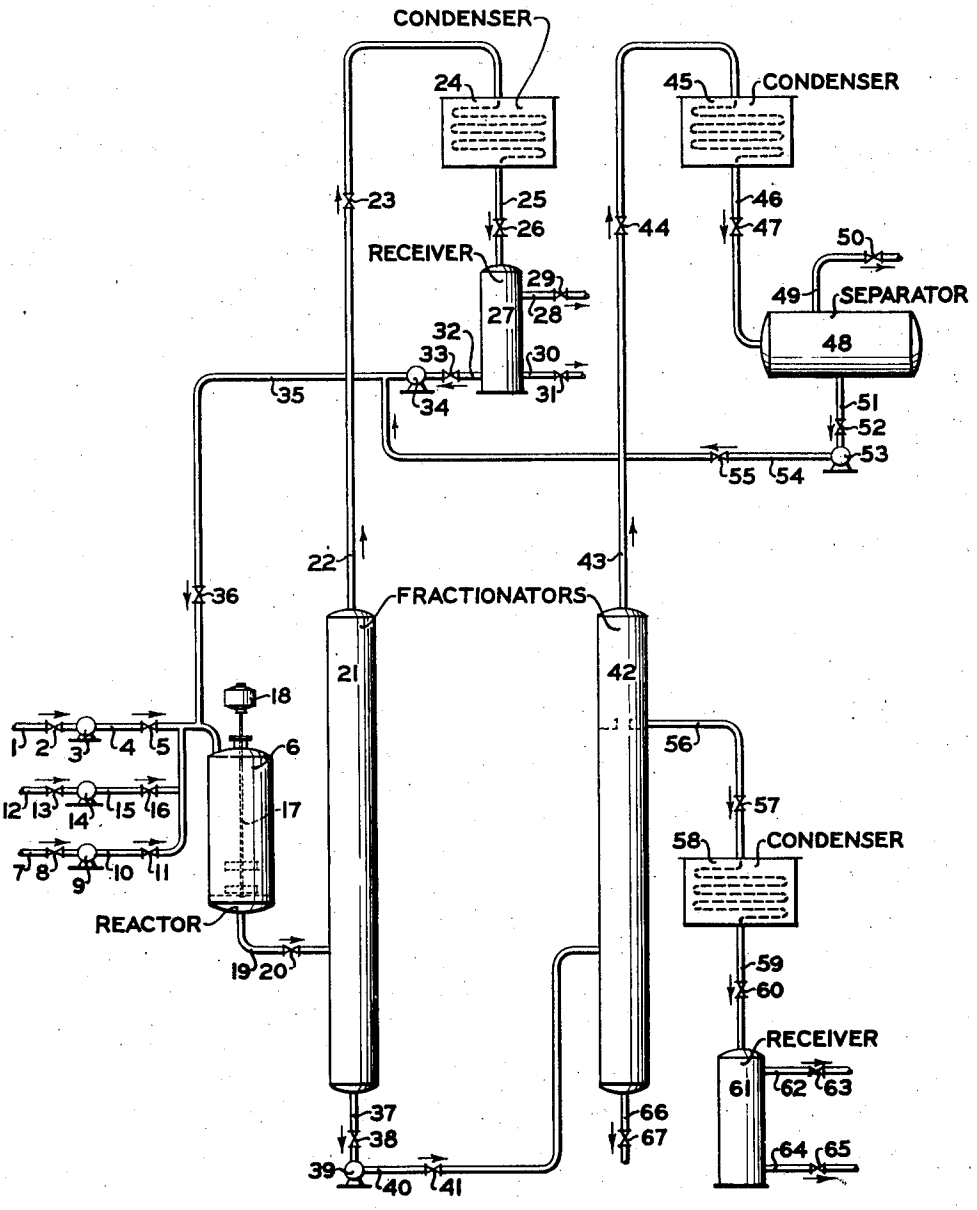
Jan. 4, 1944. L. S. KASSEL 2,338,248

ALKYLATION OF ISOPARAFFINIC HYDROCARBONS

Filed Dec. 29, 1941



INVENTOR

LOUIS S. KASSEL

BY Lee J. Gary

ATTORNEY

Patented Jan. 4, 1944

2,338,248

UNITED STATES PATENT OFFICE

2,338,248

ALKYLATION OF ISOPARAFFINIC HYDROCARBONS

Louis S. Kassel, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application December 29, 1941, Serial No. 424,768

14 Claims. (Cl. 260—683.4)

This invention relates to the treatment of isoparaffinic or branched-chain paraffinic hydrocarbons to produce therefrom branched-chain paraffinic hydrocarbons of higher molecular weight. In a more specific sense this invention is concerned with a novel process for alkylating isoparaffinic hydrocarbons comprising isobutane and relatively low boiling normally liquid-branched-chain paraffins with normally gaseous or liquid olefins to produce therefrom normally liquid saturated hydrocarbons which may be utilized as components of gasoline suitable for use in airplane or automobile engines.

The cracking process, which is operated principally with the object of producing gasoline from heavier and less valuable petroleum fractions incidentally produces considerable yields of fixed gases consisting of hydrogen, methane, ethane, propane, and butanes, as well as ethylene, propene, and butenes in varying quantities and proportions. In most instances, these gases are considered to be valuable merely as fuel, although attempts have been made from time to time to utilize the olefinic constituents for the manufacture of hydrocarbon derivatives on a commercial basis.

In one application of the present process the isobutane and olefins present in cracked gas mixtures are utilized as a source of additional yields of motor fuel fractions to augment those produced primarily by cracking. While the process is particularly applicable to the utilization of the hydrocarbons in cracked gas mixtures and in selected fractions produced therefrom in the stabilizers of cracking plants, it is also applicable to the treatment of branched chain paraffins and olefins produced from any other source. Efforts to alkylate normal paraffin hydrocarbons with olefins in the presence of catalysts have thus far failed unless concurrent isomerization of the normal to branched-chain paraffin occurs. Isobutane is the isoparaffin commonly subjected to alkylation although higher molecular weight isoparaffins also react with olefins under similar or modified conditions of operation to produce branched chain paraffins of higher boiling point than the isoparaffins charged to the process. However, as the higher molecular weight isoparaffins such as isopentane, isohexane, etc., are themselves valuable constituents of gasoline, they are consequently used less commonly as charging stocks for the alkylation process than is isobutane. Mono-olefins and particularly those containing from 3 to about 16 carbon atoms per molecule are utilizable for alkylating isoparaffins in the presence of mixed catalysts comprising both hydrogen fluoride and sulfur dioxide, although the common olefin-containing charging stocks are often limited to hydrocarbon fractions containing propene and butenes. Normal paraffins frequently present in hydrocarbon fractions containing propene and butenes dilute the reacting hydrocarbons but are separable from the alkylation products by distillation. Thus propane and normal butane may be removed from the alkylation product while an isoparaffin such as isobutane, which is also separated from the reaction product, is recycled to further alkylation treatment.

In one specific embodiment the present invention comprises a process for synthesizing substantially saturated hydrocarbons of gasoline boiling range by alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons in the presence of a composite of liquid hydrogen fluoride and sulfur dioxide.

Whereas previous work in alkylating various classes of paraffins with olefins indicates that the reactions can be brought about in the presence of composites containing boron fluoride, hydrogen fluoride and nickel and in the presence of mixtures of hydrogen fluoride and sulfuric acid, these alklylation reactions are brought about more effectively by the process of the present invention utilizing as catalyst a composite of hydrogen fluoride and sulfur dioxide. Since hydrogen fluoride boils at about 20° C. and sulfur dioxide at about —10° C., mixtures of these two materials may be handled readily as liquids under a relatively low superatmospheric pressure, generally not more than about 20 atmospheres or even at atmospheric pressure when the reaction mixture is cooled to a temperature below the normal boiling point of the catalyst components and hydrocarbons charged to alkylation.

The hydrocarbon conversions which occur when an isoparaffin is alkylated with an olefin in the presence of a catalyst involve not only simple combinations of isoparaffins with olefins to form branched-chain paraffins of higher molecular weight, but also some reactions of polymerization and certain amounts of decomposition so that the net result is the production of a mixture of substantially saturated hydrocarbons having a considerable boiling range but containing a large proportion of alkylated hydrocarbons boiling within the range of gasoline and having a relatively high antiknock value. Polymerization is kept relatively low when a moderate excess of isoparaffin to olefin is maintained throughout

the entire reaction. While the normal ratio of isoparaffins to mono-olefinic hydrocarbons may be as low as about 1 or as high as about 10, with a preferred ratio of about 5, the exact ratio of isoparaffin to olefin for good operation depends somewhat upon the particular isoparaffin and olefin-containing hydrocarbon mixtures charged to alkylation.

The proportions of liquid hydrogen fluoride and sulfur dioxide used as the preferred catalyst mixture will also depend upon the hydrocarbons being reacted and upon the conditions of operation. Generally the use of mixtures containing relatively small amounts of hydrogen fluoride and relatively large amounts of sulfur dioxide results in the formation of products containing organic fluorides or other fluorine-containing compounds, whereas the use of catalyst mixtures containing relatively large amounts of hydrogen fluoride and relatively small amounts of sulfur dioxide effects the formation of alkylation products which are substantially free from fluorine-containing compounds. It is therefore seen that catalyst composites containing different proportions of hydrogen fluoride and sulfur dioxide are not necessarily equivalent in their action and that the catalyst activity can be controlled within certain limits by the choice of the proportions of hydrogen fluoride and sulfur dioxide used in the catalyst composites.

The alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons in the presence of a mixture of hydrogen fluoride and sulfur dioxide is preferably carried out at temperatures between about 0° and about 50° C., although satisfactory results are also obtainable at temperatures as low as about −30° C. and as high as about 100° C. Since different isoparaffins and olefins have different reactivities, the alkylation of isobutane with propene, for example, may require more severe conditions such as a somewhat higher temperature or a catalyst containing a higher proportion of hydrogen fluoride than those used for catalyzing the reaction of isobutane with a more reactive olefin such as isobutene. The alkylation reaction mixture is generally maintained under a superatmospheric pressure of up to about 20 atmospheres when alkylating the lower-boiling isoparaffins, as isobutane or isopentane by normally gaseous olefins, but these operating conditions may be altered when carrying out similar reactions between higher boiling isoparaffins and olefins of varying structures. Superatmospheric pressures are generally used which are sufficient to maintain the hydrocarbons and catalyst in substantially liquid state or to effect liquefaction of a portion of the reaction mixture including the catalyst.

The amount of hydrogen fluoride-sulfur dioxide composite catalyst employed is preferably from about 10 to about 100 parts by weight of catalyst per 100 parts by weight of hydrocarbons undergoing treatment at any one time, although in some operations other ratios of catalyst to hydrocarbon mixtures may be used.

The charge rate, expressed as volumes of hydrocarbon per volume of hydrogen fluoride in the reactor per hour, and the amount of mixing in the reactor are two important variables which are suitably correlated with each other, as well as with other process variables in order to obtain best results. The charge rate is ordinarily between about 0.5 and about 20 volumes of hydrocarbons per volume of catalyst mixture per hour; other things being equal, higher hydrocarbon charge rates generally require a greater amount of mixing. Indications by which unfavorable operating conditions may be recognized are usually the production of a less completely saturated product and the presence of excessive amounts of alkyl fluorides in the product. The results can then be improved in most cases by reducing the charge rate or by increasing the mixing. An unnecessarily high extent of mixing, at least within moderate limits, does not have a markedly harmful effect on product quality. With these general rules as a basis, it is easy to determine optimum conditions for any particular charging stock.

While the alkylation of isobutane with olefins in the presence of a composite catalyst comprising hydrogen fluoride and sulfur dioxide is not understood completely, it is believed that the catalyst is miscible with the hydrocarbons present in the alkylation reaction mixture since it is known that the C_3 and C_4 hydrocarbons are miscible with sulfur dioxide at alkylation temperatures and that sulfur dioxide is also miscible with hydrogen fluoride at these temperatures. This miscibility of the catalyst with the hydrocarbons therefore appears to be a factor favoring alkylation since the concentrations of hydrocarbons are accordingly increased in the regions where alkylation occurs.

The process of the present invention may be carried out in either batch or continuous types of operation. In a simple batch process an isoparaffin to be alkylated, such as isobutane, is brought to the alkylation temperature within the approximate range specified and in the presence of the necessary amount of catalyst mixture, and alkylation is effected by the gradual introduction thereto of an olefin, or preferably of an olefin-isoparaffin mixture while the mixture is stirred mechanically to effect intimate contact between the catalyst and the reacting hydrocarbons. The mixture of alkylation products and catalyst composite is removed periodically from the batch type reactor and fractionally distilled to separate a mixture of unreacted isoparaffins and catalyst from higher boiling alkylation products of gasoline boiling range. The recovered mixture of unreacted isoparaffin and used catalyst is returned to further use in a later run for alkylation of an additional quantity of an isoparaffin with an olefin.

It is usually preferable to carry out the alkylation reaction continuously by withdrawing from the alkylation reactor a complex mixture of excess unreacted isoparaffins and admixed normal paraffins, an alkylate of gasoline boiling range, higher boiling hydrocarbons, and catalyst composite, said complex mixture being withdrawn at substantially the same rate as that at which the hydrocarbons and catalyst are supplied to the alkylation reactor. As the process is usually operated, sufficient pressure is maintained upon the reaction mixture to keep a substantial proportion thereof in liquid state. The exact pressure necessary depends both upon the composition of the reaction mixture and the temperature employed. The alkylation reactor used in the process consists quite often of a coil or tower provided with baffles, orifice plates or other mixing devices, or a vessel provided with a stirrer or other mechanical means of agitation, although any method may be employed which satisfactorily effects intimate contact of the reacting hydrocarbons and catalyst composite employed. It may sometimes be advantageous to use two or more reaction vessels,

and the flow may be either in series or in parallel.

The accompanying diagrammatic drawing shows one specific arrangement of interconnected apparatus units which may be used in carrying out the process of this invention, although alternatively other types of apparatus may also be employed.

Referring to the drawing a butane fraction containing a relatively high proportion of isobutane is introduced through line 1 and valve 2 to pump or compressor 3 which discharges through line 4 and valve 5 into reactor 6. Another hydrocarbon fraction containing both butanes and butenes is admitted through line 7 and valve 8 to pump or compressor 9 which discharges through line 10 and valve 11 into line 4 already mentioned through which the mixture of isobutane and normal butane is introduced into reactor 6. The liquid catalyst mixture used in the process and consisting of both hydrogen fluoride and sulfur dioxide is introduced through line 12 and valve 13 to pump 14 which discharges through line 15, valve 16, and lines 10 and 4 to reactor 6.

Reactor 6 comprises a vessel of suitable construction for carrying out the process. The reaction mixture contained in reactor 6 is mixed by means of stirrer 17 operated by a motor, or other prime mover 18. The mixture of hydrocarbons and catalyst is continuously withdrawn from reactor 6 through line 19 and valve 20 to fractionator 21 of conventional design in which vapors of unconverted isobutane and the mixed hydrogen fluoride-sulfur dioxide catalyst are removed and directed therefrom through line 22, valve 23, condenser 24, run-down line 25, and valve 26 to receiver 27 provided with conventional gas release line 28 containing valve 29. From receiver 27 the liquefied mixture comprising essentially unconverted isobutane, hydrogen fluoride, and sulfur dioxide may be withdrawn therefrom through line 30 and valve 31. However, the major proportion of the liquefied material collected in receiver 27 is withdrawn therefrom through line 32 and valve 33 by pump 34 which discharges through line 35 and valve 36 into line 4, already mentioned. In this way the recovered mixture of unconverted isobutane and catalyst is recycled to further use in reactor 6.

The normally liquid alkylation product admixed with normal butane, the latter present in one or both of the hydrocarbon fractions charged to the process, is directed from near the bottom of fractionator 21 through line 37 and valve 38 to pump 39 which discharges through line 40 and valve 41 into fractionator 42 of conventional design in which hydrocarbon mixture introduced thereto is separated into a normal butane fraction, a substantially saturated alkylate of gasoline boiling range (containing a substantial amount of branched chain octanes), and a mixture of higher boiling hydrocarbons. The mixture introduced to fractionator 42 may also contain relatively small amounts of hydrogen fluoride which was not separated from the normal butane and alkylate in fractionator 21. Vapors of normal butane and the hydrogen fluoride which may be present are directed from fractionator 42 through line 43, valve 44, condenser 45, and the liquefied material is directed through rundown line 46, and valve 47 to separator 48 in which normal butane separates as an upper layer in separator 48. The upper layer containing normal butane is withdrawn from separator 48 through line 49 and valve 50 to storage or other use not illustrated in the attached diagrammatic drawing. The lower hydrogen fluoride layer is withdrawn from separator 48 through line 51 and valve 52 by pump 53 which discharges through line 54 and valve 55 into line 35, already mentioned, through which the recovered mixture of unconverted isobutane and catalyst is recycled to further alkylation treatment.

From fractionator 42 vapors of a substantially saturated alkylate of gasoline boiling range are directed through line 56, valve 57, condenser 58, and the condensate is passed through run-down line 59, and valve 60 to receiver 61 provided with conventional gas release line 62 containing valve 63, and with liquid draw-off line 64 containing valve 65. The substantially saturated alkylate, which is the desired product of the process, is withdrawn through line 64 and valve 65 to storage. Alkylation products boiling higher than the desired gasoline fraction are withdrawn from the bottom of fractionator 42 through line 66 and valve 67 to cooling and storage not shown in the diagrammatic drawing.

The following example is given to indicate results obtained by the use of the present process, although it is not intended to limit the generally broad scope of the invention in exact correspondence with the data given.

A mixture of 90 grams of liquid hydrogen fluoride and 80 grams of sulfur dioxide was placed in a nickel-lined autoclave of 1100 cc. capacity provided with a motor driven stirrer. The autoclave and catalyst mixture contained therein were maintained at 15° C. while charging thereto, over a period of 2.5 hours, a total of 800 cc. (approximately 435 grams) of a liquefied hydrocarbon mixture containing 20 mole per cent of propene, 1.8 per cent propane, 52.8 per cent isobutane, 25.8 per cent normal butane and 0.6 per cent higher boiling hydrocarbons. The resultant reaction mixture, which was under a pressure of 4.5 atmospheres, was then stirred for an additional hour, after which the product was stabilized to remove a substantial proportion of the unconverted gaseous hydrocarbons and catalyst from higher boiling alkylation products. The recovered unconverted gaseous hydrocarbons consisted of 0.6 per cent of propane and 99.4 per cent of butanes. The higher boiling alkylation product, after washing with alkali and water, and drying, amounted to 100 grams, a yield of 152 per cent based upon the weight of the propene converted.

The stabilized, washed, and dried hydrocarbon product was separated by distillation into the following fractions:

Fraction No.	Boiling point, °C.	Volume, percent
1	20–78	3
2	78–82	2
3	82–100	62
Residue	Above 100	33

Thus more than 60 per cent of the normally liquid alkylation product consisted of heptanes, probably 2,2-dimethylpentane and 2,4-dimethylpentane. The residue boiling above 100° C. contained some unsaturated hydrocarbons and also small amounts of componds containing fluorine.

The foregoing specification and example serve to indicate the character of the process of the present invention and the nature of the results obtained therefrom, although neither section is

introduced with the idea of unduly limiting the generally broad scope of the invention.

I claim as my invention:

1. A process for synthesizing hydrocarbons which comprises alkylating an isoparaffin with an olefin in the presence of a mixture of hydrogen fluoride and sulfur dioxide.

2. A process for producing liquid hydrocarbons from hydrocarbon gases which comprises alkylating a normally gaseous isoparaffin with a normally gaseous olefin in the presence of a mixture of hydogen fluoride and sulfur dioxide.

3. A process for producing hydrocarbons boiling in the gasoline range which comprises alkylating isobutane with a normally gaseous olefin in the presence of a mixture of hydrogen fluoride and sulfur dioxide.

4. A process for producing heptanes which comprises alkylating isobutane with propene in the presence of a mixture of hydrogen fluoride and sulfur dioxide.

5. A process for producing octanes which comprises alkylating isobutane with a butene in the presence of a mixture of hydrogen fluoride and sulfur dioxide.

6. A process for converting normally gaseous hydrocarbons into normally liquid substantially saturated hydrocarbons of relatively higher molecular weight which comprises alkylating a normally gaseous isoparaffin with a normally gaseous monoolefin in the presence of a mixture of hydrogen fluoride and sulfur dioxide while maintaining the reactants in essentially liquid state.

7. A process for producing substantially saturated hydrocarbons having molecular weights suitable for use as motor fuel constituents which which comprises alkylating an isoparaffin of relatively low molecular weight with a mono-olefin of relatively low molecular weight in the presence of a mixture of hydrogen fluoride and sulfur dioxide at a temperature between about −30° and about 100° C.

8. A process for producing substantially saturated hydrocarbons having molecular weights suitable for use as motor fuel constituents which comprises alkylating an isoparaffin of relatively low molecular weight with a mono-olefin of relatively low molecular weight in the presence of a mixture of hydrogen fluoride and sulfur dioxide at a temperature between about −30° and about 100° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reacting hydrocarbons and mixture of hydrogen fluoride and sulfur dioxide.

9. A process for producing heptanes which comprises alkylating isobutane with propene in the presence of a mixture of hydrogen fluoride and sulfur dioxide at a temperature between about −30° and about 100° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reacting hydrocarbons and mixture of hydrogen fluoride and sulfur dioxide.

10. A process for producing octanes which comprises alkylating isobutane with isobutene in the presence of a mixture of hydrogen fluoride and sulfur dioxide at a temperature between about −30° and about 100° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reacting hydrocarbons and mixture of hydrogen fluoride and sulfur dioxide.

11. A process for producing octanes which comprises alkylating isobutane with normal butenes in the presence of a mixture of hydrogen fluoride and sulfur dioxide at a temperature between about −30° and about 100° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reacting hydrocarbons and mixture of hydrogen fluoride and sulfur dioxide.

12. A process for synthesizing substantially saturated hydrocarbons of gasoline boiling range which comprises subjecting at least one molecular proportion of an isoparaffinic hydrocarbon and one molecular proportion of an olefinic hydrocarbon to contact under alkylating conditions in the presence of a mixture of hydrogen fluoride and sulfur dioxide.

13. A process for synthesizing substantially saturated hydrocarbons of gasoline boiling range which comprises subjecting at least one molecular proportion of an isoparaffinic hydrocarbon and one molecular proportion of an olefinic hydrocarbon to contact at a temperature between about −30° and about 100° C. in the presence of a mixture of hydrogen fluoride and sulfur dioxide.

14. A process for synthesizing substantially saturated hydrocarbons of gasoline boiling range which comprises subjecting at least one molecular proportion of an isoparaffinic hydrocarbon and one molecular proportion of an olefinic hydrocarbon to contact at a temperature between about −30° and about 100° C. in the presence of a mixture of hydrogen fluoride and sulfur dioxide and under a pressure sufficient to maintain in liquid state a substantial proportion of the reacting hydrocarbons and the mixture of hydrogen fluoride and sulfur dioxide.

LOUIS S. KASSEL.