Patented Nov. 9, 1943 2,334,099

UNITED STATES PATENT OFFICE

2,334,099

TREATMENT OF HYDROCARBONS

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No Drawing. Application May 29, 1939, Serial No. 276,414

4 Claims. (Cl. 260—666)

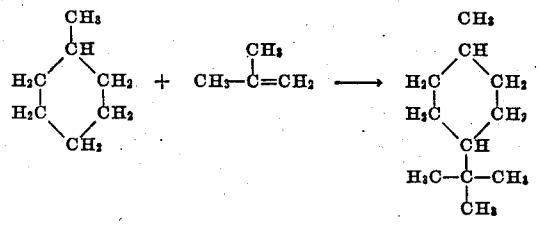
This invention relates particularly to the interaction of naphthenic and mono-olefinic hydrocarbons in the presence of catalysts. It is more specifically concerned with the conversion of naphthenic hydrocarbons and particularly of alkyl naphthenes into more highly alkylated naphthenic hydrocarbons.

In one specific embodiment the present invention comprises a process for contacting a mixture of naphthenic and mono-olefinic hydrocarbons, said mono-olefinic hydrocarbons containing more than three-carbon atoms per molecule, with sulfuric acid whereby to produce a substantial yield of alkylated naphthenic hydrocarbons.

In general, the naphthenic hydrocarbons contained in petroleum fractions may be converted into more highly alkylated naphthenes by the process of this invention. The resulting alkyl naphthenes constitute saturated products of good octane number suitable for use as high grade motor fuel. Furthermore, alkyl naphthenes, particularly alkyl cyclohexanes, may be dehydrogenated to yield alkyl benzenes which are useful as raw materials for the preparation of dyes, pharmaceuticals, etc.

The term "olefin," used within the concept of the present invention, comprises compounds of carbon and hydrogen of open chain structure containing one double bond per molecule. Beginning with olefins of four-carbon atoms, a number of isomers are possible corresponding to different positions of the double bond in the presence of secondary or tertiary carbon atoms, the number of possible isomers increasing with the increasing number of carbon atoms in the molecule. From these considerations it is evident that a large number of different olefins may be employed either singly or in admixture for interacting with naphthenic hydrocarbons according to the process of the invention. The reactions involved in these alkylations are complicated further by the large number of possible naphthenic hydrocarbons which may be present in a hydrocarbon mixture to which the reaction may be applied.

To illustrate the course of an alkylation reaction, the following equation is given which represents the changes occurring when a naphthene, such as methylcyclohexane, is subjected to the action of isobutene, according to the process of this invention:



Methylcyclohexane — Isobutene — p-Methyl-tertiary butyl cyclohexane

Where olefins are contacted with sulphuric acid some polymerization of olefins will occur, as well as the alkylation reactions described. However, these reactions may be controlled to a substantial degree by the use of an excess of the naphthenic hydrocarbons to dilute the olefins employed and thus decrease the tendency toward polymerization and the formation of compounds of high molecular weight.

The process of this invention may be carried out either as a batch operation or continuously. In the simplest case, sulfuric acid of approximately 85–100% concentration may be stirred into the naphthenic hydrocarbon in a batch agitator under a pressure of the approximate order of 1–40 atmospheres and a stream of olefin-containing gases bubbled into the reaction mixture. Alternatively, when utilizing a liquid olefin, a mixture of the olefinic and naphthenic hydrocarbons may be added slowly to a stirred suspension of the acid in another portion of the naphthenic hydrocarbons.

The use of towers or reaction chambers makes possible continuous operation as the acid, olefins, and naphthenic hydrocarbons may be injected separately into a mixing device of suitable character at the top of the column and the mixture allowed to flow downwardly so that more or less complete reaction is assured by the time the reaction constituents reach the bottom of the tower. In some cases the acid and naphthenic hydrocarbons may be caused to flow downwardly counter-current to the stream of olefinic gases directed upwardly through the tower. In such operations other modes of procedure will present

themselves to those conversant with the reactions involved.

The following numerical data are introduced to indicate typical results obtainable by the present process, although it is not intended to limit the scope of the invention in strict accordance therewith.

Three molecular proportions of methylcyclohexane were reacted with two molecular proportions of isobutene in the presence of one molecular proportion of 97% sulfuric acid at a temperature which varied from 0° to 25° C. The hydrocarbon layer was separated from the acid catalyst layer (which was recycled to further use) and then the hydrocarbon layer was washed, dried, and distilled. A fraction boiling at 160–190° C. was separated which consisted mainly of 1-methyl-4-tertiary-butylcyclohexane admixed with relatively minor proportions of triisobutene formed by polymerization of isobutene.

The character of the process of the present invention, and particularly its commercial value, are evident from the preceding specification and limited numerical data presented, although neither section is intended to be unduly limiting in respect to its generally broad scope.

We claim as our invention:

1. A process for the production of poly alkyl derivatives of cyclohexane which comprises reacting an alkyl cyclohexane with a mono-olefin of more than three carbon atoms to the molecule in the presence of sulfuric acid and under alkylating conditions.

2. A process for the production of poly alkyl derivatives of cyclohexane which comprises reacting an alkyl cyclohexane with a mono-olefin of more than three carbon atoms to the molecule in the presence of 85–100% sulfuric acid and at a temperature in the approximate range of −20 to +60° C.

3. A process for the production of poly alkyl derivatives of cyclohexane which comprises reacting methylcyclohexane with isobutene under alkylating conditions in the presence of sulfuric acid.

4. A process for the production of poly alkyl derivatives of cyclohexane which comprises reacting methylcyclohexane with isobutene in the presence of sulfuric acid at a temperature of from about 0° C. to about 25° C.

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