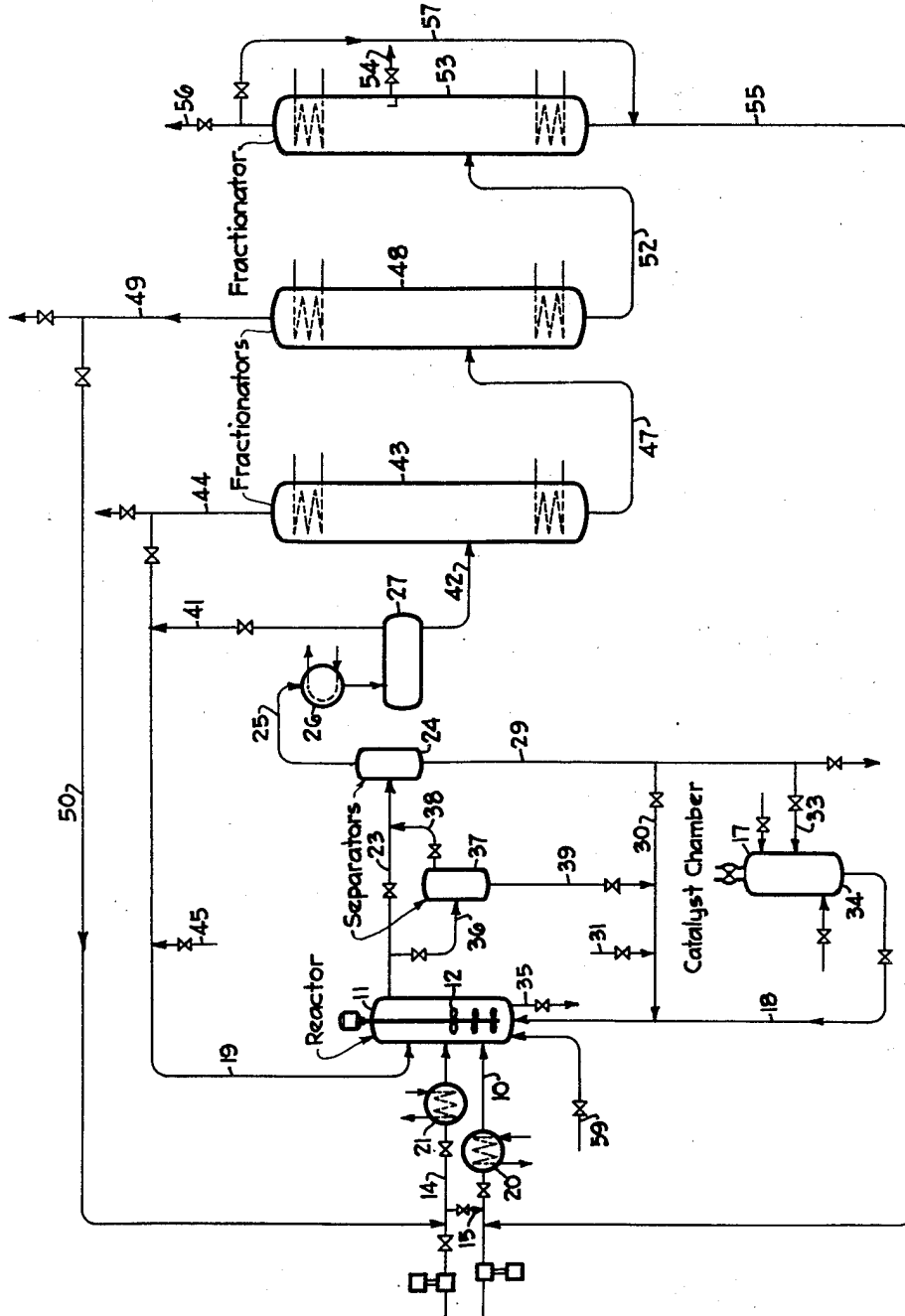


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OF HIGH BOILING PARAFFINS
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PRODUCTION OF IMPROVED DIESEL ENGINE FUELS BY THE CATALYTIC ISOMERIZATION OF HIGH BOILING PARAFFINS

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This invention relates to the conversion of normally liquid high molecular weight hydrocarbons and relates more particularly to the production of high quality Diesel engine fuels.

The relative suitability of a hydrocarbon or a hydrocarbon mixture as a fuel for Diesel engines is dependent not only upon the possession of a high ignition value, as generally expressed by cetane number, but upon the combination therewith of a high heating value and a low pour point. The more readily available hydrocarbons boiling in the Diesel engine fuel boiling range such as those obtainable by distillation from naturally occurring petroleum and from cracked crudes generally possess too low an ignition value. High cetane paraffinic stocks, on the other hand, generally are lacking in a sufficiently low pour point to enable their efficient utilization under conditions of relatively low temperatures. Processes have been disclosed heretofore for the production of hydrocarbons possessing properties approaching more nearly the combination of characteristics desired in a high quality Diesel fuel. Such processes as used heretofore, however, often have been handicapped by the utilization of one or more such steps as, for example, cracking, solvent extraction, extractive distillation, etc., which enables the conversion of only a relatively small proportion of the charge to a product having the physical and chemical properties falling within the relatively narrow range of a high quality Diesel fuel. Such processes, furthermore generally, provide no means for the variation of the pour point over a relatively wide range without substantial reduction in ignition and/or heating value. Practical operation of such processes directed primarily to the production of only Diesel fuels is often rendered highly uneconomical because of their complexity and resultant high cost of operation.

It is an object of the present invention to provide an improved process for the more efficient production, in the absence of any substantial hydrocarbon decomposition, of high quality Diesel engine fuels possessing a high heating value, high ignition value and low pour point.

A further object of the invention is the provision of an improved process for the more efficient conversion of a high cetane paraffinic stock having a relatively high pour point to a paraffinic Diesel engine fuel of low pour point without substantial reduction of ignition value and in the absence of any substantial hydrocarbon decomposition.

Another object of the invention is the provision of an improved process for the more efficient conversion of a saturated normally liquid isomerizable high molecular weight hydrocarbon of straight or branched structure to a saturated hydrocarbon of branched and more highly branched structure having substantially the same molecular weight

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in the absence of any substantial hydrocarbon decomposition.

Another object of the invention is the provision of an improved process for the more efficient conversion of normally liquid high molecular weight paraffins of straight and branched chain structure to paraffins of branched and more highly branched chain structure, respectively, having the same molecular weight, in the absence of any substantial hydrocarbon decomposition.

Still another object of the invention is the provision of a high quality Diesel engine fuel combining relatively high ignition and heating values with a low pour point. Other objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the process of the invention, a normally liquid isomerizable saturated hydrocarbon of high molecular weight such as, for example, a paraffin having at least ten carbon atoms of the molecule, of straight chain or branched structure, is converted by contact with a catalyst comprising a modified metal halide of the Friedel-Crafts type in the presence of a cracking suppressor under conditions described fully herein, converting high molecular weight normally liquid paraffins of straight and branched structure to normally liquid paraffins of branched and more highly branched structure having the same molecular weight as the hydrocarbons charged, in the absence of any substantial hydrocarbon decomposition. By the term hydrocarbon "decomposition," as used in the present specification and appended claims, is meant the rupture of carbon to carbon bonds of the hydrocarbon molecule to result in the formation of hydrocarbons of substantially lower molecular weight than the normally solid hydrocarbon charged, or recombination of hydrocarbon fragments to form higher molecular weight tars and sludges.

In processes disclosed heretofore involving the conversion of high molecular weight hydrocarbons such as, for example, the paraffins having at least 7 or 8 carbon atoms to the molecule, with the aid of a metal halide of the Friedel-Crafts type, such as aluminum chloride, hydrocarbon decomposition is generally the predominant reaction. For, although aluminum chloride is known to promote such reactions as the conversion of normal butane to isobutane in the absence of any substantial hydrocarbon decomposition at certain conditions, the effect of this catalyst in the presence of a higher paraffin is to favor the cracking reaction over the isomerization reaction. Thus, in the presence of pentane, aluminum chloride will cause the cracking reaction to predominate, whereas in the presence of still higher paraffins, the cracking reaction will generally prevail to the substantial exclusion of isomerization. Resort is therefore had in the isomerization of

normal pentane with aluminum chloride to the use of agents capable of suppressing the cracking reaction. The agents suppressing the cracking of the lower boiling paraffins, however, also suppress to a varying degree the isomerization of these materials. Since the cracking proceeds at a progressively more active rate with increase of molecular weight of the lower boiling paraffins, the inordinately large amount of cracking suppressor required to inhibit substantially all cracking of, for example, a C₈ paraffin, results in a concomitant suppression of the isomerization reaction to a degree rendering the isomerization on a practical scale of such more readily cracked paraffins highly uneconomical. The treatment of paraffins of still higher molecular weights with aluminum chloride on a practical scale in the absence of any substantial degree of cracking has, therefore, heretofore been held unfeasible.

In contrast to the methods employed heretofore in the treatment of normally liquid paraffin hydrocarbons of high molecular weight, and notwithstanding the behavior of the lower boiling paraffins of progressively increasing molecular weight in the presence of aluminum chloride and a cracking suppressor, it has now been found that the high molecular weight normally liquid hydrocarbons such as, for example, the normally liquid paraffins having at least 10 carbon atoms to the molecule can be catalytically converted to normally liquid hydrocarbons of improved properties, having the same molecular weight as the normally solid hydrocarbon charge, in the absence of any substantial degree of hydrocarbon decomposition, with the aid of certain catalysts comprising a modified metal halide of the Friedel-Crafts type in the presence of a cracking suppressor under the conditions described fully herein.

The normally liquid high molecular weight hydrocarbons converted in accordance with the process of the invention comprise broadly the high molecular weight normally liquid isomerizable hydrocarbons, such as, for example, the normally liquid paraffin hydrocarbons of straight chain and/or branched structure having at least 10 carbon atoms to the molecule. Examples of this class of hydrocarbons are, for example, *n*-decane, the several methylnonanes, dimethyl-octanes and ethyloctanes; *n*-undecane, the several methyldecanes, dimethylnonanes and ethylnonanes; *n*-dodecane, the several methylundecanes, dimethyldecanes and ethyldecanes; *n*-tridecane, the several methyl-dodecane, dimethylundecanes and ethylundecanes; *n*-tetradecane, the several methyltridecane, dimethyl-dodecane and ethylundecane; *n*-pentadecane, the several methyltetradecane, dimethyl-tridecane and ethyltridecane; *n*-hexadecane, the several methylpentadecane, dimethyltetradecane and ethyltetradecane; the several trimethyl, methylethyl and propyl isomers of the above normal paraffins and the several diethyl and butyl isomers thereof; further examples are 2-methylheptadecane, 3,12 - diethyltetradecane; 7,8-diethyltetradecane; 5,6 - dibutyldecane; 2-methylnonadecane; 3-ethyloctadecane; 4-propylnonadecane; 2,9 - dimethyl-5,6-diisoamyldecane; 5-butyleicosane; 9-octylheptadecane; 7-butyl-docosane; 9-butyl-docosane; 11-amylnonadecane; 10-nonylnonadecane; 9-octyl-docosane; 11-decyl-docosane; etc.

The high molecular weight normally liquid hydrocarbon charge to the system may consist predominantly of a single hydrocarbon or a mixture

of two or more high molecular weight hydrocarbons. They may be obtained from any suitable source such as, for example, by separation, as by fractional distillation, from naturally occurring hydrocarbon mixtures such as petroleum, or from the distillate products obtained upon the thermal or catalytic treatment of such naturally occurring hydrocarbons, or any other hydrocarbons or carbonaceous materials. Another source of the high molecular weight paraffins comprises the products obtained in the synthesis of hydrocarbons or hydrocarbon-containing materials as, for example, the high molecular weight normally liquid paraffins obtained in the synthesis of hydrocarbons from carbon monoxide and hydrogen, by such methods as the Fischer-Tropsch process and modifications thereof. The high molecular weight hydrocarbon or hydrocarbons need not necessarily be introduced into the system in pure or highly concentrated form and they may comprise a lesser amount of other hydrocarbons capable or not of undergoing conversion under the conditions of the execution of the process. A suitable charge to the system comprises, for example, a high boiling normally liquid hydrocarbon fraction consisting predominantly of paraffinic hydrocarbons having at least 10 carbon atoms to the molecule as obtained by fractional distillation of hydrocarbon mixtures of relatively wide boiling range. The invention is furthermore not limited to the treatment of only the paraffinic hydrocarbons but comprises the conversion of, for example, such isomerizable hydrocarbons as the hydrocarbons comprising an isomerizable alkyl group attached to a cycloparaffinic or aromatic ring.

In order to set forth more fully the nature of the invention, it will be described in detail with reference to the accompanying drawing, wherein the single figure illustrates more or less diagrammatically one form of apparatus suitable for executing the process of the invention.

Referring to the drawing, a normally liquid, high molecular weight, isomerizable hydrocarbon such as, for example, a straight chain paraffin having from ten to sixteen carbon atoms to the molecule, is passed from an outside source through valved line 10 into a conversion zone. The conversion zone may comprise any suitable reactor, or plurality of reactors connected in series or in parallel optionally in combination with soaking vessels or a zone of restricted cross-sectional area such as a coil. In the drawing the reaction zone is represented by reaction chamber 11 provided with suitable stirring means 12. Though the invention is in no wise limited by the type of reactor or reactors employed, those providing intimate contact of catalyst and reactant are preferred. Efficient execution of the process, it has been found, is materially aided by intimate contact, preferably in the form of an emulsion or other dispersion of catalyst and reactants.

In addition to the normally liquid high molecular weight hydrocarbons to be converted, there is introduced into the reaction zone a cracking suppressor. Suitable cracking suppressors comprise any materials capable of suppressing the cracking of hydrocarbons in the presence of the catalysts comprising a modified metal halide of the Friedel-Crafts type, under the conditions of execution of the reaction. The cracking suppressors employed may be normally liquid or normally gaseous materials, as well as normally solid materials which are liquid at the temperature of reaction or which can be adequately dissolved

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In materials liquid at the temperature of reaction. Suitable cracking suppressors comprise, for example, the butanes, the cycloparaffins and alkyl substituted cycloparaffins, such as cyclopentane, methylcyclopentane, ethylcyclopentane, dimethylcyclopentane, cyclohexane, methylcyclohexane, dimethylcyclohexane and ethylcyclohexane, binuclear alicyclic hydrocarbons such as decalin (decahydronaphthalene), hydrindan, methylhydrindan, bicyclopentyl, cyclopentylcyclohexane, bicyclohexyl, dimethylbicyclohexyl, dimethylbicyclohexyl, dicyclo alkyl methanes, dicycloalkylethanes, perhydroanthracene, tricyclopentyl, dicyclopentylcyclohexane, cyclopentylbicyclohexyl, dicyclohexylcyclopentane, tricyclohexyl, and homologs thereof. Other suitable cracking suppressors include saturated terpenes, saturated dicyclopentadienes, adamantane, spirocycloparaffins, and homologs thereof.

A single cracking suppressor or a mixture of two or more cracking suppressors may be employed. The cracking suppressors need not necessarily be introduced into the system in pure or concentrated form, but may comprise other materials such as hydrocarbons having no deleterious effect under the conditions of execution of the process. The cycloparaffinic cracking suppressors may be introduced into the system in the form of cycloparaffin concentrates obtained by separating a cycloparaffin-containing fraction of narrow boiling range from naturally occurring or synthetically produced hydrocarbon mixtures. A dimethylcyclopentanes fraction containing from about 60 to about 85 per cent or more of cycloparaffins is effective as a cracking inhibitor under the conditions employed in the process of the invention.

The cracking suppressor is introduced into the system as such or as a solution in a portion of the charge or in a suitable solvent, by means of a valved line 14. It may be introduced directly into reactor 11. In a preferred method of operation, however, at least a part of the cracking suppressor introduced into reactor 11 is mixed with the high molecular weight paraffins to be converted, prior to their introduction into the reaction zone. To this intent, a valved line 15 is provided for the passage of the cracking suppressor into charge line 10 to mingle therein with the hydrocarbon charge to be converted.

The rate of introduction of cracking suppressor into the system is controlled to effect the suppression of any substantial amount of hydrocarbon decomposition within reactor 11. The proportion of suppressor introduced will vary within the scope of the invention, depending upon the particular suppressor employed as well as the conditions and particular catalyst maintained in reactor 11. A ratio of cracking suppressor to normally liquid hydrocarbons to be converted in reactor 11 of from about 0.5:1 to about 10:1 by weight and higher may be employed. It is preferred, however, particularly when employing hydrocarbons as cracking suppressors, to maintain the ratio of suppressors to normally liquid hydrocarbon to be converted in excess of about 1:1 by weight and preferably in the range of from about 2:1 to about 8:1 by weight. Excellent results are obtained with the aid of the cycloparaffinic cracking suppressors employed in the ratio of suppressor to hydrocarbons to be converted of from about 2:1 to about 5:1 by weight.

Within reactor 11 the reactants are contacted with a modified isomerization catalyst which, in

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the presence of the cracking suppressor, will enable the conversion of the normally liquid high molecular weight hydrocarbons. Suitable catalysts comprise an isomerization catalyst containing a modified metal halide of the Friedel-Crafts type. Modification of the catalyst is essential to the attainment of the objects of the invention. Thus, the use of $AlCl_3$ per se in the absence of inhibitor at a temperature of about $100^\circ C$. will result in substantial decomposition of the high molecular weight hydrocarbons. Addition of sufficient methylcyclohexane to suppress completely any cracking, on the other hand, will generally repress to an inordinate degree the conversion of the high molecular weight paraffins in the presence of aluminum chloride per se. Of the catalysts comprising a modified metal halide of the Friedel-Crafts type, those comprising a halide of aluminum, such as the chloride or bromide or mixtures thereof, are preferred. By the term "modified metal halide" employed throughout the specification, and attached claims, is meant a metal halide which has been modified by combining a portion of it with a reactive material to form a fluid medium in which the remaining metal halide and HCl can be dissolved or suspended in a catalytically active state. The isomerization catalysts, comprising the modified metal halide, employed in the process of the invention, are obtained by combining a metal halide of the Friedel-Crafts type with a suitable modifying agent under conditions resulting in a combination of the metal halide with the modifying agent. The resulting combination may be in the form of an actual complex compound of the metal halide and the modifying agent or in the form of a loose combination in which no actual compound formation between the metal halide and modifier occurs, and the actual compositions and structures of which, because of their complexity, do not lend themselves to ready determination. Suitable modifying agents which are combined with metal halides of the Friedel-Crafts type to result in isomerization catalysts comprising the modified metal halide include, for example, the aromatic hydrocarbons as exemplified by benzene, toluene, dimethyl benzene, trimethyl benzene, ethyl benzene, triethyl benzene, propyl benzene, ethyl propyl benzene, the isopropyl benzenes, the normal butyl benzenes, the tertiary butyl benzenes, the amyl benzenes, the mixed alkyl benzenes, such as ethyl toluene, dipropyl toluene, etc.; aromatic hydrocarbon fractions such as kerosene extracts obtained by the extraction of kerosene with a solvent possessing preferential solvent action for aromatics; aromatic extracts derived from thermally or catalytically cracked, reformed, or dehydrogenated petroleum or synthetic petroleum fractions, cyclic olefins such as cyclopentene or cyclohexene; paraffinic and olefinic hydrocarbons of straight or branched chain structure; halogen substituted paraffin hydrocarbons such as propyl chloride and butyl chloride, organic carboxylic acids of the fatty acid series, such as formic, acetic, propionic, butyric oleic, naphthoic and the like; ethers such as diethyl ether, ethyl phenyl ether, and the like; the esters, such as isobornyl acetate, pyroboric acetate, ethyl benzoate, and the like; organic nitro compounds of which the nitroparaffins, the nitro-aralkyl and the nitroisocyclic compounds such as nitrobenzene, nitronaphthalene, nitromethane, nitroethane, nitrocyclohexane and the like, are representative; alcohols such as isobornyl, glycerine, phenol, ethyl alcohol, pro-

pyl alcohol, isopropyl alcohol, dodecanol and the like; the ketones of aliphatic, aralkyl, aromatic or mixed character, such as acetone, methyl ethyl ketone, methyl propyl ketone, acetophenone, ethyl phenyl ketone, benzophenone and the like, their homologues and substitution products; aliphatic, aralkyl or aromatic carboxylic acid halides, particularly the aromatic carboxylic acid halides as benzoyl chloride, benzoyl bromide, etc.; organic sulphones, such as the aryl and aralkyl sulphones as diphenyl sulphone, benzyl sulphone; organic compounds broadly possessing a dipole moment and capable of reacting with aluminum halides, such as aluminum chloride.

The catalysts comprising a modified metal halide are obtained by combining with stirring one or more of the above catalyst modifiers with the metal halide, such as aluminum chloride, and allowing the mixture to stand at room temperature or at an elevated temperature up to, for example, about 150° C., generally in the presence of an added hydrogen halide, for a sufficient length of time to result in the formation of a liquid, or sludge, consisting essentially of an organo-metal halide complex. Although the above modified catalysts consisting of complex reaction product containing the metal halide are preferred, the invention is in no wise limited to the manner in which the activity of the metal halide is modified.

Thus suitable modified metal halide-containing catalysts are obtained by contacting a metal halide, such as aluminum chloride, with a portion of the hydrocarbon charge in the absence of a cracking suppressor, thereby obtaining a complex reaction product comprising modified aluminum chloride. Another source of modified metal halide catalysts comprises the metal halide-containing complex reaction products obtained during the isomerization of lower boiling paraffins with a metal halide of the Friedel-Crafts type such as aluminum chloride. The aluminum chloride-containing complex mixtures or sludges thus rejected from processes isomerizing lower paraffins which are completely spent with respect to their ability to promote the isomerization reaction are converted to suitable modified aluminum chloride catalysts for use in the present invention by the addition thereto of fresh aluminum chloride.

Other methods of modifying the metal halides to render them suitable in the process of the invention comprise their combination with at least one other metal halide. Thus suitable catalysts comprise a solution of $AlCl_3$ in molten $SbCl_5$; the melts consisting of $AlCl_3$ in combination with a halide of one or more of the following elements: Na, K, or other alkali metals, Zn, etc.

The modified catalyst may be prepared, for example, by the introduction of the modifying agent and the metal halide of the Friedel-Crafts type, such as $AlCl_3$, into a chamber 17. From chamber 17 the modified aluminum chloride is passed to reactor 11 by means of valved line 18. The ratio of catalyst to hydrocarbon within reactor 11 may vary within the scope of the invention. Catalyst to normally liquid high molecular weight hydrocarbon charge ratios may range, for example, from about 1:20 to about 10:1, and preferably from about 1:4 to about 4:1. Higher or lower proportions of catalyst may, however, be employed within the scope of the invention.

The conversion within reactor 11 is preferably executed in the presence of added hydrogen

halide such as, for example, hydrogen chloride, or a material capable of liberating hydrogen halide under the operating conditions. The hydrogen chloride is introduced into reactor 11 by means of a valved line 19. The hydrogen chloride is preferably added in sufficient amount to saturate the reactants in reactor 11 therewith. A lesser or greater amount of hydrogen halide promoter may be employed, however.

The temperature within reactor 11 is maintained in the range of from about 20° C. to about 150° C. and preferably from about 50° C. to about 120° C. Particularly preferred temperatures comprise those in the range of from about 80° C. to about 110° C. The temperature within reactor 11 is maintained by suitable heating means such as, for example, heat exchangers 20 and 21 in lines 10 and 14, respectively. Additional temperature controlling means not shown in the drawing to permit the addition or removal of heat from reactor 11 may be provided. Subatmospheric, atmospheric or superatmospheric pressures up to, for example, about 100 atmospheres, may be maintained in reactor 11. A slightly superatmospheric pressure ranging, for example, from about atmospheric to about 25 atmospheres, is generally preferred. The contact time of catalyst and normally liquid hydrocarbons to be converted may vary considerably within the scope of the invention. The use of a contact time of from about 5 minutes to about 2 hours is satisfactory. A contact time in the range of from about 15 minutes to about 30 minutes is somewhat preferred. Higher or lower contact times may, however, be established within the scope of the invention.

Under the above-defined conversion conditions, straight and branched chain normally liquid hydrocarbons of high molecular weight are converted to normally liquid hydrocarbons of branched or more highly branched structure possessing the same molecular weight as the normally liquid hydrocarbon charge from which they are derived, in the absence of any substantial hydrocarbon decomposition. The straight chain paraffinic hydrocarbons having from ten to sixteen carbon atoms to the molecule are converted to branched paraffins having the same number of carbon atoms to the molecule, comprising high quality Diesel engine fuels, in the absence of any substantial hydrocarbon decomposition. Without intent to limit the scope of the invention by any theories advanced herein to set forth more fully the nature of the invention, it is believed that the effect of the conversion conditions maintained in reactor 11 is to convert the normal and branched chain high molecular weight paraffins charged, to isomers thereof having an increased number of alkyl side chains in which the alkyl side chains formed during the reaction consist essentially only of methyl groups.

Effluent from reactor 11 comprising branched chain normally liquid hydrocarbons of high molecular weight in the Diesel engine fuel boiling range cracking suppressor, catalyst and hydrogen chloride promoter, is passed through valved line 23 into a separating zone, for example, a chamber 24. Within chamber 24 a lower liquid layer comprising catalyst is separated from an upper liquid layer comprising hydrocarbons. The upper layer comprising hydrocarbons, as well as any normally gaseous materials such as hydrogen chloride, is passed from chamber 24 through line 25 and condenser 26 into accumulator 27.

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Liquid comprising catalyst is drawn from chamber 24 and returned through valved lines 29, 30 and 18 to reactor 11. Inlet 31 is provided for the addition of make-up aluminum chloride to the recirculating catalyst. Such addition is preferably controlled to provide sufficient aluminum chloride to the system to combine with excess catalyst modifier present. Catalyst withdrawn from chamber 24 through line 29 is passed in part through valved line 33 into drum 34 wherein it is subjected to reactivation or employed as a component in the production of additional modified catalyst. Removal of spent catalyst from the system may be effected by continuous or intermittent withdrawal from valved line 29.

In a modified form of operation at least a portion of the reactor effluent is diverted from line 23 through valved line 36 into a chamber 37, wherein at least partial separation of catalyst from hydrocarbons is effected. Hydrocarbons at least partially freed of catalyst are passed from chamber 37 through valved lines 38 and 23 into chamber 24. Liquid comprising catalyst is withdrawn from chamber 37 and passed through valved line 39 into valved line 30. The use of at least two separating chambers is advantageously resorted to in view of the desirability of maintaining intimate contact of reactants and catalyst in reactor 11. The maintenance of such a high degree of contact, preferably in the state of an emulsion, is at times aided by the use of the plurality of separators enabling a rapid partial separation, under conditions favorable to such separation, in the first of the separators.

Normally gaseous materials comprising hydrogen chloride may be flashed intermittently or continuously from accumulator 27 and passed through valved line 41 into line 19 leading to reactor 11.

Liquid comprising unreacted charge and reaction products, as well as cracking suppressor and dissolved hydrogen chloride, may be taken from accumulator 27 and passed to any suitable separating zone capable of effecting the separation of reaction products therefrom. Any conventional methods involving one or more such steps as distillation, fractionation, solvent extraction, filtration, etc., may therein be applied. The particular method of product separation will, of course, be governed to some degree by the properties such as the boiling ranges of the components present in the reactor effluent. In the present illustrative presentation of the invention, separation is shown for conditions in which the cracking suppressor is lower boiling than the products of the reaction. Liquid is drawn from accumulator 27 and passed through line 42 into fractionator 43. Within fractionator 43 a fraction comprising normally gaseous material such as hydrogen chloride, and optionally at least a part of the cracking suppressor, is taken overhead through valved line 44 and passed, at least in part, through valved line 19 to reactor 11. A valved line 45 leading into line 19 is provided for the introduction of make-up hydrogen chloride into the system. Bottoms comprising unconverted hydrocarbons and hydrocarbon reaction products are taken from fractionator 43 and passed through line 47 into a fractionator 48. Within fractionator 48 a fraction comprising the cracking suppressor is separated, taken overhead through valved line 49, and passed at least in part through valved line 50 into cracking suppressor charge line 14.

A liquid fraction comprising branched chain paraffins in the Diesel engine fuel boiling range

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and unconverted hydrocarbons is taken from the lower part of fractionator 48 and passed through line 52 into a fractionator 53. Within fractionator 53 branched chain paraffins boiling in the Diesel engine fuel boiling range and having substantially the same molecular weight as the high molecular weight paraffinic charge are separated as an intermediate fraction and removed through valved line 54 as a final product.

A liquid fraction comprising unconverted hydrocarbons is separated from the lower part of fractionator 53 and removed therefrom through valved line 55 and passed into line 10 leading into reactor 11. Material boiling between the boiling range of the branched chain paraffin reaction products and the cracking suppressor, which may have been introduced into or formed within the system, is separated as vapor fraction within fractionator 53 and removed overhead therefrom through valved line 56. Material thus eliminated overhead from fractionator 53 through valved line 56 may be returned in part or entirety to the reactor 11. To this effect a valved line 57 leading from line 56 into line 55 is provided.

For the purpose of clarity, parts of apparatus such as, for example, pumps, valves, accumulators, reboilers, reflux circuits, and other auxiliary equipment not essential to a full and complete description of the invention, have been omitted from the drawing. The separation indicated above, as effected within certain fractionators shown in the drawing, may in practical operation involve the utilization of a greater number of fractionators.

Although the above-detailed description of the invention has stressed the use of normally liquid cracking suppressors, it is to be understood that the invention is not limited to the use of only this specific type of cracking suppressor. Thus, in a modification of the invention, the cracking suppressor may comprise, for example, a normally gaseous suppressor such as hydrogen in addition to the hydrocarbon suppressor. Such gaseous cracking suppressors may be introduced into the system by means of a valved line 59 leading into reactor 11. Other materials which may be introduced into the reaction zone in addition to the hydrocarbon cracking suppressor employed comprise, for example, a metal capable of inhibiting cracking under the operation condition such as, for example, fragmented, granular or powdered aluminum. Additional suitable cracking suppressors comprise, for example, one or more of the following which are preferably added to the reaction zone in an amount ranging from about 0.5% to about 3% by weight of the normally liquid hydrocarbons charged: benzene and alkyl-substituted benzenes such as, for example, toluene, the xylenes, ethyl benzene, propyl benzene, isopropylbenzene, tetramethylbenzene, pentamethylbenzene, hexamethylbenzene, naphthalene.

When employing in addition to the hydrocarbon suppressor a normally solid cracking suppressor, diluent material may be employed in sufficient amount to assure intimate contact of catalyst and reactants in reactor 11, or to facilitate the flow of reactants through the system. Suitable diluent materials which may be employed comprise, for example, normally liquid solvents, or normally gaseous as well as normally solid solvents which are in the liquid state under the operating conditions and which have no adverse effect upon the execution of the reaction. Suitable solvents which may be employed in addi-

tion to the cracking suppressor comprise, for example, the paraffins such as propane, normal pentane, isopentane, neopentane and hexanes. The use of such diluents, in relatively small amounts, in addition to a normally liquid cracking suppressor may be used within the scope of the invention.

The ability to enable the conversion of substantially all of a high molecular weight hydrocarbon charge to branched and/or more highly branched paraffins in the absence of any substantial hydrocarbon decomposition, provides a highly economical method for the production of relatively pure high molecular weight branched chain hydrocarbons on a practical scale. An advantage of the process resides in the ability to control within a wide range the degree of branching of the final product. Thus the degree of branching of the final product is increased by lengthening the contact time or by the recycling of insufficiently branched product through the reaction zone. The process of invention is, however, of particular value in its ability to prepare high quality Diesel engine fuels as determined by heating value, ignition value and pour point, from readily available hydrocarbon materials on a practical scale with an unusually high degree of efficiency. Thus the readily available normally liquid high molecular weight paraffinic hydrocarbons of low pour point and cetane number are converted by means of the invention to branched chain products combining a relatively high cetane number with a low pour point. Readily available paraffinic hydrocarbon fractions predominating in straight chain paraffins having from about ten to sixteen carbon atoms to the molecule, as obtained by fractional distillation of naturally occurring hydrocarbon mixture and possessing cetane values of the order of from about 20 to 100 are readily converted in the absence of any substantial hydrocarbon decomposition by means of the process of the invention to high quality Diesel engine fuels having a cetane number of from about 50 to about 90 and a pour point below about -10° C. A particular advantage of the invention resides in the ability to control within a wide range the pour point of the final product. Thus the pour point of the final product is lowered materially by increasing the contact time or by recycling the product of insufficiently low pour point through the reaction zone until a sufficiently low pour point is obtained. A particularly valuable application of the process of the invention resides in the conversion of Diesel engine fuels materially to lower the pour point thereof. Thus Diesel engine fuels, which though possessing high ignition values, are handicapped by insufficiently low pour points, when treated in the process of the invention are converted to a product of materially reduced pour point without any substantial degradation of desirable qualities such as ignition and heating values. Thus the processing of hydrocarbons in the Diesel fuel boiling range in the process of the invention enables the efficient reduction of a pour point, for example, in the range of from about 0 to about 18° C. to one as low as -60° C. and lower. The ability to control within a wide range such properties as the pour point of relatively pure hydrocarbons in the Diesel fuel boiling range, as well as mixtures thereof, in the absence of any substantial hydrocarbon decomposition, renders the process of particular value in the production of products valuable as blending agents for Diesel engine fuels deficient in such properties.

The products of the process of the invention are, however, not limited to their use to Diesel fuels, but are of value wherever normally liquid high molecular weight branched hydrocarbons are applied. Thus the branched paraffins of high molecular weight obtained in accordance with the process of the invention are of particular value as components in insecticides and spray oils generally. The process of the invention provides a valuable means for increasing the octane rating of motor fuels in the gasoline boiling range by enabling the more efficient conversion of the straight chain paraffins having from ten to twelve carbon atoms to the molecule to the branched chain isomers thereof possessing substantially superior ignition values. Straight chain paraffins having from ten to sixteen carbon atoms to the molecule are efficiently converted by means of the invention to branched chain isomers thereof of valuable in the production of aviation safety fuels.

The following examples are illustrative of the present invention:

Example I

A modified aluminum chloride catalyst was prepared by reacting 500 grams of tertiary butyl chloride with 200 grams of anhydrous aluminum chloride at room temperature and stirring until evolution of HCl ceased. To 125 grams of the resulting mixture there was added an additional 50 grams of anhydrous $AlCl_3$. 100 grams of n-cetane in admixture with 400 grams of cyclohexane was contacted with vigorous stirring with the modified $AlCl_3$ catalyst thus obtained at 100° C. and 30 minutes contact time. The hydrocarbon layer was decanted from the reaction mixture, washed with hot water, and distilled to remove cyclohexane and traces of hydrocarbon by-products formed during reaction. The residue, boiling above 250° C., was fractionally crystallized from 10 volumes of methyl ethyl ketone at -35° C. to remove unreacted cetane, and an oily product equivalent to 28% conversion based on the cetane charged was recovered by flashing off the methyl ethyl ketone solvent. The boiling range of the product was 250° C. to 286° C., refractive index n_D^{20} 1.4355, pour point -30° C., bromine number 0.0.

Example II

In a series of experiments cetane was catalytically isomerized in the presence of four parts by weight of cyclohexane under the conditions set forth in Example I with the exception that the temperature and contact time indicated in the following for each of the runs were employed. The conversion of cetane to isocetane obtained in each of the runs was determined and is set forth in the following table:

Temperature, $^{\circ}$ C.	Contact Time, Min.	Percent Conversion to Isocetanes
65	60	26.5
75	60	30.2
75	30	19.0
85	30	24.8

The isomerized products from these experiments were combined and tested as a Diesel fuel. The pour point of the composite sample was -24° C.

Example III

In a series of experiments cetane was con-

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tacted with vigorous stirring with a modified aluminum chloride catalyst, prepared as set forth in Example I, at a temperature of 100° C. The contact time employed in each run was controlled to result in a reaction of 30% of the cetane charged. In one of the experiments no cycloparaffin inhibitor was employed. In the remainder of the runs methylcyclohexane was admixed with the cetane charge. The weight ratio of methylcyclohexane inhibitor to cetane charge, the conversion of cetane to isocetanes in per cent and the yield of isocetanes in per cent for each of the experiments is indicated in the following table:

Wt. Ratio of Methylcyclohexane to Cetane	Per Cent Conversion to Isocetanes	Per Cent Efficiency of Reaction
0	0	0
1:4	10.2	34
2:1	22.5	75
4:1	26.4	88
8:1	29.1	97

The invention claimed is:

1. A process for the production of high quality Diesel engine fuels which comprises contacting hydrocarbons comprising straight chain paraffins having from ten to sixteen carbon atoms to the molecule with a preformed catalyst comprising an aluminum chloride-hydrocarbon complex in the presence of a cycloparaffinic hydrocarbon at a temperature of from about 20° C. to about 150° C., and maintaining the ratio of said cycloparaffin to said paraffins in the range of from about 2:1 to about 8:1 parts by weight, thereby effecting the conversion of said straight chain paraffins to branched chain paraffins having substantially the same molecular weight and possessing a high ignition value and low pour point, in the absence of any substantial hydrocarbon decomposition.

2. A process for the production of high quality Diesel engine fuels which comprises contacting hydrocarbons comprising straight chain paraffins having from ten to sixteen carbon atoms to the molecule with a preformed catalyst comprising an aluminum halide-hydrocarbon complex in the presence of a saturated cyclic hydrocarbon at a temperature of from about 20° C. to about 150° C. and maintaining the ratio of said cyclic hydrocarbon to said straight chain paraffins in the range of from about 2:1 to about 8:1 parts by weight, thereby effecting the conversion of said straight chain paraffins to branched chain paraffins having substantially the same molecular weight and possessing a high ignition value and low pour point, in the absence of any substantial hydrocarbon decomposition.

3. A process for the production of high quality Diesel engine fuels which comprises contacting hydrocarbons comprising straight chain paraffins having from ten to sixteen carbon atoms to the molecule in the presence of an amount of alicarbocyclic hydrocarbons at least equal by weight to said straight chain paraffins at a temperature of from about 20° C. to about 150° C. with a preformed catalyst comprising an aluminum halide complex obtained by the interaction of an aluminum halide and an organic compound, thereby effecting the conversion of said straight chain paraffins to branched chain paraffins having substantially the same molecular weight and possessing a high ignition value and low pour point, in the absence of any substantial hydrocarbon decomposition.

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4. A process for the production of high quality Diesel engine fuels which comprises contacting isomerizable hydrocarbons consisting essentially of normally liquid paraffinic hydrocarbons having at least ten carbon atoms to the molecule in the presence of an amount of alicarbocyclic hydrocarbons at least equal by weight to said isomerizable hydrocarbons at a temperature of from about 20° C. to about 150° C. with a preformed complex catalyst comprising a metal halide of the Friedel-Crafts type obtained by the interaction of a metal halide of the Friedel-Crafts type and an organic compound, thereby converting said isomerizable hydrocarbons to a branched chain hydrocarbon Diesel fuel having a low pour point and a high ignition value in the absence of any substantial hydrocarbon decomposition.

5. A process for lowering the pour point of a hydrocarbon Diesel engine fuel without substantially altering the molecular weight thereof in the absence of any substantial hydrocarbon decomposition which comprises contacting said hydrocarbon Diesel engine fuel with a catalyst comprising aluminum chloride-hydrocarbon complex in the presence of an amount of cycloparaffinic hydrocarbons equal to from about 2 to about 8 times the weight of said Diesel engine fuel at a temperature of from about 20° C. to about 150° C.

6. A process for the conversion of a straight chain paraffin having from ten to sixteen carbon atoms to the molecule to a branched chain paraffin having substantially the same molecular weight in the absence of any substantial hydrocarbon decomposition which comprises contacting said straight chain paraffin in the presence of a promoter affording a hydrogen halide under the conditions of execution of the reaction and of an amount of cycloparaffinic hydrocarbons equal to from about 2 to 8 times the weight of said straight chain paraffin with a preformed catalyst comprising an aluminum halide-hydrocarbon complex at a temperature of from about 20 to about 150° C.

7. A process for the conversion of normally liquid straight and branched chain paraffins having at least ten carbon atoms to the molecule to branched and more highly branched paraffins respectively having the same molecular weight as said paraffins charged in the absence of any substantial hydrocarbon decomposition which comprises contacting said normally liquid paraffin hydrocarbons at a temperature of from about 20° C. to about 150° C. and in the presence of a hydrocarbon decomposition suppressor consisting essentially of a saturated cyclic hydrocarbon present in an amount at least equal by weight to said normally liquid paraffins with a preformed metal halide complex obtained by the interaction of a metal halide of the Friedel-Crafts type with an organic compound.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,382,815	Sutton et al.	Aug. 14, 1945
2,393,104	Grosse et al.	Jan. 15, 1946
2,404,436	Crawford et al.	July 23, 1946
2,406,634	Pines et al.	Aug. 27, 1946