

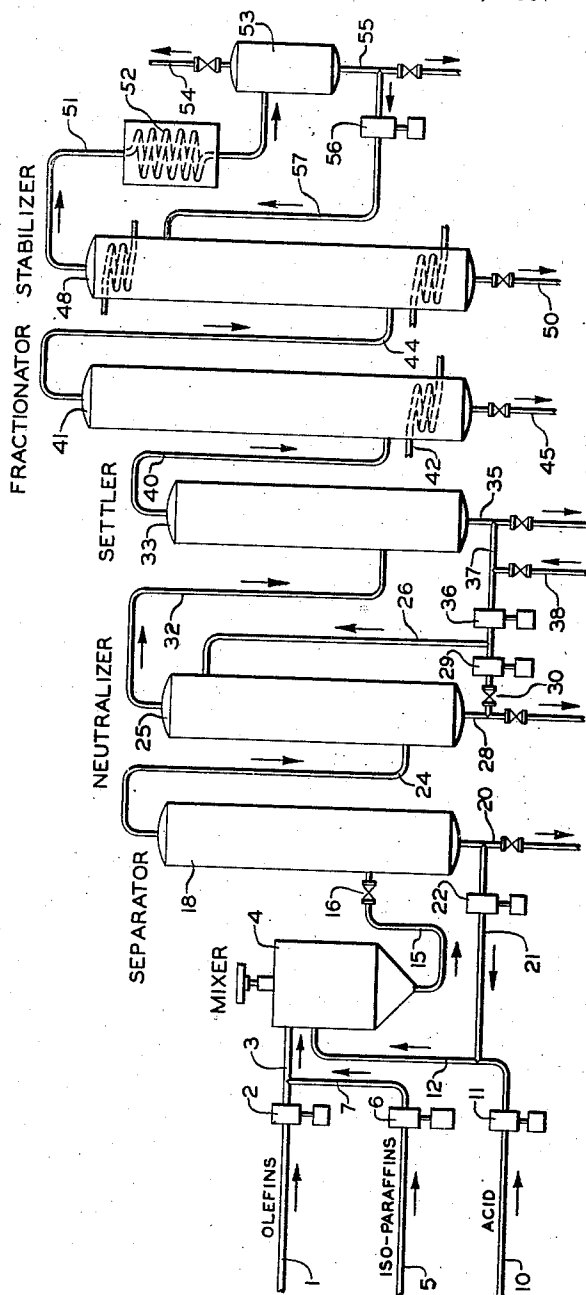
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ALKYLATION OF HYDROCARBONS

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ALKYLATION OF HYDROCARBONS

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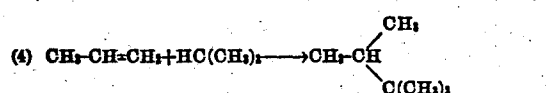
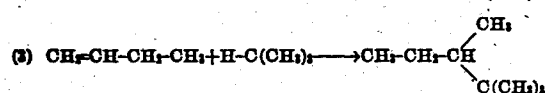
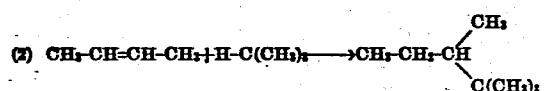
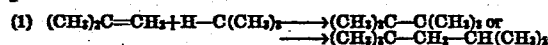
This invention has to do with the alkylation of hydrocarbons by the union of paraffins and olefins.

In particular the invention is concerned with the production of motor fuel hydrocarbons of improved antiknock value from gaseous hydrocarbons by reacting iso-paraffins with olefins in the presence of a catalyst.

This is a division of our copending application Serial No. 148,978, filed June 18, 1937.

It is well known in the art that aromatic hydrocarbons, such as benzene, may be alkylated by condensation with olefins in the presence of a suitable catalyst. This reaction apparently is possible because of the reactivity of the hydrogen atoms in the benzene molecule.

Iso-paraffins contain hydrogen attached to tertiary carbon atoms which possess unusual reactivity and in some cases even surpass that of the benzene hydrogen. It has been found that alkylation of iso-paraffins may be effected by olefins under proper conditions and with a suitable catalyst. Reactions of this type may be symbolized as follows, using isobutane as the iso-paraffin:



The above type of reactions is essentially the union of an olefin with an iso-paraffin to obtain a higher molecular weight iso-paraffin. By reacting hydrocarbons of the proper molecular weight, it is possible to obtain products of the gasoline boiling range and possessing a high antiknock value.

In accordance with the present invention, it is preferable to utilize hydrocarbons containing about 4 carbon atoms whereby a high yield of products of predominantly 8 carbon atoms or octanes is obtained. It has been found, for example, that by reacting isobutane with a C₄ unsaturated hydrocarbon fraction, a good yield of high antiknock motor fuel may be obtained.

Although it is preferable to utilize the olefin

stocks of about 4 carbon atoms because a higher octane product may be produced, the process is applicable to, and a good product may be obtained from olefin stocks of 3 carbon atoms. In some cases this may be preferable due to the larger quantities of propylene available, and also because a product of lower 50% point is obtained. It has been found, for example, that by reacting isobutane with propylene, a good yield of high antiknock motor fuel may be obtained.

The process may also be adapted to unsaturated hydrocarbon fractions which are comprised mainly of a mixture of C₃ and C₄ hydrocarbons. In some cases this process may be preferred to those in which a fraction of predominantly either 3 or 4 carbon atoms are used, because of the larger quantities of combined C₃ and C₄ available, and also because the product has a distillation range which requires little light blending stock to make it suitable for aviation fuel.

The invention will be further understood from the following examples of operations coming within the scope of the invention.

Example I

Isobutane and concentrated sulfuric acid (66° B_e) in the ratio of about 3 parts by volume of isobutane to 2 parts of sulfuric acid were introduced into a reaction vessel. The mixture was agitated and, during a period of about 4 hours, 7 parts of a C₄ stock, consisting of a refinery cracked gas containing about 3.3% C₃, 14.5% isobutylene and 25.8% normal butylenes, 11% isobutane, 44% normal butane and 1.4% of C₅ were slowly added. The reaction was allowed to continue 1½ hours after the olefin stock was charged. Ordinary temperatures were used and sufficient pressure to maintain the products in a liquid state. The unreacted gas was removed from the vessel by releasing the pressure and the liquid products separated from the acid.

The yield of butane-free product was about 150% by weight of the olefin charged. About 76% of the product distilled below 300° F., 17% from 300–400° F., and the remainder of 7% above 400° F. The 400 end point naphtha was stable, less than 2% unsaturated and had an octane value of 88.

Example II

Sulfuric acid (66° B_e) and a C₄ stock containing a mixture of about 2 parts of isobutane to 3 parts by volume of a C₄ fraction of cracked gases of substantially the composition given in Example I above, were mixed in the ratio of about

4 parts of acid to about 9 parts of the C₄ fraction. The olefin stock was slowly added to the mixture in 3 1/4 hours, and the reaction continued an additional 30 minutes. The unreacted gases were removed from the reaction vessel and the liquid products separated from the acid.

The product was substantially the same as that described in Example I above. The yield was about 140% by weight of the olefin charged, about 74% of the product distilled below 300° F., 20% from 300–400° F. and the remainder of 6% above 400° F.

Example III

Sulfuric acid (400 cc. of 66° Bé.) is charged into an iron reaction bomb. To the agitated acid in the bomb is charged 362 g. of a mixture, containing 32% propylene and 68% isobutane by weight, at a constant rate in 3 hours. The reaction is allowed to continue ten minutes with agitation. The unreacted gas is removed from the bomb by releasing the pressure and the liquid product is separated from the acid in a separatory funnel. The alkylation reaction took place at 85–95° F. and 60 to 80 pounds pressure per square inch gauge.

The yield of butane feed product is 166% by weight of the olefin charged. 70% of the product distills below 311° F., 21.4% from 311–400° F. and the remainder of about 7.3% above 400° F.

The 311° E. P. cut has an initial boiling point of 137° F., a 10% point of 174, a 50% point of 197° F., a 90% point of 236° F. and an end point of 283° F. by A. S. T. M. distillation, contains less than 0.5% of unsaturation, and has a C. F. R. M. octane of 81.9.

Example IV

Sulfuric acid (400 cc. of 66° Bé.) is charged into an iron reaction bomb. To the agitated acid in the bomb is charged 377 g. of a mixture, containing by weight 12.5% propylene, 13.7% C₄ olefin, 38.4% isobutane and the majority of the remainder n-butane, at a constant rate in 3 hours. The reaction is allowed to continue ten minutes with agitation. The unreacted gas is removed from the bomb by releasing the pressure and the liquid product is separated from the acid in a separatory funnel. The alkylation reaction took place at 85–95° F. and 50 to 65 pounds pressure per square inch gauge.

The yield of butane free product is 20% by weight of the olefin charged. 66.8% of the product distills below 311° F., 22.4% from 311–400° F., and the remainder of about 10.8% above 400° F.

The 311° F. cut was combined with the 311° F. cut of a similar run to obtain sufficient material for distillation and C. F. R. M. octane. The mixture has an initial boiling point of 112° F., a 10% point of 159° F., a 50% point of 223° F., a 90% point of 268, and an end point of 300° F. by A. S. T. M. distillation, contains less than 0.5% unsaturation and has a C. F. R. M. octane of 81.

In Examples III and IV it will be observed that the time of contact of the reacting hydrocarbons in the presence of the sulfuric acid catalyst during the alkylation operation is from 10 minutes for the hydrocarbons last introduced to an average for all the hydrocarbons of about 100 minutes. In Examples I and II an even longer average time of contact is used.

Also it will be observed with respect to Example I above that the rate of olefin feed to

the alkylation operation is less than 1 unit volume of olefin per minute for about 170 unit volumes of acid in the alkylation operation. In the other examples the rate of olefin feed per unit volume of acid is even less.

Further it will be observed with respect to Example I that the amount by weight of sulfuric acid catalyst in admixture with isoparaffin is in excess of the amount by weight of isoparaffin. This is also true in the case of Examples II, III and IV.

Also it will be observed with respect to Example I that the rate of feed to the alkylation operation of olefin in units of volume per minute is less than about 1/10 the minimum of units of volume of excess unreacted isoparaffin in the reacting mixture.

The process may be operated either as a batch or continuous operation, but in general the continuous operation is preferable. In operating continuously, as hereinafter described, the isoparaffin and olefin hydrocarbons are fed simultaneously into the reaction zone containing the sulfuric acid catalyst, as is likewise true of the batch operations described in Examples III and IV above. It is desirable to maintain the isoparaffin concentration quite high, for example at least equal to the olefin concentration in the mixture, and in some instances from 2 to 3 times the olefin concentration. In continuous operation, it is advantageous to keep the initial reaction product between the acid and olefin low. The concentration of the initial products, probably the sulfuric acid esters, can be kept low by controlling the quantity of acid and the agitation.

The process has been operated successfully at temperatures of 75–90° F. and pressures of about 30–50 pounds. Lower temperatures from the above, of around 75–80° F., are preferable but lower temperatures of down to zero or below may be used. It is desirable to maintain sufficient pressure to keep the materials in liquid phase.

The acid is strong sulfuric acid and preferably about 94 to 100% concentration. The ratio of acid to oil may vary considerably. For an oil mixture containing about 20% olefins, for example, the amount of acid should be at least about 5% and may run as high as 100% of the oil. In the specific examples set forth above the amounts of acid employed range from about 45% by volume of the oil in Example I to substantially higher proportions in the other examples.

It is unnecessary to use an unsaturated gas of any particular composition since substantially all the olefins react. Cracked gases of 30–40% olefin content are preferable although products containing from 5–50% or more unsaturation may be used. Typical C₄ gaseous fractions, for example, run about 15% isobutylene, about 25% normal butylene, about 10–15% isobutane and about 45% normal butane.

In the accompanying drawing there is shown one form of apparatus for carrying out the process of the invention, although other types of apparatus may be used.

Referring to the drawing, an unsaturated gaseous hydrocarbon fraction, such as a C₄ fraction or a fraction of cracked gas containing a substantial amount of or predominating in C₄ hydrocarbons, is charged through the line 1 and forced by the pump 2 through the line 3 into a mixer 4. Isoparaffin hydrocarbons, such as iso-

butane, are charged through the line 5 and forced by the pump 6 through the line 7 also into the mixer 4. A catalyst such as sulfuric acid is introduced through the line 10 and forced by the pump 11 through the line 12 into the mixer 4. The mixer may be any suitable mechanical means for agitating or effecting contact between the oil and the acid, such as mechanical mixers, orifice plates, and the like. In the mixer 4, it is intended that the acid and hydrocarbons react to produce a union between the olefins and isoparaflins to effect reactions of the nature of alkylation. The reaction products are discharged from the mixer 4 through the line 15, controlled by valve 16 to separator 18. In this separator the acid is separated and withdrawn from the bottom thereof through the line 20. This acid may be recirculated to the mixer, if desired, by means of the line 21 and pump 22. The oil is withdrawn from the top of the separator through the line 24 and introduced into the neutralizer 25. In this neutralizer the oil is contacted with a neutralizing agent, such as caustic or other alkaline material introduced through the line 26. The spent caustic, settling out in the neutralizer, is withdrawn from the bottom thereof through the line 28. This spent reagent may be recirculated, if desired, by means of the pump 29, located in the line 30. The oil after contact with the neutralizing agent is conducted from the top of the neutralizing tower 25 through the line 32 and introduced into the settling tower 33, wherein any additional alkali is allowed to settle out and the latter is withdrawn from the bottom of the tower through the line 35. This spent neutralizing agent also may be recirculated by means of the pump 36, located in the line 37. Fresh neutralizing agent, if desired, may be introduced through the line 38 in communication with line 37. The treated oil is withdrawn from the top of the settler 33, through the line 40 and charged into fractionator 41 provided with a means for heating in the lower portion thereof, such as heating coil 42. In this fractionator it is intended that a fraction of motor fuel boiling range be vaporized and taken overhead through the line 44 as a distillate fraction while material of higher boiling point than motor fuel is withdrawn from the bottom of the fractionator through the line 45. Vapors are conducted through the line 44 to stabilizer 48 wherein the motor fuel hydrocarbons are fractionated and separated from hydrocarbons of lower boiling point than motor fuel. The stabilized motor fuel product is withdrawn from the bottom of the stabilizer through the line 50 while the lighter materials comprising chiefly unreacted gaseous hydrocarbons are conducted from the top of the stabilizer through the vapor line 51 in which is located condenser 52. Condensate formed in the condenser 52 is passed to receiver 53 provided with a gas release line 54 and a liquid draw-off line 55. All or a portion of the condensate from the receiver 53 may be pumped as a reflux condensate by the pump 56 through the line 57 to the upper portion of the stabilizer. In some instances it may be of advantage to return to the system at least a part of the unreacted gases withdrawn through the gas release line 54.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What we claim:

1. A process for the manufacture of normally liquid hydrocarbons boiling within the gasoline boiling range, which comprises reacting low boiling olefins with a low boiling isoparaflin such as isobutane in the presence of concentrated sulfuric acid catalyst while maintaining alkylating conditions, and maintaining in the reacting mixture throughout the entire reaction a substantial molar excess of the isoparaflin over the stoichiometrical equivalent monomeric contents of the olefins, whereby alkylation of the isoparaflin is effected and a substantially saturated liquid reaction product is produced.
2. A process in accordance with claim 1 in which the reacting mixture is maintained substantially in liquid phase.
3. A process in accordance with claim 1 in which the low boiling olefins comprise the butylenes.
4. A process for the manufacture of normally liquid saturated hydrocarbons boiling within the gasoline boiling range which comprises simultaneously feeding into a reaction zone, containing concentrated sulfuric acid catalyst, a low boiling isoparaflin such as isobutane and a low boiling olefin while maintaining alkylating conditions in said reaction zone, the feed of the isoparaflin being maintained throughout in substantial molar excess over the stoichiometric equivalent feed of the olefin, whereby a substantial molar excess of isoparaflin to olefin is maintained in the reacting mixture throughout the entire reaction.
5. A process in accordance with claim 4 in which the total quantity of the hydrocarbons present in the reacting mixture is at all times less by weight than the quantity of sulfuric acid catalyst present therein.
6. A process in accordance with claim 4 in which the reacting mixture is maintained substantially in liquid phase.
7. A process in accordance with claim 4 in which the low boiling olefins comprise a butylene.
8. A process for the manufacture of normally liquid saturated hydrocarbons boiling within the gasoline boiling range which comprises reacting low boiling olefins with a low boiling isoparaflin such as isobutane in the presence of concentrated sulfuric acid catalyst while maintaining alkylating conditions, maintaining in the reacting mixture throughout the entire reaction a substantial molar excess of the isoparaflin over the equivalent monomeric contents of the olefins, and continuing the contact of the hydrocarbons with the acid for a time not less than 10 minutes, whereby alkylation of the isoparaflin is effected and a substantially saturated liquid reaction product is produced.
9. A process for the manufacture of normally liquid saturated hydrocarbons boiling within the gasoline boiling range, which comprises simultaneously feeding into a reaction zone, containing concentrated sulfuric acid catalyst under alkylating conditions, a low boiling isoparaflin such as isobutane and a low boiling olefin, the feed of isoparaflin being maintained throughout in substantial molar excess over the stoichiometric equivalent monomeric feed of the olefin, whereby a substantial molar excess of isoparaflin to olefin is maintained in the reacting mixture throughout the entire reaction, maintaining the reacting mixture of hydrocarbons and acid in agitation, and continuing the contact of the reacting mixture

ture of hydrocarbons and acid with agitation for not less than 10 minutes.

10. In the manufacture of normally liquid hydrocarbons boiling within the gasoline boiling range by reacting a low boiling olefin with a low boiling isoparaffin such as isobutane in the presence of concentrated sulfuric acid catalyst while maintaining alkylating conditions, the process comprising maintaining a body of concentrated sulfuric acid catalyst in agitation in a reaction zone, supplying thereto a low boiling olefin while maintaining at all times a substantial molar excess of the isoparaffin therein, and controlling the rate of supply of olefin so as not to exceed 1 unit volume thereof per minute for about 170 unit volumes of acid in said reaction zone.

11. A process in accordance with claim 10 in which a molar excess of the isoparaffin is fed into the reaction zone simultaneously with the olefin.

12. In the manufacture of normally liquid hydrocarbons boiling within the gasoline boiling range by reacting a low boiling olefin with a low boiling isoparaffin such as isobutane in the presence of concentrated sulfuric acid catalyst while maintaining alkylating conditions, the process comprising maintaining in agitation in a reaction zone a mixture of concentrated sulfuric acid and isoparaffin, supplying olefin at a slow rate to the isoparaffin and acid in said zone, and maintaining a substantial molar excess of isoparaffin therein at all times, the rate of supply of olefin in units of volume per minute being less than about $\frac{1}{80}$ the minimum of units of volume of excess unreacted isoparaffin maintained in said mixture.

13. A process according to claim 12 in which the amount by weight of sulfuric acid catalyst in the mixture with isoparaffin is in excess of the amount by weight of isoparaffin.

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CERTIFICATE OF CORRECTION.

Patent No. 2,260,945.

October 28, 1941.

KARL KORPI, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 52, for "20%" read "--120%--"; 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 20th day of January, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.