

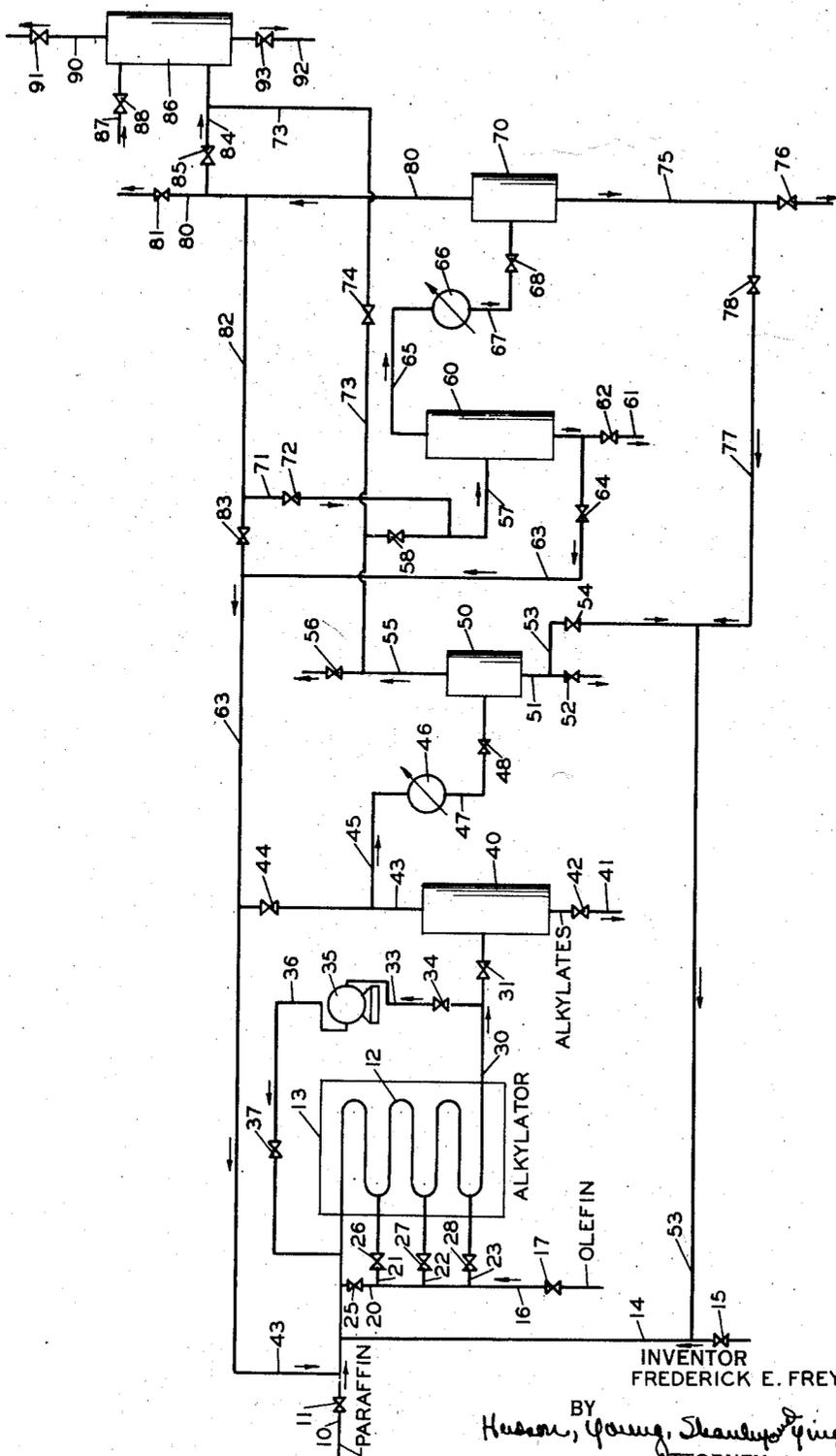
June 29, 1943.

F. E. FREY

2,322,800

CONVERSION OF HYDROCARBONS

Filed Jan. 22, 1940



INVENTOR
FREDERICK E. FREY

BY
Hudson, Young, Stanley & Singer
ATTORNEY

UNITED STATES PATENT OFFICE

2,322,800

CONVERSION OF HYDROCARBONS

Frederick E. Frey, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

Application January 22, 1940, Serial No. 315,063

8 Claims. (Cl. 196—10)

This invention relates to the catalytic production of higher boiling hydrocarbons from lower boiling hydrocarbons and more particularly to the catalytic union of paraffin and unsaturated hydrocarbons in the presence of hydrofluoric acid.

Many processes have been proposed for converting low boiling hydrocarbons into higher boiling hydrocarbons, such as the production of motor fuels and lubricants from less viscous, more volatile, or normally gaseous hydrocarbons. Some of these processes are dependent upon having olefin hydrocarbons, or other unsaturated hydrocarbons, present in large proportions in the charge stock, such as in well known thermal and catalytic polymerization processes for producing motor fuel from refinery gases containing light unsaturated hydrocarbons from cracking stills. Still other processes have been proposed to produce heavier hydrocarbons from lighter paraffin hydrocarbons, such as thermal conversion under pressure whereby scission of the paraffins and polymerization proceed concurrently to produce conversion, or multistage processes employing a dehydrogenation step as a first part of the process, followed by one or another variety of conversion polymerization involving the olefins so produced.

This invention relates particularly to the alkylation of paraffin hydrocarbons to produce alkyl derivatives thereof, or in other words, higher boiling paraffin hydrocarbons, in the presence of a new catalyst for this reaction, and it also relates to certain preferable methods and process arrangements for alkylating paraffins in the presence of this catalyst to obtain high yields of preferred paraffin hydrocarbons, or specific paraffinic hydrocarbon fractions of predetermined boiling ranges and characteristics. I have found that concentrated hydrofluoric acid, under conditions to be set forth, will act as a catalyst to effect a union of unsaturated hydrocarbons with paraffin hydrocarbons to form higher boiling paraffin hydrocarbons. I have further found that it is preferable to use as a catalyst for this reaction substantially anhydrous hydrofluoric acid, or hydrogen fluoride, and that it can be effectively and safely used over a wide range of temperatures. I have also found that, although metal halide catalysts such as boron trifluoride have been used in the presence of appreciable quantities of finely divided metallic nickel and hydrogen fluoride to catalyze the reaction of paraffins and olefins to form higher boiling paraffins, the presence of such other materials as finely divided metals and/or metal halides is not necessary for my invention, and that I can use concentrated hydrofluoric acid as a catalyst for the alkylation of paraffin hydrocarbons in the absence of finely divided nickel, metal halides, and the like. Thus, when reference is made hereinafter,

in the specification or in the claims, to concentrated hydrofluoric acid or to substantially anhydrous hydrofluoric acid, it is to be understood that I regard the hydrofluoric acid as being the sole catalytic material. Although the metal walls of the reaction chambers or vessels may at times have some fortuitous promoting effect, the process has been carried out in the presence of numerous metals without appreciable differences being noted, so that such effects of gross masses of metal are substantially negligible if at all present.

It is an object of this invention to produce higher boiling paraffin hydrocarbons by the alkylation of lower boiling paraffins in the presence of hydrofluoric acid.

Another object of this invention is to use hydrofluoric acid as a catalyst in alkylation reactions involving only aliphatic hydrocarbons.

Still another object of my invention is the conversion of low boiling isoparaffins to higher boiling isoparaffins by alkylation with unsaturated hydrocarbons in the presence of concentrated hydrofluoric acid.

A further object of this invention is to establish a process wherein synthetic conversion stocks composed of hydrocarbons of simple and controlled composition can be converted in the presence of concentrated hydrofluoric acid to produce a paraffinic liquid fraction having especially desirable characteristics and controlled properties, reflecting closely the identities of the reactant hydrocarbons selected.

An object of my invention is a process for the alkylation of paraffins with olefins in the presence of substantially anhydrous hydrofluoric acid to produce various simple branched paraffins of a single species or a mixture of simple composition within a wide range of boiling points or volatilities.

Another object is to effect the efficient recovery by physical means of hydrofluoric acid when used as a catalyst in the alkylation of paraffins with olefins.

Further objects and advantages of my invention and process will be found in the accompanying disclosure and discussion.

Catalysts which effect the alkylation of paraffins with olefins include active metal halides such as aluminum chloride, especially in the presence of small amounts of the corresponding hydrogen halide, certain complex salts such as sodium chloroaluminate, and concentrated sulfuric acid, a strong oxygen-containing, polybasic acid. However, these and similar catalysts have one or more rather distinct disadvantages, chief among which are the promotion of unwanted side reactions, and more or less rapid deactivation of the catalysts accompanied by chemical reactions involving these materials. Thus aluminum chloride, boron

trifluoride, and similar metal halides form addition compounds with olefin hydrocarbons which sooner or later degenerate into black, tar like masses which not only represent a deactivation of catalytic materials, but also represent a loss of valuable hydrocarbon material and necessitate involved procedures for eliminating such materials and recovering the metal halide in a form suitable for subsequent use. Sulfuric acid, which has recently found wide commercial application as an alkylating catalyst, has somewhat similar disadvantages. While apparently it does not form such definite intermediate compounds with olefin hydrocarbons as do various metal halides, there apparently is associated with its use a formation of various organic compounds, which after a time render the acid much less active, so that sulfuric acid which contains only 10 or 15 per cent of such organic material must be replaced with fresh, uncontaminated acid. Sulfuric acid is also a powerful oxidizing agent, so that it can not be used at temperatures much above about 100 to 125° F. without too extensive deleterious side reactions that consume both sulfuric acid and valuable organic material. The spent acid can be partly reclaimed by more or less elaborate chemical means such as hydrolysis with water, removal of the oils thereby released, and reconcentrating by distilling out the water.

Concentrated hydrofluoric acid, when used as an alkylating agent for the alkylation of paraffin hydrocarbons, apparently does not possess these deleterious characteristics. It is essentially a non-oxidizing and non-reducing material, so that it can be used, and treated, at elevated temperatures without the undesirable side reactions just mentioned. While somewhat more dilute concentrations may be used, I prefer to use it in concentrations greater than 80 per cent by weight, the other material being water, and I have found that substantially 100 per cent hydrofluoric acid, that is, substantially or completely anhydrous hydrofluoric acid or hydrogen fluoride, is very effective, and is particularly adapted to the process arrangements to be hereinafter described more fully. As will be discussed, the process is generally carried out with the hydrocarbon material substantially in liquid phase; efficient reaction results when sufficient hydrofluoric acid is employed to result in a substantial saturation of the liquid hydrocarbon material with hydrogen fluoride, and preferably sufficient hydrogen fluoride is used to form a separate liquid phase which may be maintained emulsified or intimately mixed with the hydrocarbon while reaction takes place. In most cases the hydrofluoric acid charge should be at least 10 per cent of the total charge, on a liquid volume basis, and hardly ever need exceed 50 or 60 per cent, though more can, at times, be used. In the concentrated form, hydrofluoric acid is substantially inert, or non-corrosive, toward numerous metals, such as copper, nickel, most steels, and various other alloys which can be used in the construction of plant equipment. Occasional fortuitous reactions may produce minor amounts of inorganic fluorides but, as previously discussed, insofar as this invention is concerned hydrofluoric acid is considered to be used in the substantial absence of added metals or metal halides. The reaction temperature may be varied over a wide range for any particular reaction mixture, but appears to be most dependent upon the paraffin hydrocarbon participating in the reaction. Thus, in general, I may carry out an alkylation

process at temperatures between about 0 and 300 or 400° F. For readily reacted paraffin hydrocarbons, such as isobutane or isopentane, I may readily effect an alkylation at a temperature between about 35 and 100° F., while for less reactive paraffins higher temperatures are necessary or more desirable. The use of hydrofluoric acid has a distinct advantage in such cases, in that it can be used under these more extreme conditions without promoting or entering into extensive undesirable side reactions.

I have found that when an intimate mixture of a paraffin hydrocarbon (particularly a low boiling isoparaffin such as isobutane, isopentane, or isohexane), concentrated hydrofluoric acid, and an olefin hydrocarbon is maintained at a reaction temperature, a union takes place between the paraffin and the olefin to form a higher boiling paraffin which generally represents the sum of the original paraffin and olefin not only as to molecular weight but also as to molecular structure. Butanes are ordinarily too light to be included in most motor fuels in appreciable quantities, so that they will form the usual paraffinic reactants. While pentanes are present in most motor fuels in appreciable proportions, it will at times be desirable either to utilize excess pentanes or produce a fuel of very low volatility and pentanes, or heavier paraffins, may be used as reactants in such cases. Highly branched isoctanes can be produced either by alkylating isobutane with butylenes or by alkylating isopentane with propylene, while highly branched isononanes will result from the alkylation of isopentane with butylenes and will have low volatilities and vapor pressures.

It appears that if a mixture of paraffins and olefins containing a large portion of olefins, such as 30 to 50 mol per cent, or more, of the total mixture, is reacted in the presence of concentrated hydrofluoric acid, the molecular weight of the hydrocarbon product tends to be higher than would result if the same amount of olefin and paraffin were reacted by adding small amounts or portions of olefin to a predominantly paraffinic mixture in the presence of hydrofluoric acid, while allowing reaction to take place between and during the addition of olefins. While it seems that, in many instances with various particular olefin and paraffin reactants, some type of olefin-consumption reaction occurs very rapidly, so that immediately after olefin-containing material is introduced to the reaction zone the concentration of free olefin rapidly approaches a low value—often less than one per cent—and is difficult to determine experimentally as to amount, more lower molecular weight products generally result, especially with the more reactive olefins, if high momentary concentrations of olefins in the reacting mixture are not obtained or permitted to result. Any olefin-consumption reaction which takes place under these conditions is exothermic, and for a close control of the reaction, heat should be removed as it develops. It is, of course, possible to produce a paraffinic product when the total charge stock contains more than 50 mol per cent of olefins. When there is a high initial concentration, such as first mentioned, it appears that in some cases a certain amount of polymerization first takes place, which of course reduces the mol per cent of olefin, and a heavy product forms with these polymers as reactants. In other cases, the initial paraffinic product again is alkylated with additional olefin.

The ultimate result is somewhat similar in both cases but not always the same.

It has, therefore, been found to be quite desirable to supply small amounts of olefins as these are consumed. When separate streams of paraffins and olefins are available, this can be accomplished in a continuous process by dispersing olefins in the reacting stream as reaction progresses, as by adding olefins at a plurality of points along the course of the reacting stream in a manner designed to effect rapid dispersal within the reacting medium. When the olefins and paraffins to be reacted are in the same mixture, with olefins in a rather high concentration, a suitable low concentration may be established and maintained by recirculating a portion of the effluent of the reaction zone back through this reaction zone, using it to dilute the incoming charge stock. When this latter modification is used, a portion, or portions, of the charge stock may be added at various points along the course of the reacting stream, thus reducing the amount of the recycle stream necessary to maintain an initial low concentration. In these modifications opportunity should, of course, be provided for abstraction of heat as reaction proceeds, and before further olefin addition. I have found that the most desirable results are obtained when the amount of olefin added to any particular part of the reacting mixture is not greater than about 10 mol per cent of the total hydrocarbon material present, at the immediate zone of addition. Thus, in a continuous operation, wherein an olefin-containing stream is added at a point or zone of introduction to a paraffinic stream, this is to mean that the amount of olefin in this olefin-containing stream does not exceed the specified mol per cent of this stream plus the reactant stream. A suitable time for reaction, and abstraction of heat, should be allowed before again adding olefin, and generally 50 to 75 per cent or more of the olefin previously added should be allowed to react before additional olefin is added. When reacting some paraffin and olefin mixtures, especially those containing less reactive olefins, olefin consumption reactions are not so rapid and somewhat higher olefin concentrations may be maintained in the reacting stream without resulting in too great an increase in the proportion of products of higher molecular weights. When the charge stock is especially reactive the added olefins may need to be kept as low as 1 or 2 per cent for any particular point or zone of olefin introduction, but generally satisfactory conditions will be found when the added olefins are between 2 and 8 per cent of the total stream. When an easily polymerizable olefin, such as isobutylene, is one of the principal olefin reactants, or when the process is carried out at elevated temperatures with somewhat less reactive paraffins, such as temperatures between about 125 and 300° F., it will generally be desirable to add only small amounts of olefins at any one point, with a substantial amount of recycle and/or many points of olefin addition.

Olefins over a wide range of molecular weights and structures are suitable to use in the alkylation of paraffins in the presence of concentrated hydrofluoric acid. One of the principal commercial applications of my invention at present is the production of paraffin hydrocarbons in the motor fuel range from lower boiling hydrocarbons, and for this reason olefins of five or fewer carbon atoms per molecule are more often preferred. Of these, ethylene enters into reac-

tion least readily, especially in the absence of olefins of more carbon atoms per molecule. While pentenes are generally considered to be in the motor fuel boiling range, it will often be desirable to decrease the amount of C₅ hydrocarbons in a final product for reasons of volatility, or a high boiling fuel of low vapor pressure may be desired, so that it will not be unusual to use pentenes. Hexenes, heptenes, octenes, and the like are more often of greater value as they are, although they are not to be excluded in the broadest concepts of this invention. Cycloolefins, such as cyclopentene, cyclohexene, and the like, also enter into reaction as ordinary aliphatic olefins. Ordinarily the process is operated under only moderate superatmospheric pressures, such as between about 20 and 200 pounds per square inch gauge. Since the alkylation reaction represents a decrease in the total number of molecules, a certain amount of pressure favors the reaction. However, since the reactants are generally readily maintained in liquid phase with only moderate pressure at reaction temperatures in the lower part of the range indicated, only sufficient pressure to insure liquid phase operation is generally adequate. When higher reaction temperatures are used, higher pressures may also be used, and pressures as high as 1500 or 2000 pounds per square inch or more may be used, if desired. While such high pressures favor reaction, lower pressures are generally successfully used with the pronounced activity of hydrofluoric acid to induce the alkylation reaction. Since very moderate temperatures usually suffice in the presence of hydrofluoric acid, for thermodynamic reasons the pressure can, accordingly, be moderate and can, of course, be as low as can be shown by trial to permit effective alkylation. In most instances the process will be operated under a pressure between 20 and 500 pounds per square inch.

The reaction period, during which olefin is introduced, reacted and consumed to produce eventually an isoparaffinic product, is dependent to a certain extent upon the reaction temperature and the total amount of olefins reacted. A period between 15 minutes and 2 hours has been found satisfactory in most cases, but at higher temperatures a reaction period as low as about 5 minutes, or somewhat less, will often be sufficient. At lower temperatures and low olefin concentration, which is preferred at times when preparing certain especially pure products, periods as high as 4 or 5 hours may be found most desirable.

It will be understood, of course, that all these reaction variables are more or less interdependent, and that when one is arbitrarily fixed the limits within which others may be varied are somewhat restricted. The more desirable ranges for ordinary applications of my invention have been indicated, and can also be ascertained from the specific examples presented hereinafter. However, for any particular application of my invention, the most desirable conditions can be readily determined by trial by one skilled in the art, such a determination being facilitated by the discussion of trends of these variables presented herewith.

Reference will now be made to the accompanying drawing which forms a part of this specification, and which illustrates diagrammatically by means of a flow sheet one arrangement of apparatus suitable for practicing my in-

vention. It will be described as a specific embodiment for the production of paraffinic hydrocarbons in the boiling range of motor fuel from butanes and/or pentanes, and also serves as one example of my invention. However, it will be understood that other charge stocks may be used and products of other boiling ranges produced, with suitable modifications for any particular case as will be readily ascertained, as just discussed.

In this particular application of my invention, a paraffinic hydrocarbon material, such as a butane fraction from natural gas containing a substantial proportion of isobutane, enters the system under a suitable pressure, such as 20 to 200 pounds per square inch gauge, thru pipe 10 and valve 11, and is passed to a reaction zone 12 in alkylator 13, such as the tube coil diagrammatically shown. Concentrated hydrofluoric acid, preferably between 80 and 100 per cent hydrofluoric acid, is passed thru pipe 14 and valve 15, and is thoroughly mixed with the paraffinic stream passing thru pipe 10. This stream should be in such amount that, when the subsequent reaction takes place in liquid phase as will most often be the case, the liquid hydrocarbon material is substantially saturated with hydrogen fluoride, and preferably about 10 per cent or more of the total mixture is hydrofluoric acid. Olefin hydrocarbons enter the system thru pipe and manifold 16 and valve 17, and may be accompanied by a certain amount of paraffinic material similar to that entering thru pipe 10, such as butane. Active churning action may be obtained by stirring means in an enlarged reaction zone, or by baffles, orifices, and the like, in a tube coil of restricted cross section, whereby hydrofluoric acid and hydrocarbons are intimately intermixed, and churned, as is shown in this particular modification.

The olefins are added to the paraffin stream at one or more points, as may be desirable, thru pipes 20, 21, 22, and 23, controlled by valves 25, 26, 27, and 28, respectively, which lead to various points in the reaction zone. These olefins may be produced by dehydrogenation, cracking, depolymerization, or polymerization, or the like, and are ordinarily somewhat diluted with saturated material. Thus when butenes are reacted with butanes to produce octanes, the butenes may previously be produced by dehydrogenation of butane, and may be accompanied by unreacted butane. At other times, when the olefins are originally in more concentrated form, such as when polymers are used or an olefin concentrate is formed by depolymerization, paraffin hydrocarbons such as butane may be deliberately added, if desired. It will be noted that pipe 20 introduces olefins into the paraffin stream immediately before it enters the reaction zone 12, and at times this may be the only point of addition. Also, when a hydrocarbon material containing a relatively low amount of olefins is available, such as less than about 15 or 20 per cent, this material can be added thru pipes 10 or 16 as the sole charge to the process. Such a modification is preferably used in connection with a recirculation of a part or portion of the effluent of the reaction zone passing thru pipe 30. Such a recirculation is accomplished by passing a portion of the effluent from pipe 30 thru pipe 33, valve 34, pump 35 and pipe 36 controlled by valve 37 back to pipe 10 at the inlet of the reaction zone. In any method of olefin addition it is well to keep the amount of olefin added low at any one point

of olefin addition, such as below 10 mol per cent of the total hydrocarbon present, and the olefin concentration maintained may sometimes be very low, below 1 per cent, as previously discussed.

However, by the practice of my process a large amount of reaction can be secured by continuously adding olefin to the reacting stream as previously added olefin is consumed, as by a plurality of points of addition represented by pipes 20 to 23, inclusive. With such controlled addition of olefins, the reaction time may be somewhat extended to produce a substantial total yield. At reaction temperatures of 40 to 100° F., which ordinarily are suitable for the alkylation of paraffins such as isobutane, a reaction time should preferably not be less than 5 minutes, and with very small amounts of olefin addition, and low temperatures, may be as much as 3 hours or more. Generally a satisfactory time will be found between 15 minutes and 2 hours for such materials.

The reaction effluent, comprising primarily paraffins and hydrofluoric acid, passes thru pipe 30 and valve 31 to fractionating means 40, wherein a separation is made between the product, or alkylate, and lower boiling material, comprising predominantly unreacted paraffins and hydrofluoric acid. The alkylate is withdrawn thru pipe 41 and valve 42, and may be subjected to such other treatment, such as fractionation, caustic washing, and the like, as may be desired or necessary. Traces of the acid and of alkyl fluorides may be removed by suitable treatment, as by contacting with hot or cold alkali. The fractionating means 40 is diagrammatically represented as a single fractionating column, which is to be supplied with suitable bubble trays or the like, heating means for the bottom and cooling means for the top, as is well known in the art, but which are not shown. However, if necessary or desirable, the fractionating means may comprise two or more fractionators and their auxiliary equipment, as will be readily understood. Lower boiling material is removed thru pipe 43, and may be returned entirely or in part directly to the reaction zone thru valve 44 for further reaction.

More often, however, it will be desirable to subject at least a part of this material to further treatment, and in such an event all or a part of the stream is passed from pipe 43 thru pipe 45, cooler and condenser 46, pipe 47 and valve 48 to separator 50. The pressure prevailing in the system at this point is appreciably above atmospheric, a pressure of the order of 30 to 150 pounds per square inch gauge is effective, and the cooler and condenser 46 is operated so as to reduce to liquid condition both hydrocarbon and hydrofluoric acid and permit a separation of liquid hydrocarbons from the denser liquid hydrofluoric acid to take place. Generally ordinary cooling water will provide sufficient cooling, and if the pressure is not sufficient at this temperature to result in a condensation, it may be boosted by a compressor not shown in pipe 45. Hydrofluoric acid is withdrawn through pipe 51, and may be discharged thru valve 52. Any portion of this material may be returned to the reaction thru pipe 53, and valve 54, passing to pipe 14, and generally a substantial portion is so recycled.

A hydrocarbon fraction, still containing a minor amount of dissolved hydrofluoric acid, but comprising principally unreacted butane is removed from separator 50 thru pipe 55, and may be discharged thru valve 56. However, it will

generally be desirable to subject this material to further treatment, and any part or all of it is then passed from pipe 55 thru pipe 57 and valve 58 to fractionating means 60. Again, this may be a simple fractionating column, with suitable bubble trays, heating means, and cooling means, not shown, or may be a combination of two or more fractionators and/or separators. A paraffin hydrocarbon material, such as butane, is recovered in a substantially pure state as a kettle product, which is removed thru pipe 61, and may be recovered for further use or treatment thru valve 62. In most cases it will be desirable to recycle directly at least a substantial portion of this material, and such a portion is passed from pipe 61 thru pipe 63 and valve 64, to pipe 43 and on to the reaction zone. With the previous removal of the major part of the hydrofluoric acid as a liquid thru pipe 51, only minor amounts will remain in the hydrocarbon stream passing thru pipe 55. In such low concentrations in the charge to fractionating means 60, it can be made to pass overhead thru pipe 65, even in the presence of some lower boiling hydrocarbons, as a part of an azeotropic mixture, leaving substantially pure hydrocarbons in the kettle to be withdrawn thru 61 as discussed. The vapor fraction, which contains appreciable quantities of hydrofluoric acid, is removed thru pipe 65, cooler and condenser 66, pipe 67 and valve 68 to separator 70. The cooling in 66 is sufficient to cause a condensation of hydrofluoric acid and a separation of a major part of it from the hydrocarbon material as a separate heavy liquid phase, which is withdrawn thru pipe 75, and may be either returned to the system thru pipe 77 and valve 78, and pipes 53 and 14, or removed in part, or entirely, thru valve 76. The light hydrocarbon material, which will contain only a small amount of hydrofluoric acid, is removed from separator 70 thru pipe 80, and is preferably returned to fractionating means 60 thru pipes 82 and 71, and valve 72. If desired, a part may be recirculated thru valve 83.

With this preferred arrangement, a state of equilibrium can be reached whereby even relatively light hydrocarbons can be recovered from the kettle product of fractionating means 60, and removed thru valve 82, with substantially all of the hydrofluoric acid being recycled thru pipes 53 and 77, and such a mode of operation forms a modification of this invention. However, if desired a part, or all, of the material passing thru pipe 80 may be removed from the system thru valve 81. If the hydrofluoric acid content renders this material difficult to handle or undesirable to let free, it may be treated in scrubber 86 by being passed thru pipe 84 and valve 85. Water, or an alkali solution such as sodium hydroxide, or the like, is introduced thru pipe 87 and valve 88, and is used to wash the hydrocarbon stream entering thru pipe 84. Purified hydrocarbons are removed thru pipe 90 and valve 91, while the wash liquid is removed thru pipe 92 and valve 93. If desired, a part or all of the stream passing thru pipe 55 may be sent to scrubber 86 thru pipe 73 and valve 74.

It will be understood that the flow diagram presented and described herewith is schematic only, and that many additional pieces of equipment, such as pressure gauges, valves, flow meters, pumps, heat exchangers, controllers, reflux accumulators, reflux lines, and the like, will be necessary for any particular installation, and can be installed by anyone skilled in the art. How-

ever, the essential equipment and material flow have been described in sufficient detail to serve as an efficient guide.

When a normally liquid paraffin, such as isopentane or isohexane is charged to the process, and a motor fuel fraction is being produced, it may often be desirable to retain at least a part of the unreacted isoparaffin in the product. This can be accomplished, as desired, by a proper control and operation of fractionating means 40. Substantially anhydrous hydrofluoric acid has the added advantage that it boils below the usual motor fuel range, and this fact, coupled with the fact that it can be heated in the presence of hydrocarbons without entering into oxidizing or reducing reactions, enables it to be readily separated by distillation from the paraffinic product, and recycled to the reaction zone along with low boiling unreacted paraffins. Alkyl fluorides, which may be formed in minor amounts, generally will accompany the alkylate product. They may be separated therefrom by any desirable means, as by solvent extraction using methyl or ethyl alcohol. While it will generally be more desirable to practice my invention as a continuous process, it will, of course, be understood that at times it may be practiced as a batch process as well.

Example I

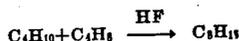
A liquid mixture of isobutane and substantially anhydrous hydrofluoric acid in a volume ratio of 1.2:1 was maintained in a steel bomb at a temperature of about 60 to 70° F. While the liquid mixture was vigorously stirred, a mixture of isobutylene and isobutane, containing 68 per cent isobutylene, was slowly added, the total addition time being 15 minutes, after which agitation of the mixture was continued for about 50 minutes. A sufficient amount of isobutylene and isobutane was added to make the total mol ratio of isobutane to isobutylene about 3:1, although at no time did the actual concentration of unreacted isobutylene approach this figure. After the reaction, most of the unreacted light hydrocarbons and some unreacted hydrofluoric acid were removed from the effluent by distillation, and the normally liquid residue was washed with water and a sodium hydroxide solution. The combined liquid product had the following physical properties.

Specific gravity at 73° F.....	0.7014
Refractive index.....	1.3973
Unsaturation.....per cent..	0.9

A. S. T. M. distillation:	
I. B. P.....° F.....	115
5%.....	175
10%.....	195
20%.....	211
30%.....	218
40%.....	223
50%.....	230
60%.....	238
70%.....	254
80%.....	302
90%.....	400
E. P.....	442
Rec.....	97.0
Res.....	1.5
Loss.....	1.5

From this distillation it can be seen that a large portion of the product consists of isooctanes, this simple product being formed in large amounts with a relatively large amount of

butane in the charge stock, according to the equation:



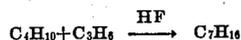
It is also readily seen that the product is aliphatic and saturated, and that the entire product is well suited for use in an internal combustion, spark ignition, engine.

Example II

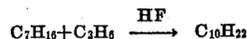
An intimate mixture of liquid isobutane and liquid concentrated hydrofluoric acid, in a liquid volume ratio of 1.4:1, was vigorously stirred in an iron reaction chamber, which was not attacked by the hydrofluoric acid. To this mixture was added propylene over a period of about 30 minutes. The reaction temperature during this period was between about 70 and 80° F., and the pressure was allowed to be the vapor pressure of the reacting mixture, which never exceeded 50 pounds per square inch gauge. The mol ratio of total isobutane to total propylene added was 2.2:1, but was always appreciably greater than this during the reaction period. After addition of propylene the mixture was maintained in the chamber with continuous agitation for 45 minutes more, during which the temperature fell to 65° F. and the pressure decreased to about 40 pounds per square inch gauge. The high residual pressure was presumably due to some propane, which was present in the propylene and which was not appreciably reacted under these conditions. The total yield of liquid product was about 150 per cent based on the propylene reacted, and was separated by fractional distillation into fractions which had the following properties:

Fraction	Boiling point	Density	n_D^{20}	Unsaturation rates	Volume
	° F.			Percent	Percent
C_5 and C_6	86-172	0.6472	1.3700	0.25	10.6
C_7	172-179	0.6702	1.3811	0.00	15.7
C_7	179-208	0.6860	1.3886	0.12	31.2
C_8	208-257	0.7032	1.3965	0.12	11.5
C_9	257-302	0.7170	1.4053	0.36	6.2
C_{10}	302-347	0.7337	1.4135	0.48	12.4
C_{11}	347-410	0.7491	1.4209	0.42	4.5
C_{11}	>410		1.4440		7.9
Total product.....		0.7025	1.3970	0.30	100.0

It is readily seen that nearly 47 per cent of this product consisted if isoheptanes which were formed by the following reaction:



and that 12.4 per cent consisted of isodecanes which were presumably formed by the reaction



The presence of other products is probably due to secondary reactions which are not clearly understood at this time, but which also appear to produce paraffinic products. Over 90 per cent of the total product was in the present day gasoline boiling range, and possessed good motor fuel properties.

Many modifications and variations of this invention may obviously be used, and can be adapted by one skilled in the art without departing from the spirit of the disclosure. The restrictions used in the examples, and in connection with the drawing, need not necessarily be used as limits for any particular operation or set of conditions, as they are presented primarily as illustrative examples.

I claim:

1. A process for the production of a normally liquid paraffinic hydrocarbon material, which comprises reacting a low boiling isoparaffin with an olefin in the presence of substantially anhydrous hydrofluoric acid as the effective alkylation catalyst to form normally liquid paraffin hydrocarbons, passing at least a portion of the effluent to fractionating means, separating as a liquid from said fractionating means liquid paraffins so produced, separating as a gas from said fractionating means a mixture comprising unreacted hydrocarbons and hydrofluoric acid, cooling and condensing at least a portion of said gas mixture to condense and separate as liquids hydrocarbons and hydrofluoric acid, separating said hydrofluoric acid as a heavy liquid from a lighter hydrocarbon liquid and returning said hydrofluoric acid to the aforesaid reaction, subjecting said lighter hydrocarbon liquid to a fractional distillation to separate a hydrocarbon material substantially uncontaminated with hydrofluoric acid as a liquid kettle product and removing at least a portion thereof from the system, passing as a gas from said fractional distillation a mixture comprising hydrocarbons and hydrofluoric acid, cooling and condensing said gas mixture to condense and separate as liquids hydrocarbons and hydrofluoric acid, separating said hydrofluoric acid as a heavy liquid from a lighter hydrocarbon fluid and returning said hydrofluoric acid to the aforesaid reaction, and returning at least a portion of said hydrocarbon fluid to said fractional distillation.

2. A process for producing paraffin hydrocarbons in the motor fuel boiling range from lower boiling isoparaffins and olefins, which comprises subjecting a mixture comprising such a low boiling isoparaffin and an olefin of three to five carbon atoms per molecule in a reaction zone to the action of concentrated hydrofluoric acid as the effective alkylation catalyst to alkylate said isoparaffin with said olefin to produce normally liquid paraffins in the motor fuel boiling range, passing the effluent to fractional distillation means and separating and recovering said normally liquid hydrocarbons so produced as a liquid from a vaporized mixture of unreacted hydrocarbons and hydrofluoric acid, cooling and condensing at least a portion of said vaporized mixture to condense as liquids hydrocarbons and hydrofluoric acid, passing the condensed mixture to separating means, removing from said separating means a heavy liquid comprising hydrofluoric acid and returning at least a portion of the same to said reaction zone, and removing also from said separating means a light liquid comprising unreacted hydrocarbons.

3. A process for the production of higher boiling hydrocarbons from lower boiling paraffin hydrocarbons, which comprises passing a stream of predominantly alkylatable paraffinic hydrocarbon material in which olefinic material is dispersed at an alkylation pressure and temperature and in admixture with an alkylation promoting amount of concentrated hydrofluoric acid as the effective alkylation catalyst through a reaction zone in indirect heat exchange with a heat absorbing medium, maintaining said stream in said reaction zone for a reaction time sufficient to effect substantial alkylation of said alkylatable paraffinic material, dispersing additional olefinic material in said paraffinic stream during said reaction time as olefinic material is consumed by said reaction in a total amount not

greater than the total alkylatable paraffin charged and in such a manner that the concentration of unreacted olefin present in the mixture at a point of olefin dispersal does not exceed the equivalent of about 2 mol per cent of the hydrocarbons present, removing heat from said reaction zone during said reaction time by means of said heat absorbing medium to maintain a relatively constant alkylation temperature, passing a liquid mixture effluent from said reaction zone and containing a hydrofluoric acid phase and a hydrocarbon phase to separating means, separating said hydrofluoric acid phase and returning at least a portion thereof to said reaction zone, separating also said hydrocarbon phase containing dissolved hydrofluoric acid, passing said hydrocarbon phase to a fractional distillation means, separating from said means a vaporous fraction comprising all said dissolved hydrofluoric acid and a low-boiling paraffinic hydrocarbon, cooling and condensing said vaporous fraction to form a liquid hydrocarbon phase and a liquid hydrofluoric acid phase, separating and returning said hydrocarbon phase to said distillation means, and recovering also from said distillation means a liquid hydrocarbon fraction essentially free of hydrofluoric acid and containing higher boiling paraffin hydrocarbons so produced.

4. A process for separating a hydrocarbon fraction substantially free of hydrogen fluoride from a mixture containing low-boiling hydrocarbons and hydrogen fluoride, which comprises subjecting said mixture to fractional distillation, separating from said fractional distillation a low-boiling fraction comprising essentially all said hydrogen fluoride together with only sufficient low-boiling hydrocarbon material to form a minimum boiling azeotropic mixture with said hydrogen fluoride, and separating also from said fractional distillation a higher-boiling hydrocarbon fraction which is essentially free of hydrogen fluoride and containing all of said initial low-boiling hydrocarbons in excess of those contained in said azeotropic mixture.

5. In the process of claim 4, cooling and condensing said low-boiling fraction to form a hydrogen fluoride phase and a hydrocarbon phase, recovering said hydrogen fluoride phase, and returning said hydrocarbon phase to said fractional distillation.

6. In a process for the production of a normally liquid paraffinic hydrocarbon material by the alkylation of low-boiling alkylatable paraffinic hydrocarbons with olefinic hydrocarbons in the presence of concentrated hydrofluoric acid as

the alkylation catalyst, the improvement which comprises passing a mixture effluent from said alkylation and containing a liquid hydrogen fluoride phase and a hydrocarbon phase to a phase separating means, separating said hydrogen fluoride phase, passing said hydrocarbon phase to a fractional distillation means, separating from said means a vaporous fraction comprising a mixture of a low-boiling paraffinic hydrocarbon and hydrofluoric acid, cooling and condensing said vaporous fraction to form a liquid hydrofluoric acid phase and a hydrocarbon phase, recovering said hydrofluoric acid phase, returning said hydrocarbon phase to said fractional distillation, and separating also from said means a liquid fraction comprising a low-boiling alkylatable paraffinic hydrocarbon fraction substantially free from hydrofluoric acid.

7. A process for separating a hydrocarbon fraction substantially free of hydrogen fluoride from a mixture containing low-boiling hydrocarbons and hydrogen fluoride, which comprises subjecting said mixture to fractional distillation, separating from said fractional distillation a low-boiling fraction comprising essentially all said hydrogen fluoride together with at least sufficient low-boiling hydrocarbon material to form a minimum-boiling azeotropic mixture with said hydrogen fluoride, cooling and condensing said low-boiling fraction to form a hydrogen fluoride phase and a hydrocarbon phase, recovering said hydrogen fluoride phase, and returning said hydrocarbon phase to said fractional distillation, and separating also from said fractional distillation a high-boiling hydrocarbon fraction which is essentially free of hydrogen fluoride.

8. A process for separating a hydrocarbon fraction from a liquid mixture comprising low-boiling paraffin hydrocarbons and hydrogen fluoride dissolved therein, which comprises subjecting said mixture to fractional distillation, separating therefrom a low-boiling fraction comprising essentially all said dissolved hydrogen fluoride together with at least sufficient low-boiling paraffin hydrocarbon material to form a minimum-boiling azeotropic mixture with said hydrogen fluoride, cooling and condensing said low-boiling fraction to form a liquid hydrogen fluoride phase and a liquid hydrocarbon phase, returning said hydrocarbon phase to said fractional distillation, and separating also from said fractional distillation a higher boiling hydrocarbon fraction which is essentially free of hydrogen fluoride.

FREDERICK E. FREY.