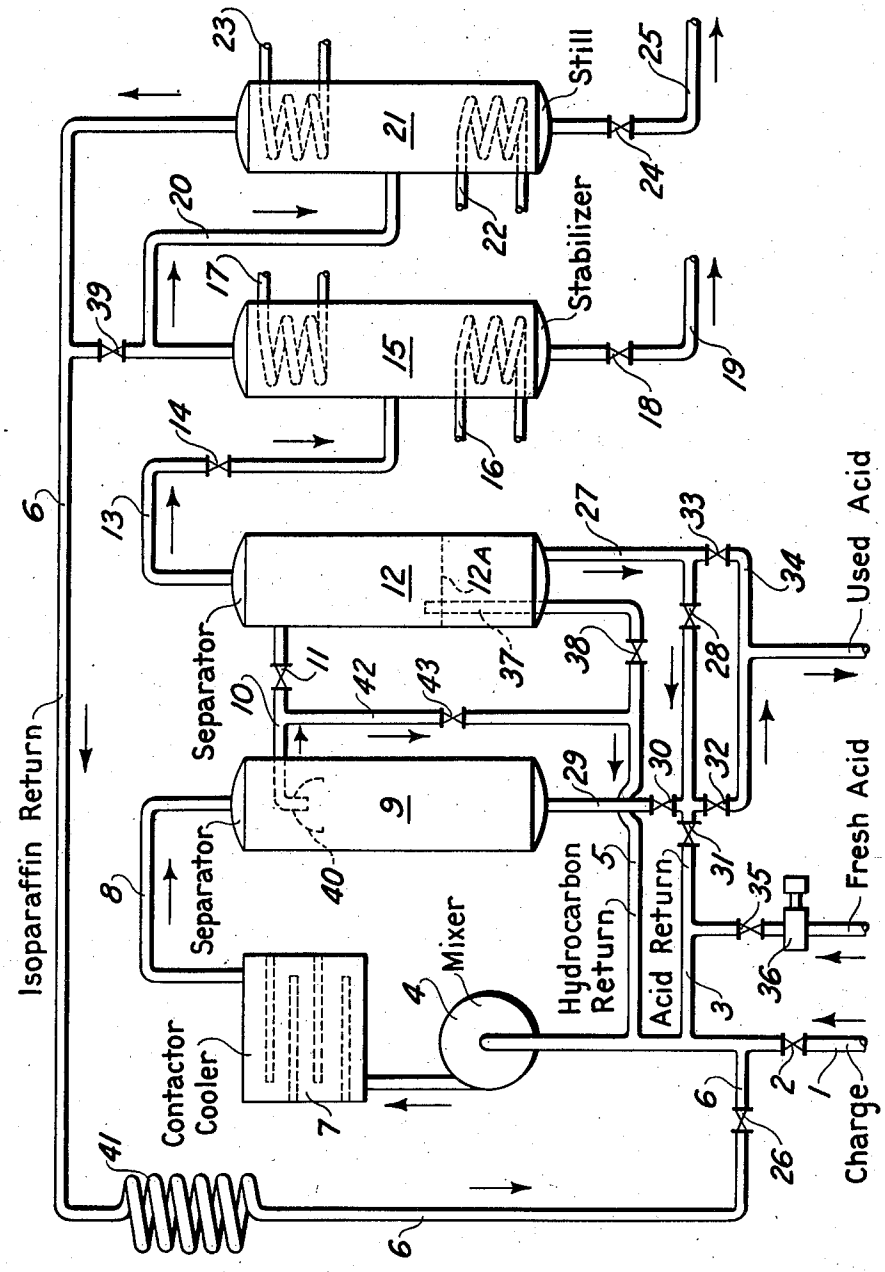
June 10, 1941. M. M. HOLM ET AL 2,245,038

HYDROCARBON REACTION

Filed Oct. 14, 1940



INVENTORS

MELVIN M. HOLM

EUGENE H. OAKLEY

BY J. Madams

ATTORNEY

Patented June 10, 1941 2,245,038

UNITED STATES PATENT OFFICE

2,245,038

HYDROCARBON REACTION

Melvin M. Holm, San Francisco, and Eugene H. Oakley, El Cerrito, Calif., assignors to Standard Oil Company of California, San Francisco, Calif., a corporation of Delaware

Application October 14, 1940, Serial No. 361,084

11 Claims. (Cl. 196—10)

This invention relates to an improved process for the alkylation of isoparaffins with olefins by means of a liquid acid catalyst, and more particularly to said process when employed for the production of liquid motor fuels of high antiknock value.

This application is a continuation-in-part of our copending application Serial No. 282,724, filed July 3, 1939.

It is known that the isoparaffinic hydrocarbons, such as isobutane and isopentane, may be caused to react with the normally gaseous olefins, such as propylene and the butenes, by means of liquid acid catalysts, such as concentrated sulfuric acid. The products of the reaction correspond in substantial part to the union of one molecule of isoparaffin with one molecule of olefin and are usually referred to as alkymers. The alkymers produced from the isoparaffins and olefins containing less than six carbon atoms per molecule have a high antiknock value and are therefore particularly desirable in the preparation of motor fuels.

It has been found that while the above alkylation reaction of, for instance, isobutane by a butene is at first readily catalyzed by concentrated sulfuric acid, the acid soon becomes inactive, apparently due to the accumulation of the products of side reactions, and the alkylation reaction substantially stops. Accordingly, alkylation may be effected by charging a batch of acid to an appropriate alkylating system, using it until its catalytic activity is spent and then discarding it. Such a batch or intermittent method of operation is, however, not well adapted to large scale commercial operation and the consumption of acid by this method is so high as to be entirely uneconomical in the production of alkymers for motor fuel.

It is the broad object of the present invention to provide an entirely continuous process for the alkylation of isoparaffins with olefins by means of a liquid acid catalyst.

It is a more specific object of the present invention to provide a continuous process for the alkylation of isoparaffins with olefins by means of a liquid acid catalyst which is economical of acid and well adapted to large scale commercial operation.

It is a still more specific object of the present invention to provide a continuous process for the manufacture of isoparaffinic motor fuels of high antiknock value by alkylating isoparaffins of less than six carbon atoms with normally gaseous olefins by means of a liquid acid alkylation catalyst, such as concentrated sulfuric acid.

Other and further important objects of the invention will become apparent from the following description and the appended claims.

While it is to be understood that we are not to be limited to any mere theoretical explanation, as mentioned above, the deterioration of an acid alkylation catalyst, such as sulfuric acid, is apparently due to the formation and accumulation of certain hydrocarbon compounds resulting from reactions which accompany the main alkylation reaction. These hydrocarbon compounds apparently enter into complex combination with the acid molecules and thus interfere with their ability to catalyze the alkylation reaction. We have found, however, that the alkylating activity of sulphuric acid remains substantially constant for a time and then falls off very rapidly to substantially zero. It appears probable that this is due to the accumulation of a certain critical concentration of the hydrocarbon-acid complex, or possibly better stated, to the reduction of the concentration of free acid molecules below a certain minimum value. In any event, we have found that if a relatively small fraction of the acid catalyst is continuously withdrawn and replaced by fresh acid, this rapid loss of catalytic activity may be entirely prevented and the catalyst maintained active for promoting the alkylation reaction for very long periods of time.

It will thus be apparent that the process of our invention relates to the alkylation of isoparaffins with olefins by contacting said isoparaffins and olefins together or in appropriate sequence with a liquid acid alkylation catalyst which is being continually replenished with fresh acid, thus making possible an operation which is entirely continuous and adapted to commercial use.

In our copending application Serial No. 282,724 it was disclosed that by making this rate of replenishment such that the concentration of free acid in the catalyst is maintained constantly above a critical minimum value its alkylating ability may be kept in the above-mentioned constant range and the rapid loss of efficiency may be entirely prevented, thus making possible a truly continuous process in which the acid consumption is not excessive. We have now discovered that when, in addition, certain ratios of acid to hydrocarbon are maintained in the several reaction zones of the process disclosed the consumption of catalyst acid may be still further reduced.

In our process as disclosed three distinct zones

are present. In the first the isoparaffin, olefin and acid catalyst are intimately mixed and thoroughly contacted by violent mechanical agitation and the alkylation reaction is thereby largely completed in this zone. The second is a dual purpose zone of residual reaction and of primary separation of hydrocarbons from the acid catalyst while the third is a substantially quiescent zone of final separation.

According to one embodiment of the process of the present invention the ratio of acid to hydrocarbon maintained under conditions of reaction in the first two zones is materially lower than in previously known alkylation processes and hence the rate of acid deterioration and the expenditure of acid per unit of product is substantially reduced. This is accomplished by maintaining a high ratio of acid catalyst to hydrocarbon reactants in the first zone of major reaction, which is preferably of restricted volume and cross-section relative to the second zone, and maintaining a much lower ratio in the second or residual reaction zone. The ratio of total acid to hydrocarbon in the two zones under reaction conditions is thus materially less than is necessary in the initial zone of primary reaction. This is in contrast to the more usual process in which the relatively high proportion of acid required in the zone of initial reaction is maintained throughout the whole region of reaction.

The invention will be further explained with particular reference to sulfuric acid as the liquid alkylation catalyst and the alkylation of isobutane with butene for the production of aviation motor fuel of high antiknock value as the alkylation reaction, though it is by no means limited thereto, since it may be applied, as indicated above, equally well with other liquid acid alkylation catalysts of the sulfuric acid type, such as chlorosulfonic acid, and to mixed liquid acid alkylation catalysts, such as sulfuric and phosphoric, sulfuric and chlorosulfonic acids, etc., and to other alkylation combinations, such as isobutane with propylene, isopentane with butene, isopentane with propylene, etc.

The point at which sulfuric acid rapidly loses its ability to catalyze the alkylation of isoparaffins with olefins will depend somewhat on the temperature at which the alkylation reaction is effected, the concentration of the original acid, the composition of the hydrocarbon feed subjected to alkylation, etc. Starting with commercial acid containing 96 to 98% H_2SO_4, and alkylating isobutane with butene, we have found that the titrated acidity of the acid catalyst, substantially free of butyl acid sulfate, progressively decreases to about 86% by weight, calculated as H_2SO_4, as more fully explained hereinafter, while the rate of alkylation and the quality of alkymers produced remain substantially constant. If the reaction is then continued further without the addition of fresh acid, the gravity and the acidity of the catalyst decrease very rapidly while both the yield and the quality of alkymers produced also show a rapid and extensive decrease. In accordance with the foregoing discovery it is a significant feature in the process of our invention that the sulfuric acid catalyst is maintained above about 86% by weight H_2SO_4, on a butyl acid sulfate free basis, by continuously removing a portion of the used acid and replacing it with fresh acid whereby the catalyst is maintained highly active for effecting the alkylation of isoparaffins with olefins, the consumption of acid is materially decreased and the quality and yield of alkymers produced are high. This replacement of catalyst may be either strictly continuous or by intermittently withdrawing and replacing a small portion of the acid.

When the concentration of the acid catalyst is so controlled it has been found desirable to maintain the volume ratio of acid to hydrocarbon reactants in the initial reaction zone of restricted volume, in which a major part of the alkylation reaction is effected under violent mechanical agitation, at about one to one or above. It has, however, been found possible to reduce this ratio in the subsequent zone of residual reaction and relatively larger volume to about one to five and sometimes as low as one to ten. By thus maintaining a substantially reduced proportion of acid catalyst in the zone of residual reaction and initial separation and by, at the same time, keeping the zone of initial reaction and high acid content less than half of the total reaction space, the quantity of acid catalyst that is continuously under reaction conditions is very substantially less than in previously disclosed processes and hence the rate of utilization of acid per unit of product is correspondingly reduced.

This invention may be better understood by reference to the accompanying drawing wherein one specific embodiment exemplifying the invention is shown. In this embodiment a mixture of hydrocarbons containing an isoparaffin to be alkylated, such as isobutane, and the olefin for effecting the alkylation, such as butene, is introduced through line 1 and valve 2 to a mixing device 4 which may be in any convenient form, such as a centrifugal pump or turbo-mixer or other instrumentality for effecting a high degree of dispersion of one immiscible liquid in another. Acid catalyst is added through line 3 and isoparaffin recycled from the process, as presently to be described, through line 6 and valve 26. The hydrocarbon reactants are thoroughly mixed with the acid catalyst by the violent mechanical agitation effected in 4 and the mixture is then discharged through a further contacting and cooling zone 7, provided with baffles or other elements for effecting turbulence, and is then led through line 8 to a residual zone of reaction and initial separating chamber 9 wherein the acid catalyst tends to separate by gravity from the hydrocarbon phase. From the chamber 9 a hydrocarbon phase, which may contain some dispersed acid, is taken through a hooded drawoff 40 into line 10 and through valve 11 to a final zone of separation 12, the acid collected therein being indicated by 12a.

From separator 12 the substantially acid-free hydrocarbon reaction mixture may then be led through line 13 and valve 14 to a stabilizer 15, equipped with an appropriate heating element 16 and a refluxing device 17, wherein the alkymer product may be freed from C_4 and lighter hydrocarbons. If the hydrocarbon raw material charged to the process contained both normal and isobutane the overhead from stabilizer 15 may be led through line 20 to a butane still 21, equipped with heating element 22 and reflux element 23 wherein the isobutane is separated from the normal butane and led back to the initial alkylation zone through line 6, condenser 41 and valve 26 for further reaction while the normal butane is discharged from the system through valve 24 and line 25. In the event that no normal butane is present the overhead from stabilizer 15 may be led directly through valve 39 into line 6 for return to the reaction zone.

As already indicated, the acid catalyst tends to

separate by gravity from the reaction mixture in vessel 9. However, according to the present invention this separation is not permitted to reach the point at which a continuous acid phase is formed, a mixture of hydrocarbon and coarsely dispersed acid catalyst being led from the bottom of the chamber 9 through line 29, valves 30 and 31 and line 3 for admixture with fresh reactants and return to the zone of primary reaction in mixer 4 and contactor 7. By regulating the rate of passage of the reaction mixture through the zone of residual reaction and initial separation in chamber 9 and by adjusting the relative rates of hydrocarbon removal through line 10 and hydrocarbon and acid removal through line 29, it is possible to keep the acid content of the stream removed through line 10 at a low value, usually not over a few per cent, while the acid content of the mixture passing through line 29 may be of the order of 50 to 60%. It is thus possible to maintain any desired high ratio of acid to hydrocarbon, as for instance one to one by volume or above, in the zone of initial alkylation comprising mixer 4 and contactor-cooler 7, while maintaining a substantially lower ratio in the zone of residual reaction and primary separation in chamber 9. In order to derive the greatest benefit from this feature of our invention it is desirable to keep the volume of the zone of initial alkylation as small a fraction as possible of the total reaction space as for instance less than 40% and preferably not more than 10% while maintaining a ratio of acid to hydrocarbon in the remaining 60 to 90% of the reaction mixture of not more than 1 to 2 and preferably 1 to 10 or less. The quantity of acid maintained under reaction conditions is thus maintained low relative to the quantity of alkymers produced as compared with other known alkylation processes and a substantial operating economy is thus effected.

Under some conditions it may be desirable, in order to maintain the desired acid-hydrocarbon balance throughout the system, to recycle a portion of the hydrocarbon phase, containing some alkymer product, from line 10 through line 42 and valve 43 or from separator 12 through line 37 and valve 38 into line 5 and mixer 4.

The acid collected in separator 12 is removed through line 27 from which it may be returned to the reaction zone through valve 28, line 3 and valve 31 or may be discharged from the system through valve 33 and line 34. Fresh acid for initially charging the system and for maintaining the concentration and the activity of the acid in the reaction zone, as described above, may be added by pump 36 through valve 35 and line 3, or through other convenient connection to the reaction zone.

The arrangement of the hooded drawoff connection 40 through which the hydrocarbon phase is drawn from vessel 9 into line 10 is a significant feature in the smooth operation of the process as described herein. By locating this element at a lower level than and on the downstream side of the point of entry of acid-hydrocarbon mixture into the vessel 9 the acid droplets are permitted to attain a directed velocity which serves to carry them past the hydrocarbon drawoff hood and thus produce a region of very low acid content within the hood from which a hydrocarbon liquid substantially free of acid may be drawn, thus reducing the load on final separator 12 to a minimum and contributing to the flexibility of operation of the process.

In alkylating isobutane with normal or mixed butenes and concentrated sulfuric acid as the catalyst, it is found convenient to maintain a temperature between about 15° and 100° F. from the point of mixing in 4 through contactor 7 into the settling zone 9 wherein the alkylation reaction is substantially completed. It may thus be desirable to so construct the contactor 7 that it may also serve as a cooling device. Sufficient pressure to maintain the hydrocarbon reactants in liquid phase is usually desirable though not absolutely necessary.

It is also found desirable to maintain a high ratio of isoparaffin to olefin and a high concentration of isoparaffin at the point at which the olefin first contacts the acid catalyst and throughout the zone of active alkylation, and for this reason the hydrocarbon charged to the system should contain a greater molecular proportion of isoparaffin than olefin and the rate of recycling isoparaffin through line 6 and valve 26 should be as high as convenient. Recycle of the isoparaffin rich reaction mixture through lines 3 and 5, as above described, is also useful in maintaining the desired high ratio of isoparaffin to olefin in the zone wherein the major portion of the alkylation reaction is effected. It is preferred that the molecular ratio of isoparaffin to olefin at the point of mixing with the acid catalyst and in the primary reaction zone 4 be at least about fifty to one and for the best results it should be of the order of one hundred to one or above, ratios between about one hundred and seven hundred to one being preferable. Since the olefin is rapidly taken up by the acid the molecular ratio of isoparaffin to alkyl acid sulfate in the reaction zone would thus be above one hundred to one. The concentration of isoparaffin in the hydrocarbon phase should be high, at least above 50% by liquid volume and preferably well above 60%.

We have found that when the C_4, butane-butene, cut from a petroleum cracking operation, to which isobutane is added to give an appropriate ratio of isoparaffin to olefin, as described above, is alkylated according to the method described, the sulfuric acid catalyst may be maintained at maximum and substantially constant activity by keeping its titrated acidity above about 94–95% by weight, when expressed as H_2SO_4, and its gravity above about 64° Bé., as more fully explained below, and that this may be accomplished by adding fresh 95 to 98% acid at the rate of usually not more than about 1.5 pounds per gallon of alkymer produced while a corresponding amount of used acid is withdrawn.

The material which is accumulated by the acid during the course of the alkylation reaction and which is responsible for its decrease in gravity and concentration and its ultimate loss of alkylating activity is rather complex in character and variable in amount, dependent upon the original concentration of the acid, the composition and purity of the raw material and particularly the temperature of alkylation, so that it is impossible to give an exact value of either acid concentration or gravity that must, under all conditions, be maintained in order to maintain a satisfactory catalytic activity. The used sulfuric acid catalysts have been found to contain a highly unsaturated terpene-like hydrocarbon material and alkyl sulfonic acids, both of which apparently play a part in the inactivation of the acid. Both would, of course, lower its gravity in proportion to the respective quantities present while obviously only the former

would lower its titrated acidity in direct proportion to the amount present. A used acid catalyst will also contain alkyl acid sulfate varying in amount with the point in the system at which it is withdrawn and also with the specific combination of conditions being employed in effecting the alkylation reaction. The presence of the alkyl acid sulfate, however, while it lowers the measured acidity and the gravity of the catalyst, apparently is not significant in a determination of the immediate activity of the catalyst.

While the ultimate test of the alkylating activity of a used acid catalyst would, of course, be to use it in a standard control alkylation reaction, we have found that a fairly reliable indication of the condition of used sulfuric acid may be obtained from its titrated acidity or its gravity when determined in view of the foregoing complications. The acid withdrawn at a point in the system at which the alkylation reaction is substantially complete would contain, at most, only a few tenths of a per cent by weight of alkyl acid sulfate, which can be disregarded. However, in the event that acid containing more than, for instance, 0.2 to 0.3% of alkyl acid sulfate is to be evaluated, the ester should be either removed in known manner or appropriate correction made for it in the gravity or acid concentration values used in such evaluation.

When observing the foregoing conventions, we have found that a Baumé gravity of about $60° \pm 2°$ represents the gravity above which the sulfuric acid, substantially free of alkyl acid ester, must be held, under all combinations of conditions so far tested, in order that its activity may be maintained for effecting the alkylation reaction to produce a product of the highest quality. The titrated acidity of the catalyst, substantially alkyl acid sulfate free, while not so quick and easy a test to apply, is a somewhat more reliable indicator of the catalyst activity. In order that its highest alkylating activity may be preserved, we have found that the titrated acidity, expressed as H_2SO_4, should be kept above about 86% by weight and that the range within which the minimum satisfactory concentration may vary with varying conditions of operation is between about 82% and 90%.

The rate at which used acid must be withdrawn and fresh acid added in the practice of the present invention in order to maintain the catalyst active for alkylation is also dependent upon a number of variables, of which the temperature at which the alkylation reaction is effected is apparently highly significant. For an average set of conditions, as outlined above, when alkylating isobutane with butene and producing alkymers boiling substantially within the range of aviation gasoline, the addition rate for various temperatures has been found to be about as follows:

Temperature, °F.	Pounds of 96-98% acid per gallon of alkymers
Below 15	0.2 to 0.5
15 to 40	0.3 to 1.0
40 to 70	0.5 to 2.0
70 to 100	1.0 to 4.0
Above 100	Above 3.0

While the foregoing figures are believed to cover the range of practical operating conditions of the various specific methods of operation now known, it will, of course, be realized that the exact value for any particular method, feed composition and set of operating conditions could only be determined by actual experiment.

Operation of the process of our invention and the advantages to be derived therefrom may be better appreciated from the following example:

Example.—A normal C_4 cut from the liquid phase cracking of a heavy petroleum oil was passed through a polymerization plant wherein 76.5% of the olefins were removed. The residual gas was enriched with isobutane until the ratio of isobutane to olefin was 13.7 to 1. The mixture was then charged to a continuous alkylation plant of the three zone type described hereinabove. The fresh acid catalyst charged was 98% sulfuric acid and the catalyst was maintained at about 64.6° Bé. (about 95.6% H_2SO_4) throughout the system by continuously replacing a small portion of the used catalyst with fresh acid. Operation and recirculation rates were maintained, as described, so that the isobutane to butene ratio at the point of mixing with the acid was 515 to 1, the concentration of isobutane in the hydrocarbon phase was 63.2% and the concentration of acid in the primary reaction zone of high dispersion was between 50 and 55% while the concentration of acid in the large volume zone of residual reaction and initial separation was about 15% by volume. The capacity of the primary reaction zone containing the high proportion of acid was only 15.5% of the total capacity of the two zones of reaction so that the quantity of acid continuously under reaction conditions was only 40% of what it would have been in a conventional system, of the same capacity, having a constant ratio of acid to hydrocarbon throughout. Under these conditions the alkylation product amounted to 165% by weight of the olefins charged, had a gravity of 68.0° A. P. I. and contained 99.5% of aviation gasoline having a bromine number of 0.1 and an octane number of 96.5.

While the present invention has been explained with respect to one specific embodiment, as set out in the drawing and described in detail above, it will be appreciated that the principles of maintaining the acid catalyst above a critical minimum strength by continuous acid replacement and of maintaining a higher ratio of acid catalyst to hydrocarbon reactants in the zone of initial high reaction than in a subsequent zone of residual reaction which constitute essential features of our invention, may be applied to substantially any alkylation system in which a liquid catalyst of the sulfuric acid type is employed.

In addition to providing an entirely continuous system for alkylating isoparaffins with olefins, it is also a feature of our invention that by the continuous replacement of the sulfuric acid catalyst while maintaining a high ratio of acid to hydrocarbon only in that limited portion of the system in which the major part of the alkylation reaction is effected the acid consumption is reduced from between 4 and 10 pounds per gallon of alkymer product, as experienced in former batch methods of operation, to an entirely practical amount between about 0.5 and 1.5 pounds per gallon of alkymers.

Having thus disclosed and exemplified our invention of an improved process for continuously and economically alkylating isoparaffins with olefins by means of a liquid acid catalyst, we claim:

1. Process for the alkylation of hydrocarbons which comprises maintaining two zones of reaction in series, the first of which is of smaller

capacity than the second and contains a means of mechanical agitation for intimately contacting two immiscible liquids, continuously charging olefins, a molecular excess of low boiling isoparaffins and strong sulfuric acid into the mixing device of the first reaction zone wherein the hydrocarbon and acid phases are thoroughly mixed under alkylating conditions, introducing the resulting mixture into the upper portion of an enlarged vessel constituting the second zone of reaction in which at least a partial separation of acid and hydrocarbon phases is effected so that the acid-to-hydrocarbon ratio leaving the bottom of said enlarged vessel is higher than the average ratio existing in the vessel, maintaining a higher volume ratio of acid to hydrocarbon in the first zone than in the second, maintaining the acid gravity in both zones of reaction above at least 60° Bé. by continuously replacing a portion of the used acid catalyst with fresh acid, recycling a portion of the acid and hydrocarbon reaction mixture from said second zone to said first zone, withdrawing another portion of the reaction mixture from the upper portion of said second zone through a hooded connection whereby the ratio of acid to hydrocarbon withdrawn may be regulated and passing said withdrawn mixture to a separating zone wherein acid is separated from hydrocarbons.

2. Process for the alkylation of isoparaffinic hydrocarbons which comprises maintaining two zones of reaction in series, the first of which is of smaller capacity than the second and contains a means of violent mechanical agitation for intimately contacting two immiscible liquids and the second of which consists of a vessel of relatively large cross-section free from any mechanical obstruction that would materially interfere with the quiet flow of liquids therethrough, continuously charging a normally gaseous olefin, a molecular excess of a low boiling isoparaffin and strong sulfuric acid into the mixing device of the first reaction zone wherein the hydrocarbon and acid phases are thoroughly mixed under alkylating conditions, maintaining at least 50% by volume of acid catalyst in said first reaction zone, introducing the resulting mixture into the upper portion of a vessel of enlarged cross-section which constitutes the second zone of reaction, in which at least a partial separation of acid and hydrocarbon phases is effected, maintaining the proportion of acid to hydrocarbon in said second zone of reaction below about 20% by volume, maintaining the acid gravity in both zones of reaction above at least 60° Bé. by continuously replacing a portion of the used catalyst with fresh acid, maintaining the proportion of isoparaffin in the hydrocarbon phase in both zones of reaction above 50% by volume, recycling a portion of the acid and hydrocarbon reaction mixture from said second reaction zone to said first reaction zone and passing another portion of the reaction mixture from said second reaction zone to a separating zone wherein acid separates from hydrocarbons by gravity.

3. Process for the alkylation of isobutane which comprises maintaining two zones of reaction in series, the first of which is of smaller volume than the second and contains a means of violent mechanical agitation for intimately contacting two immiscible liquids and the second of which consists of a vessel of relatively large cross-section free from any mechanical obstruction that would materially interfere with the quiet flow of liquids therethrough, continuously charging isobutane and butene in molecular ratio above about 100 to 1 to said first reaction zone and intimately contacting said hydrocarbon mixture with strong sulfuric acid in the mixing device of said first reaction zone wherein the hydrocarbon and acid phases are thoroughly mixed under alkylating conditions, maintaining the proportion of acid in the reaction mixture in said first reaction zone at least above 50% by volume, introducing the resulting mixture into the upper portion of the vessel of enlarged cross-section which constitutes the second zone of reaction, maintaining the proportion of said acid to hydrocarbon in said second zone of reaction below about 20% by volume, maintaining the acid gravity in both zones of reaction above at least 60° Bé. by continuously replacing a portion of the used acid with fresh acid, maintaining the proportion of isobutane in the hydrocarbon phase in both zones of reaction above 50% by volume, recycling a portion of the acid and hydrocarbon reaction mixture from the bottom of said second reaction zone to said first reaction zone and passing a second portion of the reaction mixture containing a lower ratio of acid to hydrocarbon from said second reaction zone to a separating zone wherein acid separates from hydrocarbons by gravity.

4. Process for the alkylation of isobutane which comprises maintaining two zones of reaction in series, the first of which is of less than about one-fourth the capacity of the second and contains a means of violent agitation for intimately contacting two immiscible liquids and the second of which consists of a vessel of relatively large cross-section free from any mechanical obstruction that would materially interfere with the quiet flow of liquids therethrough, continuously charging isobutane and butene in molecular ratio above about 100 to 1 to said first reaction zone and intimately contacting said hydrocarbon mixture with strong sulfuric acid in the mixing device of said first reaction zone wherein the hydrocarbon and acid phases are thoroughly mixed under alkylating conditions, maintaining the proportion of acid in the reaction mixture in said first reaction zone at least above 50% by volume, introducing the resulting mixture into the upper portion of the vessel of enlarged cross-section which constitutes the second zone of reaction, maintaining the proportion of said acid to hydrocarbon in said second zone of reaction below about 20% by volume, maintaining the acid gravity in both zones of reaction above at least 60° Bé. by continuously replacing a portion of the used acid with fresh acid, maintaining the proportion of isobutane in the hydrocarbon phase in both zones of reaction above 50% by volume, recycling a portion of the acid and hydrocarbon reaction mixture from the bottom of said second reaction zone to said first reaction zone and passing a second portion of the reaction mixture containing a lower ratio of acid to hydrocarbon from the upper portion of said second reaction zone to a separating zone wherein acid separates from hydrocarbons by gravity.

5. Process for the alkylation of hydrocarbons which comprises maintaining two zones of reaction in series, continuously charging to the first such zone olefins, a molecular excess of low boiling isoparaffins and strong sulfuric acid in such quantities as to maintain at least 50% by volume of isoparaffin in the hydrocarbon phase and a ratio of about one volume of acid per volume of hydrocarbon in said first zone, violently agitating the acid and hydrocarbon phases in said

first zone to produce a large surface of contact therebetween in order to expedite the alkylation of isoparaffins in the hydrocarbon phase by components in the acid phase, passing reaction mixture from said first zone of violent agitation to a second zone which is clear of baffles and similar obstructions to free flow whereby a partial separation of the acid and hydrocarbon phases is promoted, maintaining a ratio of acid to hydrocarbon in said second zone which is substantially less than in the aforesaid first zone, recycling acid and hydrocarbon from said second zone to said first zone and withdrawing hydrocarbon containing alkymer product from said second zone to a substantially quiescent zone of separation.

6. Process for the alkylation of isoparaffins which comprises maintaining in series a first zone of primary reaction wherein reactants are subjected to violent mechanical agitation and a second zone of residual reaction and primary separation under substantially less agitation, said first zone being of smaller volume and smaller cross-section than said second zone, the rate of passage of fluid reactants through said first zone thus being greater than through said second zone, continuously charging isoparaffin and concentrated sulfuric acid containing alkyl acid sulfate to said first zone in quantities such that the molecular ratio of isoparaffin to alkyl acid sulfate is always greater than 100 to 1, passing reaction mixture from said first zone to the upper part of said second zone, returning acid and hydrocarbon from the bottom of said second zone to said first zone, withdrawing hydrocarbons including alkymer product from the upper portion of said second zone and maintaining the concentration of sulfuric acid in the acid phase in both zones above 94% by weight H_2SO_4 by continuously replacing a small portion of it with fresh strong acid.

7. In a process for the alkylation of isoparaffins with olefins by means of an acid alkylation catalyst, the improvement which comprises maintaining two zones of reaction in series, maintaining the concentration of isoparaffin to be alkylated at least about 50% by liquid volume of the hydrocarbon phase in said first zone and effecting therein a high degree of dispersion between relatively immiscible acid alkylation catalyst and hydrocarbon phases to produce a large surface of contact therebetween in order to expedite the alkylation of isoparaffins in the hydrocarbon phase with components in the acid catalyst phase, introducing the resulting mixture into said second zone in which said dispersed acid catalyst the hydrocarbon phases are subjected to a force tending to effect a separation therebetween due to the relative difference in densities between said two phases resulting in an increase of the volume ratio of acid catalyst to hydrocarbon in the mixture in said second zone in the direction of said force, maintaining a higher volume ratio of acid catalyst to hydrocarbon in said first zone than the average volume ratio of acid catalyst to hydrocarbon in said second zone, recycling a portion of the acid catalyst and hydrocarbon mixture from a location in said second zone where the ratio of acid catalyst to hydrocarbon is higher than the average in said second zone, withdrawing another portion of the reaction mixture from a location in said second zone where the acid catalyst to hydrocarbon ratio is lower than at said first-mentioned location, and passing said portion so withdrawn to a separating zone where acid catalyst is separated from hydrocarbons.

8. Process as defined in claim 7 in which the volume ratio of acid catalyst to hydrocarbon is maintained less than about 1 to 5 in said second zone.

9. Process as defined in claim 7 in which said other portion of the reaction mixture is withdrawn from where in said second zone the acid catalyst to hydrocarbon ratio is lower than the average in said second zone.

10. In a process for the alkylation of isoparaffins with olefins by means of an acid alkylation catalyst the improvement which comprises maintaining two zones of reaction in series, maintaining the concentration of isoparaffin to be alkylated at least about 50% by liquid volume of the hydrocarbon phase in said first zone and effecting therein a high degree of dispersion between relatively immiscible acid alkylation catalyst and hydrocarbon phases to produce a large surface of contact therebetween in order to expedite the alkylation of isoparaffins in the hydrocarbon phase with components in the acid catalyst phase, introducing the resulting mixture into an upper portion of said second zone in which said dispersed acid catalyst and hydrocarbon phases tend to separate by gravity resulting in a gradual increase of the volume ratio of acid catalyst to hydrocarbon downwardly in the mixture in said second zone, maintaining a higher volume ratio of acid catalyst to hydrocarbon in said first zone than the average volume ratio of catalyst to hydrocarbon in said second zone, recycling a portion of the acid catalyst and hydrocarbon mixture from where in said second zone the ratio of acid catalyst to hydrocarbon is higher than the average in said second zone, withdrawing another portion of the reaction mixture from where in said second zone the acid catalyst to hydrocarbon ratio is lower than the average in said second zone, and passing said portion so withdrawn to a separating zone where acid catalyst is separated from hydrocarbons.

11. Process as defined in claim 10 in which the volume ratio of acid catalyst to hydrocarbon is maintained less than about 1 to 5 in said second zone.

MELVIN M. HOLM.
EUGENE H. OAKLEY.