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PROCESS FOR MANUFACTURE OF
BRANCHED CHAIN ALIPHATIC
COMPOUNDS

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This invention relates to the manufacture of branched chain aliphatic compounds by an improved method from straight chain aliphatic compounds derived from hydrocarbons occurring largely in natural gas and light distillates of crude petroleum. More particularly, it has to do with an efficient transformation of olefinic and water-soluble oxygenated derivatives of straight chain aliphatic hydrocarbons into more complex hydrocarbons of high anti-knock value and high solubility in hydrocarbon oils.

With augmented production of normally gaseous hydrocarbons and their low molecular weight oxygenated derivatives, a need has arisen for changing these products into better utilizable liquid fuels for automotive engines. In my Patent No. 2,175,359 of October 10, 1939, is disclosed a very useful method for obtaining high octane number fuels from such products, but improvements in this method were found desirable for increasing the yield rate.

A principal object of this invention is to provide a more efficient catalytic reaction for converting low molecular weight aliphatic compounds into the desired more complex compounds of improved motor fuel value with increased yield rates, as will be explained fully hereinafter.

One of the principal features in obtaining this object involves what may be briefly termed a co-alkylation of the aliphatic reactants into iso-aliphatic compounds of lower oxygen content. While the complete mechanism of the reaction in high probability involves many other inter- and intramolecular changes, from results obtained, it may be analyzed as involving a condensation of the oxygen containing aliphatic compounds with one another and partly with any olefins present, the condensation ostensibly not being accompanied by splitting out of water molecules. By use of the carbon monoxide and/or olefin reagents to control the process, the oxygen atoms, which ordinarily are forced out in combination with hydrogen, are made to combine to any desired extent with carbon monoxide and olefins, thereby forming hydrated, oxygenated, or carboxylated olefin derivatives which, also, must enter into the condensation reaction. This reaction calls for the use of specific types of catalysts to direct the reaction in a reducing atmosphere of a restricted water vapor content and in the presence of gaseous reagents which actively suppress the formation of water vapor.

In accordance with this novel method low molecular weight normal alcohols and their analogous higher oxidation derivatives, such as ketones and

acids, are transformed into higher boiling iso-aliphatic compounds, the starting materials being obtained for example by methods outlined in my Patent No. 2,175,359 and in my co-pending application Serial No. 268,286 of April 17, 1939, but preferably by a restricted partial oxidation of unsaturated and highly volatile hydrocarbon products formed in a cracking or reforming operation, or synthesized by reduction of carbon monoxide. The thus obtained products may include in addition to normal alcohols such as methyl, ethyl, propyl and butyl alcohols varying amounts of ketones, aldehydes, acids and aliphatic hydrocarbons containing from 1 to about 6 carbon atoms per molecule, i. e., compounds boiling chiefly below 300° F. or lower boiling than heavy ends of gasoline.

The straight chain oxygen containing aliphatic compounds, including compounds such as normal alcohols, aldehydes, ketones and esters are brought into contact with the catalysts admixed with suitable gaseous reagents and with their water vapor content limited to as low an amount as possible. More particularly, the water vapor content of the gaseous mixture should be held below 8 per cent by volume, and preferably below 5 per cent by volume to prevent poisoning of the catalyst and retarding of the reaction.

The reactants are brought into contact with a catalyst having a high dehydrating and co-alkylating power. A catalyst of this type is in general selected from groups of hygroscopic compounds which contain a strong mineral acid radical, most notably a sulphuric or phosphoric acid radical, for example, the anhydrous acids and their salts, to wit; sulphates and phosphates of magnesium, calcium, aluminum and other common metals, more generally of the di- and trivalent metals. The compounds may contain combinations of metals as in copper uranium phosphate and may contain the simple and complex forms of the acid radicals as for example the pyro-phosphate, the ortho-phosphate and heteropoly acids. In place of or supplementary to the salt type catalysts which may include also non-volatile hygroscopic salts, salts of other acids such as salts of halogen acids (metal halides such as aluminum chloride or boron fluoride, which readily react with water to form hydrogen halides), carbonic acid, etc., and difficultly reducible dehydrating metal oxides may be employed, e. g., thoria, alumina, and magnesia.

In reacting aliphatic compounds comprising normal aliphatic acids, e. g., acetic, propionic, and butyric, or similar oxygenated acid forming substances, it is desirable to have present alkaline

compounds capable of saponifying fatty acids or of combining with acyl groups.

The catalyst may be advantageously used supported by an adsorptive carrier, either one that is relatively inert or one that has catalytic dehydration activity, e. g., unglazed porcelain, activated charcoal, clay, asbestos, diatomaceous earth, weathered or hydrolyzed feldspar, kieselguhr, silica gel, and the like. The catalysts to be used with these carriers prepared by methods which make them highly water absorbent are compounds having relatively high or predominating dehydrating activity.

In the selection of a catalyst for the present purposes a chief desideratum is that the catalyst mass have a strong dehydrating action with little reducing or hydrogenating activity. For this reason it is desirable to omit metals of the iron group and to use compounds of trivalent heavy metals in minor proportions. However, the co-alkylation catalyst may have a limited amount of hydrogenating activity which is preferably supplied by trivalent heavy metal oxides, e. g., chromic oxide, tungstic oxide, etc. A mixture of a divalent metal oxide with a trivalent metal oxide may be used with the catalyst favoring hydrogenation present in a minor proportion, for example, the catalyst may contain 80 to 90 per cent of magnesia and 10 to 20 per cent of chromic oxide.

Avoidance of more than a minor amount of hydrogenation appears to be desirable in order to prevent active olefinic and oxygen containing compounds from becoming converted into more inert compounds before they undergo the desired transformation by co-alkylation and to suppress formation of water vapor. By thus controlling the catalytic tendencies among other factors, the desired rearrangements and combination of the reactants are accomplished. Although according to this method the final product tends to contain a larger proportion of unsaturated compounds, if saturation of double bonds in the compounds is desired, the products may be subsequently hydrogenated using known suitable catalysts and hydrogenating conditions. The gaseous reactants may be brought into contact with one or more of the dehydrating catalysts in successive stages, and in a final stage the gaseous products may be subjected to a hydrogenation treatment with added hydrogen in the presence of a hydrogenation catalyst.

The temperature at which the co-alkylation reaction proceeds at a substantial rate is above 400° F., but preferably for a higher yield rate the temperature should be in the range of 600 to 1100° F., with the pressure at 1 atmosphere or higher e. g. up to 50 atmospheres, but preferably in the range between 5 to 30 atmospheres, and the time of contact is a period of 5 seconds to 1 minute, or several minutes depending upon the temperature. A fraction of a minute is sufficient for the reaction at temperatures in the range of 900° to 1100° F. With the temperature within the preferred range a suitable space velocity of the gaseous reactants over the catalysts is within the range of 500 to 8000 cu. ft./hr. cu. ft. of catalyst.

Preferably the reducing gas reagent admixed with the reactants should contain an excess of carbon monoxide and a limited amount of hydrogen. Water gas containing at least one mole of carbon monoxide per mole of hydrogen may be used, but the carbon monoxide content is preferably increased to aid in restricting water vapor formation. Substantially dry hydrocarbon gases

containing a substantial portion of olefins are also supplied as oxygen absorbing reagents and reactants, the olefins having the effect of absorbing oxygen by undergoing hydration and taking part as reactants in the co-alkylation, as already explained. In order to insure that the water vapor in the reaction zone is maintained below 5 per cent of the gaseous material contacted with the catalyst the combined carbon monoxide and olefin hydrocarbon content of the gaseous material should at least be equal to the volume of the oxygen containing compounds, and the free hydrogen gas should be kept preferably below 25 per cent by volume of the gaseous reaction mixture.

Vapor reaction products from the co-alkylation zone may be fractionated in any conventional type of fractionating device to obtain as an overhead a vapor comprising a series of hydrocarbons and oxygenated derivatives boiling in the gasoline or naphtha motor fuel range, and intermediate reflux fraction condensed from vapor reaction products contains compounds boiling above 400° F., 500° F., or even 600° F. which may be used in Diesel fuels, cracking stocks, and to some extent in lubricants.

The importance of this process may be well appreciated by considering that it enables one to convert low anti-knock value straight chain aliphatic compounds, which are too volatile to serve as stable liquid fuel ingredients, into higher boiling branched compounds of high octane rating without requiring preliminary extremely high temperature conversions of gaseous paraffins into olefins and special gas fractionating and recovery systems. For the present process the reducing and dehydrating gaseous reagents comprising principally carbon monoxide and gaseous olefins may be supplied by coal gas, particularly low temperature carbonization coal gas, water gas, cracking process or reforming process fixed gases, and mixtures of such gases. Converted natural gases may likewise be used.

As an example of the initial oxygenated aliphatic feed material composition, typical components which would be present in the largest concentrations are: ethyl alcohol, propyl alcohol, amyl alcohol, acetone, methyl ethyl ketone, acetaldehyde, acetic acid, propionic acid, ethers, methylene oxides, esters, etc. To increase the efficiency of the process by maintaining the water content at a minimum, such a feed material may have to be preliminarily dried by using well known desiccants, e. g., dehydrated clays, silica gel, anhydrous inorganic salts, such as calcium sulphate, calcium chloride, phosphates, or the like. In the event the lower alcohols or fatty acids are present to a large degree, the highly alkaline or reactive type of dehydrating agent should be avoided in a preliminary drying, but may be present in the reaction zone.

Using the catalysts and directions which have been given, the fractionated motor fuel product recovered is of a complex nature difficult to analyze and comprises oily compounds which are at the most, slightly soluble in water and water-soluble compounds. The desired iso-aliphatic end products are the oily compounds, of which some of the following may be identified: secondary and tertiary alcohols, branched ketones and esters, phorones, other unsaturated branched aliphatic oxygen containing compounds, iso-olefins, and some cyclic compounds including aromatics, terpenes, and heterocyclic compounds. The water-soluble compounds may be extracted and re-

cycled for improvement by the co-alkylation reaction.

As an example, stabilizer gases containing 1 to about 6 carbon atom hydrocarbons obtained in a vapor phase cracking of hydrocarbons are mixed with coal gas rich in carbon monoxide then passed over a dehydrating catalyst with an equal quantity of a dried overhead product from the synthesis of oxygenated compounds by the reduction of carbon monoxide. With the pressure at about 10 atmospheres, the temperature regulated to lie in the range of 600° to 700° F. and the space velocity maintained between 800 to 750 cu. ft. per hr. per cu. ft. of catalyst (copper-uranium phosphate on activated alumina) a substantial yield of yellowish motor fuel liquid products has been obtained. The water-insoluble product recovered by washing this crude product with water boils at temperatures ranging from 250° F. up to and even exceeding the end point of gasoline and is soluble in gasoline or kerosene. Tests show that even small amounts of this product, about 5 per cent, blended with a commercial gasoline of 70 octane number eliminates knocking in an engine which requires a fuel of 76 octane number for substantially non-knocking operation.

While this invention has been described with reference to specific reactants, reaction conditions, proportions, and catalysts, it is to be understood that the scope of this invention is not limited thereto. In actual practice various forms of alloy or metal reaction apparatus may be used, e. g. enameled, tinned, copper or aluminum lined vessels. Any of the known types of control instruments, control apparatus, pumps to supply pressure, and general refinery apparatus may be used to obtain and regulate the operating conditions.

This application is a continuation-in-part of my co-pending application Serial No. 268,286 of which no application has been filed in any foreign country or countries except in England filed June 22, 1939; France filed July 10, 1939; and that no application has been filed in any country or countries than those mentioned.

Having described my invention, what I claim and desire to secure by Letters Patent is as follows:

1. The method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons into higher boiling iso-aliphatic compounds of higher anti-knock value which comprises contacting a mixture of said oxygenated derivatives, normally gaseous olefins, and a reducing gas composed primarily of carbon monoxide with a dehydrating catalyst at a temperature in the range of 400-1100° F., while maintaining the water vapor content of the reactants below 8% by volume.

2. A method according to claim 1 in which the process is operated under superatmospheric pressure.

3. A method in accordance with claim 1 in which the dehydrated catalyst comprises essentially a hygroscopic compound containing a strong mineral acid radical.

4. A method in accordance with claim 1 in which the catalyst comprises essentially a hygroscopic phosphate compound.

5. A method in accordance with claim 1 in which the catalyst comprises essentially a dehydrated copper-uranium phosphate.

6. A method in accordance with claim 1 in which the catalyst comprises a metal halide

which readily reacts with water to form hydrogen halide.

7. A method in accordance with claim 1 in which the catalyst comprises a difficultly reducible oxide of a metal, other than iron, having a low hydrogenating activity.

8. A method in accordance with claim 1 in which the catalyst is supported by an adsorbent carrier having high catalytic dehydration activity.

9. A method in accordance with claim 1 in which the catalyst is supported by an adsorptive carrier comprising a hygroscopic metal oxide of low hydrogenating activity.

10. The method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons, selected from the group comprising normal alcohols and their more highly oxidized derivatives having a boiling range mainly lower than the gasoline boiling range, into higher boiling iso-aliphatic compounds of higher anti-knock value which comprises reacting said oxygenated derivatives with olefinic hydrocarbons in a reducing atmosphere composed principally of carbon monoxide and containing less than 5% by volume of water vapor content in the presence of a dehydration catalyst at a temperature in the range of 600-1100° F. at superatmospheric pressure and with a space velocity of 500-8,000 cu. ft. per hour per cu. ft. of catalyst, and condensing motor fuel ingredients from the resulting reaction products.

11. The method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons having 1 to about 6 carbon atoms per molecule into higher boiling iso-aliphatic compounds of higher anti-knock value which comprises reacting said oxygenated derivatives with normally gaseous olefins in a reducing atmosphere composed principally of carbon monoxide in the presence of a dehydration catalyst at a temperature in the range of 400-1100° F., the gaseous reactants having a rate of flow of 500-8,000 cu. ft. per hour per cu. ft. of catalyst, while maintaining the water vapor content below approximately 5% by volume.

12. The method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons into higher boiling iso-aliphatic compounds of higher anti-knock value which comprises contacting a mixture of said oxygenated derivatives, normally gaseous olefins, and a reducing gas composed primarily of carbon monoxide, with a dehydrating phosphate catalyst at a temperature in the range of 400-1100° F., while maintaining the water vapor content of the reaction mixture below 8% by volume.

13. The method of converting low boiling straight chain water-soluble oxygenated derivatives of normal aliphatic hydrocarbons into higher boiling iso-aliphatic compounds of higher anti-knock value which comprises reacting said oxygenated derivatives with normally gaseous olefins and carbon monoxide in contact with a dehydrating phosphate catalyst at a temperature in the range of 600-1100° F., while maintaining the water vapor content of the reaction mixture below approximately 5% by volume.

14. The method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons into higher boiling iso-aliphatic compounds of higher anti-knock value which comprises mixing said oxygenated derivatives with normally gaseous olefins and a reducing gas composed primarily of carbon monoxide,

contacting such mixture with a dehydration catalyst at a temperature in the range of 600-900° F., while maintaining the water vapor content of the reactants below approximately 5% by volume, and fractionating and condensing a liquid motor fuel fraction from the reaction products.

15. The method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons into higher boiling isoaliphatic compounds of higher anti-knock value which comprises mixing said oxygenated derivatives with normal gaseous olefins and a reducing gas composed principally of carbon monoxide and containing less than 25% by volume of hydrogen, the combined carbon monoxide and olefin content of the gaseous material being at least equal to the volume of said oxygenated derivatives, contacting such mixture with a solid catalyst composed of water absorbent material including essentially a hygroscopic compound of high dehydrating but low hydrogenating catalytic activity at a temperature above 400° F., while maintaining the water vapor content of the reactants at less than 5% by volume.

16. A method of converting low boiling straight chain oxygenated derivatives of normal aliphatic hydrocarbons, selected from the group comprising normal alcohols and their more highly oxidized derivatives having a boiling range mainly lower than the gasoline boiling range, into higher boiling branched chain compounds of higher octane rating which comprises mixing said oxygenated derivatives with normally gaseous olefins and a reducing gas composed primarily of carbon monoxide and containing less than 25% by volume of hydrogen, the combined carbon monoxide and olefin content of the gaseous material being at least equal to the volume of said oxygenated derivatives, contacting said mixture with a dehydrating catalyst comprising copper-uranium phosphate supported on a carrier comprising activated alumina at a temperature in the range 600-900° F., while maintaining the water vapor content of the reaction mixture below approximately 5% by volume, and fractionating and condensing a liquid motor fuel fraction from the reaction products.

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