated

	Per cent by volume
Uncondensible	4.1
Propene	40.9
Propane	0.8
Isobutene	51.6
n-Butene	1.7
Butanes	0.9

This mixture was passed over a bed of solid phosphoric acid catalyst granules of approximately 4–10 mesh in size which contained approximately 65% by weight of equivalent of phosphoric acid calculated as P_2O_5. To determine the best conditions for the production of low boiling polymers having high octane number, a number of combinations of conditions were employed and the results of these experiments are indicated in the following table:

Mixed polymerization of isobutene and propene

Average temp., ° F.	324	257	217	200	319	312
Pressure, lbs./sq. in.	550	570	550	550	280	280
Gas charged, cu. ft./hr./pound catalyst	11.8	4.5	3.7	3.9	5.5	4.6
Exit gas, cu. ft./hr./pound catalyst	0.7	0.9	0.9	0.8	0.6	0.7
Polymerization of—						
Propene, percent	89	60	55	62	80	69
Isobutene, percent	99	98	96	93	99	99
Propene and isobutene	95	80	77	79	90	85
Ratio polymerized propene: isobutene	42:58	33:67	31:69	35:65	38:62	35:65
Polymer—						
Gal. / 1,000 cu. ft. charged	19.7	17.1	16.0	16.2	18.1	17.3
Fraction IBP–300° F., percent	68	66	72	66	60	64
Fraction 300–437° F.	28	27	21	26	37	34
Bottoms and loss	4	7	7	8	3	2
Hydrogenated IBP–300° F.—						
Fraction, octane number			90	93	93	91
Gravity, ° A. P. I. at 60° F.			70.3	71.5	72.3	70.0
A. S. T. M. distillation—						
IBP, ° F.			186	186	180	182
10 percent			194	194	193	191
20 percent			197	196	195	196
50 percent			204	204	199	203
90 percent			241	226	207	239
E. P., ° F.			324	293	226	295
Percent over			98.5	99.0	99.0	98.5
Percent bottoms			1.0	1.0	1.0	1.0
Percent loss			0.5	0.0	0.0	0.5
Vol. percent over at 212° F. based on:						
IBP–300° F. hydrogenated fraction			70	75	95	70
Total polymer			47	49	68	43
Percent by weight of gas charged converted into—						
IBP–300° F. hydrog.	62	52	56	52	52	53
IBP–212° F. hydrog.	43	39	53	50	36	37

It will be seen from the above table that the best results when considering the 95% yield of material boiling below 212° F. and the 93 octane number of the material boiling to 300° F., as well as the ratio of the propene to the isobutene undergoing mixed polymerization that the best conditions of operation for the particular mixture employed corresponded to from 200–220° F., a pressure of 550 lbs. per square inch and a charging rate of about 4 cu. ft. per hr. per lb. of catalyst. These conditions will of course be modified considerably when dealing with mixtures of different composition and olefin concentration and when using different types of plant equipment in respect to both absolute and relative capacities of units.

The nature of the present invention and its practical and commercial aspects will be evident from the foregoing specification and numerical data respectively although neither section is intended to be unduly limiting upon the proper scope of the invention.

We claim as our invention:

1. In the polymerization of an olefinic mixture containing isobutene and propene in the presence of solid phosphoric acid catalyst, the method of producing high yields of isoheptenes which comprises subjecting the olefinic mixture to the action of the solid phosphoric acid catalyst at a temperature of the order of 200 to 325° F. and under a pressure of about 500 to 600 lbs. per square inch whereby to effect mixed polymerization of isobutene and propene as the primary reaction in the process.

2. In the polymerization of an olefinic mixture containing isobutene and propene in the presence of solid phosphoric acid catalyst, the method of producing high yields of isoheptenes which comprises subjecting the olefinic mixture to the action of the solid phosphoric acid catalyst at a temperature of from about 200 to 220° F. and under a pressure of approximately 550 lbs. per square inch whereby to effect mixed polymerization of isobutene and propene as the primary reaction in the process.

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Certificate of Correction

Patent No. 2,270,302. January 20, 1942.

VLADIMIR IPATIEFF ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, lines 23 to 52 inclusive, strike out the table and insert instead the following—

Mixed polymerization of isobutene and propene

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Polymerization of—						
Propene, percent	89	60	55	62	80	69
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Propene and isobutene	95	80	77	79	90	85
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Fraction, octane number	90	93	93		91	
Gravity, ° A. P. I. at 60° F.	70.3	71.5	72.3		70.0	
A. S. T. M. distillation—						
IBP, ° F.	186	186	180		182	
10 percent	194	194	193		191	
20 percent	197	196	195		196	
50 percent	204	204	199		203	
90 percent	241	226	207		239	
E. P., ° F.	324	293	226		295	
Percent over	98.5	99.0	99.0		98.5	
Percent bottoms	1.0	1.0	1.0		1.0	
Percent loss	0.5	0.0	0.0		0.5	
Vol. percent over at 212° F. based on:						
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Total polymer	47	49	68		43	
Percent by weight of gas charged converted into—						
IBP–300° F. hydrog.	62	52	56	52	52	53
IBP–212° F. hydrog.	43	39	53	50	36	37

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of April, A. D. 1945.

[SEAL]

LESLIE FRAZER,
Acting Commissioner of Patents.