

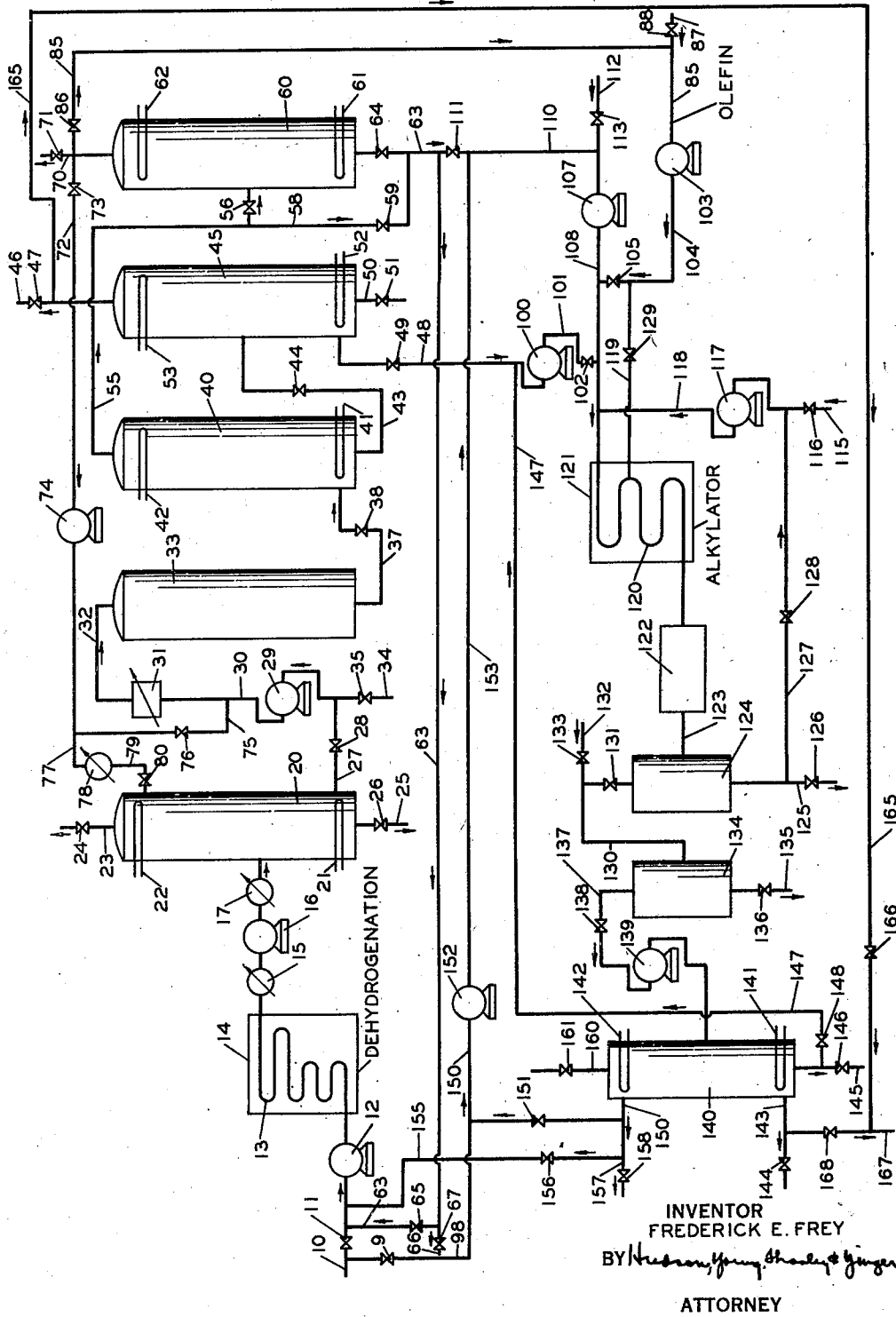
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MOTOR FUEL PRODUCTION

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MOTOR FUEL PRODUCTION

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This invention relates to the production or manufacture of motor fuel from low boiling hydrocarbons, and more particularly to the production of hydrocarbons in the gasoline boiling range suitable for premium motor fuels from paraffin hydrocarbons having three to five carbon atoms per molecule. This application is a continuation-in-part of my copending applications Ser. No. 297,600 filed October 2, 1939, now Patent 2,327,633, granted August 24, 1943, and Serial No. 315,063 filed January 22, 1940, now Patent 2,322,800, granted June 29, 1943.

Many processes have been proposed for converting normally gaseous hydrocarbons into hydrocarbons having higher molecular weights, such as motor fuels and lubricants. Some of these processes are dependent upon having olefin 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 unsaturated components from cracking stills. Still other processes are adapted to produce motor fuel from normally gaseous paraffins, such as unitary thermal conversion processes, or multistage processes employing a dehydrogenation step as a first part of the process, followed by a conversion of olefins so produced. Still other processes have been proposed wherein a paraffinic hydrocarbon stream and an olefinic hydrocarbon stream are charged to a process, and the paraffins and olefins are caused to interreact, or as it is generally stated, the paraffins are alkylated by the olefins to form paraffins having higher molecular weights.

As disclosed in my abovementioned copending application Serial No. 315,063, now Patent No. 2,322,800, I have found that concentrated hydrofluoric acid will act as a catalyst to effect a union of unsaturated hydrocarbons, such as olefins, with paraffins to form higher boiling paraffin hydrocarbons. I have also found that concentrated hydrofluoric acid can be used as the sole alkylating catalyst, without the presence of such other materials as finely divided metals, metal halides, and the like, and that it is preferable to use as a catalyst substantially anhydrous hydrofluoric acid, or hydrogen fluoride.

I have now found that when low boiling paraffins such as butane or pentane are reacted in the presence of concentrated hydrofluoric acid with certain higher boiling olefins, especially those formed by the polymerization of simpler lower boiling olefins, a paraffinic product results which, although higher boiling than the original paraffin, is not necessarily higher boiling than the

high boiling olefin reacted, and in fact may at times be lower boiling than the olefin. Thus I have found that when a butane fraction, boiling between about 10 and 35° F., is reacted in the presence of concentrated hydrofluoric acid with an olefin material such as triisobutylene, boiling between about 345 and 355° F., a paraffinic product results of which the predominant part boils between 200 and 240° F. and which appears to contain large portions of isomeric octanes. Similarly, isooctenes will react with such a butane fraction in the presence of hydrofluoric acid to produce a paraffinic product containing large portions of isooctanes.

The process of one modification of the present invention involves a cooperation between a polymerization step, for the production of motor fuel range hydrocarbons by the polymerization of lighter olefins, and an alkylation step, for the production of motor fuel range hydrocarbons by the alkylation of lighter paraffins with olefins which may be heavier and/or lighter than the final product. The polymerization step is preferably one carried out with the aid of a solid polymerization catalyst, such as silica-alumina or the like, "solid" phosphoric acid, acid copper phosphate, or the like; and the alkylation step is carried out in the presence of concentrated hydrofluoric acid, using olefins which have been recovered from the effluent of the polymerization step. It has been found that the paraffins charged to the alkylation step may be either isoparaffins or normal paraffins, but preferably the paraffinic material should contain appreciable portions of isoparaffins such as isobutane (2-methyl propane) or isopentane (2-methyl butane) or the like, and such may be separated from the unreacted hydrocarbons which have passed through the polymerization step, or may be independently introduced to the process as a separate charge to the alkylation step.

In one particular manner of practicing my invention, isobutane is thermally dehydrogenated forming propene and isobutene, and hydrogen and methane are removed from the effluent. A fraction consisting of hydrocarbons having three and more carbon atoms per molecule and comprising predominantly propene, isobutene and isobutane is passed at an elevated pressure over a solid polymerization catalyst under conditions such that essentially all of the isobutene is polymerized along with a substantial portion of the propene, forming polymers in the gasoline boiling range. Under optimum conditions, consid-

erable amounts of isohexenes and isooctenes are formed, and the polymerization effluent also contains higher boiling olefinic polymers and some unreacted propene. In this particular case the material which is lower boiling than isobutane contains a large portion of propene and is readily separated from the polymerization effluent by fractional distillation in a depropanizer. Likewise, the higher boiling olefinic polymers are readily separated from the gasoline range polymers. Either, or both, of these olefinic fractions constitute a valuable part of the charge to the alkylation step. In this particular instance the unreacted paraffins in the polymerization effluent are predominantly isobutane, and a portion of such a fraction may constitute the paraffinic portion of the hydrocarbon charge to the alkylation step. This fraction will contain a small amount of unreacted isobutene which will also undergo a desirable reaction in the alkylation step. Isopentane may be blended with the isobutane fraction charged to the alkylation step or may constitute the entire isoparaffinic portion of the charge, or isobutane from some other source may be charged to the alkylation step. Even when higher boiling olefinic polymers are the sole olefinic charge to the alkylation, the alkylation products will be isoparaffins in the gasoline boiling range, since it appears that such high boiling polymers undergo concomitant scission reactions, substantially all of the fragments being olefinic and taking part in the reaction, rather than that these higher boiling olefins join directly to the charged isoparaffin to form still higher boiling products. The gasoline boiling range isoparaffins have high antidetonating qualities and octane numbers, and the olefin polymers in the gasoline boiling range are also superior in these respects. These gasoline products may be used separately as motor fuels or blending stocks, the olefin polymer may be hydrogenated before use; or these fractions may be blended together to form a premium motor fuel. In those cases where an olefinic motor fuel is not undesirable, this latter procedure is especially effective, since the olefins have "blending" octane numbers even higher than their straight octane numbers in the pure state, and to blend them with isoparaffins gives a still more superior result.

While the catalytic polymerization produces a polymer which has a superior octane number, both as it is and after hydrogenation to form a paraffinic material, it fails to convert all of the olefins charged and generally also produces a certain amount of polymer which may be undesirably heavy. Although catalytic alkylation of hydrocarbon material to give a product in the same boiling range produces a paraffinic product directly which also has a superior octane number, the octane number will generally not be quite as high as that of the former product resulting from polymerization.

The cooperative combination of the present invention not only gives a total product with a high octane number, but also depletes the olefin content of the hydrocarbon stream produced by dehydrogenation and charged to the alkylation step, and thus aids in producing a desirable alkylmer by raising the ratio of paraffin to olefin in this stream and facilitates control of this reaction. Thus, the combination gives a total product having an octane number higher than could be produced by alkylation alone, and also results in a better utilization of olefin hydrocarbons and production of isoparaffinic hydrocarbons

in the gasoline range than would result from catalytic polymerization alone.

Concentrated hydrofluoric acid, when used as an alkylating agent for the alkylation of paraffin hydrocarbons, apparently does not possess the deleterious characteristics of other alkylating agents such as aluminum chloride, boron trifluoride, sulfuric acid, and the like. It has only a limited tendency to form black, tar-like masses, and it is essentially a nonoxidizing and nonreducing material, so that it can be used and treated at elevated temperatures without undergoing undesirable side reactions. 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, such as normal paraffins, higher temperatures of the order of 150 to 300 or 500° F. 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.

As just mentioned, higher temperatures are necessary for the alkylation of normal paraffins, and they may be caused to react with olefins in the presence of concentrated hydrofluoric acid at temperatures above about 100 to 120° F., preferably within the range of 150 to 300° F., but in some instances as high as 500 or 600° F. While the alkylation of normal paraffins may be carried out under only slight superatmospheric pressures, it is preferable to operate under substantial superatmospheric pressures, such as about

100 to 1,000 or 2,000 pounds per square inch or more. The process is preferably conducted with at least an appreciable portion of the reactant material in liquid phase, although this is not necessary for all reactants. When the process is conducted with a substantial portion of the reactants in liquid phase, the reaction temperature should not be above the critical temperature of the highest boiling reactant, and the pressure should be at least no less than the vapor pressure of this reactant, and preferably should be at least 500 pounds per square inch. Since the alkylation temperatures, even in the upper part of the range indicated, are still rather moderate, the pressures ordinarily need not be excessively above the vapor pressure of the reacting mixture and can, of course, be as low as can be shown by trial to permit effective alkylation. In many instances normal paraffins can be alkylated in the presence of hydrofluoric acid at pressures between 50 and 500 pounds per square inch. With some of the lower boiling and less reactive of the paraffins, it may be desirable to conduct the alkylation at a temperature in the upper part of the range indicated and such that the reactants are predominantly in gaseous phase, even under substantial elevated pressures.

It is an object of my invention to react normally liquid unsaturated hydrocarbons with low boiling paraffin hydrocarbons to form paraffin hydrocarbons in the motor fuel boiling range.

Another object of my invention is to react polymeric olefins with low boiling paraffins in the presence of concentrated hydrofluoric acid to form paraffin hydrocarbons boiling in the motor fuel range.

A further object of my invention is to provide a process for the production of hydrocarbons boiling in the motor fuel range from low boiling hydrocarbons by a combination of an olefin polymerization step and an olefin-paraffin alkylation step conducted in the presence of concentrated hydrofluoric acid.

A still further object of this invention is to react polymeric olefins boiling in or above the motor fuel range with low boiling paraffins, especially low boiling isoparaffins, in the presence of concentrated or anhydrous hydrofluoric acid to form paraffin hydrocarbons boiling near or below the range of said olefins.

Further objects and advantages will become apparent from the accompanying disclosure and discussion.

Reference will now be made to the drawing which forms a part of this specification and which shows diagrammatically one arrangement of apparatus for practicing my invention.

A low boiling saturated hydrocarbon material, such as a butane fraction of natural gas containing a high concentration of isobutane, enters the system through pipe 10 and valve 11 and is passed by pump 12 through the coil 13 in the dehydrogenating furnace 14. In many cases where such a hydrocarbon stream comes directly from a fractional distillation process or from some other separation step it may be under a pressure sufficiently high to obviate the necessity of the pump 12 and in such a case, of course, the pump may be omitted. The dehydrogenation which takes place in the unit represented by the coil 13 and the furnace 14 may be any type of dehydrogenation process known to the art and may be either thermal or catalytic or a combination of both. The pressure will generally not be in excess of about 200 pounds per square inch, and prefer-

ably will be lower; and the temperature will be between 850 and 1250° F.

From the dehydrogenation furnace 14 the effluent passes through cooler 15, pump or compressor 16 and cooler and condenser 17 to separating means represented by the fractionating column 20, supplied with heating means 21 at the bottom and cooling means 22 at the top. Hydrogen and any light hydrocarbons formed in the dehydrogenation are removed from the system through pipe 23 and valve 24; and any heavy hydrocarbons, tar and/or carbon may be removed from the system through pipe 25 and valve 26. This separation may be aided by the use of cooled, unreacted hydrocarbons, (which may be flashed to provide direct vaporization and refrigeration as has been more fully described by Hays et al. in their copending application Serial No. 336,250, filed May 20, 1940), introduced through pipe 29 and expansion valve 30. A hydrocarbon stream, comprising unreacted paraffins and olefins produced by the dehydrogenation, passes from the separating means 20 through pipe 27 and valve 28, and is passed at a suitable polymerization pressure, preferably between 200 and 2000 pounds per square inch, by pump 29 through pipe 30, heater 31 and pipe 32 to the polymerization unit 33. Normally gaseous unsaturated hydrocarbons, such as propylene and/or butenes as may be recovered from an oil cracking process, may be introduced through pipe 34 and valve 35, and such a stream may constitute the only hydrocarbon material charged to this part of the process. In such a case the dehydrogenation part of the system just described may not be used, or may be used only to dehydrogenate paraffin hydrocarbons in the stream entering through pipe 34 which pass through the polymerization system and are ultimately passed through pipe 63 to the pipe 10.

The polymerization carried out in unit 33 will preferably be a catalytic polymerization rather than a thermal one and may be carried out with any known polymerization catalyst which promotes the formation of simple, low boiling polymers from light olefins such as propylene and/or butylenes. Such catalysts may be silica-alumina, solid phosphoric acid, diluted aqueous solutions of liquid acids such as sulfuric acid, or the like. If the hydrocarbon stream charged to this polymerization step contains two or more species of olefins such as the mixture of propylene and isobutene which results from the thermal dehydrogenation of isobutane, the unit may be so operated as to secure interpolymerization of these olefins, one such method being described in Frey's copending application Serial No. 294,377, filed September 11, 1939.

The polymerization effluent passes through pipe 37 and valve 38 to separating means represented by the fractionating column 40, supplied with a heating coil 41 at the bottom and a cooling coil 42 at the top. The entire polymer fraction, comprising olefin polymers boiling in the motor fuel range and also higher boiling polymers, passes from the bottom of means 40 through pipe 43 and valve 44 to fractionating column 45, wherein a separation is made between light polymers suitable for motor fuel or as a motor fuel blending stock which is removed from the system through pipe 46 and valve 47, and heavier polymers which may be removed through pipe 48 and valve 49. Extremely heavy polymers or tar and the like may be removed

from the system through pipe 50 and valve 51. Separation and fractionation in the column 45 is aided by heating coil 52 in the bottom and cooling coil 53 in the top.

Light hydrocarbons which have passed through the polymerization step unaffected, including paraffin hydrocarbons along with unreacted olefins, pass from the means 40 through pipe 55 and valve 56 to the fractionator 60, wherein a separation is made between lighter unreacted hydrocarbons and heavier unreacted hydrocarbons, the separation being aided by a heating means 61 and cooling means 62. Heavier unreacted hydrocarbons, which will be substantially entirely paraffins, pass from the bottom of fractionator 60 through pipe 63 controlled by a valve 64, and may be passed through valve 65 to pipe 10 and the dehydrogenation step, or any part or all of this stream may be withdrawn from the system through pipe 66 and valve 67. A stream of light unreacted hydrocarbons, which will contain the majority of the unreacted olefins, is removed from the top of fractionator 60 through pipe 70, and part or all of the stream may be removed through valve 71 when it is not possible or desirable to take care of this stream by the methods to be hereinafter described, or when the content of paraffins is sufficiently high to warrant a discard of a part of this stream or to warrant a separation of paraffins from olefins in apparatus not shown, with subsequent reintroduction to the process of either one or both of these fractions as will be readily appreciated. A portion of the olefin-containing stream passing through pipe 70 may be diverted through pipe 72 and valve 73 and returned to the polymerization step by pump 74. This may be done by addition of this stream through pipe 75, and valve 76 directly to pipe 30, or by passing a part or all of the stream through pipe 77, cooler 78, pipe 79 and valve 80 as a refrigerating agent to the top of the fractionator 20, as previously mentioned. Alternatively, or concomitantly, a portion of the stream passing through pipe 70 may be passed through pipe 85 and valve 86 to the hydrofluoric acid alkylation step to be more fully hereinafter discussed. When the charge to the polymerization step contains appreciable amounts of both propylene and butenes, or when a propane-butane mixture is dehydrogenated or when a refinery C₃-C₄ fraction is directly charged, or when isobutane is thermally dehydrogenated, the stream passing from fractionator 60 through pipe 63 will contain predominantly paraffin hydrocarbons such as butanes, while the stream passing from this fractionator through pipe 70 will contain the major part of the unpolymerized olefins, mainly propene, at least a part of which can conveniently be recycled to the polymerization step. If the polymerization step has been so conducted that practically all of the olefin material charged has undergone polymerization, the stream passing through pipe 55 may be passed directly to pipe 63 through pipe 58 and valve 59, with suitable control of valves 56 and 64.

As has been previously discussed, it is an object of this invention to react olefins, which are present in the polymerization effluent and which are unsuitable by reason of their boiling range or molecular weight for direct inclusion in motor fuel, with low boiling paraffins and especially low boiling isoparaffins in the presence of a concentrated hydrofluoric acid to form further quan-

titles of hydrocarbons in the motor fuel range. When the polymerization is so conducted that substantially all the light olefins charged are polymerized, the only olefins unsuitable for motor fuel will have high molecular weights, but generally, the polymerization conditions will not be so drastic and both light and heavy olefins can be sent to the alkylation step and reacted there, and a process involving this modification is also a part of my invention.

Heavy olefins are passed from pipe 48 through pump 100, pipe 101 and valve 102 to the alkylation process, and light olefins are passed from pipe 85 through pump 103, pipe 104 and valve 105 to the alkylation process. A suitable hydrocarbon stream, such as one consisting of or comprising large quantities of isoparaffins such as isobutane and/or pentane is passed through pump 107 and pipe 108 to the alkylation process. The paraffin hydrocarbons in the effluent of the polymerization step may comprise or consist of a portion of the stream passing through pipe 63, which is passed through pipe 110 and valve 111 to pump 107. If such is not the case, or if additional paraffin charge is needed, paraffins may be introduced through pipe 112 and valve 113 into pipe 110. Light olefins separated from the stream discharged through valve 71 and in a more concentrated form may also be introduced through pipe 112, or through pipe 87 and valve 88 into pipe 85. Polymeric olefins from some suitable outside source may also be introduced to the process through pipe 87 or 112, and may at times constitute the sole olefin charge to the process.

Hydrofluoric acid is charged to the process through pipe 115, valve 116, pump 117 and pipe 118, which in this case leads into pipe 108. As one method of performing the alkylation, the paraffins, olefins and hydrofluoric acid may be rapidly and intimately mixed at the juncture of pipes 108 and 118, and the mixture is rapidly passed through the tube coil 120 in the reactor-heat-exchanger 121. Since the alkylation reaction is exothermic, it is preferable that this initial part of the reaction should be carried out with a removal of heat sufficient to maintain a desired operating temperature. A tube coil of a type similar to that used in tube stills effects a turbulent mixing of the material passing through it, and thus contributes to the efficiency of the alkylation reaction. This reaction may be continued and completed in an enlarged chamber 122, which may be insulated and which affords an extended reaction time to the mixture without much mixing or turbulence. It may at times be desirable to have a part or all of the light olefins enter the alkylation system at some intermediate point or points, and in such an event this may be accomplished by passing any desired portion of the stream from pipe 104 through one or more pipes illustrated by pipe 119, controlled by a valve 123, to one or more intermediate points of the coil 120, with suitable control of valve 105. From the chamber 122 the mixture, substantially completely reacted, passes through pipe 123 to a separator 124, wherein a separation takes place between the hydrocarbon material and the hydrofluoric acid phase. This latter is removed through pipe 125, and may be removed from the system through valve 126, or any part or all of it may be passed through pipe 127 and valve 128 to pipe 115 to be used again in the process.

The hydrocarbon material, containing the

products of the alkylation along with unreacted hydrocarbons is removed from the top of the separator 124, either as a liquid or as a vapor, through pipe 130 and valve 131. It will generally be desirable to effect an intimate contact of this hydrocarbon material with an acid-neutralizing agent such as sodium hydroxide or carbonate or the like, and such material as an aqueous solution or a slurry in some hydrocarbon-miscible material can be introduced through pipe 132 and valve 133 and the combined mixture passed to separator 134. Any excess neutralizing agent and products of the neutralization are removed, as through pipe 135 and valve 136, while hydrocarbon material is passed through pipe 137, valve 138, and through pump 139 to hydrocarbon separating means illustrated by the fractionator 140 which is equipped with a heating coil 141 at the bottom and a cooling coil 142 at the top. A hydrocarbon fraction comprising a large proportion of hydrocarbons in the motor fuel boiling range produced by the alkylation, or in other words the alkylmer fraction, is removed from a low point of the fractionator 140 through pipe 143 and valve 144, and may be used directly as a premium motor fuel; or it may be used as a blending stock, or may be subjected to further fractionation to recover certain narrow boiling fractions of simple composition comprising certain highly desirable individual hydrocarbons. Heavier hydrocarbons are removed from a lower point of the fractionator through pipe 145 and may be discharged from the system through valve 146. This fraction may at times contain an appreciable proportion of higher boiling olefin polymers, suitable for reaction in the alkylation step. In such cases, a portion of the stream may be passed from pipe 145 through pipe 147 and valve 148 to pipe 48, where it is mixed with the heavy polymer passing from the polymerization step to the alkylation step.

A hydrocarbon steam lighter than the alkylmer, and comprising low-boiling unreacted paraffins, is removed from an upper part of the fractionator 140 through pipe 150, and may be passed through valve 151, pump 152 and pipe 153 to pipe 110 for further passage through the alkylation stem. A portion or all of this stream may be passed to the dehydrogenation step by being passed from pipe 150 through pipe 155 and valve 156 to pipe 10. If desired, this stream may be discharged from the system through pipe 157 and valve 158. Any light hydrocarbons which it is desired not to have retained in the system may be discharged from the top of fractionator 140 through pipe 160 and valve 161. When the initial charge to the dehydrogenation step, entering the system through pipe 10, is suitable also for the alkylation charge, this material may also be used as a part or all of the fresh paraffin charge to the alkylation step. In case a portion of the stream entering the system through pipe 10 is used as charge to the alkylation step it may be passed from this pipe through pipe 98 and valve to pipe 150 and is passed by pump 152 to the alkylation step.

When isopentane is a part of the hydrocarbon material charged to the alkylation step and is present in excess so that an appreciable portion passes through this step unreacted, a part or all of this unreacted isopentane may be retained in the alkylmer fraction removed through pipe 143, and at times a part may also be recycled to this step through pipe 150, pump 152 and pipe 153 and 110, as is readily understood. Isopentane

in itself is a valuable ingredient of premium motor fuels. Its introduction to the alkylation step thus produces a fuel having a desirably wide boiling range and having a good volatility. A combination motor fuel having a high antiknock rating may be formed by blending the material produced in the polymerization step with the fuel discharged from the alkylation step. This may be accomplished by passing all or any part of the fuel flowing through pipe 46, through pipe 165 and valve 166, and mixing it with a stream withdrawn from pipe 143 through pipe 167 and valve 168, with suitable control of valves 47 and 144. Both these streams comprise motor fuel hydrocarbons having high antiknock qualities, and since one, the alkylmer, is paraffinic and the other, the polymer, is olefinic, the resultant blend will be quite high as to antiknock value or octane number, since the "blending" octane number of the olefinic component when blended with a paraffinic stock, is not infrequently much higher than the octane number of the olefinic component by itself.

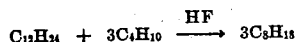
Example I

As one example of the practice of my invention, a refinery C₄ fraction containing both normal butylenes and isobutylene, to the extent of about 18 percent, along with butane, and a small amount of propane, was passed over a silica-alumina catalyst in liquid phase under a pressure of about 1500 pounds per square inch and at a temperature of about 350° F. The silica-alumina catalyst was prepared by treating a hydrous silica gel with an aluminum sulfate solution, whereby alumina was adsorbed, and washing and drying the resultant material, as described in U. S. Patent 2,142,324. The reaction time of the polymerization was such that about 45 percent of the olefins in the charge were polymerized, forming an olefinic polymer of which over 80 percent boiled below 360° F.

From this olefinic polymer a fraction was separated, by fractional distillation, which boiled between 345 and 355° F., and which consisted essentially of dodecenes. About three volumes of a liquid butane fraction from natural gas, containing a predominant portion of isobutane, were mixed with about one volume of substantially anhydrous liquid hydrofluoric acid and to the mixture was added about 0.76 volume of the above described polymer fraction. The mixture was vigorously agitated and maintained under a pressure between 45 and 55 pounds per square inch gauge, and the olefin fraction was added during an initial period of 48 minutes, the reaction temperature being maintained between 65 and 80° F. After the initial reaction period during which olefin was added the reaction mixture was maintained under similar reaction conditions for an additional period of 65 minutes. The normally liquid hydrocarbon product was removed from the effluent and was subjected to fractional distillation with the following results.

Boiling range, ° F.	Approximate formula	Density	Refractive index at 68° F.	Weight per cent of total	Per cent unsat.
88-167....	C ₆ H ₁₄	0.6444	1.3689	4.2	0.00
167-203....	C ₇ H ₁₆	0.6736	1.3841	5.8	0.10
203-257....	C ₈ H ₁₈	0.6934	1.3951	61.6	0.05
257-306....	C ₉ H ₂₀	0.7183	1.4066	5.8	0.05
306-365....	C ₁₀ H ₂₂ and C ₁₁ H ₂₄	0.7445	1.4219	12.7	0.36
>365....	C ₁₂ H ₂₆ and heavier	0.7670	1.4312	9.9	0.60
				100.0	

It is of considerable interest to note that the predominant fraction of the total product was a mixture of octanes, formed by the general reaction



and that substantially all the original dodecenes have disappeared, since very little of the liquid product boiled in the range of the dodecene charged, and what there was, was practically completely saturated. The presence of other products than octanes and dodecanes was probably due to secondary reactions which are not clearly understood at this time, but which also appear to produce paraffinic products. Well over 90 percent of the total product was in the present day gasoline boiling range, and possessed good motor fuel properties.

Example II

As an example of the operation of another modification of my invention, a hydrocarbon stream containing about 95 percent isobutane was thermally dehydrogenated by being passed through a tube coil maintained at a temperature between 1100° and 1220° F., and under an inlet pressure of about 150 pounds per square inch gage, for a period of time sufficient to produce an effluent stream containing about 20 mol percent of gaseous olefins which were about half isobutene and half lighter olefins predominantly propene. All but a negligible fraction of the material lower boiling than propene was removed from this dehydrogenation effluent, a portion of unreacted propene was added as a recycle stock, and the mixture was passed under a pressure of about 1410 pounds per square inch over a granular silica-alumina catalyst at a temperature between 300 and 475° F. for a period sufficient to convert over 90 percent of the isobutene in the charge to polymers; about 50 percent of the total propene in the charge also entered into the reaction producing some interpolymers such as isohexenes with the isobutene. The normally liquid hydrocarbons, that is, the polymer fraction, were readily separated from the butanes and lighter portion of the effluent. About one-third of this polymer had more than eight carbon atoms per molecule, and about one-eighth of it was too heavy to be included in a motor fuel having an end-point of 400° F. The normally gaseous fraction separated from the polymers consisted of C₃ and C₄ hydrocarbons, which were readily separated by fractionation into a saturated part containing about 2 percent olefins and over 95 percent isobutane, and an unsaturated part containing about 40 percent propene. A portion of this latter fraction was returned to the polymerization step as recycle stock.

The polymer material was separated by fractionation into two parts, one boiling below about 360° F. constituting about 82 percent of the total polymer. This material, after being saturated by non-destructive hydrogenation, is a premium blending stock for aviation fuel, having an octane number of about 91 and a high response to the addition of an antiknock agent such as tetraethyl lead. The second portion contained the higher boiling polymers and, although a substantial portion would have been included in a gasoline having a higher endpoint, such as about 400° F., such a fraction is considered as a higher-boiling polymer fraction for the purpose of this specification.

This liquid higher-boiling polymer fraction is blended with approximately an equal liquid volume of the light unsaturated, unreacted hydrocarbons mentioned above, and the combined stream is mixed with about 4 liquid volumes of the above mentioned isobutene fraction. The combined hydrocarbon stream, as a liquid, is continuously and intimately mixed with concentrated hydrofluoric acid of a strength greater than 95 percent in a ratio of about 2:1 and is passed through a tube coil at a velocity sufficient to insure turbulent flow. The tube coil is immersed in a bath to regulate the temperature and keep it below 100° F., and is of sufficient length that the reaction time is about 40 minutes. The effluent is passed as a liquid to a separator, wherein a separation takes place between the heavier liquid hydrofluoric acid and the hydrocarbon material. The hydrofluoric acid is removed and returned to the inlet of the tube coil. The hydrocarbon fraction is neutralized by being passed over soda ash, and from it a liquid product is separated, boiling below 400° F. and constituting about 95 percent of the total normally liquid product. It is over 98 percent saturated, contains a large proportion of isoparaffins, has an initial octane number of nearly 90 and has an excellent response to the addition of tetraethyl lead.

As previously mentioned the dehydrogenation step should be conducted at a pressure below about 200 pounds per square inch and may be either thermal or catalytic or a combination of both. Thermal dehydrogenation is preferably carried out between about 1000 and 1250° F., and catalytic dehydrogenation may be carried out between about 850 and 1100° F. In a combination of both, the thermal dehydrogenation should precede the catalytic. It has been found that the most desirable catalysts comprise or consist of chromium oxide, preferably the black, unglowed variety. Suitable modifications are disclosed in U. S. Patents 1,905,383 and 2,098,959, and in the copending applications, Serial Numbers 113,091 of Morey, (now Patent 2,288,320, granted June 30, 1942) 173,708 of Matuszak et al., (now Patent 2,294,414, granted September 1, 1942) 173,709 of Morey et al., (now Patent 2,312,572, granted March 2, 1943) and 263,000 of Schulze (now Patent 2,291,581, granted July 28, 1942).

The polymerization step, while it may be thermal or catalytic, is preferably a catalytic one carried out in the presence of solid granular catalysts. A preferred catalyst is a silica-alumina catalyst, such as described in U. S. Patent 2,142,324 or 2,147,985; or a catalyst of somewhat similar properties may be prepared by intimately mixing an acidic hydrous silica jelly and hydrous alumina jelly, preferably with the latter being present only to an extent of about 1 to 5 percent by weight, and subsequently drying and granulating the resultant material. As mentioned, other solid catalysts may be used. The pressure will generally be at least 200 pounds per square inch and need not be in excess of about 2000 pounds per square inch. Pressures sufficient to insure a substantially liquid phase operation are the most desirable, as brought out in the copending application, Serial No. 747,964, now Patent 2,198,937, granted April 30, 1940, of which I am a coinventor. The temperature should be between 100 and 600° F., with the most usual operation between 250 and 550° F. The temperature and reaction time are interdependent, and with either one fixed the other can be varied as

necessary to give a more or less constant or steady polymerization of the olefins.

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 restriction used in the examples, and in connection with the drawing, need not necessarily be used as limits for all particular operations or sets of conditions, since they are presented primarily as illustrative examples. It will be understood that the flow diagrams presented and described as a part of the disclosure are schematic only, and that many additional conventional pieces of equipment, such as pressure gauges, valves, pumps, heat exchangers, reflux lines and accumulators, heaters and coolers, and the like, will be necessary for any particular installation, and can be supplied to meet the requirements of any particular case by anyone skilled in the art. The essential equipment and conditions have been described and the modifications discussed in sufficient detail to serve as efficient guides.

I claim:

1. A process for the production of premium aliphatic hydrocarbons boiling in the motor fuel range from isobutane, which comprises dehydrogenating isobutane to produce isobutene and a substantial portion of propene, subjecting a hydrocarbon fraction containing isobutene and propene so produced, together with unreacted isobutane, to a catalytic polymerization under polymerization conditions such as to polymerize only a portion of the propene and substantially all of the isobutene to form olefin polymers boiling in and above the motor fuel range, passing the polymerization effluent to separating means, separating therefrom a fraction comprising olefin polymers boiling in the motor fuel range and removing same from the process as a product thereof, separating also a fraction comprising higher boiling polymers, a fraction comprising unreacted isobutane, and a fraction comprising unreacted propene, passing through an elongated reaction zone a stream comprising an intimate liquid mixture of concentrated hydrofluoric acid and said isobutane fraction and said heavy poly-

mer fraction, removing heat from said mixture in said zone during a reaction period to maintain an alkylation temperature, adding at a plurality of points along the length of said reaction zone said propene fraction to supply additional olefin reactant to said zone and in amounts such as to maintain a relatively low olefin concentration, and recovering from an effluent of said zone a hydrocarbon fraction containing paraffins boiling in the motor fuel range so produced.

2. A process for alkylating a low-boiling isoparaffin hydrocarbon of four to five carbon atoms per molecule to produce isoparaffins boiling in the motor fuel range, which comprises passing a stream comprising an intimate, liquid admixture of such an isoparaffin, concentrated hydrofluoric acid and olefin polymers boiling above the motor fuel range through an elongated reaction zone under alkylating conditions to produce isoparaffins in the motor fuel range, adding at a plurality of points subsequent to the inlet of and along the length of said reaction zone a normally gaseous olefin of at least three carbon atoms per molecule to supply additional olefin reactant to said zone and in amounts such as to maintain a relatively low olefin concentration in said reaction zone, and recovering from an effluent of said reaction zone a hydrocarbon fraction containing isoparaffins boiling in the motor fuel range so produced.

3. A process for reacting a low-boiling isoparaffin with low-boiling olefins and olefin polymers, which comprises passing a stream comprising an intimate liquid mixture of a hydrofluoric acid alkylation catalyst and a low-boiling isoparaffin and normally liquid olefin polymers through an elongated reaction zone under alkylating conditions to produce isoparaffins in the motor fuel range, adding at at least one point subsequent to the inlet of and along the length of said reaction zone a normally gaseous olefin to supply additional olefin reactant to said zone and in amounts such as to maintain a relatively low olefin concentration in said reaction zone, and recovering from an effluent of said zone a hydrocarbon fraction containing isoparaffins boiling in the motor fuel range so produced.

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