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REACTION OF PARAFFINIC
HYDROCARBONS

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This invention relates to improvements in the production of highly desirable components of motor fuels and pertains particularly to the production of relatively low boiling saturated aliphatic hydrocarbons which have been found to be useful in the production of gasolines.

It has heretofore been proposed to produce motor fuel constituents and motor fuel according to a number of well known processes, such as thermal and catalytic cracking of heavier hydrocarbons, polymerization and then hydrogenation of normally gaseous olefins, treating of crude and straight run gasoline cuts with olefins to improve their octane number by alkylating the aromatic constituents thereof with the olefins, etc. It has been found possible to react paraffinic hydrocarbons with olefins to produce saturated hydrocarbons boiling within the motor fuel range. This reaction has been denoted as alkylation. It is then readily apparent that a saturated branched chain normally liquid paraffin may be produced directly by alkylating a normally gaseous branched chain paraffin, for example, isobutane, by treating such a compound with a normally gaseous mono-olefin without the necessity of including a subsequent hydrogenation treatment in the process as would be the case where a polymerization process had been used.

Another advantage of the use of an alkylation process in contrast to the well known polymerization process lies in the fact that the petroleum industry is constantly seeking methods whereby it may be possible to utilize by-products of the industry and in this respect, alkylation is a distinct advance in the art. Large supplies of field butanes, refinery C₄ cuts from cracking units, debutanizer units, etc., each containing substantial quantities of gaseous olefins and paraffins both straight and branched chain are available. Such gaseous mixtures have heretofore been fed to polymerization processes which are able to utilize only the olefinic content of the mixtures. In consequence, the industry has found it expedient to dehydrogenate the inert paraffinic gases coming from such units, to convert them to olefins and to then refeed these olefin containing gases to the polymerization process. Such a procedure is obviated in a comparable alkylation process, the prior dehydrogenation and subsequent hydrogenation necessary on the polymerization process being wholly eliminated, yet a gasoline having improved octane number is produced.

Still another advance has been made in the alkylation of paraffins. It has been above-stated that the alkylation process involved the reaction

of a paraffin with an olefin to produce a paraffinic compound. It has now been discovered that analogous results may be accomplished by effecting a reaction between two paraffins, one of which is branched chain or between 2 mols of a single isoparaffin. It is preferable to have the reactants contain branched chains but it is not essential to success of the reaction that this condition prevail as to all the reactants, but it is necessary that at least one of the paraffins contain at least one tertiary carbon atom.

It is an object of the present invention to react a paraffin with a paraffin in such manner as to produce saturated liquid hydrocarbons.

It is a further object of the invention to react liquid paraffinic hydrocarbons of relatively low octane number with normally gaseous branched chain paraffins containing at least one tertiary carbon atom to produce motor fuels of improved octane number.

It is a still further object of this invention to produce a mixture of liquid saturated hydrocarbons suitable for use in motor fuels by reacting waste paraffinic refinery gases with liquid branched chain paraffins in the presence of alkylation catalysts and at temperatures below that at which the reactants substantially thermally decompose.

To accomplish such objects, it is a feature of the present invention to carry out the reaction under optimum reaction conditions in the presence of alkylation catalysts which have been found to be particularly effective in promoting the desired reaction. It is obvious that the optimum reaction conditions will vary for each particular catalyst employed. In general, it may be said that reaction conditions are favored when the feed rates are adjusted to provide longer contact time than would be used in corresponding polymerization reactions. Production of saturated hydrocarbons was also noticeably favored by more intimate contact between the reactants. The feed stock therefore is preferably introduced into the reaction zone through jets, porous thimbles, turbomixers and the like.

It was also found to be advantageous for the production of a high quality motor fuel, to return the heavier hydrocarbon fractions and those fractions boiling intermediate the reactants and the desired motor fuel fraction removed from the process as the final product, to the reaction zone. However, it is sometimes desirable to leave the products formed intermediate the reactants and the desired fraction in the final product since these lighter saturated hydrocarbons are readily

volatilized and have excellent anti-knock properties, in general. Likewise, any unreacted reactants are separated from the fractions desired and returned to the reaction zone. Increased yields of the desired fraction result whether this recycle step is carried out continuously or intermittently, whether only part or all of the recycle stock is fed into the alkylation zone together with the fresh feed.

The invention is not limited to the use of reactants from any particular source. Single hydrocarbons may be employed, such as isobutane, isopentane, etc. However, it is commercially more feasible to use mixtures of hydrocarbons containing the essential paraffinic constituents. As the normally gaseous paraffins used, the butanes and pentanes may be employed. Where the liquid paraffin used is a straight chain compound, then branched chain pentanes and/or isobutane or mixtures containing at least one of them are usually employed. Field butanes may be used directly or may be used after first having been subjected to a catalytic polymerization or alkylation reaction to remove substantially all of their olefinic content. Likewise refinery C_3 - C_5 and C_6 cuts after being treated to alkylating or polymerizing conditions, having had their olefinic content substantially depleted, are suitable sources of supply of the gaseous paraffins used as reactants in the present invention's process. The normally liquid paraffins used may be either straight or branched chain compounds, but at least one of the reactants should be a branched chain compound, preferably a compound containing a tertiary carbon atom where the other employed is a straight chain hydrocarbon. In the preferred embodiment of the invention, both types of reactants may contain tertiary carbon atoms in their molecules although the reaction of other branched chain compounds is contemplated. Paraffins ranging from the hexanes to the dodecanes either as single chemical compounds or as mixtures with others of the same homologous series or admixed with inert compounds may be used as reactants in the process of the present invention. Mixtures of branched chain and straight chain liquid paraffins may be satisfactorily employed. Thus isooctane and normal heptane may be employed together with isobutane as a suitable reaction mixture. Isododecane, isobutane and butane; isodecane and isopentane; etc. are suitable reaction mixtures as well. A preferred mixture for use as the liquid paraffinic reactant of the present invention is obtained from the catalytic alkylation of isobutane with isobutylene, its polymers, copolymers, etc., separation of the desired gasoline fraction and the isolation of the C_6 and heavier fraction, for use in the present invention. Specifically, the following may serve as the liquid paraffins useful in the reaction although it is to be distinctly understood that this enumeration is but representative and it is not intended that the operation of the invention be restricted to these compounds or mixtures containing the same. 2-methyl pentane, 3-methyl pentane, 2-3 dimethyl butane, 2-2 dimethyl butane, n-hexane, 2 methyl hexane, 3 methyl hexane, 2 ethyl pentane, 3 ethyl pentane, 2,3 dimethyl pentane, 2,4 dimethyl pentane, 2,2 dimethyl pentane, 3,3 dimethyl pentane, and higher homologues may be used either separately or in mixtures of one or more. In particular, however, the invention is directed to the use of liquid hydrocarbons containing a total of six or

more carbons in each molecule and of low octane values and their normally liquid isomers.

To insure high yields of products it is preferred to have at least 2 mols of normally gaseous paraffin present in the reaction mixture for each mol of the normally liquid present. In cases where, for example, an isododecane is reacted with isobutane, it is preferred to have present at least three mols of the latter per mol of the former. In most instances it is advisable to have an excess of the normally gaseous paraffin over that amount theoretically required. Thus, where isooctane is reacted with isobutane, from about two to ten mols, or even more, of isobutane may be present per mol of isooctane. The same degree of molecular excess is equally applicable in the alkylation of isobutane using heavier liquid paraffins such as an isododecane.

More specifically, it has been found that certain catalysts effectively promote such alkylation reactions. Thus the invention contemplates the use of halides of metals such as aluminum, zinc, antimony, tin, iron, nickel, tungsten, tantalum, zirconium, molybdenum, etc., specifically the chlorides and bromides of these metals or mixtures of these, or mixed with small amounts for example, between about 2.2 and about 11.5% by weight based on the feed stock, of an alkyl halide such as ethyl chloride, propyl chloride, tertiary butyl chloride, tertiary or secondary amyl chloride, the bromides thereof, etc. The ethyl halides promote the activity of these catalysts, their effect being to increase the formation of lower boiling saturates at the expense of higher boiling paraffins.

Another particularly desirable catalyst is the metal halide-aluminum halide complex wherein the aluminum halide is present in from about 0.5 to about 2.5 moles per mol of other metal halide. Specifically $AlCl_3$ - $NaCl$ in varying molecular proportions has been found to be a particularly effective catalyst. Likewise, a catalyst composed of KBr - $FeCl_3$ complex has been very effective in promoting alkylation. Other similar double salt complexes which are within the scope of the invention are lithium chlor aluminate, antimony brom aluminate, sodium brom aluminate, mercury brom aluminate, potassium chlor aluminate, etc., each in the varying molar ratios above designated. These complex double salts may be prepared by mixing the alkali metal halide, alkaline earth metal halide or other corresponding metal halide, for example, sodium chloride, with slightly more aluminum halide, for example, aluminum chloride, than is necessary for the catalyst of the desired mol ratio. The excess aluminum chloride is added in order to compensate for losses due to volatilization on heating. The mixture is heated in an open vessel until fusion occurs and a clear liquid results. At a temperature of 400-450° F. some solid sodium chloride usually is present and the liquid portion of the mixture is therefore poured off through a wire gauze.

Another catalyst found to be highly useful in the process of the present invention is concentrated sulfuric acid. It is preferred to use this catalyst in concentrations of between about 70 and 110%, usually about 96-98% concentration. Organic metallic compounds, such as methyl aluminum chloride and dimethyl aluminum chloride are also suitable catalysts for the reaction.

The above mentioned catalysts, as well as any number of well known alkylation catalysts not specifically mentioned hereinbefore, but nevertheless suitable for use in the process of the invention, may advantageously be impregnated or

deposited upon carriers either inert or activated. Suitable aluminous and/or siliceous carriers are activated alumina, silica gel, bauxite, fuller's earth, bentonite, kieselguhr, pumice, celite, Sil-O-Cel, infusorial earth, montmorillonite, Marsil clays, Tonsil, Super Filtrol, activated Floridin, etc. These substances not only serve as excellent carriers for alkylation catalysts, but in many instances, they serve as highly useful catalysts when used alone. These clays of the bentonite and montmorillonite type acid activated according to the process of Chappell et al. U. S. Patent 1,642,871, September 20, 1927, are particularly desirable. Clays have also been found to be advantageously used when they contain small percentages of alkyl halides, for example, tertiary butyl chloride.

In cases where the double salt type complex is used as the catalyst it has been found that they eventually lose their catalytic alkylation activity under the operating conditions of the invention. Any suitable reactivation or regeneration process may be employed, for example, treatment of the catalyst mass with inorganic acidic gases such as the hydrogen halides, HCl, HBr, or the free halogens, Cl₂ and Br₂ or by treatment with heat and pressure to free the pores of the catalyst mass of residual heavier hydrocarbon compounds and decomposition residues that accumulate during the alkylation process. Such a process of reactivation is also applicable in the cases where activated clays or catalytically impregnated activated clays are used.

The reaction may be carried out at temperatures ranging from between about 0° F. to about 550° F. and under pressure ranging from between about atmospheric to about 3000 lbs./sq. in. gauge and at a throughput of between 0.5 and about 7.0 volumes/volume of catalyst/hour.

The reaction may be materially assisted if a dehydrogenation catalyst is admixed with the alkylation catalyst. Such catalysts as chromium oxide, chromium oxide-aluminum oxide, silica gels or precipitates impregnated with the salts of nickel, chromium, aluminum, vanadium, or other dehydrogenating metals, may be admixed with the alkylation catalysts in an amount between about 0.2% and about 25% of the total alkylation catalyst. It is, however, not advisable to mix such dehydrogenation catalysts with a strongly basic or strongly acidic alkylation catalyst, since it would obviously defeat the very purpose for which they are added to have such catalysts react with acids or alkalis to any appreciable extent.

No particular provision has been made for collecting and utilizing the hydrogen evolving during the alkylation, although it, together with any other gaseous by-products may be collected and used in any convenient manner such as, for example, in hydrogenating polymers of olefins to saturated compounds.

Experimental evidence points to the theory that the liquid paraffin, in the presence of the alkylation catalyst and under the reaction condition obtaining, is split to yield low boiling saturates and unsaturates, the unsaturates then reacting with the normally gaseous isoparaffin present to produce saturated liquid hydrocarbons of increased branchiness of the chain thereby creating a compound of enhanced octane number. While some such mechanism is required to explain the yield of 168% based on the weight of isooctane in the feed stock, see subsequent Example 1, it is

nevertheless to be distinctly understood that the invention is not limited to any theory of operation and is restricted only to the extent indicated by the appended claims.

No specially designed apparatus is necessary for the successful operation of the invention. Conventional apparatus now customarily used in effecting acid polymerization and catalytic alkylation reactions is quite suitable. Provision, however, should be made for the regular and controlled escape of hydrogen evolved during the alkylation process of the invention, especially in cases where dehydrogenation catalysts are employed. In the case of effecting alkylations under pressures of 1800 to 3000 lbs./sq. in. and temperatures of around 400-500° F. it has been found to be advantageous to introduce the reactants into the catalyst chamber from the top and allow them to flow through the reactor in a downward direction, whereas, in cases where the alkylation proceeds at room temperatures slightly below or up to 50° F. and under substantially atmospheric pressure and up to 1000 lbs./sq. in. it is advantageous to introduce the reactants into the catalyst chamber at the bottom and remove the reacted mixture from the top of the reactor. C₄ saturates and liquid saturates are thus fed to the reactor containing the desired alkylation catalyst. In cases where a once-through passage of reactants through the reactor is not sufficient to effect complete reaction they may be conveniently recycled through the reactor any number of times sufficient to effect substantially complete reaction. The reacted mixture, under at least sufficient pressure to maintain the reactants as well as reacted products in a liquid state is passed to a stabilizer (fractionating tower) where the unreacted reactants are separated and returned to the original feed line. The bottoms may then be further fractionated and the heavier ends likewise recycled to the original feed line to suppress any substantial further formation of such compounds. The fraction distilling over from this second fractionation step contains the desired C₅-C₈ product and may have an end point of about 400° F.

It is apparent that the process and conventional apparatus readily lend themselves to the carrying out of a continuous process and it is within the spirit and scope of this invention to so carry out the novel alkylation.

The following examples are intended to be only illustrative of the invention and are in no way considered to be limiting the scope of the invention hereinbefore disclosed.

Example 1

Into a continuous unit having a catalyst chamber holding 100 cc. of sodium chloride-aluminum chloride mixture made up in a ratio of 1 mol of NaCl to 1.8 mols of AlCl₃, the mass being deposited on celite, there was introduced a feed stock consisting of 89.8% isobutane and 10.2% isooctane. This feed, while at 3000 lbs./sq. in. and at 400° F., was passed through the catalyst chamber at 3 volumes/volume of catalyst/hour continuously. The resulting product, after separation from the unreacted reactants, constituted 168% yield based upon the original isooctane in the feed stock, had a bromine number of 20, and contained 90% by weight of saturates. It was fractionated into the following cuts: 22% C₅ fraction, 5% C₆ fraction, 8% C₇ fraction, 40% C₈ fraction, and 25% C₉ and heavier fractions.

Example 2

Into a suitable pressure vessel a mixture of 88% isobutane and 12% isooctane was treated with a mixture of aluminum chloride containing 3.2% by weight of the total reactants of tertiary butyl chloride. The amount of catalyst used represented 14.1 grams per 100 grams of feed stock and only sufficient pressure was maintained to keep the reaction medium liquid at the reactive temperature of 15° F. After 4.5 hours had elapsed the reacted product was freed of unreacted reactants and the isolated product was obtained in a 74% yield based upon the weight of the isooctane treated. The product had a bromine number of 1 and was 99% saturated. It fractionated to 20% by weight of C₅—C₇ cut, 70% C₈ cut and 10% C₉ and heavier hydrocarbon cut.

Example 3

Into a continuous unit having a catalyst chamber holding 100 cc. of sodium chloride-aluminum chloride mixture made up in a ratio of 1 mol of NaCl to 1.7 mols of AlCl₃ deposited on celite, there was introduced a feed stock comprising 9.3% normal heptane and 90.7% of isobutane. This feed at 2000 lbs./sq. in. gauge and at 400° F. was passed through the catalyst chamber at 3 V./V./hour continuously. The resulting product, after separation from the unreacted reactants, constituted 179% yield based upon the original heptane in the feed stock, had a bromine number of 27 and contained 85% by weight of saturates. It was fractionated into the following cuts or fractions: 50% C₅—C₇ fractions, 40% C₈ fraction, and 10% C₉ and heavier fractions. The final boiling point of the total product was 401° F.

It is to be understood that where mention is made of "double salt complex" or the equivalent thereof in the description or in the claims, it is intended to include the mixtures of metal halide-aluminum halide compositions containing other than requisite molecular quantities of each component for known complex salts although it is realized that such mixtures may not be true double salt complexes but may be, at least partially, physical mixtures thereof. The description and claims are to be construed in such a light for want of a more convenient term to cover the catalysts involved.

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

1. A process for the production of a composi-

tion composed predominately of saturated normally liquid hydrocarbons boiling in the gasoline range which comprises reacting isobutane with a relatively high molecular weight acyclic paraffin in the presence of a metal halide-aluminum halide double salt complex, wherein the metal is other than aluminum.

2. A process as in claim 1 wherein the catalyst is deposited upon celite and wherein the mol ratio of aluminum halide to other metal halide is between about 1.1 and about 2.0 to 1.

3. A process for the production of a composition composed predominately of saturated liquid hydrocarbons boiling within the gasoline range which comprises reacting isobutane with isooctane in the presence of NaCl—AlCl₃ double salt complex supported on celite, the mol ratio of AlCl₃ to NaCl being between about 1.1 and about 2.0 to 1, at a temperature between about 300 and about 500° F. at a pressure between about 1000 and about 3000 lbs./sq. in. gauge at a throughput of between about 0.5 and about 7.0 volumes/volume of catalyst/hour.

4. A process as in claim 3 wherein the isooctane is replaced by normal heptane.

5. A process for the production of a composition composed predominantly of saturated, branched chain, normally liquid hydrocarbons boiling in the gasoline range which comprises reacting at least one low boiling isoparaffin with at least one normally liquid paraffin of different molecular weight than the low boiling isoparaffin, under alkylation reaction conditions in the presence of a metal halide-aluminum halide double salt complex wherein the metal is other than aluminum.

6. A process for the production of a composition composed predominantly of saturated, branched chain, normally liquid hydrocarbons boiling in the gasoline range which comprises reacting an isoparaffin of less than six carbon atoms per molecule with a normally liquid paraffin of at least six carbon atoms per molecule under alkylation reaction conditions in the presence of a metal halide-aluminum halide double salt complex wherein the metal is other than aluminum.

7. A process as in claim 6 wherein the catalyst employed is sodium chloride-aluminum chloride double salt complex supported on celite, the mol ratio of aluminum chloride to sodium chloride being about 1.1:1 to about 2.0:1.

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