

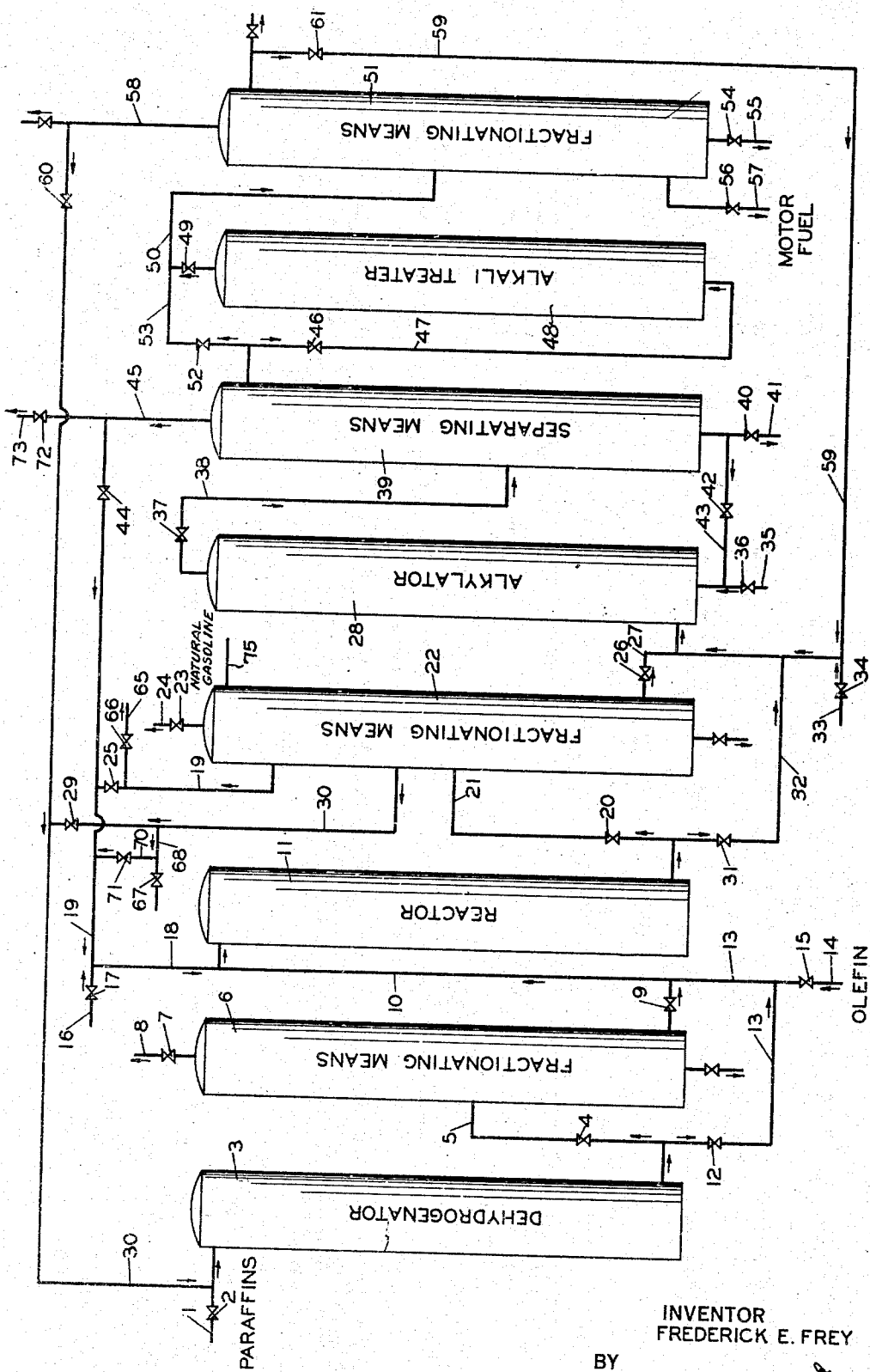
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F. E. FREY

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# PARAFFIN ALKYLATION

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INVENTOR  
FREDERICK E. FREY

BY

BY  
Hudson, Young, Shandys & Ginger  
ATTORNEY

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## PARAFFIN ALKYLATION.

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

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This invention relates to a process of manufacturing hydrocarbons of relatively high molecular weight from hydrocarbons of lower molecular weight, and more particularly to the manufacture of motor-fuel hydrocarbons from lower-boiling hydrocarbons. It is a continuation-in-part of my copending application Serial No. 312,964, filed January 8, 1940.

I have found that relatively high-boiling hydrocarbons may be manufactured from lower-boiling hydrocarbons, such as paraffins and/or olefins, by converting the lower-boiling hydrocarbons into alkyl halides, such as chlorides or fluorides, and subsequently alkylating paraffins, especially isoparaffins, with the alkyl halides under suitable alkylation conditions. I have further found that the alkylation reaction is favored by the paraffin having a branched structure with a tertiary hydrogen atom and by the alkyl group of the alkyl halide being non-primary, that is, secondary or tertiary. Furthermore, I have found that alkyl chlorides are more advantageous than other halides for the alkylation of paraffins.

An object of this invention is to effect the manufacture of relatively higher-boiling hydrocarbons from lower-boiling hydrocarbons.

Another object is to convert lower-boiling hydrocarbons into motor fuel by alkylation of paraffins with alkyl halides formed from low-boiling hydrocarbons.

Another object is to convert hydrocarbons having two to six carbon atoms per molecule into alkyl chlorides suitable for the alkylation of isoparaffins.

Another object is to decrease the volatility of paraffins, especially isoparaffins.

Another object is to utilize hydrogen chloride in a process of manufacturing motor-fuel hydrocarbons from lower-boiling hydrocarbons having two to eight carbon atoms per molecule.

A further object is to produce, entirely from lower-boiling paraffins, higher-boiling paraffins.

A further object is to produce preselected paraffin hydrocarbons from lower-boiling paraffin hydrocarbons.

Another object is to recover and to utilize olefins from gaseous mixtures by converting them into halides, which are readily condensable or extractable, and then reacting them with paraffins to yield higher-boiling paraffins.

Other objects and advantages of the invention will be obvious to those skilled in the art.

The invention will be readily understood from the following description and the accompanying

drawing, which shows a flow-diagram for a preferred mode of operation, adapted to produce hydrocarbons boiling in the motor-fuel range.

A feed stock comprising at least one paraffin hydrocarbon having from two to six carbon atoms per molecule enters the system through inlet 1 having control-valve 2. It passes into dehydrogenator 3, in which part of the feed stock is converted into at least one unsaturated hydrocarbon. For example, dehydrogenator 3 may be a cracking coil in which the paraffin hydrocarbon is cracked into unsaturated hydrocarbons; more advantageously, it may be a catalytic dehydrogenator in which one or more of the known catalysts for cracking and/or dehydrogenating hydrocarbons into unsaturated hydrocarbons are used. Particularly efficient catalysts for this purpose comprise black unglowed chromium oxide; but many other catalysts, such as bauxite and alumina, with or without promoters such as compounds of chromium, zirconium, molybdenum, etc., may be used with good results.

As paraffins having more than four carbon atoms per molecule may be readily incorporated as such in motor fuel, the feed stock to be dehydrogenated may comprise advantageously chiefly at least one paraffin having two to four carbon atoms per molecule; furthermore, as isobutane may be utilized efficiently in a subsequent step, the feed stock advantageously may comprise chiefly at least one of the normally gaseous unbranched paraffins, ethane, propane, and normal butane.

From dehydrogenator 3, the products and unreacted hydrocarbons may be passed through valve 4 and conduit 5 into fractionating means 6, which serves chiefly to remove light gases such as hydrogen and methane; these are withdrawn as a light-gas fraction through valve 7 and outlet 8. If desired under some conditions of operation, ethane and ethylene may be removed with hydrogen and methane. The residual hydrocarbons are passed through valve 9 and conduit 10 to reactor 11.

If desired, under some conditions of operation, at least part of the effluent from dehydrogenator 3 may be passed through valve 12 and by-pass conduit 13 directly to conduit 10 and thence to reactor 11 without undergoing fractionation in fractionating means 6. Also, if desired, a feed stock comprising at least one olefin having two to six carbon atoms per molecule may enter the system, as through inlet 14 having control-valve 15, and be passed to reactor 11, as by conduits 13 and 10.

Simultaneously with the passage of olefinic hydrocarbon material into reactor 11, a hydrogen halide, preferably hydrogen chloride, enters the system at inlet 16 having control-valve 17 and passes through conduit 18, together with recycled hydrogen halide from conduit 19, to reactor 11. Although hydrogen chloride is preferred, other halides, especially hydrogen fluoride, may be used; hydrogen bromide and hydrogen iodide are undesirable under some conditions of operation because the alkyl bromides and iodides they form are subject to loss by oxidation into by-products that are difficult to reclaim.

In reactor 11, the mixture comprising olefinic hydrocarbon material and hydrogen halide is subjected to conditions favoring union of the olefins with the hydrogen halide to form alkyl halides. The conditions depend somewhat upon the particular reactants, but a suitable temperature and a suitable pressure may be readily found between 0 and 400° F. and between 1 and 10 atmospheres, respectively; however, temperatures and pressures outside these ranges at times may be useful. In general, a temperature below about 150° F. is advantageous for the production of tertiary alkyl halides, and one above this temperature for the production of secondary and primary alkyl halides. Although the reaction is capable of occurring in the absence of a catalyst, the rate of reaction under most conditions is advantageously increased by a catalyst comprising at least one corresponding halide of a polyvalent metal. Among suitable catalysts are the halides of tin, zinc, antimony, aluminum, bismuth, vanadium, manganese, barium, calcium, cadmium, copper, chromium, iron, mercury, nickel, and similar polyvalent metals. Of these catalysts, the chlorides of barium, tin, zinc, and antimony are preferred for the reaction involving hydrogen chloride. Other catalysts, including metallic oxides and mineral acids and acid salts and even water catalyze the reaction, and suitable catalysts and conditions are readily determined by trial.

The catalyst may be supported on a porous material such as charcoal, silica gel, alumina gel, fire brick, and similar well-known supports, or it may be dispersed in a liquid medium such as chlorinated hydrocarbon, which preferably has a boiling point higher than that of the alkyl chloride to be formed and into which the reactants are injected.

After the reaction between olefins and the hydrogen halide is substantially completed, the resultant mixture is passed from reactor 11 through valve 20 and conduit 21 into fractionating means 22, wherein it is fractionally distilled and separated or wherein the alkyl halide in some instances is separated from the mixture by condensation or simple absorption in a low-boiling hydrocarbon liquid, such as natural gasoline, introduced through conduit 75. Any undesired light gases, such as hydrogen and hydrocarbons having less than two carbon atoms per molecule may be removed as a light-gas fraction through valve 23 and outlet 24. Unreacted hydrogen halide may be recycled to reactor 11 through valve 25 and conduits 19 and 18, or may be discharged from the system, entirely or in part, through conduit 65 and valve 66. The alkyl halide, together with, if desired, at least a part of the unreacted hydrocarbons, is passed as a heavy fraction through valve 26 and conduit 27 into alkylator 28.

If desired, unreacted hydrocarbons having two carbon atoms per molecule and a part or all of the other unreacted hydrocarbons may be recycled as

an intermediate fraction through valve 29 and conduit 30 to dehydrogenator 3, or may be discharged from the system, entirely or in part, through conduit 68 and valve 67, or may be returned to reactor 11, entirely or in part, from conduits 30 and 68 through conduit 70 and valve 71 to conduits 19 and 18. Also, if desired, at least part of the effluent from reactor 11 may be passed through valve 31 and conduits 32 and 27 directly to alkylator 28 without undergoing fractionation in fractionating means 22. Furthermore, if desired, a feed stock comprising at least one isoparaffin having four to eight carbon atoms, such as natural-gas gasoline, "wild" extracted hydrocarbons from natural gas, light petroleum distillates, and the like, may enter the system through inlet 33 having control-valve 34 and pass through conduits 32 and 27 into alkylator 28; such isoparaffin advantageously may be isobutane, as heavier paraffins may be incorporated as such in motor fuel more readily than isobutane.

In place of going through the steps of dehydrogenating the paraffins charged to the process through conduit 1, and reacting the olefins with a hydrogen halide, or in case an olefin-containing stream is not available to be charged through conduit 14, paraffins may be reacted directly with free halogen to produce alkyl halides and the corresponding hydrogen halide. In such a modification, the use of chlorine is to be preferred, not only because alkyl chlorides are preferred for subsequent use, but because chlorine is cheap and the chlorides are readily handled. In this modification, the paraffin hydrocarbon material from which alkyl halides are to be made is charged through conduit 14 and valve 15, and a free halogen is charged through conduit 16 and valve 17. These materials are reacted in reactor 11, under reaction conditions which are well known to the art, and which in themselves form no part of this invention, forming alkyl halides by substitution reactions. In such a case, of course, dehydrogenator 3 and fractionating means 6 need not be included, and subsequent parts, and operation, of the process will be substantially the same. This modification results in the production of substantial amounts of a hydrogen halide which may be removed from the process or which may be used for producing additional alkyl halides from olefins in another reactor in the manner already described. If the hydrogen halide is not used to react with olefins, free halogen can be regenerated from it, if desirable, by chemical oxidation, electrolysis, or the like, and re-used in the halogenation step. The halogenation does not require drastic reaction conditions, and the conditions are readily controlled, when paraffins of more than two carbon atoms per molecule are used, so as to produce high yields of non-primary alkyl halides, which form the most desirable charge to the subsequent alkylation step.

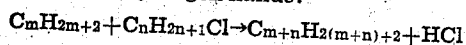
If a hydrocarbon stream containing both olefins and paraffins is charged to the process, the olefins may be reacted in reactor 11 with a hydrogen halide, and unreacted paraffins, separated from the effluent, either may be dehydrogenated, as previously discussed, or may be reacted with free halogen to form alkyl halides in supplemental apparatus similar to that shown and discussed; the effluent from such a halogenation step may be added to the material flowing through conduit 21, as will be readily appreciated.

In alkylator 28 the mixture entering it through conduit 27 and comprising an alkyl halide and a paraffin having four to eight carbon atoms per

molecule is subjected to suitable alkylation conditions. These conditions comprise the presence of an alkylation catalyst such as aluminum halides, double salts of aluminum halides, such as sodium chloride-aluminum chloride, and other catalysts adapted to effect alkylation of paraffins with alkyl halides, such as concentrated sulfuric acid. If a mobile catalyst, such as sulfuric acid, is used, it enters the alkylator through inlet 35 having control valve 36.

The choice of a suitable catalyst depends somewhat upon the alkylation reactants. For example, primary halides, especially ethyl halides, react relatively difficultly and require a catalyst more powerful than that which is adequate for non-primary alkyl halides. Thus, when a primary alkyl halide, such as ethyl chloride, is used, catalysts of the aluminum chloride type are more advantageous than catalysts of the sulfuric acid type.

Various reactions occur in alkylator 28, but the primary reaction is believed to be alkylation of paraffins, especially isoparaffins, which are alkylated more easily than normal paraffins, with an elision of a hydrogen halide:



The primary alkylation product appears to undergo secondary reactions that form lower-boiling and higher-boiling products; it doubtless also undergoes isomerization.

As alkylation in the presence of catalysts other than sulfuric acid is well-known to the art, additional description of the alkylation step will be limited, primarily for the sake of brevity, to sulfuric acid alkylation. When sulfuric acid is used as the catalyst, the alkylation reaction appears to proceed most efficiently for isoparaffins having four to eight carbon atoms per molecule and for non-primary alkyl halides in which the alkyl group has three to six carbon atoms per molecule. Of non-primary alkyl halides, the tertiary react somewhat more rapidly than do the corresponding secondary alkyl halides; hence, as tertiary alkyl halides are produced from the reaction of hydrogen halide with only isolefins, it is advantageous for the feed stock to the dehydrogenation step to comprise chiefly an isoparaffin, especially isobutane, if an adequate supply of such isoparaffin is available. Conversely, if a secondary alkyl halide is used in the alkylation step, it is advantageous to use a relatively high strength of acid, such as 100 to 105 per cent sulfuric acid, especially if the halide is a chloride. The reaction is favored by a relatively high ratio of sulfuric acid to hydrocarbons; the acid should have a volume within the range of 0.1 to 2 times the volume of hydrocarbons, advantageously within the range of 0.5 to 1. The sulfuric acid should have a composition equivalent to a strength within the range of 90 to 105 per cent by weight, preferably between 95 and 102 per cent; the reaction temperature may be in the range of 0 to 125° F., preferably between 50 and 100° F. If desired, the acid may contain emulsifiers, such as for example alkyl sulfates. As alkyl sulfates or equivalent compounds are formed to some extent during the reaction, a small portion of spent acid advantageously may be added to fresh acid to increase its ability to form good emulsions with the alkylation reactants.

The reaction requires some time to approach completeness, but a period of from 5 minutes to 3 hours is usually sufficient. Much longer periods preferably should be avoided, as they favor

secondary reactions that convert the primary alkylation product into lower-boiling and higher-boiling products. Some indication of the progress of the reaction may be obtained from the rate of evolution of hydrogen halide, which is a product of the primary alkylation reaction. The hydrocarbon products boil chiefly in the motor-fuel range, are substantially completely saturated, and have excellent anti-knock ratings.

After substantially all of the alkyl halide has reacted, the resultant mixture is passed through valve 37 and conduit 38 into separating means 39, in which the sulfuric acid is separated from the mixture as a heavy layer by gravity or, if desired, by centrifuging. The sulfuric acid may be withdrawn through valve 40 and outlet 41, and thence it may be subjected to a process of reclamation, if desired; or, alternatively, it may be returned, partly or entirely as trial indicates is desirable, to alkylator 28 through valve 42 and conduit 43. The hydrogen halide is passed through valve 44 and conduits 45, 19, and 18 to reactor 11, in which it is used again to form alkyl halides, or it may be discharged, entirely or in part, through conduit 73 and valve 72. The hydrocarbon material is passed through valve 46 and conduit 47 to alkali treater 48, in which it is freed from acidic material by a washing treatment with an alkali.

From alkali treater 48, the hydrocarbon stream is passed through valve 49 and conduit 50 to fractionating means 51.

Under some conditions of operation, a small amount of acidic material in the hydrocarbon material passed to fractionating means 51 may be tolerated; under such conditions, if desired, at least part of the hydrocarbons from separator 39 may be passed through valve 52 and conduits 53 and 50 directly to fractionating means 51 without being subjected to an alkali treatment in alkali treater 48.

In fractionating means 51, the hydrocarbons are fractionated into a heavy-oil fraction, which is withdrawn through valve 54 and outlet 55; into a motor-fuel fraction, which is withdrawn through valve 56 and outlet 57; and into one, or two, low-boiling fractions, which may be recycled to dehydrogenator 3 and/or alkylator 28 through conduits 58 and/or 59 in proportions controlled by valves 60 and 61. If desired, either or both of these fractions may include at least part of the relatively low-boiling motor-fuel hydrocarbons, such as those containing up to about eight atoms of carbon per molecule, as such hydrocarbons may undergo an effective decrease in volatility by being reprocessed; furthermore, the fraction recycled to alkylator 28 through conduit 59 may include any alkyl halide that escaped reaction. Either or both of these streams may be discharged from the system, entirely or in part, through the valved conduits shown.

It will be understood that auxiliary equipment, not shown in the drawing, such as pumps, automatic controls of various kinds and purposes, and the like may be used wherever they are desirable or necessary.

The term isoparaffin, as used in this specification in connection with the charge stock, refers to paraffin hydrocarbons such as isobutane (2-methyl-propane), isopentane (2-methylbutane) and the like, that is, hydrocarbons which contain at least one tertiary hydrogen atom. Other examples of such hydrocarbons are the isohexanes 2- and 3-methyl-pentane, isoheptanes such as 2- and 3-methyl-hexane, 2, 3- and 2,4-

dimethylpentane, and, 3-ethylpentane, and the like.

When it is desired to produce a gasoline having particularly desirable characteristics, such as an aviation gasoline, or some certain valuable hydrocarbon or hydrocarbons boiling in the motor-fuel range, it will generally not be desirable to use an isoparaffin having a molecular weight higher than that of isobutane or of isopentane, or possibly of isohexane. When it is desired to produce paraffins boiling above the motor-fuel range, correspondingly heavier paraffins should be charged. It has been found that highly branched isoparaffins of relatively high molecular weight are somewhat readily decomposed by prolonged contact with sulfuric acid; when these are used the reaction conditions should be so modified, as indicated by trial; that extensive deleterious decomposition does not take place, or at times it may be more desirable to charge a simple isoparaffin such as 2-methylheptane or 2,4-dimethylhexane than to charge a complex isoparaffin such as 2,2,4-trimethylpentane.

It will, of course, generally be impractical to charge any particular hydrocarbon in an absolutely pure state, especially when relatively high-boiling hydrocarbons are used. When some particular individual paraffin is desired to be obtained in a relatively pure state, as by fractional distillation of the reaction mixture, the hydrocarbon mixture charged should be relatively free of readily reactive paraffins other than those necessary to produce the desired product. When isoparaffins are reacted, the presence of limited amounts of normal paraffins is generally not deleterious, and may at times be advantageous in controlling the reaction; at other times, less pure hydrocarbon fractions may be used.

As previously mentioned, it is preferable to use either secondary or tertiary alkyl halides, and it is also preferable that the halides be chlorides. It is one of the features of my invention that the alkyl halides produced in the first part of my process are readily separated from the other constituents of the reaction mixture and are also of the most desired type for the subsequent alkylation step. Hydrocarbons of relatively low molecular weight are readily reacted in this first part of the process, with the minimum of side reactions, and the resultant alkyl halides are readily obtained in a pure state when desirable, such as when it is desired to produce a gasoline, or some certain valuable hydrocarbon or hydrocarbons boiling in the motor-fuel range. In any case where such a particular hydrocarbon product is desired, the individual hydrocarbons suitable for the charge stock may be readily selected by trial, in the light of the present disclosure.

For the acid-alkylation step, the temperature, the reaction time, and the relative amount of sulfuric acid are interrelated. With relatively high temperatures and/or large amounts of acid, relatively short reaction times may be used. When it is desired to produce a relatively pure product, short reaction times and low yields per pass should characterize all the steps of the process, and when a certain appreciable amount of side reactions or secondary reactions may be tolerated, all the steps of the process may be operated so as to have longer reaction times and higher yields per pass. The most desirable conditions in any particular instance can be readily determined by trial.

When sulfuric acid strength in excess of 100

per cent is mentioned, reference is made to "fuming" sulfuric acid which, when titrated with an alkali, reacts with sufficient alkali to be equivalent to the amount of acid indicated.

The following examples are given purely for the purpose of illustrating a few of the many possible modes of operation of the process; they are not necessarily to be taken as establishing limitations of the invention.

#### Example I.

A feed stock comprising chiefly isobutane is dehydrogenated with a catalyst comprising black-unglazed chromium oxide at a pressure in the neighborhood of atmospheric, at a temperature within the range of about 750 to 1020° F., and at a space velocity of about 2000 volumes of isobutane, calculated to 32° F., and 1 atmosphere; per volume of catalyst per hour. The effluent is cooled and compressed until the four-carbon hydrocarbons are liquefied; the hydrogen and uncondensed light hydrocarbons are removed. The residual material is mixed with anhydrous hydrogen chloride approximately equivalent in amount to the isobutylene, whereupon tertiary butyl chloride is formed; the reaction occurs rapidly at ordinary temperatures and pressures. The resultant mixture of isobutane and tertiary butyl chloride is intimately mixed as a liquid at room temperature with about three-fifths of its own volume of concentrated sulfuric acid having a strength of about 96 per cent, by a motor-driven stirrer, and the mixture is allowed to react for about four hours. The hydrogen chloride regenerated by the reaction is recycled to form more butyl chloride. The sulfuric acid is removed by settling, and the hydrocarbon material is freed from residual acidic material by washing with dilute alkali. This hydrocarbon material is substantially completely paraffinic and has a substantial content of hydrocarbons having more than four carbon atoms per molecule; it is fractionated into an isobutane fraction, which is recycled to the dehydrogenation step, and into a motor-fuel fraction, which is withdrawn from the system and has a high antiknock rating.

#### Example II

Tertiary butyl chloride is prepared from isobutane and hydrogen chloride as in Example 1. It is freed from isobutane by fractional distillation, the isobutane being recycled to the dehydrogenation step. It is then mixed with about 1.5 times its own weight of a feed stock comprising chiefly isopentane, and the resultant mixture is emulsified by mechanical stirring, with about three-fourths of its own volume of concentrated sulfuric acid having a strength of 96 per cent by weight. After about four hours at a temperature of about 70° F., during which the regenerated hydrogen chloride is recycled to the step for forming butyl chloride, the emulsion is allowed to settle into two layers. The lower or acid layer is removed, and the upper or hydrocarbon layer is washed with dilute alkali and then fractionally distilled. Of the hydrocarbons other than isopentane, about 96 per cent by weight boil between 85 and 410° F.; this fraction amounts to about 83 per cent by weight of the theoretical yield based on the formation of nonane. The motor-fuel fraction of the product so formed has a good antiknock rating and a Reid vapor pressure of less than 4 pounds.

*Example III*

A feed stock comprising chiefly normal butane is dehydrogenated, in the presence of dehydrated bauxite, at a pressure of about 1 atmosphere, at a temperature of about 1000 to 1200° F., and at a space velocity of about 1000 volumes of butane, calculated to 32° F. and 1 atmosphere, per volume of catalyst per hour. The effluent is cooled and compressed until the four-carbon hydrocarbons and most of the three-carbon hydrocarbons are liquefied; hydrogen and uncondensed light hydrocarbons are removed. The residual material is mixed with anhydrous hydrogen chloride slightly in excess of the amount chemically equivalent to the olefins present, and is subjected to the action of a catalyst comprising zinc chloride supported on active charcoal at a temperature in the range of 100 to 300° F. After the butylenes and the propylene have reacted to form secondary butyl chloride and isopropyl chloride, respectively, the unreacted hydrocarbons are removed from the chlorides by fractional distillation and recycled to the dehydrogenation step. The chlorides are mixed with about 1.5 times their weight of a feed stock comprising chiefly isopentane, and the mixture is emulsified, by vigorous mechanical stirring, with about three-fourths of its own volume of sulfuric acid having 102 per cent H<sub>2</sub>SO<sub>4</sub> by weight. After about three hours at a temperature of about 68° F., during which the hydrogen chloride regenerated is recycled to the step for making chlorides, the emulsion is allowed to settle into two layers. The lower or acid layer is removed, and the upper or hydrocarbon layer is washed with dilute alkali and then fractionally distilled. Of the hydrocarbons other than isopentane, about 98 per cent by weight boil between 85 and 410° F.; this fraction, which is completely paraffinic, amounts to about 90 per cent by weight of the theoretical yield based on the formation of nonane.

*Example IV*

A feed stock comprising chiefly propane is dehydrogenated with the aid of a dehydrated-bauxite catalyst, at a pressure slightly above atmospheric, at a temperature within the range of about 1050 to 1300° F., and at a space velocity of about 1000 volumes of propane, calculated to 32° F. and 1 atmosphere, per volume of catalyst per hour. The resultant mixture is cooled to between about 100 and 195° F., mixed with an excess of anhydrous hydrogen chloride and subjected to the action of stannic chloride deposited on dehydrated bauxite. After the reaction forming isopropyl chloride is substantially complete, the reaction mixture is fractionally distilled into a light-gas fraction comprising chiefly hydrogen and methane, which is discarded; into a hydrogen chloride fraction, which is recycled to the step for the formation of isopropyl chloride; into a propane fraction, which is recycled to the dehydrogenation step; and into an isopropyl chloride fraction, which is mixed with about 1.8 times its own weight of a feed stock comprising chiefly isopentane. The mixture comprising isopropyl chloride and isopentane is emulsified with about three-fourths of its own volume of sulfuric acid having a strength equivalent to 102 per cent H<sub>2</sub>SO<sub>4</sub> by weight. After being kept vigorously stirred for about four hours at about 70° F., the emulsion is allowed to settle, and the lower or acid layer is removed. The upper or hydrocarbon layer is washed with

dilute alkali and fractionally distilled. After removal of isopentane, the fraction boiling from 85 to 410° F. amounts to about 99 per cent by weight of the hydrocarbon product and to 78 per cent by weight of the theoretical yield based on the formation of octane.

*Example V*

There is mixed with a stream of commercial propane, consisting of over 95 per cent propane, a stream of chloride, with a mole ratio of propane to chlorine of about 8 to 1. This mixture is rapidly heated to a temperature of about 630° F. and is maintained at that temperature for a time long enough for at least 90 per cent of the chlorine to react. The reaction products are rapidly cooled and passed to fractionating equipment. A propyl chloride fraction is separated, of which the major constituent is isopropyl chloride. This fraction is mixed with a butane stream comprising over 80 per cent of isobutane, the mole ratio of isobutane to isopropyl chloride being about 3 to 1. The resultant liquid mixture is continuously and intimately mixed, by a mechanical mixing pump, with one half its own volume of sulfuric acid having a strength of about 103 per cent and consisting of a blend of approximately equal parts of fresh and recycled acid. The resultant liquid mixture, or emulsion, is passed rapidly through an elongated tube coil of restricted cross-sectional area, which is immersed in a liquid bath which takes up the heat of reaction and maintains the reaction temperature in the neighborhood of 75° F. The turbulence in the stream, as a result of the rapid flow through the tube coil, aids to maintain an intimate mixture of the liquid reactants. After a reaction time of about 12 minutes the effluent is passed to a separating system, wherein the hydrocarbon material is separated from the sulfuric acid material and from hydrogen chloride. The free acid in the hydrocarbon material is neutralized and removed by an alkali wash, and the stream is passed to a fractionating system. In the fractionating system there is separated a butane fraction, a portion of which is recycled to the alkylation step, a propyl chloride stream, and a hydrocarbon fraction boiling within the motor-fuel range and containing considerable quantities of isoheptanes that have excellent antidetonating and blending characteristics.

*Example VI*

Natural gas is cracked at low pressure to convert the paraffins having two or more carbon atoms per molecule into olefins, chiefly ethylene and propylene. Hydrogen chloride is admixed to the resultant effluent from the cracking coil, and the mixture is passed at low pressure over zinc chloride adsorbed on pumice at about 300° F., whereby alkyl chlorides, chiefly ethyl chloride and isopropyl chloride, are formed. The resulting mixture is cooled, and the alkyl chlorides are extracted by absorption in natural gasoline in a countercurrent absorption tower. The resultant mixture of natural gasoline and alkyl chlorides is subjected to the action of aluminum chloride under alkylation conditions, whereby alkylation of natural-gasoline constituents is effected with elision of hydrogen chloride. The gasoline recovered from the reaction mixture, by fractional distillation and washing with dilute caustic, is much superior to the original natural gasoline by being less volatile and by having an increased antiknock rating.

In view of the many possible modifications of the process that will be obvious to those skilled in the art, the invention should not be limited unduly by the foregoing specification and examples, but it should be understood to be extensive in scope and equivalents, within the scope of the appended claims.

I claim:

1. A process for the manufacture of motor-fuel hydrocarbons, which comprises cracking natural gas at low pressure to form olefins, reacting the resultant olefins with hydrogen chloride to form alkyl chlorides, extracting the resultant alkyl chlorides by absorption with natural gasoline, subjecting the resultant mixture of natural gasoline and alkyl chlorides to the action of aluminum chloride under alkylation conditions, whereby motor-fuel hydrocarbons are formed by alkylation of natural-gasoline constituents, and separating the resultant motor-fuel hydrocarbons.

2. A process for the production of branched-chain paraffin hydrocarbons, which comprises converting an aliphatic hydrocarbon selected from the group consisting of olefins and paraffins of low molecular weight into non-primary alkyl halides, passing a gaseous effluent of said conversion comprising an alkyl halide so produced and unreacted hydrocarbons to an absorption zone, contacting said gaseous effluent in said absorption zone with a liquid paraffinic hydrocarbon fraction boiling in the lower part of the motor fuel range and containing at least one branched-chain paraffin to separate alkyl halides so produced from said conversion effluent, reacting said alkyl halides with said low-boiling branched-chain paraffin hydrocarbon under suitable alkylation conditions to form branched-chain paraffin hydrocarbons of higher molecular weight and in the boiling range of motor fuel, and subsequently separating from the reactants a hydrocarbon fraction comprising said branched-chain paraffin hydrocarbons of higher molecular weight so produced.

3. A process for the production of hydrocarbons boiling in the motor fuel range, which comprises passing a normally gaseous paraffin hydrocarbon to a dehydrogenating zone to form normally gaseous unsaturated hydrocarbons, passing the resultant unsaturated hydrocarbons without separation from accompanying saturated hydrocarbons to a reaction zone to convert said unsaturated hydrocarbons into alkyl halides, passing the resultant mixture to a separating means to separate alkyl halides from accompanying hydrocarbons by absorption of said alkyl halides with a normally liquid saturated hydrocarbon fraction boiling in the lower part of the motor fuel range and higher than said accompanying hydrocarbons, subjecting the resultant mixture of normally liquid saturated hydrocarbons and alkyl halides to suitable alkylation conditions to form paraffin hydrocarbons in the motor fuel range, and subsequently passing the alkylation effluent to a separating means to remove a hydrocarbon fraction in the motor fuel range so produced.

4. A process for the manufacture of hydrocarbons boiling in the motor fuel range, which comprises dehydrogenating normally gaseous paraffin hydrocarbons to form normally gaseous unsaturated hydrocarbons, subjecting the resultant unsaturated hydrocarbons without separation from accompanying saturated hydrocarbons

to reaction with a hydrogen halide to form alkyl halides, separating resultant alkyl halides from accompanying hydrocarbons by absorption with a normally liquid saturated hydrocarbon fraction boiling in the lower part of the motor fuel range, subjecting the resultant mixture of said normally liquid saturated hydrocarbons and alkyl halides to the action of aluminum chloride under alkylation conditions to form hydrocarbons in the motor fuel range by alkylation of said normally liquid saturated hydrocarbons with said alkyl halides, and separating from the alkylation effluent a hydrocarbon fraction in the motor fuel range so produced.

5. A process for manufacturing hydrocarbons boiling in the motor fuel range from lower boiling hydrocarbons, which comprises dehydrogenating normally gaseous paraffin hydrocarbons having more than two carbon atoms per molecule to form gaseous olefins, reacting substantially all the resultant olefins with hydrogen chloride under conditions adapted to form alkyl chlorides therefrom, separating from the reaction products resultant alkyl chlorides by absorption with a normally liquid saturated hydrocarbon material of high isoparaffin content and of relatively high volatility, separating also a fraction comprising essentially unreacted normally gaseous paraffin hydrocarbons and returning at least a portion thereof to said dehydrogenation step, reacting a resultant mixture containing said saturated hydrocarbon material of relatively high volatility with said alkyl chlorides in the presence of sulfuric acid under conditions adapted to alkylate said saturated hydrocarbon material, separating from the alkylation effluent hydrogen chloride as a light gaseous phase and returning at least a portion thereof for reaction with additional olefin and separating also a hydrocarbon material as a liquid phase and recovering therefrom normally liquid hydrocarbons of less volatility than the absorbent material and boiling in the motor fuel range.

6. A process for the production of branched-chain saturated hydrocarbons, which comprises converting a low-boiling aliphatic hydrocarbon to form an alkyl halide, passing a gaseous effluent of said conversion comprising an alkyl halide so produced and unreacted hydrocarbons to an absorption zone, contacting said gaseous effluent in said absorption zone with a liquid saturated hydrocarbon fraction boiling in the lower part of the motor fuel range and comprising an alkylatable hydrocarbon to separate an alkyl halide so produced from said conversion effluent, passing a resulting rich absorption liquid from said absorption zone to an alkylation zone and therein subjecting said rich liquid to alkylation conditions to form a branched-chain saturated hydrocarbon of higher molecular weight by reactions involving said alkyl halide and said alkylatable hydrocarbon, and subsequently separating from an effluent of said alkylation zone a fraction comprising said branched-chain saturated hydrocarbon of higher molecular weight so produced.

7. The process of claim 6 in which said low-boiling aliphatic hydrocarbon converted to an alkyl halide is a normally gaseous paraffin, said alkylatable hydrocarbon is a low-boiling isoparaffin and a liquid acid alkylation catalyst is employed in said alkylation zone.

FREDERICK E. FREY.