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ALKYLATION OF HYDROCARBONS IN THE PRESENCE OF SULFURIC ACID

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This invention relates to the synthesis of hydrocarbons of a saturated nature from lower boiling saturated and unsaturated hydrocarbons. It relates especially to the synthesis of saturated hydrocarbons of suitable boiling point for use as constituents of motor fuel.

More specifically the invention relates to a chemical process carried on under controlled conditions involving the catalytic combination of unsaturated aliphatic hydrocarbon compounds with aromatic or isoparaffinic hydrocarbon compounds to form synthetic derivatives of a mixed or branched chain character.

Many processes have been proposed for converting normally gaseous hydrocarbons into hydrocarbons having higher molecular weights, such as motor fuel and lubricants. Some of these processes are dependent upon having olefin hydrocarbons present in large proportions in the charge stock such as in well-known thermal and catalytic polymerization processes for producing motor fuel and other liquid hydrocarbons from refinery gases containing unsaturated components from cracking stills. Still other processes are adapted to produce motor fuel stocks from normally gaseous paraffins, such as unitary thermal conversion processes, or a multistage process employing a dehydrogenation step as a first part of the process, followed by a conversion of olefins so produced. Still other processes have been proposed wherein a paraffinic hydrocarbon stream and an olefinic hydrocarbon stream are charged to a process, and the paraffins and olefins are caused to interact, or as it is generally stated, the paraffins are alkylated by the olefins to form paraffins having higher molecular weights. The olefins may be in the simple normally gaseous or liquid form or they may be in the form of higher molecular weight polymers.

This invention comprises treatment of reactive hydrocarbons of an alkylatable non-olefinic nature, particularly aromatic hydrocarbons, and/or low boiling isoparaffinic hydrocarbons, with simple olefinic hydrocarbons and/or their polymeric counterparts, in the presence of sulfuric acid and an emulsifier to produce hydrocarbon compounds of a character and boiling range suitable for use as gasoline and/or as antiknock constituents of gasolines. The reaction between isoparaffins and olefins, or aromatics and olefins in the presence of an alkylating catalyst of the type of sulfuric acid is presumably of a simple character. For example, the alkylation reaction can be expressed by the following general equation:

$$xRH + (C_nH_{2n})_x \xrightarrow{(H_2SO_4)} xR—C_nH_{2n+1}$$

where R represents an aryl, aralkyl or alkyl radical and $(C_nH_{2n})_x$ is a simple olefinic hydrocarbon or polymer thereof, with x a relatively small whole number. An equation for the reaction of specific reactants such as isopentane and propylene

in the presence of sulfuric acid may be expressed as:

$$\underset{\text{Isopentane}}{C_5H_{12}} + \underset{\text{propylene}}{C_3H_6} \xrightarrow{(H_2SO_4)} \underset{\text{Iso-octane}}{C_8H_{18}}$$

In this and similar alkylation reactions we have found that certain organic materials will act as emulsifiers in a mixture of sulfuric acid and hydrocarbons, that their presence is accompanied by a more intimate mixture of the components, and that the result of their use is that during an alkylation reaction a better yield of heavier hydrocarbons, and especially of desirable hydrocarbons, is obtained than if no such emulsifying material had been added, other conditions being equal, or that less stringent or drastic operating conditions are necessary to produce similar results. Heretofore, sulfuric acid alkylation reactions have been performed in reactors wherein violent mechanical agitation was necessary to keep reactants and catalyst in intimate contact. When 90–97 per cent sulfuric acid is employed as substantially the only constituent of the catalytic material long reaction times are required to insure a maximum yield of product in view of relatively low temperature conditions which are necessary to prevent decomposition of parts of the reactant material. Birch et al. in an article appearing in Ind. Eng. Chem. 31, 884, 1079 (1939), apparently tried to overcome these difficulties by employing high acid-hydrocarbon ratios in addition to violent agitation. In this article it is stated that a high acid-hydrocarbon ratio is essential in sulfuric acid alkylation reactions; without it the intimacy of mixing necessary for successful operation is not possible. Also, it is stated that unsatisfactory agitation, especially when accompanied by a low acid-hydrocarbon ratio leads to olefin polymerization without addition or alkylation. We have found that we can make less rigorous the requirements of high acid-hydrocarbon ratios, long reaction times and/or violent agitation deemed as necessary by prior art in the sulfuric acid alkylation of saturated or aromatic hydrocarbons by unsaturated hydrocarbons, by the practice of our present invention.

One object of our invention is to effect an alkylation of hydrocarbons of a saturated nature to produce alkyl derivatives thereof.

Another object of our invention is the production of hydrocarbons which can be used as high antiknock constituents of motor fuel.

Another object of our invention is to produce an increased yield of a premium liquid motor fuel having high antiknock qualities from normally gaseous hydrocarbons.

A further object of our invention is to produce an increased yield of motor fuel and/or motor fuel constituents, having a high octane number and boiling within the gasoline range, by alkylating isoparaffins and/or aromatics with mono-olefins either in the form of monomers or polymers in the presence of novel alkylation catalysts.

A still further object of our invention is to provide a process wherein the alkylation reaction shall be favored in preference to the simple polymerization of the olefins introduced into the reaction zone for the purpose of combining with the isoparaffinic or other alkylatable hydrocarbons.

Still another object is a reduction in the time and/or acid-hydrocarbon ratio, and/or severe mechanical agitation formerly employed in alkylating hydrocarbons with olefins in the presence of sulfuric acid.

Other objects and advantages of our invention can be found from the accompanying disclosure and discussion.

We have found that when small amounts of an organic compound of relatively high molecular weight and capable of acting as an emulsifying agent for a mixture of low boiling paraffins and concentrated sulfuric acid is contained in an alkylation reaction mixture wherein sulfuric acid comprises substantially the entire catalytic material and the reactants comprise isoparaffinic hydrocarbons and olefins or aromatic hydrocarbons and olefins, said mixtures are more easily and/or more completely reacted. Also, in general, as a result of the addition of said organic compounds which act as emulsifiers of the constituents of the alkylation reaction mixture, the acid-hydrocarbon ratio can be decreased to a lower value than when sulfuric acid is used as a catalyst in the absence of such organic emulsifiers. We have further found that such organic compounds of acidic characteristics are particularly useful, such as certain organic acids, hydrolyzable metal salts of said acids, and esters of said acids. Previously, relatively large quantities of acid were needed to insure intimate contact of reactants and catalysts, but this feature is no longer necessary in view of the present invention. Furthermore, as a result of our invention the percentage yield of product, especially of desirable material, from sulfuric acid alkylation reactions wherein a small amount of an organic emulsifier is present has been found to be greater than when sulfuric acid is not accompanied by such an agent.

oleic, ricinoleic and like acids to be satisfactory emulsifiers. As other organic acids for the purposes of this invention we include those acidic organic compounds such as sulfonic acids and alkyl hydrogen sulfates of which naphthalene-β-sulfonic acid and lauryl hydrogen sulfate are representative examples, respectively. Also, important in this classification are hydrolyzable metal salts of said fatty acids, sulfonic acids and alkyl hydrogen sulfates. Especially the alklali metal salts of alkyl hydrogen sulfates have been found to create desirable emulsion conditions in mixtures of sulfuric acid and hydrocarbons wherein the alkyl group includes lauryl, myristyl, palmityl, oleyl, stearyl and the like radicals and the alkali metal group includes sodium and potassium. Preparations containing these latter organic compounds or mixtures of same are available commercially. Presumably, when esters or hydrolyzable salts of such organic acids are added to the reaction mixture, it is actually the corresponding organic acid which is producing the desirable effect which results, although we are unable definitely so to state. However, the results indicate such a mechanism, so that when we state that the reaction is carried out in the presence of a suitable organic acid it is to be understood that the acid may have been added as such or may have been added as an ester or hydrolyzable metal salt.

Table I shows the amount of time necessary for a paraffin-sulfuric acid emulsion to break completely, if at all, into distinct liquid phases, when using various organic emulsifying agents representative of ones discussed herein. In each of the examples recorded in this table a standardized procedure was used. Twenty-five cubic centimeters of 96 per cent sulfuric acid were charged to a 100-cc. graduated mixing cylinder which contained the tabulated quantities of promoter or emulsifier. The contents of the cylinder were then agitated until the emulsifying agent dissolved or until it was considered that the system was at equilibrium. Fifteen cubic centimeters of isopentane were then added and the mixture agitated for two minutes. The cylinder plus contents was then set aside and at intervals the volume of separated isopentane was noted. These values in cubic centimeters appear in Table I.

Table I

Emulsifier in 25 cc. 96% H_2SO_4 and 15 cc. i-pentane	Cubic centimeters of i-pentane separating after mixture is allowed to set—											
	0.50 min.	0.75 min.	1.00 min.	1.25 min.	1.50 min.	1.75 min.	2.00 min.	3.00 min.	4.00 min.	6.00 min.	8.00 min.	Variant
None	11.0	------	13.0	------	15.0	------	------	------	------	------	------	
Naphthalene-β-Sulfonic acid (1.1%)	2.0	3.0	5.0	10.0	------	15.0	------	------	------	------	------	
Naphthalene-β-Sulfonic acid (1.1%)[1]	0.0	------	1.0	3.0	7.0	8.0	[1]10.0	------	------	------	------	
Stearic Acid (1.1)%[2].												
Fatty alcohol sulfate (1.1)%	------	------	---	------		--- --	1.0	2.0	5.0	10.0	15.0	
Butyl Ricinoleate	7.0	------	7.5	------	7.5	------	------	------	------	7.5	------	8.0 at 26.0 min. 8.0 at 5 hrs.

[1] In this experiment only 10 cc. of i-pentane was mixed with the 25 cc. of 96% sulfuric acid.

[2] There was no separation of an i-pentane layer even after 35 minutes.

In preliminary experiments we have found that small amounts of organic acids, especially of high molecular weight fatty acids of at least ten carbon atoms per molecule such as lauric, myristic, palmitic, stearic, oleic, ricinoleic and the like promote an emulsion with a satisfactory breaking out time after being agitated in a mixture of sulfuric acid and hydrocarbons. Also we have found esters of said fatty acids such as butyl ricinoleate, and/or methyl, ethyl, propyl, butyl, amyl and the like esters of lauric, myristic, palmitic, stearic,

Of the materials listed in Table I, stearic acid produced the most persistent emulsion between sulfuric acid and isopentane. No isopentane separated even after allowing this mixture to remain undisturbed for a relatively long period of time. The relative emulsification effectiveness of other materials appearing in Table I is readily apparent to anyone familiar with emulsification experiments.

The effectiveness of previously mentioned organic compounds and materials in sulfuric acid alkylation reactions wherein hydrocarbons comprise the reactants has been found to relate more or less directly to the emulsifying ability of said materials in said alkylation reactions, and the amounts and types of compounds to be used in any particular case may be readily determined in most instances by means of correlation with simple emulsification tests such as are outlined herein. It has been found that the better the emulsifying ability of the added agents the greater the yield of alkylated material and especially of desirable material, and within reasonable limits the less the acid-hydrocarbon ratio can be without excessive adverse effects in sulfuric acid alkylation reactions. In general, the organic compound should be present in an amount of at least about 0.1 per cent by weight of the concentrated sulfuric acid, and in few if any cases need exceed about 10.0%. For most of the organic compounds disclosed we have found that between about 0.5 and 5.0 per cent is sufficient.

In order to show clearly the advantages of using an organic compound which acts as an emulsifier in connection with alkylation processes, Table II is presented containing data obtained from two sulfuric acid alkylation runs.

Table II

Run	A	B
Olefin	Propylene	Propylene.
Paraffin	Isopentane	Isopentane.
Weight olefin, grams	84	84.
Weight paraffin, do	288	288.
Emulsifier	1.0% Stearic Acid.	None.
Volume H_2SO_4, cc. (96%)	500	500.
Mol ratio, Paraffin to Olefin	2:1	2:1.
Volume Ratio, Hydrocarbons to acid.	1.25:1	1.25:1.
Pressure	Atmospheric	Atmospheric.
Temperature	68° F	68° F.
Time of Addition, minutes	80	76.
Additional Reaction Time, do	30	30.
Total Reaction Time, do	110	106.
Increase in Acid Volume	15	30.
Volume Product, cc	251	233.
Density Total Product at 68° F	0.7041	0.7109.
n_D^{20} Total Product	1.3966	1.4013.
Per Cent Olefin in Total Product	0.0	0.0.
Weight Per Cent Yield Based on Olefin (86–410° F.)	205	187.7.
(Total)	210	196.1.
Weight Per Cent Theoretical Yield (86–410° F.).	75.6	69.2.
(Total)	77.3	72.3.
Volume Per Cent 86–410° F. of Total Product.	98.2	95.7.
Volume Per Cent:		
C_6 Fraction	10.6	9.6
C_7 Fraction	5.9	6.7
C_8 Fraction	61.0	51.5
C_9 Fraction	7.5	8.2
C_{10} Fraction	7.2	8.2
C_{11}-C_{12} Fraction	6.0	11.5
Heavier than C_{12}	1.8	4.3
	100.0	100.0
Density at 68° F.:		
C_6 Fraction	0.6539	0.6493
C_7 Fraction	0.6805	0.6791
C_8 Fraction	0.7010	0.7041
C_9 Fraction	0.7232	0.7201
C_{10} Fraction	0.7384	0.7356
C_{11} and C_{12} Fraction	0.7498	0.7476
n_D^{20}:		
C_6 Fraction	1.3718	1.3699
C_7 Fraction	1.3861	1.3859
C_8 Fraction	1.3963	1.3972
C_9 Fraction	1.4072	1.4059
C_{10} Fraction	1.4154	1.4139
C_{11} and C_{12} Fraction	1.4211	1.4209

The sulfuric acid catalyst of run A contained 1.0 per cent by weight of organic emulsifier and run B contained no organic emulsifier. The emulsifier chosen for run A was stearic acid and the reactants in both runs were propylene and isopentane. The runs were made by placing isopentane and sulfuric acid in a reaction vessel equipped with a stirrer capable of effecting thorough and intimate mixing of the reactants, and adding the propylene to the mixture as it was stirred. Conditions of agitation, quantity and quality of reactants and catalyst and temperature and pressure of the reaction were maintained as near alike in each run as was possible within experimental error. A small difference between the two runs existed in the period used for the addition of the olefin to the paraffin. Previous experimentation, however, had shown that variation of such a magnitude would cause no significant difference in the ultimate yield or character of product and could well be considered as being within the experimental error of the technique employed.

By an inspection of the data in Table II it is readily apparent that the run containing the organic emulsifier yielded a larger amount of product (251 cc. or 210 per cent of the weight of the olefin) than did the run containing no emulsifier (233 cc. or 196 per cent of the weight of the olefin). Also, the amount of useful material obtained in run A is a greater percentage of the total product than that obtained in run B. By useful material we refer to that part of the product boiling between 86° F. and 410° F. and especially the iso-octanes and branched pentanes, hexanes and heptanes. For example, the C_8 fraction of run A is 18 per cent larger than the C_8 fraction of run B, and in run A there is 25 per cent less material boiling in the C_9—C_{12} range than there is in run B.

Furthermore, the quantity of material boiling above the C_{12} range of hydrocarbons was almost 60 per cent less in run A than in run B. These differences in favor of run A constitute some of the biggest advantages obtained by the use of a promoter which acts as an emulsifier such as stearic acid, for example, in sulfuric acid alkylation reactions, and show some of the advantages which result from our invention even when the other reaction conditions are similar to those used in the art.

Run A is intended to be but illustrative of the invention and is not to be considered as necessarily limiting the scope of the invention. Other emulsifiers, which may be chosen on the basis of emulsification tests such as recited herein, may be substituted for stearic acid with similar results. In carrying out the invention the apparatus used and the conditions of operation chosen in respect to temperature, pressure, proportioning of the reacting constituents, choice of acid strength and of the promoters, etc., will be varied to suit the individual case. Thus, although the alkylation reaction specifically described in the example was realized at substantially atmospheric temperature and pressure, under certain conditions lower or higher temperatures and/or pressure may be employed. The reaction is preferably carried out at temperatures ranging from between about 0° F. and 120° F. and under pressures ranging from about atmospheric to about 1200 pounds per square inch. However, it is desirable to employ a pressure which is sufficient to maintain the reactants in the liquid state, and in most cases the pressure need not be greatly in excess of such a value.

Also, the reaction time need not be limited to that shown in Table II. Although an object of the invention is to materially reduce the reaction time of those sulfuric acid alkylation reactions wherein no emulsifier is used, the reaction time when practicing my invention may be between about 5 minutes and 3.5 hours, as may be found by trial to be best suited for any particular case.

As reactants it is desirable to use isobutane, isopentane and similar isoparaffins, benzene, toluene, xylenes or such substituted derivatives of said hydrocarbons as will be normally alkylated by olefins in the presence of sulfuric acid alone providing sufficient agitation, reaction time and catalyst are employed. However, our invention gives the best results when applied to the alkylation of nonaromatic hydrocarbons. As the olefinic reactant, ethylene, propylene, n-butylenes, isobutylene, pentenes, hexenes and similar hydrocarbons are desirable; although ethylene is generally not very suitable in the absence of other olefins. In place of the monomeric mono-olefins, the dimers, trimers, tetramers, and higher polymers of these mono-olefins, the co-, cross- and interpolymers and analogous condensation products of these mono-olefins may also be used.

The molecular proportions of isoparaffin to olefin or aromatic to olefin may vary widely, i. e., say from about an equimolecular ratio to a ratio of about 100 to 1 or more. The acid-hydrocarbon ratio can often be less when such an organic emulsifier is used than when such emulsifier is absent, although, as shown, beneficial results are realized when the conditions are otherwise the same as those used heretofore. The quantity of the emulsifier, as well as the concentration and quantity of the sulfuric acid catalyst, may be increased or decreased from amounts specifically recited in various examples herein, as is well appreciated by anyone skilled in the art.

In the example the reaction was conducted in batch operation. It is, however, expressly within the scope of the present invention to carry out alkylation processes in a continuous manner. It is also to be appreciated that if, after the alkylation reaction is completed, the emulsified condition of liquid effluent persists, a small amount of a demulsifying agent can be added to the effluent to facilitate and hasten the breaking out. We have found that small amounts of formamide or the commercial products containing sulfonated hydrocarbons and their alkali metal salts act as demulsifiers under the conditions existing after said alkylation reaction in presence of an emulsifier. In choosing an emulsifier from the group of organic compounds as disclosed, it may at times prove expedient to choose one which does not have an exceedingly long breaking out time as stearic acid and the like, but rather one which when steadily agitated in an alkylation reaction mixture will provide intimate contact between reactants and which after the reaction is considered complete and agitation is stopped, will break out more or less completely in from 2 to 30 minutes, of its own accord, without the use of a demulsifying agent. The use of such an emulsifier may preclude the use of a demulsifier after said alkylation reaction is complete.

In view of 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.

We claim:

1. In a process of reacting isoparaffinic hydrocarbons with olefinic hydrocarbons to produce alkylated isoparaffinic hydrocarbons, the step of conducting said alkylation reaction in the presence of a catalyst containing concentrated sulfuric acid and relatively small percentages of a higher fatty acid of at least ten carbon atoms per molecule.

2. A process according to claim 1 wherein the organic acid is stearic acid.

3. In a process for reacting a low boiling isoparaffin with an olefin in the presence of concentrated sulfuric acid to form a heavier paraffin product in the boiling range of gasoline, the improvement which comprises conducting the reaction in the presence of stearic acid in an amount about 1 per cent by weight of the sulfuric acid.

4. In a process for reacting an alkylatable hydrocarbon with an olefin hydrocarbon to produce a higher-boiling hydrocarbon, the step of conducting said alkylation reaction in the presence of a catalyst containing concentrated sulfuric acid and a relatively small percentage of a higher fatty acid of at least ten carbon atoms per molecule.

5. An improved process for reacting a low-boiling alkylatable hydrocarbon with an olefin in the presence of concentrated sulfuric acid as alkylation catalyst, which comprises conducting said reaction in the presence of between about 0.1 and about 10 per cent by weight, of the sulfuric acid, of a fatty acid having 10 to 18 carbon atoms per molecule.

6. An improved process for reacting a low-boiling isoparaffin hydrocarbon with an olefin in the presence of concentrated sulfuric acid as alkylation catalyst, which comprises conducting said reaction in the presence of between about 0.1 and about 10 per cent by weight, of the sulfuric acid, of a fatty acid having 10 to 18 carbon atoms per molecule.

7. An improved process for reacting a low-boiling aromatic hydrocarbon with an olefin in the presence of concentrated sulfuric acid as alkylation catalyst, which comprises conducting said reaction in the presence of between about 0.1 and about 10 per cent by weight, of the sulfuric acid, of a fatty acid having 10 to 18 carbon atoms per molecule.

8. In a process for reacting a low-boiling alkylatable hydrocarbon with an olefin in the presence of concentrated sulfuric acid to form a higher-boiling hydrocarbon product, the improvement which comprises conducting the reaction in the presence of stearic acid in an amount between about 0.5 and 5 per cent by weight of the sulfuric acid.

9. In a process for reacting a low-boiling aromatic hydrocarbons with an olefin in the presence of concentrated sulfuric acid to form a higher-boiling hydrocarbon product, the improvement which comprises conducting the reaction in the presence of stearic acid in an amount between about 0.5 and 5 per cent by weight of the sulfuric acid.

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