

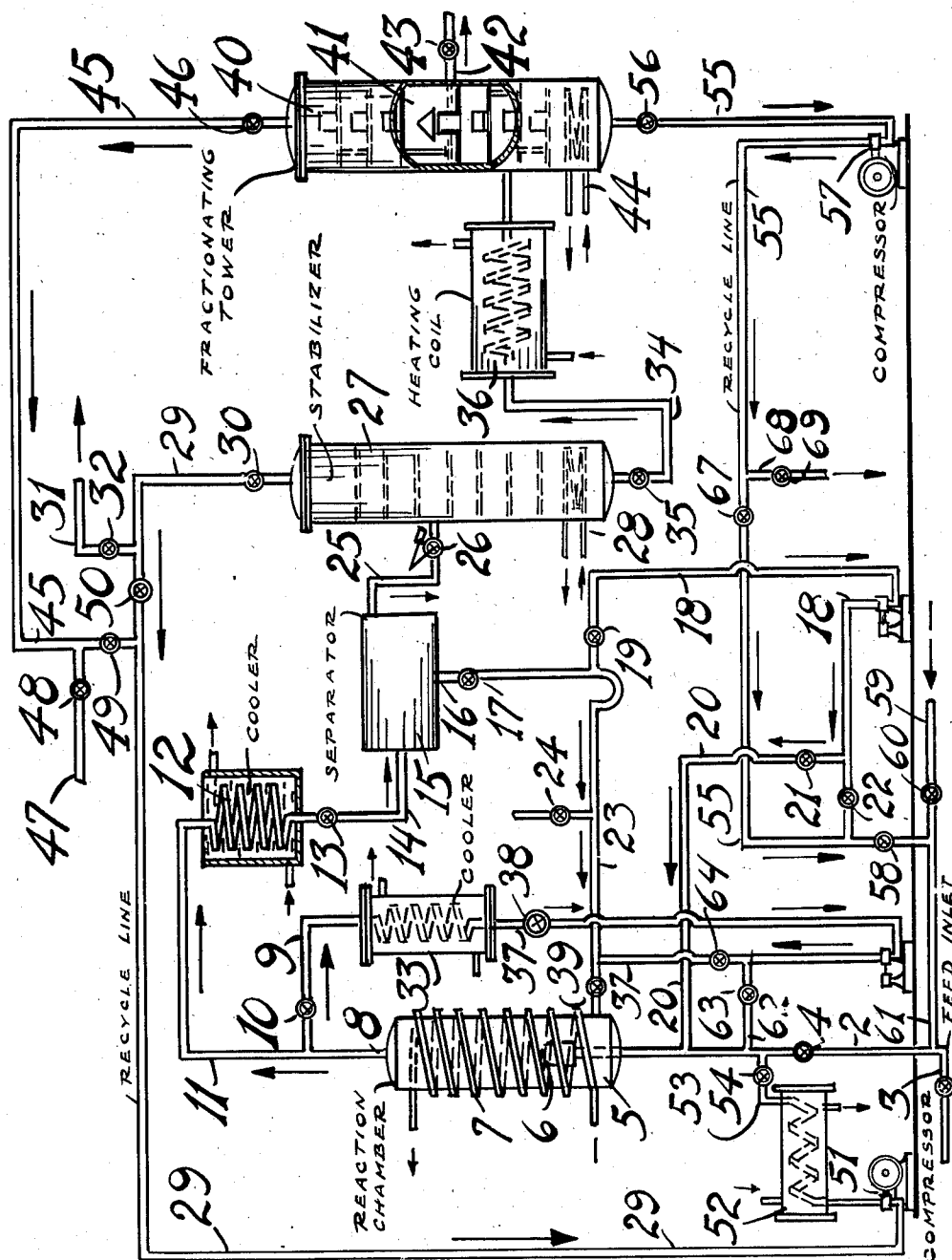
June 22, 1943.

E. E. STAHLY ET AL

2,322,482

PRODUCTION OF MOTOR FUELS BY ALKYLATION

Filed Dec. 30, 1938



Eldon E. Stahly Inventors
Erwin M. Hattox
By *P. H. Young* Attorney

UNITED STATES PATENT OFFICE

2,322,482

PRODUCTION OF MOTOR FUELS BY
ALKYLATION

Eldon E. Stahly and Erwin M. Hattox, Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

Application December 30, 1938, Serial No. 248,422

10 Claims. (Cl. 196—10)

The present invention relates to the process of reacting olefins with other hydrocarbons, and pertains, more particularly, to the production of saturated hydrocarbons boiling within the motor fuel boiling range by the alkylation of normally gaseous straight or branched chain mono-olefins. More particularly, the present invention is directed to a method for controlling the type of product by such a reaction.

It is known that saturated hydrocarbons containing tertiary carbon atoms, hereinafter referred to as tertiary hydrocarbons, will react with olefins in the presence of concentrated mineral acids to produce a wide range of products. The reactions involved are extremely complicated and are little understood. It is known that the nature of the reaction product will vary with the reaction conditions and with the type of mixture employed as starting materials. For any given mixture of starting materials and for a given set of operating conditions, however, the nature of the products produced by the procedure heretofore followed is beyond the control of the operator.

According to the present invention, the nature of the product of such a reaction is controlled to a considerable degree by adding to the feed stock one or more hydrocarbons normally contained in the product under the conditions employed, the formation of which it is desired to suppress. It has now been established that the formation of one of the normal components of the product can be substantially completely prevented by addition to the feed stock of that component, or fraction of components the formation of which it is desired to suppress if these components are added in at least an amount in which they would be normally produced.

The process of the present invention is particularly adapted to the preparation of the so-called safety fuels which find wide usage as aircraft fuels at the present time. Safety fuels are characterized by high flash point, a high octane number, good volatility and gum stability. In general, a good safety fuel should have a Tag closed cup flash point of 100° F. or more, and a boiling range of about 300 to about 500° F. It has heretofore been proposed to produce safety fuels by several methods such as the destructive hydrogenation of selected distillates or crudes, the extraction with sulfur dioxide of certain distillates or crudes, and the catalytic cracking under selected conditions of such extract. The fuels produced by the first method are rather high priced due to the limited quantity of suitable raw

material. The fuels produced by the latter two methods have so low an initial octane number and so low a lead susceptibility that the amount of lead required to convert them into 100 octane fuels makes their cost well nigh prohibitive. In contrast thereto, it has been found that the present process readily lends itself to the production of highly satisfactory safety fuels.

In the production of safety fuels by the present alkylation process, it is possible to convert substantially all of the new feed into C₁₀ and higher fractions by recycle of C₅ to C₉ fractions. It is readily apparent to one skilled in the art, however, that the invention is not confined to the addition or suppression of the C₅ to C₉ fractions alone, but it is readily understood that any desired light fraction may be returned and recycled to the reaction zone. If an extremely high boiling fuel is desired, it is contemplated to return to the original alkylation zone fractions boiling below the C₁₂ fraction, or, for example below the C₁₀ fraction, depending upon the degree of safety required in the fuel. Usually a fuel having a Tag closed cup flash in excess of 100° F. is entirely suitable for safety fuel. Likewise, it has been found entirely feasible, for the purposes of the present invention, to retain as a bottoms in the final fractionating tower hydrocarbons having a boiling point above the C₁₄—C₁₆ fractions. These heavy fractions may be returned to the alkylation reactor. While the final products produced by the process of the present invention do not, in most cases, attain an octane number of 100, nevertheless they form an extremely desirable base stock for the preparation of safety fuels. Usually they have an octane number clear of somewhere in the neighborhood of 90 to 94. It is, therefore, a relatively simple matter to raise that octane number by the use of lead tetraethyl, for example, to the required aviation standard.

The invention may be illustrated by one specific embodiment of the reaction in which an isoparaffin, such as isobutane, is caused to react with olefins, such as C₄ olefins and particularly isobutylene. The ultimate objective of the invention is the production of hydrocarbons boiling in the range of about 300 to about 500° F. and having the required flash point. Normally, however, the products of this reaction boil over the whole gasoline range and include hydrocarbons ranging from isopentane through C₁₂ and heavier hydrocarbons. In accordance with the present invention, alkylated hydrocarbons produced in the reaction and boiling above about 500° F. may

be separated from the final product and recycled to the original reaction zone. By employing this procedure, the percentage of these higher hydrocarbons ultimately produced is reduced considerably more than would normally be the case, but there is a resulting increase in the fraction boiling below these heavier recycled fractions. However, the production of the lighter ends, such as those hydrocarbons boiling below 300° F., may also be suppressed by separating from the final product these lighter fractions and returning them in substantial amounts to the original reaction zone. The return of both the heavier and the lighter undesired fractions of the final product to the reaction zone results in a material increase in the amount of the desired fractions, that is, those fractions, say from C₁₀ to C₁₄ or even as high as C₁₆.

It may be desirable, at times, to produce a motor fuel having a slightly lower flash point, in which case only C₅ to C₇ fractions, and possibly a C₈ fraction as well, are recycled to the original reaction zone. If a final product is desired having an end point of about 275–300° F., then it is desirable to recycle to the original reaction zone hydrocarbon fractions from the product composed of C₉ and higher hydrocarbons. For such a fuel, a suitable procedure is to add to the initial material being alkylated both C₁₀ and heavier hydrocarbons and C₅ to C₇ fractions so as to force the reaction to as great an extent as possible toward the production of C₈ hydrocarbons. Such a procedure normally produces high octane number gasoline which would be considerably lighter in character than the average safety fuel.

Another specific embodiment of this reaction is found in reacting an isoparaffin, such as isobutane, with olefins, such as C₄ olefins, and particularly isobutylene. The principal objective of this reaction is the production of C₈ hydrocarbons of the branch type. Normally, however, the products of this reaction boil over the whole gasoline range and include hydrocarbons ranging from isopentane through C₁₂ hydrocarbons, or higher. If, in accordance with the present invention, C₈ and higher hydrocarbons of the type ordinarily produced by this reaction are added to the feed stock, the percentage of C₈ and higher hydrocarbons in the product is much lower than would normally be the case, with a resulting increase in the C₈ fractions. By the same token, the production of C₆ and C₇ hydrocarbons can be suppressed by addition of these hydrocarbons. The preferred procedure, according to the present invention, is to add to the initial material both C₈ and heavier, and C₅ to C₇ fractions so as to force the reaction to as great an extent as possible, toward the production of C₈ hydrocarbons.

The present invention is best practiced by contacting a suitable mixture of tertiary hydrocarbons and olefins with a catalyst or activating agent under proper conditions, separating from the products produced the fractions the formation of which it is desired to suppress and recycling this fraction to the fresh feed. This procedure is to be distinguished from a procedure in which unreacted initial material is recycled or in which a recycle stock containing all of the constituents of the final product is recycled. In the former case the nature of the product is influenced only by change in the ratio of tertiary hydrocarbons to olefin in the fresh feed. In the latter case the recycle stock contains all of the products normally produced and naturally re-

sults in the formation of more of the same products. In other words, it is to be understood that according to the present invention, the material recycled, in addition to unconverted fresh feed, is a portion of the normal final product the formation of which it is desired to suppress.

The present invention is applicable to all reactions between olefins and other hydrocarbons regardless of the catalyst or activating agent which may be employed, or the presence or absence of such an agent. It has been found that the desired effect of the selective recycle operation is realized in the reaction between olefins and tertiary hydrocarbons whether the catalyst is concentrated sulfuric acid, concentrated sulfuric acid plus an oxide of a fifth group element, such as phosphorus pentoxide, a metal halide, such as boron chloride or aluminum chloride, or aluminum chloride alone or in conjunction with an alkyl halide; acid treated clays, phosphoric acid, etc. The desired effect is realized in reactions such as that between isobutane and ethylene, whether the olefin is employed in its monomeric or polymeric form.

The conditions of operation of the reaction to which the present invention is applicable are well known and need not be dealt with in great detail here. In general, it may be stated that when sulfuric acid is employed as a catalyst it should be of a strength of at least 90% and preferably between about 95% and 100%. The operating temperature can vary over a fairly wide range beginning at about 20° F. and extending to about 175° F. With other catalysts this temperature may be as high as 500° F. Temperatures lower than 20° F. can be used with sulfuric acid but slightly higher temperatures are preferred. The operation may be conducted on a batch basis or on a continuous basis. In the former type of operation, in the case of the reaction between isobutane and isobutylene, the use of molecular proportions of the former to the latter as high as 4:1 have been suggested. In the continuous operation of this process, it has been found that this ratio of 4:1 may be used in the fresh feed stock but that the ratio of isobutane: olefin in the reaction mass at the point of introduction of the feed stock should be at least 30:1. Likewise, it has been established that certain recycle ratios should be observed for the procurement of the best results, and more especially that certain minimum ratios of acid to olefins at the point of introduction into the reaction mass of the latter should be maintained.

Furthermore, it is contemplated to carry out the process either under atmospheric or superatmospheric pressure. In carrying out the reaction at superatmospheric pressures, pressures may range from a few pounds over atmospheric up to and including 3000 lbs./sq. in., but it is generally preferable to operate between about 40 and about 200 lbs./sq. in., gauge. The desire to adequately mix the reactants plus the obvious advantages of operating a continuous process make it attractive to use pressure sufficient to maintain the reactants in the liquid phase. In the case of batch operation, vigorous mechanical stirring is adequate to insure excellent yields of the final product. However, in a continuous system, the maintenance of the reactants in the liquid phase is quite desirable, since the reactants may then be readily dispersed into the reactor by means of dispersion plates, jets of restricted internal diameter, porous thimbles, turbo-mixers, centrifugal mixing pumps, etc.

A predetermined minimum amount of low boiling reaction products and, if desired, a predetermined amount of high boiling reaction products are maintained within the reaction zone. The amount of these added reaction products maintained within the reaction zone will vary with the nature and concentration of the olefins and paraffins reacted. Such variations will also be affected by the various operating conditions, such as pressure, temperature, throughput, nature of the catalyst, etc., each of which should, of necessity, be interdependently correlated with the others for best operating conditions so that as a practical matter it is not possible to accurately state the specific quantities of any given light and/or heavy condensed product which should be present in order to meet all conditions of operation.

It has been found, however, that in a continuous process, the continuous recycle of undesired reaction products to the alkylation chamber eventually builds up the equilibrium concentration of the undesired reaction products so that as a practical matter, the determination of the exact amount of recycle feed to the reaction chamber is of little moment. If desired, it is possible to determine this concentration of undesired products to be present by laboratory tests, either by a determination of the percentage of the reactor charge composed of products found in previous reactions (in cases where the reaction and recycle has been running sufficiently long to have determined that no greater quantity of undesired products are being discharged from the reactor than are being introduced into the same) or by progressively increasing the quantity of lighter reaction products charged to the reactor until a point is reached at which smaller quantities of lighter reaction products are being evolved from the reactor than are being introduced into it.

Having thus described the general nature and the objects of the invention, a more detailed description of the invention will be made by reference to the accompanying drawing which is a diagrammatic representation of one form of apparatus suitable for carrying out the process and securing the results contemplated by the invention.

For illustrative purposes only, there is shown in the accompanying drawing a diagrammatic illustration representing a process adapted to alkylate paraffinic gases in the liquid phase by means of olefins in the liquid phase in the presence of a liquid catalyst such as an inorganic mineral acid. It is to be understood, however, that the process may be readily adapted to use a solid alkylation catalyst in place of the liquid catalysts and that the process, in its broader aspects, is not restricted to any particular method of alkylation or alkylation catalyst, but contemplates a process applicable to any catalytic alkylation process. The specific embodiment of the invention described below in connection with the description of the drawing is intended to be purely illustrative of the principles of the invention and in no sense is it to be considered as limiting of the invention involved.

A suitable mono-olefin-paraffin mixture is compressed and fed into line 2 through open valves 3 and 4 so that the liquid feed stock is dispersed into the alkylation reactor 5 by any suitable dispersion device 6 such as a porous thimble, a jet, perforated disc, turbo mixer or the like, where the dispersed feed is contacted with a liquid cata-

lyst, for example, concentrated sulfuric acid, which has been introduced through valve 24 into pipe 23 and into reactor 5 through valve 39. The liquid acid catalyst may be also compressed and introduced through line 59 through valve 60 into feed line 2 where it undergoes a partial mixing with the feed stock prior to the passage through the dispersion device 6 into reactor 5.

Reactor 5 is equipped with temperature control coils 7 by means of which it is possible to either heat the reactor, as has been found to be desirable where certain catalysts are employed, or to cool the reactor by circulating ice water or cooled brine through the coils 7 in cases where it is desirable to maintain a fairly low temperature in the reactor. This latter temperature control has been found to be desirable when using concentrated sulfuric acid as the catalyst.

It has also been found desirable to recycle the olefin-paraffin-sulfuric acid mixture leaving reactor 5 through line 8 back to reactor 5. Fairly long periods of reaction under rather mild reaction conditions have proved to be more desirable than short reaction periods under more drastic reaction conditions. Accordingly, the partially reacted mixture above mentioned is passed into line 9 through valve 10 (valve 13 being closed) into heat treater 33, which may be either a heating or cooling unit depending upon the type of catalyst used. In the case of a sulfuric acid catalyst, the effluent from reactor 5 is cooled in unit 33 and then passed through valve 38 into line 37. The cooled hydrocarbon-acid partially reacted mixture is then reintroduced into the reactor 5 in one of two methods. This mixture may be reintroduced into the reactor by closing valve 64, opening valve 63 and allowing the mixture to pass through pipe 62 into feed pipe 2 thereby permitting the mixture to be redispersed through mixing and dispersion device 6 into reactor 5, or valve 63 may be closed and valves 39 and 64 opened, thereby permitting the mixture to be conducted into the reactor 5 through pipes 23 and 37.

After the mixture has been subjected to sufficient reaction to form a recoverable amount of product, valves 10 and 13 are adjusted so that only part of the reaction mixture is recycled, and pipe 11 conducts the remainder of the reaction mixture into cooler 12 and pipe 14 conducts the cooled reaction mixture into acid separator 15 where the acid settles to the bottom of the separator and is drawn off through valve 17 into pipe 16. Valves 19 and 24 may be closed and the separated acid returned to reactor 5 through line 23 and opened valve 39. The separated acid may also be commingled with the feed stock and reintroduced into reactor 5 through the dispersion and mixing device 6 by closing valves 22, 24, 39, and opening valves 19 and 21, the acid then flowing from line 16 into lines 18 and 20 into feed line 2. It is also advantageous at times to close valve 21 and open valves 22 and 58, thereby permitting the separated acid to be fed into recycle lines 55 and 61 prior to its mixing with the feed stock and being reintroduced into the reactor 5. The contents of these recycle lines will be described in detail hereinafter. It is also possible, by closing valves 19, 24 and 39 and opening valve 64, to directly introduce the separated acid into the feed line 2 by causing its flow through pipes 23, 37 and 62.

As previously pointed out, fresh acid may be introduced into the system either through valve

24 or 60. However, it is preferred to draw the spent acid from the system through valve 24. In such a case, valves 17 and 24 are open while valves 19 and 39 remain closed.

The upper hydrocarbon layer in separator 15 is drawn off through pipe 25 and led through pressure reducing valve 26 and then immediately conducted into stabilizer 27 where any normally gaseous hydrocarbons are flashed. To insure substantially complete removal of these hydrocarbons, stabilizer 27 may be equipped with heating coils 28 although this is not always necessary. The normally gaseous and lighter liquid hydrocarbons flashed from stabilizer 27 are led through valve 30 into pipe 29. These may be either conducted from the system by closing valve 50 and opening valve 32, or they may be returned in whole or in part to the reaction zone 5 by means of pipes 29 and 53, to be more fully described hereinafter.

The liquid product leaving the bottom of stabilizer 27 through valve 35 and line 34 is passed through heating coil 36 and thence into fractionator 40 provided with any desired number of trap out trays, such as 41, arranged at the desired levels to obtain any suitable fractions. Thus, when operating with an isobutylene-isobutane feed, a C₈ cut might be the only one withdrawn from a trap out tray in fractionator 40, or, if desired, a C₈-C₉ cut and a C₁₀-C₁₂ might both be withdrawn, in which case two trap out trays suitably spaced would be required. The desired products are withdrawn through a line or lines 42 by opening a valve or valves 43. The fractionator may be provided with a reboiler or heating coil 44 to insure a sharper fractionation. Products lighter than those desired are removed from fractionator 40 through valve 46 and pipe 45 and products heavier than those desired are removed from fractionator 40 through valve 56 and line 55. Both of these undesired fractions may be removed from the system through valve 48 and pipe 47, valve 49 being closed, and through valve 69 and line 68, valve 67 being closed, respectively.

As was the case in connection with the lighter effluent from stabilizer 27, these products may be recycled to the reactor 5 either in whole or in part. In recycling the lighter fractions from vessels 40 and 27, valves 32 and 48 are closed and valves 30, 46, 49, 50 and 54 are opened. This allows any unreacted reactants from vessel 27 and all fractions boiling below the boiling point of the fraction removed from the trap out trays of vessel 40 to be returned through pipes 29, 45 to compressor 51, cooling or heating coil 52, the use of a cooling or heating medium being determined by the optimum temperature requirements for the particular catalyst being used, and thence into feed pipe 2 by means of pipe 53.

The heavier products of the reaction are returned to reactor 5 by opening valves 56, 67, 58 and 4 and closing valves 69, 22 and 60. The flow is then through pipes 55, 61 and 2. Compressor 51 serves to compress the recycled heavier products to the operating pressures of reactor 5. If desired, valve 58 may be closed and valves 21 and 22 may be opened so that the recycled products of reaction are contacted with the fresh feed just prior to their introduction into the reactor 5, lines 18 and 20 being used for this purpose. It is therefore possible to mix the acid and then the heavier recycled fractions prior to the introduction of the reaction mixture into the reactor 5.

The undesired products of the reaction and the unreacted hydrocarbons which may be removed from the system through pipes 31, 47 and 69 may be either used for some extraneous purpose or they may be piped directly to another similar unit and used therein. In other words, it is not intended that the scope of the present invention should be restricted to recycling of the undesired products of reaction to the same reactor in which they were formed. It may be found to be advantageous to pipe these products to an analogous or similar unit operated in series or parallel with the above described unit, in which case, the undesired products of one unit are equally suitable for use in the reactor of a second, third, etc., unit operating upon the same or slightly different feed stock but, at any event, carrying out an alkylation reaction using substantially the same conditions of operation, catalyst, and substantially the same type of feed stock.

It will, of course, be readily understood that the heavier products of the reaction are not necessarily completely recycled to the reaction zone, but part of these heavier products may be removed from the system and the remainder recycled to the reaction zone. It is at times desirable to maintain the temperature of the stabilizer sufficiently high to distill off all lighter fractions of products as well as unreacted reactants which are not desired in the final product. These products and unreacted reactants together may then be returned to the alkylation zone. In such a case, the fractionating equipment is operated to secure a separation of the desired fractions, for example, safety fuels, say up to 500° F. end point, and the remainder of the product is taken from the fractionating unit as bottoms and may be returned to the alkylation zone to suppress their further formation.

This specific embodiment of the process has been described as applied to the use of a liquid catalyst. In cases where the catalyst is solid, such as aluminum chloride, sodium aluminum halide complex, zinc chloride, etc., the alkylation reactor 5 may be packed with such a catalyst or the catalyst may be supported on a carrier such as pumice, celite, bauxite, acid activated clays, activated carbon, etc., or the catalyst, either supported or unsupported, may be placed on a series of trays mounted within the reactor 5. In place of a single reaction chamber, two or more chambers, arranged in series or parallel, may be used whereby the catalyst contained in one or more of the chambers may be "on stream" while the other chambers containing catalysts are undergoing regeneration, thus providing for a continuous process in cases where solid catalysts are used. When solid catalysts are used, the need for separator 15 and its return lines is obviated.

The invention is not limited to the use of reactants from any particular source. Single paraffinic and olefinic hydrocarbons may be employed. However, it is commercially more feasible to use mixtures of hydrocarbons containing the requisite paraffins and olefins. The reacted mixture from catalytic and thermal polymerization units, including the gaseous constituents thereof, may be directly introduced as reactants into the alkylation reactor 5. Gaseous mixtures evolved from catalytic and thermal cracking units may also be advantageously employed.

It is an essential requirement in the practice of the specific embodiment of the present invention described with reference to the drawing that the feed stock contain at least one isoparaffin,

preferably boiling below the boiling point of the desired final product fraction, and that the feed stock contain at least one mono-olefin. Partially dehydrogenated field butanes, refinery C₃—C₄ and C₄ cuts, paraffinic mixtures containing iso-
 5 paraffins and which have been enriched with mono-olefins from extraneous sources, etc., are suitable. The invention contemplates the reactions of isobutane, pentanes, etc., with ethylene, propylene, normal or isobutylenes, normal and
 10 branched chain amylenes, their dimers, trimers, tetramers, etc., their codimers, cotrimers, cotetramers, etc., their cross- and inter-polymers, etc. It is desirable to have in the fresh feed between about 2 and about 12 mols of isoparaffin present per mol of mono-olefin. Likewise,
 15 from 4 to 24 mols of isobutane should be contacted with each mol of diisobutylene, etc.

The invention is not limited to any particular catalyst. Any suitable catalyst known to promote alkylation may be employed. Halides of
 20 metals, such as iron, nickel, aluminum, zinc, etc., either alone or admixed with small amounts of a halide, such as hydrogen halide or its equivalent, are known to be excellent alkylation catalysts. Boron fluoride, sodium aluminum complex halides, concentrated inorganic mineral acids, such
 25 as sulfuric acid or oxides of elements of the 5th group of the periodic system when used in conjunction with concentrated sulfuric acid are also quite desirable alkylation catalysts. It has also
 30 been found advantageous to use acid treated clays, such as Marsil clay, montmorillonite, bentonite, Floridin, Super Filtrol, etc., not only as suitable carriers for other catalysts but also as catalysts per se.

As a guide in carrying out the invention and toward a better understanding of the principles involved therein, the following examples are presented, it being distinctly understood that such
 40 examples are illustrative rather than limitative.

Example 1

A feed stock composed of 11.3% of isobutylene, .8% of normal butylene, 69.8% of isobutane and 12.1% of a C₅—C₇ fraction obtained from a similar experiment conducted in the absence of said
 45 fraction from the feed was subjected with stirring in an autoclave at 50–55 lbs./sq. in. gauge pressure and at a temperature of 70° F. for 2½ hours to reaction in the presence of 98% sulfuric acid in an amount equal to 93 grams of catalyst per 100
 50 grams of feed. Analysis of the total product indicated a 99% reduction of the olefin content of the feed. The debutanized product which was obtained in a yield of about 148% based upon the olefin content of the feed, was fully saturated since it exhibited no bromine number. The newly
 55 formed product comprised 13.4% of C₅—C₇ fraction, 36.1% of C₈ fraction and 50.5% of C₉ and heavier fraction.

Example 2

A feed stock comprising 7.8% of isobutylene, 4% of normal butylene, 31.6% of isobutane, 41.5% of a C₅ and heavier fraction obtained from a previous alkylation reaction and 18.7% of a C₅—C₇
 65 fraction obtained from a previous alkylation reaction was reacted for 2½ hours at 30 lbs./sq. in. gauge pressure and at a temperature of between about 65 and about 70° F. in the presence of 75 grams of 93% sulfuric acid per 100 grams of feed. The total product had a bromine number of less than 1, indicating a 97.7% reduction of the olefin content of the feed stock. The composition of the debutanized product was 24.9% of C₅—C₇,
 70

19.6% of C₈ and 55.5% of C₉ and heavier. An analysis of the newly formed product in this reaction revealed no further formation of C₅—C₇ fraction, 91% of C₈ fraction and 9% of C₉ and heavier fraction. This newly formed product was obtained in a 195% yield based upon the total butylene content of the feed stock.

In Example 1, the addition of C₅—C₇ to the feed (equivalent to 12.1% of the total feed) resulted in the formation of no new C₅—C₇ hydrocarbons. In fact, less C₅—C₇ cut was found in the product than was present in the feed which indicates that some of those components were alkylated to produce heavier paraffins. The results of Example 2 demonstrate the effect of recycling both heavy and light ends. Less C₅—C₇ was found in the product than was added to the feed and only a small increase in C₉ and heavier fractions was noted. Approximately 91% of the newly formed product boiled in the C₈ range. The high yield of 195% indicates that it is an extremely efficient reaction and that this reaction is unquestionably made more efficient by the recycling of heavy and light ends.

The above examples are batch operations, but it is readily understood that the novel recycle feature of the present invention is adapted to the process carried out continuously with continuous recycle of heavier and/or lighter products which are undesired or with continuous removal only of the desired products from the reaction zone, allowing the concentration of the heavier and lighter products to build up to an equilibrium within the said alkylation zone.

It will be noted that in the procedure described with reference to the drawing, there is continuous recycle of the reaction mixture containing all components of the product as well as the return to the reaction mixture of selected fractions of the product. Such procedure is desirable in continuous operations where it is desired to maintain a high hydrocarbon content in the reaction mixture. It will be understood, therefore, that the practice of the present invention does not exclude the recycling of a large portion of all components of the reaction product, but is satisfied by such an addition of those selected fractions of the product, the formation of which it is desired to suppress, as will build up in the reaction mixture a higher ratio of undesired product to desired product than would normally obtain under the usual conditions of working.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and desired to be secured by Letters Patent is:

We claim:

1. In a process which comprises reacting a mono-olefin and a paraffinic hydrocarbon containing at least one tertiary carbon atom per molecule to produce alkylated hydrocarbons, the improvement which comprises introducing into the reaction mixture a fraction of a previously formed product of said reaction taken from the group consisting of a normally liquid fraction boiling below that of the ultimately desired final product and a fraction composed of hydrocarbons boiling below that of the ultimately desired final product with hydrocarbons boiling above that of the ultimately desired final product.

2. A process as in claim 1 wherein the process is continuously carried out and wherein the undesired fractions are returned to an alkylation zone as formed and separated from the desired final product.

3. In the process of catalytically alkylating isoparaffins with mono-olefins, the improvement which comprises fractionating the resultant reacted mixture to separate from the alkylate produced at least one fraction of a desired boiling range, a lower boiling fraction, and a higher boiling fraction, and returning to an alkylation zone substantially all of said latter fractions in substantially the amount and at substantially the same rate as that at which they are formed in the reaction.

4. A process as in claim 3 wherein the process is conducted continuously.

5. A process for the production of normally liquid hydrocarbons boiling within the gasoline boiling range which comprises alkylating normally gaseous isoparaffins with monoolefins having a boiling point below that of the desired final product at temperatures between about 10 and about 100° F. in the presence of between about 90% and about 100% sulfuric acid and carrying out the reaction in the presence of a fraction of the final product boiling above the desired ultimate final product and in the presence of another fraction of said final product boiling below that of the ultimately desired final product.

6. A process for the production of safety fuels which comprises alkylating a normally gaseous isoparaffin with a normally gaseous mono-olefin in the presence of concentrated sulfuric acid, fractionating the resultant reaction mixture into a fraction composed predominantly of C₅ to C₇ hydrocarbons, another fraction composed of predominantly C₈ to C₁₂ hydrocarbons and a third fraction composed predominantly of C₁₃ and heavier hydrocarbons, and recycling the first and third fractions to the alkylation zone.

7. The process for the production of safety fuel which comprises alkylating a normally gaseous isoparaffin with a normally gaseous mono-olefin in the presence of concentrated sulfuric acid under alkylating conditions, fractionating the resultant reacted mixture into a fraction composed

predominantly of C₅ to C₈ hydrocarbons, another fraction composed predominantly of C₁₀ through C₁₆ hydrocarbons and a third fraction composed predominantly of C₁₈ and heavier hydrocarbons and recycling the first and third fractions to the alkylation zone in substantially the amount and at substantially the same rate as that at which they are formed in the reaction.

8. In a process for the production of saturated liquid hydrocarbons having a boiling range corresponding to that of gasoline wherein isoparaffins are alkylated with mono-olefins by passing a mixture of the reactants together with concentrated mineral acid catalyst into a reaction zone under suitable conditions of operation, and the products from said reaction zone are fractionated to separate a desired product of predetermined boiling range and wherein reaction products boiling above and below the desired range are normally formed in the process, the improvement which comprises introducing into the reaction zone a predetermined minimum quantity of said last named higher and lower boiling reaction products sufficient to substantially completely suppress the further formation of said products during the reaction.

9. A process which comprises alkylating a refinery C₄ cut containing isobutane and at least one butene in the liquid phase in the presence of 93 to 98% sulfuric acid, fractionating the resulting alkylate to separate the same into a desired motor fuel boiling range fraction and undesired higher and lower boiling fractions, and returning substantially all of the undesired fractions to the alkylation reactor in substantially the amount and at substantially the same rate as that at which they are formed in the reaction.

10. A process as in claim 9 wherein the process is carried out in a continuous manner and in which the recycle of the undesired fraction is continuously carried out.

ELDON E. STAHLY.
ERWIN M. HATTOX.