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TREATMENT OF PARAFFIN HYDROCARBONS

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This application is a continuation-in-part of my copending application Serial No. 161,588, filed August 30, 1937, which in turn is a continuation-in-part of my application Serial No. 32,638, filed July 22, 1935.

This invention relates to the alkylation of paraffin hydrocarbon with olefin hydrocarbons and in its preferred embodiment involves the alkylation of iso-paraffin hydrocarbons.

In a more specific sense the invention is concerned with a novel process for alkylating isobutane with olefins which are normally gaseous to produce saturated hydrocarbons of higher molecular weight which can be utilized as components of motor fuel for automobile and airplane engines.

The utilization of gaseous paraffins has been carried out in the past without catalysts by straight thermal treatment alone, or followed by polymerization of the olefins produced therefrom to produce motor fuels. The present process is a marked improvement on this type of operation.

In one specific embodiment the present invention comprises the alkylation of iso-paraffin hydrocarbons with olefin hydrocarbons in the presence of phosphoric acid catalysts at temperatures within the approximate range of 200–500° C. and under pressures of the order of 500–5000 lbs./sq. in.

A specific feature of the present invention is the employment of optimum temperature and pressure combinations when using phosphoric acid catalysts. It is within the scope of the invention to use aqueous ortho phosphoric or pyro phosphoric acids of different concentrations, and under certain conditions meta phosphoric acid may be employed whenever they are found to produce good results in the alkylation of a given isoparaffin with a given olefin or a mixture of isoparaffins with any olefin or a mixture of olefins but ortho and pyro phosphoric acid are preferred. It is further comprised as a special feature of the invention to employ the so-called "solid" phosphoric acid catalyst, the properties of which will be described presently in greater detail. It is to be recognized, however, that the action of these acids of phosphorus, which may be used alternatively, will not be exactly equivalent and are not necessarily interchangeable in alkylation reactions involving different isoparaffins and different olefins. Similarly, details of operation, either batch or continuous, will require modifications using the different acid catalysts specified. Such modifications usually will be determinable by those sufficiently versed in these types of catalytic reactions. As a rule, in the case of the acids of phosphorus used without carriers or supports, the higher concentrations are preferable in the case of the ortho-acid and due consideration must be given to the melting points and fluidity of the pyro and meta acids which are solid at ordinary temperatures.

The amounts of acid employed are preferably large in comparison to the amounts of hydrocarbons undergoing reaction, although in some operations, smaller volume percents of acid may be used when employing longer times of contact.

Depending upon the reactivity of the components in a given alkylation reaction, phosphoric acid of different concentrations may be employed, and temperatures and concentrations of acid may be varied to produce good results, providing they are properly coordinated. For instance, the reactions of isobutane with propylene may require more severe conditions, such as somewhat higher temperature or higher acid concentration than the reactions of isobutane with the more reactive normal butylene. Pressures may be employed to assist the reaction and to prevent undue losses of material by vaporization, and, when desirable, to maintain the hydrocarbons undergoing reaction substantially in liquid phase.

The solid phosphoric acid catalysts referred to are made by mixing a major proportion of ortho or pyro phosphoric acid by weight with a relatively inert and preferably siliceous carrier such as, for example, kieselguhr, heating at temperatures of the order of 300–400° C. to partially dehydrate the acid and fix a portion on the silica in the form of silico-phosphoric acids, grinding the cake, sizing to produce particles of usable diameter and rehydrating with steam at temperatures of the order of 260° C. to produce a catalyst having an acid of optimum concentration. The above procedure may be modified by extruding the original pasty mix and subjecting the extruded formed particles to the steps of calcination and rehydration.

The process of the invention is particularly applicable to the alkylation of isobutane with its olefinic counter-parts, the butylenes, with propylene, and in some cases with ethylene. Isobutane can be much more readily alkylated by normally gaseous olefins than normal butane which apparently has to undergo some isomerization prior to alkylation. These alkylation reactions are of particular importance in the oil industry in connection with the cracking process. The fixed gases ordinarily contain large quantities of 3 and 4 carbon atom hydrocarbons, both olefinic and saturated. Processes are in commercial operation which catalytically polymerize the 3 and 4 carbon atom olefins to form liquid products suitable as hydrocarbon motor fuel. However, the paraffinic hydrocarbons in these gases are substantally unaffected in these processes. Furthermore, the production of high octane motor fuel, such as iso-octanes, requires two steps of treatment such as butylene polymerization followed by hydrogenation, whereas in the present process iso-octanes are formed by direct alkylation, for example, of isobutane by either normal or isobutylene. The actual operation of the process admits of some modification, depending upon the normal phase of the reacting constituents and whether batch or continuous operations are employed.

The principles of the present invention also find application in the alkylation of normally liquid iso-paraffin hydrocarbons or mixtures containing the same. The temperature and pressure ranges previously mentioned are the ones most applicable when dealing with the alkylation of isobutane but in the case of other iso-paraffins, these ranges may be extended to include the temperatures most suitable for any given paraffin or mixture of paraffin hydrocarbons. In the alkylation of isobutane, the preferred temperature range is between 350 and 450° C. and preferred pressures are of the order of 500 lbs. and upward per square inch, pressures up to 3500 lbs. being advantageously utilized. Owing to the extensive possibilities in combinations of different olefins and different paraffins which might be employed in the reactions, the total range of operating conditions which the invention comprises is somewhat difficult to state.

The actual operation of the process admits of some modification depending upon the normal phase of the reacting constituents, the use of liquid phosphoric acid or solid composites made by absorbing the acid on supports, and whether batch or continuous operations are employed. In a simple type of batch operation a paraffin to be alkylated, such as, for example, isobutane is brought to a temperature within the approximate range specified in the presence of a phosphoric acid catalyst having a concentration corresponding to a sufficiently high activity and its alkylation is effected by the gradual introduction under pressure of an olefin such as, for example, isobutene while effecting intimate contact between catalyst and reacting compounds.

In another method of operation the paraffin may be mixed with an olefin at a suitable temperature, a phosphoric acid catalyst added and the reactions of alkylation induced by a sufficiently long contact with the acid catalyst chosen. Alkylation may be allowed to progress to different stages of replacement. In the case of the alkylation of isobutane with butenes, the best products from the standpoint of motor fuel usually are produced by the condensation of equimolecular quantities of paraffins and olefins. After a batch treatment is completed the spent acid catalyst is allowed to settle, and the upper hydrocarbon layer is removed by decantation and subjected to fractionation for the removal of uncombined hydrocarbons as a light overhead and the recovery of an intermediate motor fuel fraction.

In one type of continuous operation a liquid isoparaffin containing suspended therein the requisite amount of liquid phosphoric acid catalyst may be pumped through a baffled treater, the desired alkylation reactions taking place during passage through the treater and the fractionation of the product accomplished in succeeding fractionating equipment. The details of continuous processes of this general character are more or less familiar to those skilled in oil refinery operations and any necessary additions to or modifications of the above general procedures will be more or less obvious, and can be made without departing from the general scope of the invention.

When operating with solid granular catalysts such as may be produced by adsorbing phosphoric acid on various relatively inert supports, batch or continuous operations may be conducted in a generally similar manner to those employed when using the liquid acid and a further alternative method is offered which consists in passing the reacting hydrocarbons through stationary beds of granular catalytic material until the efficiency of the acid is reduced to an impractical point by unavoidable side reactions leading to the deposition of carbonaceous material. Steam may be used in this operation to maintain the activity of the catalyst.

While the present process possesses particular advantages in connection with the utilization of the gases produced in oil cracking plants, it has a broader significance and includes generally the interaction of any olefin and any iso-paraffin or mixtures thereof at temperatures at which alkylation reactions are fostered by the preferred phosphoric acid catalyst in preference to the simple polymerization of the olefins. It is further essential to the promotion of the alkylation reactions in preference to those of polymerization to maintain a considerable excess of the iso-paraffin in the reaction zone at all times. This is readily accomplished in the case of batch operations by introducing an olefin into intimate contact with an iso-paraffin in the presence of an acid catalyst, the introduction being stopped before the requisite excess of iso-paraffin is reacted, or in continuous operation by maintaining a sufficient excess of the iso-paraffin at all times. As a rule the ratio of paraffin to olefin should not be less than 3:1, although this may vary with various conditions. In other types of batch operations or in continuous operations, the proper proportions of paraffin and olefin may be mixed prior to the introduction of the catalyst and the mixture subjected to the required conditions of temperature, pressure and time.

The following data are introduced to indicate the type of results normally obtainable by the use of the present process and to indicate the effect of some of the variables involved in the reactions. The tabulations given summarize the principal data obtained in a series of runs in which temperature was varied at a constant pressure, and pressure was varied at a constant temperature. These operations were of the continuous type.

EFFECT OF TEMPERATURE

Pressure: 3,000 lbs. per square inch
Charging Stock: 13 percent C_3H_6; 87 percent i-C_4H_{10}
Catalyst: Solid phosphoric acid on kieselguhr—3–6 mesh

Temp., ° C.	Percent C_3H_6 reacted per pass	Percent C_3H_6 to liquid	Percent C_3H_6 to C_3H_8	Yield liquid from C_3H_6 reacted	Bromine number	Liquid space velocity
200	100	100	0	100	87	2.5
300	99	99	1	114	65	2.8
400	97	83	17	160	31	2.9
450	99	52	48	170	28	3.2

EFFECT OF PRESSURE

Temperature: 400° C.

Charging stock: 13 percent C_3H_6; 87 percent i-C_4H_{10}
Catalyst: Solid phosphoric acid on kieselguhr—3–6 mesh

Press., lb./sq. in.	Percent C_3H_6 reacted per pass	Percent C_3H_6 to liquid	Percent C_3H_6 to C_3H_8	Yield liquid from C_3H_6 reacted	Bromine number	Liquid space velocity	Mesh of catalyst
1,200	100	93	7	139	25	4.0	10–14
2,000	100	100	0	154	32	2.6	3–6
3,000	97	83	17	160	31	2.9	3–6

The following conclusions may be reached by an examination of the above data:

Keeping the pressure constant at 3000 lbs./sq. in. with solid phosphoric acid in the reaction chamber the yield of liquid product, based on propylene reacted is favored by increasing temperatures.

At 200° C., yield=100%
At 450° C., yield=170%

Keeping the temperature constant at 400° C. high pressures favor the yield of liquid product.

At 1200 lbs./sq. in. yield=139
At 3000 lbs./sq. in. yield=160

The liquid product formed from isobutane and propylene reacting on solid phosphoric acid at 3000 lbs./sq. in. and 400° C. is 80% saturated, consists mainly of C_5, C_6, and C_7 hydrocarbons, has an octane number of 80, and 95% boils below 400° C.

As an example of the possibilities of alkylating iso-paraffins with ethylene which is generally the least reactive of normally gaseous olefins in alkylation reactions, the following is given.

A mixture of 100 parts by weight of ethylene dissolved in 1500 parts by weight of iso-butane was passed over a solid phosphoric acid catalyst at 400° C. (752° F.) under 3000 lbs./sq. in. pressure at a liquid hourly space velocity of 3.

220 parts by weight of alkylated reaction products were obtained which were free from butane and lighter hydrocarbons. This recovered product had a bromine number of 10 (indicating more than 95% saturation), an octane number of 85 by the motor method and a density of 0.67. Less than 5% of the alkylated products boiled above 400° F. Analyses indicated that the principal compounds produced by the alkylation were iso-paraffins.

I claim as my invention:

1. A process for producing higher molecular weight hydrocarbons from isoparaffin and olefin hydrocarbons which comprises simultaneously contacting an isoparaffin and an olefin with a phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature and the proportion of olefin to isoparaffin to effect alkylation of the isoparaffin with the olefin as the principal reaction in the process with minimum olefin polymerization, thereby chemically combining the isoparaffin and olefin to form a heavier hydrocarbon.

2. A process for producing higher molecular weight hydrocarbons from isoparaffin and olefin hydrocarbons which comprises simultaneously contacting an isoparaffin and a normally gaseous olefin with a phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature and the proportion of olefin to isoparaffin to effect alkylation of the isoparaffin with the olefin as the principal reaction in the process with minimum olefin polymerization, thereby chemically combining the isoparaffin and olefin to form a heavier hydrocarbon.

3. A process for producing gasoline boiling hydrocarbons from normally gaseous iso-paraffin and olefin hydrocarbons which comprises simultaneously contacting a normally gaseous isoparaffin and a normally gaseous olefin with a phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature and the proportion of olefin to isoparaffin to effect alkylation of the isoparaffin with the olefin as the principal reaction in the process with minimum olefin polymerization, thereby chemically combining the normally gaseous isoparaffin and olefin to form a heavier hydrocarbon boiling in the gasoline range.

4. A process for producing gasoline boiling hydrocarbons which comprises simultaneously contacting isobutane and a butylene with a phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature, and the proportion of butylene to isobutane to effect alkylation of the isobutane with the butylene as the principal reaction in the process with minimum butylene polymerization, thereby chemically combining the isobutane and butylene to form a heavier hydrocarbon boiling in the gasoline range.

5. A process for producing higher molecular weight hydrocarbons from paraffin and olefin hydrocarbons which comprises simultaneously contacting an alkylatable paraffin and an olefin with a phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature and the proportion of olefin to paraffin to effect alkylation of the paraffin with the olefin as the principal reaction in the process with minimum olefin polymerization, thereby chemically combining the paraffin and olefin to form a heavier hydrocarbon.

6. A process for producing gasoline boiling hydrocarbons from normally gaseous paraffin and olefin hydrocarbons which comprises simultaneously contacting a normally gaseous alkylatable paraffin and a normally gaseous olefin with a phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature and the proportion of olefin to paraffin to effect alkylation of the paraffin with the olefin as the principal reaction in the process with minimum olefin polymerization, thereby chemically combining the normally gaseous paraffin and ole-

fin to form a heavier hydrocarbon boiling in the gasoline range.

7. A process for producing gasoline boiling hydrocarbons which comprises simultaneously contacting iso-butane and a butylene with a solid phosphoric acid catalyst at a controlled reaction temperature, and correlating the amount and concentration of the acid, the reaction temperature, and the proportion of butylene to iso-butane to effect alkylation of the iso-butane with the butylene as the principal reaction in the process with minimum butylene polymerization, thereby chemically combining the iso-butane and butylene to form a heavier hydrocarbon boiling in the gasoline range.

8. The process as defined in claim 3 further characterized in that said catalyst comprises a calcined mixture of a phosphoric acid and a siliceous material.

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