Patented June 11, 1946 2,401,865

UNITED STATES PATENT OFFICE

2,401,865

POLYMER REFORMING

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No Drawing. Application July 16, 1943, Serial No. 495,038

11 Claims. (Cl. 260—683.15)

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This invention relates to the production of liquid hydrocarbons having good antiknock characteristics from olefins. More particularly the invention relates to a process for the production of liquid hydrocarbons of high octane number and low acid heat value suitable for use as an aviation fuel from olefins of from three to five carbon atoms or from polymers thereof.

Processes for the production of liquid hydrocarbons from the normally gaseous olefins are well known, and such prior art processes are concerned with the polymerization of the olefins to form a polymer fraction, boiling in the gasoline range, suitable for use as a motor fuel. The normal polymer product, although it has a relatively high octane rating is not suitable as an aviation fuel because of its high acid heat. The polymer may be saturated by hydrogenation to reduce its acid heat, but this increases the cost of the product and considerably reduces the octane number. Many catalysts have been proposed for use in carrying out this polymerization reaction, among which are sulphuric acid, liquid phosphoric acid, solid phosphoric acid, and alumina-silica oxide mixtures.

Processes for the production of liquid hydrocarbons suitable for use as aviation gasoline by the reaction of isoparaffinic hydrocarbons with the normally gaseous olefins to produce longer chain isoparaffins, boiling in the gasoline range and having a high octane number, are also well known. These processes are generally carried out in the liquid phase with such catalysts as sulphuric or hydrofluoric acid. There have also been proposals to carry this reaction out in the vapor phase, at moderately elevated temperatures and pressures, over such catalysts as solid phosphoric acid. While such processes are satisfactory and produce an excellent grade of aviation fuel they are limited as to the type of raw materials which they can use and yet form a product having the desired high octane rating. As a result, while such aliphatic hydrocarbons as isobutane, butylene and ethylene may be effectively utilized, they are not attractive for the utilization of propylene, amylene, or isopentane and the other isoparaffins. Also with these so-called alkylation processes, for every mole of olefin utilized, one mole of isoparaffin is consumed.

It is a primary object of our invention to make liquid hydrocarbons suitable for use as aviation fuels from the normally gaseous or volatile liquid olefins such as propylene and amylene, with relatively small consumption of isoparaffin. Our

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invention is, however, equally well adapted to the use of butylene.

Another object of our invention is to produce normally liquid isoparaffinic hydrocarbons and aromatic hydrocarbons in high yield from olefins, particularly the olefins of from three to five carbon atoms or their polymers. A still further object is to effect this production of isoparaffins and aromatics with a minimum formation of propane and butane by cracking reactions.

A further object of our invention is to produce normally liquid isoparaffinic hydrocarbons and aromatic hydrocarbons from a mixture of the normally gaseous olefins and a light isoparaffin, particularly isobutane, with a minimum consumption of the isoparaffin.

Other and further objects of our invention will be apparent from the description thereof in conjunction with the appended claims.

We have found that a liquid hydrocarbon product consisting predominantly of a mixture of saturated, branched chain aliphatic hydrocarbons and aromatic hydrocarbons may be formed by passing a mixture of an olefin and from one-half to ten molar portions of a light isoparaffinic hydrocarbon at a low space velocity over a contact catalyst of the mixed oxide type. The gases may be passed over the catalyst at temperatures within the range of 275° C. to 500° C. At temperatures below 275° C. the product is largely olefinic in nature even though very long contact times are used. At temperatures above 500° C., cracking reactions become increasingly pronounced resulting in the cracking of the products as rapidly as they are formed. The preferred temperature range is from 300° C. to 450° C. The reaction is preferably carried out at relatively high pressures within the range of from 500 to 3000 pounds per square inch. By increasing the contact time, pressures as low as 100 pounds per square inch may be used, but the higher pressures are more desirable. The contact time varies with the activity of the particular mixed oxide catalyst used, the temperature of the gases in the reaction zone and the pressure employed. The contact time should be sufficient to allow desired reduction of the olefinic character of the product to be obtained.

The catalysts suitable for our process are composed of a mixture of an amphoteric oxide, such as the oxides of the metals of group II and group III of the periodic table, with a hydrated oxide of a weakly acidic nature, such as silica gel, hydrated boric oxide, thoria, zirconia, stannic acid and the like. The preferred amphoteric oxides

are those which are strongly amphoteric in character dissolving readily in both dilute aqueous acid and basic solutions. The oxide, in any event, must be capable of solution in both strong aqueous acid and basic solutions to be suitable for use as the amphoteric oxide constituent of our catalysts. The amphoteric oxide used should not be the amphoteric oxide of a metal easily oxidized to a non-amphoteric oxide of higher valence. For example, such oxides as stannous oxide and antimony trioxide are amphoteric, but the higher valence oxides of these metals are definitely acidic and the oxides of these metals are not suitable. The amphoteric oxide selected for use as the amphoteric oxide constituent of our catalysts should not be one which would be reduced to the metallic state by the hydrocarbons at the temperature at which the alkylation process was carried out. For example, lead oxide should not be used as the amphoteric oxide constituent of a catalyst since the lead oxide would be reduced when contacted with hydrocarbons at temperatures much above about 250° C. Typical suitable amphoteric oxides are alumina, zinc oxide, beryllium oxide, chromium oxide, gallium oxide, and the like. The use of mixtures of two or more of the amphoteric oxides as the amphoteric oxide constituent of our catalysts is also contemplated and is within the scope of our invention.

Our mixed oxide catalysts are characterized by being strongly acidic in character, and this strongly acidic character is the result of the method used for the preparation of the catalysts. The amount of amphoteric oxide present in our mixed catalysts may vary from a few tenths of one percent up to about fifteen to twenty percent. The amount of amphoteric oxide required to give the greatest activity varies to a certain extent depending upon the particular oxide mixture used, and varies widely with the particular method of preparation used.

We believe that the variation in the range of preferred amphoteric oxide content in the mixed oxide catalysts of the various synthetic and natural types is the result of a variation in the concentration of amphoteric oxide present at the catalyst surface with the different methods of preparation. It is our belief, although our invention should not be limited to any particular theoretical considerations, that the amount of amphoteric oxide present in the immediate neighborhood of the contact surfaces should be small relative to the amount of acidic oxide present. In the case of a catalyst prepared by the precipitation of aluminum oxide on neutral silica gel, the catalyst has good activity even though only a few tenths percent of the total catalyst is composed of alumina, and the amount of alumina on the catalyst so prepared should not be above about three or four percent. On the other hand a catalyst prepared by the coprecipitation of the mixed oxides should contain at least several percent of the amphoteric oxide, and usually will contain as much as ten to twelve percent or even higher, in order to have the greatest activity. Some naturally occurring mixed oxides, such as the alumina-silica clay known as "floridin" may be activated by suitable treatment. These naturally occurring mixed oxides should also contain at least several percent of the amphoteric oxide, and may contain as much as fifteen percent or even slightly higher. The amphoteric oxide content of the mixed oxide catalysts is probably not as accurate a way of describing the composition as

the acidic oxide-amphoteric oxide ratio, because of the presence of varying amounts of inert material, principally water, in the catalysts, depending upon their origin and mode of treatment in the case of the activated natural catalysts, or their method of preparation in the case of the synthetics. The amount of water will vary from about four or five percent to about twenty-five percent, and several percent of other materials, principally iron oxide, may be present in the natural catalytic oxide mixtures. The ratio of acidic oxide to amphoteric oxide is thus a more definite value since the variation in amount of these extraneous materials is discounted in its determination. The ratio of acidic oxide to amphoteric oxide in our active catalysts will vary from 20 to 1 to about 500 to 1 in the case of the amphoteric oxide deposited on acidic oxide type of catalyst, and from about 5 to 1 to about 50 to 1 in the case of the coprecipitated catalyst and naturally occurring catalyst.

The coprecipitated oxides and the naturally occurring mixed oxides may be activated by washing with a solution of a strong acid for controlled periods of time. Particularly with the coprecipitated oxides, an excessive washing even with a cold acid should be avoided, otherwise the amphoteric oxide will be removed to such an extent that the catalyst will be substantially inactive. The coprecipitated oxides may also be activated by treatment with a solution of a salt of a weak base with a strong acid such as an aluminum sulphate solution. One advantageous way for preparing such a coprecipitated catalyst is to precipitate a sodium silicate solution with an excess of aluminum sulphate so that the resulting supernatant solution is acid. The precipitate may then be washed with several portions of a fresh aluminum sulphate solution.

The naturally occurring oxides should be treated with rather concentrated acid solutions. Several successive treatments should be used, and these should preferably be altered with a washing with alkaline solutions although this is not essential. The final treatment should, of course, be an acid washing. A long digestion with hot, concentrated acid should be avoided, however, as this will substantially completely remove any amphoteric oxide from the catalyst surface and substantially inactivate the catalyst. In order that the contact surfaces of the catalyst will retain some amphoteric oxide, it would seem that the amount of amphoteric oxide present in the catalyst as a whole must be fairly high. The acid activation step removes most of the amphoteric oxide from the exposed surfaces of the catalyst and lowers the total amphoteric oxide content to a certain extent. In the case of a naturally occurring clay, or a synthetic catalyst of the coprecipitated, mixed oxide type, the acid treatment should not be carried out to such an extent that the acid disintegrates the structure of the catalyst, dissolving out all or nearly all of the amphoteric oxide because such treatment would substantially completely remove all amphoteric oxide from the actual contact surfaces. Such a catalyst would be relatively inactive.

In view of the great difficulty in determining the details of the actual molecular and crystalline structure of the contact surface of the catalyst, the theory advanced as to the extremely small amounts of amphoteric oxide required in the case of catalysts prepared by the precipitation of such oxide on a hydrated acidic oxide has not been proven. It does fit in well, however,

with the requirement of considerably larger amounts of amphoteric oxide in the case of catalysts prepared by coprecipitation of the mixed oxides or by acid treatment of naturally occurring oxide mixtures.

In the following examples and throughout the specification and the appended claims, by the use of the term "space velocity," we mean the volume of reactants as liquids entering the reaction zone per hour per unit volume of catalyst employed, unless otherwise indicated. By the term "contact time" we mean the actual total time of contact of the reactants in contact with the catalyst at the reaction conditions in minutes.

Our invention may be best understood by the following example illustrating a preferred mode of continuous operation thereof. The example is not to be construed, however, as limiting our invention to the mode of operation described therein.

Example

Silica gel was prepared by adding water glass to sufficient excess acetic acid so that the pH of the resultant mixture was approximately 5.0. The concentration of the reactants was such that the concentration of SiO_2 in the total mixture was 10% by weight. A hydrogel of silica was formed which was washed free of salts, and then boiled in a solution of 0.2 N aluminum sulphate for two hours. The catalyst was then washed thoroughly and dried for two hours at 90 to 100° C.

A gas mixture containing 2,322 grams of propylene (23.6 mol percent), 122 grams of propane (1.1 mol percent), and 10,603 grams of isobutane (75.3 mol percent) was passed over the alumina-silica catalyst at 410° C. and under a pressure of 1000 pounds per square inch. The space velocity of the gas mixture over the catalyst bed was adjusted so as to give a contact time of 2.68 minutes. The mass balance of the charge and product is given below:

Component	Charge		Product	
	Grams	Weight percent	Grams	Weight percent
Propylene	2,322	17.8	93	0.7
Propane	122	0.9	528	4.1
Isobutane	10,603	81.3	10,130	77.6
n-Butane			408	3.1
Isopentane			437	3.3
n-Pentane			28	0.2
C_6+			1,423	11.0
	13,047	100.0	13,047	100.0

96.5% of the propylene charged was converted. Considering the n-butane in the product as having come from the isobutane in the charge, only 65 grams of butanes were used up by the process or 2.9% on the basis of the propylene converted. The total yield of C_5+ hydrocarbons was 1,888 grams or 84.7% on the basis of the olefin converted. The front 85% of the C_5+ product may be used as an aviation naphtha, and has the following properties:

Olefin content	per cent	7.0
Aromatic content	do	21.4
Reid vapor pressure	lbs./sq. in.	9.4
A. S. T. M. octane No.:		
Neat		78.9
3 cc. T. E. L.		92.9

The higher boiling material was practically olefin free and contained principally aromatic hydrocarbons.

The foregoing example illustrates that a product having excellent qualities as an aviation fuel may be made from a normal olefin-isoparaffin mixture with very low consumption of isoparaffin. Without intending to limit our invention to any theoretical considerations, the following explanation of the possible reactions involved, where an olefin is reacted in admixture with an isoparaffin in the presence of a mixed oxide catalyst, is offered to illustrate the objects of our invention and to possibly account for the reaction condition requirements found necessary.

In U. S. Patent 2,068,016 to Frederick H. Gayer the use of alumina silica catalysts for the polymerization of the normally gaseous olefins, such as propylene is disclosed. While polymerization does, of course, take place in our process, its products, as such, are not the desired final reaction products. The olefin polymers are unsaturated and have too high an acid heat value. Generally where the polymer is later saturated, by hydrogenation, the resulting paraffin is of relatively low octane value. For example, the hydrogenated dimer of propylene consists predominantly of methyl pentanes, of low octane number.

On the other hand, while alkylation reactions can be carried out, they are subject to the disadvantages discussed previously, and, in addition, they do not proceed very satisfactorily over the mixed oxide contact catalyst.

Our process seeks, therefore, to react the olefin-isoparaffin mixture with a minimum of the alkylation reaction involving the original reactants, and a minimum of the original polymer in the final product.

The experimental facts regarding the behavior of this type of system may be correlated very well under the assumption that three types of reactions take place under the reaction conditions; namely, polymerization, hydrogen transfer, and depolymerization and disproportionation of polymer.

The initial reaction when an olefin is treated in the absence of an isoparaffin is the formation of polymer. Typical polymerization reactions in the case of propylene are written below:

(1) $2C_3H_6 \rightarrow C_6H_{12}$

(2) $C_6H_{12} + C_3H_6 \rightarrow C_9H_{18}$

At the same time, particularly at high temperature, a considerable amount of intermediate olefins are formed by disproportionation of the polymer; i. e.,

(3) $2C_6H_{12} \rightarrow C_4H_8 + C_8H_{16}$ etc.

A hydrogen transfer cyclization reaction takes place either simultaneously therewith or subsequent to more prolonged contact, depending on the exact reaction conditions employed, leading to the formation of a mixture of paraffins and aromatics in accordance with the following typical equation:

(4) $C_3H_6 + C_4H_8 + C_6H_{12} + C_8H_{16} \rightarrow$ Octene

$C_6H_4.(CH_3)_2 + C_3H_8 + C_4H_{10} + C_6H_{14}$ Xylene

The over-all result in the polymerization of olefins under reforming conditions will be the formation of a mixture of propane, butanes and higher paraffins boiling in the gasoline range and aromatic hydrocarbons, particularly xylene and heavier aromatics as well as smaller amounts of toluene and benzene.

The yield of gasoline boiling hydrocarbons is

considerably reduced in this process by the formation of propane and butanes.

When the reaction is carried out in the presence of isoparaffins, such as isobutane, a new type of hydrogen transfer reaction takes place; namely,

(5) $iC_4H_{10}+C_3H_6 \rightarrow C_4H_8+C_3H_8$

which is followed by cross polymerization and further hydrogen transfer reactions as indicated by the following equations:

(6) $C_4H_8+C_3H_6 \rightarrow C_7H_{14}$

(7) $C_7H_{14}+iC_4H_{10} \rightarrow C_7H_{16}+C_4H_8$

A series of reactions of this type will lead to alkylation of isobutane as the predominant result to produce mainly heptanes, with smaller amounts of other paraffins, such as propane, octane and the like. This result, however, is predicated on the assumption that other reactions are substantially absent, such as polymerization of the propylene and hydrogen transfer-cyclization reactions of the polymer mentioned above. The substantial absence of these latter reactions may be insured by maintaining a very high ratio of isoparaffin to olefin. Under these conditions it is possible to obtain alkylation as the predominant reaction.

As the ratio of olefin to isoparaffin is increased the other types of reactions such as polymerization and disproportionation as well as cyclization of the polymer will occur. A point is reached where as much isobutane is produced by hydrogen transfer between butene and polymer undergoing cyclization as is consumed by alkylation, and, as a net result, there is little or no consumption of isobutane. Under these conditions, because of the relatively smaller amount of propylene present and its tendency to condense with the isobutane preferentially, the amount of propane formed is very much smaller than when propylene alone is treated under these conditions. In other words, at the proper isobutane-olefin ratio, a high yield of reformed saturated polymer may be obtained without consuming any substantial amount of isoparaffin.

While the foregoing explanation has been offered assuming that the reactants involved are isobutane and propylene, the considerations are perfectly general for other light isoparaffins and other olefins. Regardless of the initial isoparaffinic reactant used, there will always be a mixture of all the various light isoparaffins once the reaction starts. The explanation offered as to the reactions involved is given to provide a theoretical basis for the results obtained only, and our invention is not to be construed as limited to any particular theory of the process described.

A specific application of our process is the production of aviation-base gasoline by the reaction of the volatile components of natural gasoline with olefins or olefinic polymers. The volatile ends of natural gasoline are rich in isoparaffins such as isopentane and isohexanes. An olefin such as propylene may be reacted for example in the presence of an excess of the C_5 and C_6 cuts of natural gasoline to produce a mixture of isobutane, some n-butane and a mixture of the original natural gasoline plus a saturated gasoline containing a large amount of aromatic rich C_7+ material. Sufficient C_4, C_5 and C_6 components are allowed to remain in the gasoline to make up an aviation-base stock of balanced volatility while the remaining C_4 to C_6 material is recycled to the olefin conversion step. The C_4 cut will eventually become rich in n-butane so that a portion of this material is preferably sent to a fractionating unit to remove n-butane. The n-butane may be isomerized and returned to the system if desired.

The novel results obtained by our process are apparently due to the fact that the acid activated, mixed oxide, catalysts are not only good polymerization catalysts and fair alkylation catalysts, but will also catalyze aromatization and disproportionation-reforming reactions under the conditions used. By having a mixture of isoparaffin and olefin in the charge stock, the desired reactions may be effected within the range of reaction conditions set forth.

In order to show the effect of isobutane upon the polymerization-disproportionation reaction of propylene a series of experiments were run under the conditions, and with the results set forth in the following table. All of the examples were carried out at a pressure of 1000 pounds per square inch, and at the temperature indicated in the table. The liquid space velocity of the reactants in all experiments was 2.4 cc. of liquid reactant mixture per cc. of catalyst per hour. The catalyst used throughout was the same as in Example 1. The results of Example 1 are also tabulated for convenient comparison.

Example No.	2	1	3	5	4	6	7
Paraffin used	$i\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$n\text{-}C_3H_8$
Temperature, °C.	410	410	410	350	350	350	350
Contact time, minutes	2.8	2.7	2.8	3.2	3.2	3.2	3.3
Mol percent C_3H_6 (basis of $i\text{-}C_4H_{10}$—C_3H_6 total)	2.5	23.9	100	2.5	24.0	100	100
Yield of C_5+:							
Weight percent C_3H_6 converted	105	85	50	114	88	56	49
Weight percent C_3H_6 charged	100	83	45	107	85	53	44
Unsaturated liquid product (balance saturated hydrocarbons):							
Weight percent C_5+, olefin	3.4	7.0	12.3	9.0	10.2	16.0	16.5
Weight percent C_5+, aromatics	14.6	21.4	36.8	15.5	23.2	38.2	37.5
Distribution of fractions:							
C_5 hydrocarbons	36.1	29.5	27.4	22.8	24.5	19.3	18.6
C_6 hydrocarbons	21.6	17.9	24.8	23.0	21.3	26.3	28.1
C_7 hydrocarbons	21.7	16.6	18.0	27.8	20.7	18.5	19.2
C_8+ hydrocarbons	20.8	36.0	29.8	26.4	33.5	35.9	34.1
Distribution of reactants:							
Propylene converted, per cent	95	97	90	94	96	94	90
$i\text{-}C_4H_{10}$ converted / C_3H_6 converted, mol per cent	64	2	0	36	2	0	0
C_3H_8 formed / C_3H_6 converted, do.	49	18	24	25	14	23	21
Yield C_5+ from $i\text{-}C_4H_{10}$ (basis of C_3H_6 converted)	54	3	0	38	2	0	0
Yield C_5+ from C_3H_6 (basis of C_3H_6 converted)	51	82	50	76	86	56	49

In Examples 3 and 6, there was a small increase in the amount of n-butane over that charged to the reactor. Presumably this was formed from the product polymer through disproportionation - reforming reactions, and amounted to 1.8% by weight of the butane charged.

A comparison of the results of the examples shows that the isoparaffin plays a definite part in the reaction, and very favorably influences the nature and quantity of the product obtained from the olefin. With extremely high isoparaffin-olefin molar ratios, above ten to one, the reaction becomes predominantly one of alkylation. This is well illustrated by a study of the results of Examples 2 and 5, wherein yields of liquid product in excess of 100% on the basis of olefin charged were obtained. With the extremely high isoparaffin-olefin ratio, the amount of aromatics and unsaturates was low, also indicative of a predominantly alkylation reaction. On the other hand, in the absence of isoparaffins, the reaction is predominantly one of aromatization and polymerization. This is shown by the high olefin and aromatic content of the product of Examples 3, 6 and 7. A portion of the polymer is, however, saturated by hydrogen liberated by the aromatization reaction, through hydrogen exchange.

The alkylation type of reaction in Examples 2 and 5, and the polymerization type reaction in Examples 3, 6 and 7, all result in the formation of considerable amounts of normal paraffin from the olefin charge. This is particularly true of the high temperature alkylation reaction of Example 2, where nearly half of the propylene converted was converted to propane. In the other examples substantially one-fourth of the propylene converted was converted to propane as compared to about a one-sixth to one-seventh conversion to propane under the conditions of Examples 1 and 4.

By carrying out the process in the presence of a moderate excess of isoparaffin, the consumption of isoparaffin on the basis of olefin converted is low. In Examples 1 and 4 but 2% as much isobutane is converted as propylene, as compared with 36% and 64% respectively in Examples 5 and 2. An interesting result is that, although in the alkylation type reactions of Examples 2 and 5 somewhat higher yield of liquid product is obtained, the amount of liquid product derived from olefin is considerably higher in Examples 1 and 4 than in any of the other examples, as is clearly shown in the last row of figures in the above table.

As indicated previously, we have found that the polymerization-aromatization reaction of olefins precedes to give a higher yield and a better product by admixing an isoparaffin with the olefin to effect hydrogen exchange, and disproportionation and reforming reactions. Considerable amounts of isoparaffins are required, about one mole of isoparaffin per two moles of an olefin such as propylene being the minimum amount required to appreciably influence the character of the product in the desired direction. On the other hand, where the amount of isoparaffin added exceeds ten moles per mole of propylene, the reaction becomes predominantly one of alkylation.

The preferred amount of isoparaffin to be added depends somewhat upon the particular olefin used, the character of the product desired, and the exact temperature and pressure used. For the longer carbon chain olefins, such as amylene, an

increased amount of isoparaffin on a molar basis should be used over that used with the short carbon chain olefin, propylene. Preferably our process is carried out with the addition of from 2 to 6 moles of an isoparaffin per mole of olefin of from 3 to 5 carbon atoms. Where polymers of the light olefins are used in our process, the ratio of isoparaffin added should be determined on the basis of the moles of original olefin in the polymer rather than on the moles of polymer. For example with a propylene polymer, the preferred amount of isoparaffin on a molar basis would be doubled; i. e. from 4 to 10 moles of isoparaffin per mole of propylene polymer. Increasing the pressure increases the tendency towards alkylation as the principal reaction, and lowers the preferred range of isoparaffin addition. By operating with the lower isoparaffin ratio the product may be made to contain more aromatic hydrocarbons, whereas by the use of the higher isoparaffin ratios the consumption of isoparaffin will increase slightly, and the aromatic and olefinic content of the product will decrease. At a certain ratio within the preferred range, the utilization of olefin in the liquid product will be at a maximum, the exact ratio again depending upon the temperature, pressure, catalyst, and the particular olefin and isoparaffin being used in the process.

Another advantageous way of carrying out our process is to first pass the olefin alone over the catalyst at a relatively low pressure, not exceeding 100 pounds per square inch (preferably below 75 pounds per square inch) and at a relatively high gas space velocity to form the polymer therefrom. The polymer product is then mixed with isoparaffin and passed over the catalyst at the much higher pressures and much lower space velocities to get the desired reactions of this invention. By conducting the reaction with a polymer-isoparaffin mixture, the hydrogen exchange reaction in the aromatization reaction would saturate polymer rather than a mixture of polymer and propylene, particularly eliminating the formation of propane in the reaction. The polymer from the first step would be condensed out and separated from the unreacted olefin. The olefin could then be recycled for further polymerization. The isoparaffin could be mixed with the polymer and passed to another reactor containing the catalyst wherein it would be subjected to a pressure in the range of from 500 to 3000 pounds per square inch.

An alternative procedure would be to treat the isoparaffin olefin mixture at low pressure in the presence of a mixed oxide catalyst and at a fairly high space velocity based upon cc. of olefin gas per cc. of catalyst per minute. The space velocities used should be greater than about four, measured at standard conditions, with an active polymerization catalyst to prevent the formation of much of the heavier polymer and to avoid any appreciable amount of aromatization before the unreacted propylene is removed. After removal of propylene from the isobutane-polymer mixture, the latter would be retreated at the higher pressures and low space velocities previously described. The temperature for the preliminary polymerization should preferably be within the range of from 200° to 400° C.

The unreacted isoparaffin in our process would preferably be separated from the liquid product and admixed with fresh olefin or polymer charge for recycling through the reaction zone.

Our invention is equally applicable to the

treatment of mixtures of olefins. For example, a propylene-butylene mixture, or a butylene-amylene mixture. The isoparaffinic component of the mixture may be mixed with normal paraffins. For example a n-butane-isobutane mixture may be used. The total isoparaffinic component of the paraffinic mixture should be in excess of one mole per two moles of total olefinic content of olefin mixture. A mixture of isoparaffins, such as isobutane, isopentane, 2-methyl pentane, may also be used, alone or in mixture with normal olefins. Such gas mixtures are frequently available from topping certain natural gasolines, crude oils, and from isobutane-butylene alkylation units.

The foregoing description of our invention is illustrative of the preferred modes of operation thereof only, and our invention should not be limited except as indicated in the appended claims.

We claim:

1. Process for the production of liquid hydrocarbons of high octane number and low acid heat value from olefins which comprises passing the olefin in admixture with from two to six moles of a light isoparaffin of from four to six carbon atoms per mole of olefin in contact with a catalyst comprising an association of an acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the final stages of its preparation, and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500 to 1, to 5 to 1, at a temperature between 275° C. and about 500° C., at a pressure in excess of 100 pounds per square inch and for a contact time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons from the olefin.

2. Process for the production of liquid hydrocarbons of high octane number and low acid heat value from propylene which comprises passing the propylene in admixture with from two to six moles of a light isoparaffin of from four to six carbon atoms per mole of olefin in contact with a catalyst comprising an association of an acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the fluid stages of its preparation, and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500 to 1, to 5 to 1, at a temperature between 275° C. and about 500° C., at a pressure in excess of 100 pounds per square inch and for a contact time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons from the propylene.

3. Process for the production of liquid hydrocarbons of high octane number and low acid heat value from propylene which comprises passing the propylene in admixture with from 2 to 6 moles of light isoparaffin of from four to six carbon atoms per mole of propylene in contact with an alumina-silica catalyst, which has been subjected to an acid environment in the final stages of its preparation, at a temperature between 300° C. and about 450° C., at a pressure of from 500 to 3000 pounds per square inch and for a contact time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons from the propylene.

4. The process of claim 3 in which the isoparaffin is isobutane.

5. The process for the production of liquid hydrocarbons of high octane number and low acid heat value from gasoline boiling olefin polymers which comprises passing the olefin polymer in admixture with from two to six moles of a light isoparaffin of from four to six carbon atoms per mole of the original olefin monomer in contact with a catalyst comprising an association of an acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the final stages of its preparation, and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500 to 1 to 5 to 1, at a temperature between 275° C. to about 500° C., at a pressure in excess of 100 pounds per square inch and for a contact time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons from the polymer.

6. The process for the production of liquid hydrocarbons of high octane number and low acid heat value from the normally gaseous olefins which comprises passing the olefin in admixture with from one-half to ten moles of a light isoparaffin of from four to six carbon atoms per mole of olefin over a catalyst comprising an association of acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the final stages of its preparation, and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500 to 1 to 5 to 1 at a temperature between 200° C. and about 400° C. and at a pressure below 100 pounds per square inch to convert a substantial portion of the olefin to gasoline boiling polymers, then raising the pressure of the mixture to within the range of from 500 to about 3000 pounds per square inch and passing the mixture over a catalyst comprising an association of an acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the final stages of its preparation, and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500 to 1 to 5 to 1, at a temperature between 300° C. and about 450° C. to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons.

7. The process for the production of liquid hydrocarbons of high octane number and low acid heat value from the normally gaseous olefins which comprises passing the olefin in admixture with from one-half to ten moles of light isoparaffin of from four to six carbon atoms per mole of olefin over an alumina-silica catalyst which has been subjected to an acid environment in the final stages of its preparation, at a temperature between 200° C. and about 400° C. and at a pressure below 100 pounds per square inch to convert a substantial portion of olefin to gasoline boiling polymers, then raising the pressure of the mixture to within the range of from about 500 to about 3000 pounds per square inch and passing the mixture over an alumina-silica catalyst which has been subjected to an acid environment in the final stages of its preparation at a temperature between 300° C. and about 450° C. to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons.

8. The process for the production of liquid hydrocarbons of high octane number and low acid heat value from propylene which comprises passing the propylene in admixture with from two to six moles of isobutane per mole of propylene over an alumina-silica catalyst which has been subjected to an acid environment in the final stages

of its preparation, at a temperature between 200° C. and about 400° C. and at a pressure below 100 pounds per square inch to convert a substantial portion of the propylene to gasoline boiling polymers, then raising the pressure of the mixture to within the range of from 500 to about 3000 pounds per square inch and passing the mixture over an alumina-silica catalyst which has been subjected to an acid environment in the final stages of its preparation, at a temperature between 300° C and about 450° C. to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons.

9. Process for the production of liquid hydrocarbons of high octane number and low acid heat value from the normal olefins which comprises passing the normal olefin in admixture with from two to six moles of a light isoparaffin of from four to six carbon atoms per mole of olefin in contact with an alumina-silica catalyst which has been subjected to an acid environment in the final stages of its preparation, at a temperature between 300° C. and about 450° C., at a pressure between 500 and 3000 pounds per square inch and for a contact time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons from the normal olefin.

10. The process of claim 9 in which the isoparaffin is isobutane.

11. The process for the production of liquid hydrocarbons of high octane number and low acid heat value from the normally gaseous olefins which comprises polymerizing the olefin under conditions such that a substantial amount of gasoline boiling polymer is formed, separating the unreacted olefin from the polymer, passing the polymer in admixture with from two to six moles of isobutane on the basis of the moles of original olefin monomer in the polymer in contact with a catalyst comprising an association of an acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the final stages of its preparation, and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500 to 1, to 5 to 1, at a temperature between 275° C. and about 500° C., at a pressure in excess of 100 pounds per square inch and for a contact time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffinic hydrocarbons from the gasoline boiling polymer.

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