

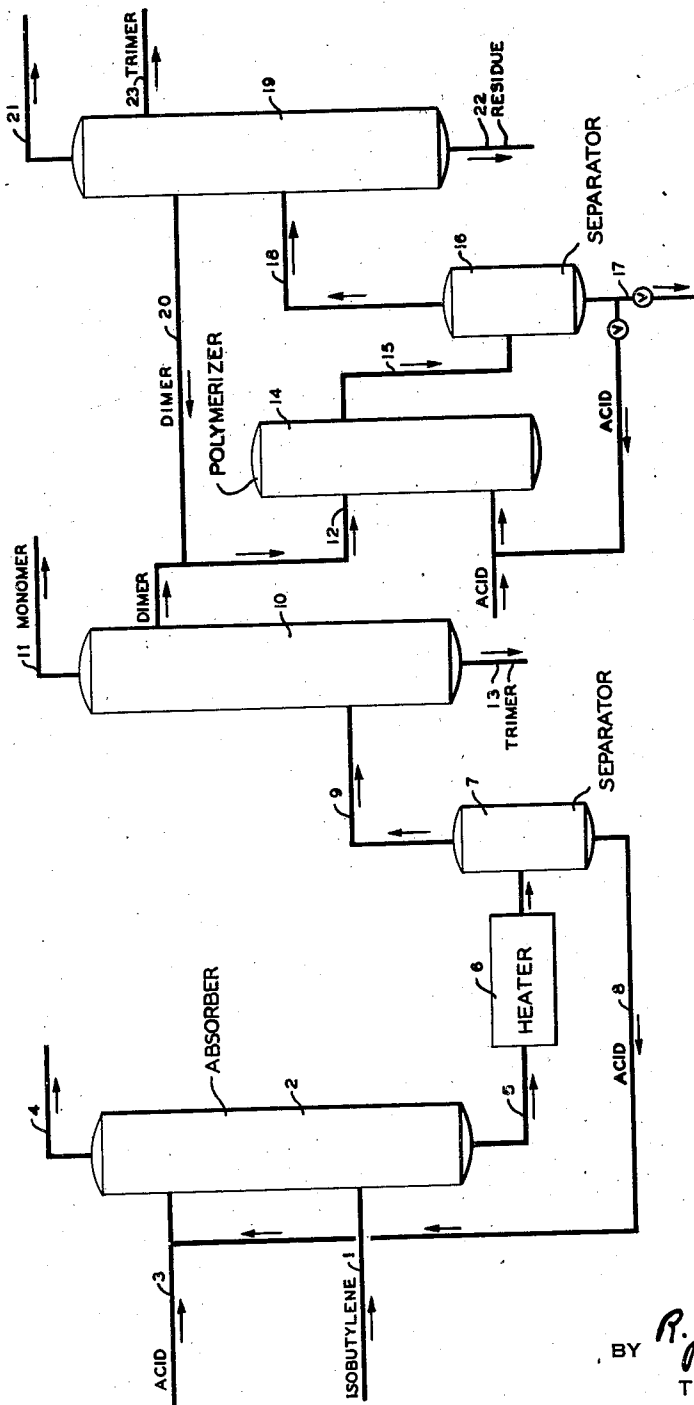
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MANUFACTURE OF HYDROCARBON PRODUCTS

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MANUFACTURE OF HYDROCARBON
PRODUCTS

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This invention relates to the manufacture of hydrocarbon products and more particularly to the manufacture of tri-isobutylene or a hydrocarbon product consisting essentially of tri-isobutylene.

The invention contemplates preparing a hydrocarbon feed consisting essentially of di-isobutylene and then subjecting the feed to the action of sulfuric acid under suitable polymerizing conditions so as to effect substantial conversion of di-isobutylene to tri-isobutylene without substantial production of polymers of higher molecular weight than tri-isobutylene.

It has been known heretofore to treat isobutylene with sulfuric acid under polymerizing conditions so as to effect polymerization. The resulting polymer product obtained contains both di-isobutylene and tri-isobutylene as well as higher molecular weight polymers. According to the information available heretofore it would be expected that when di-isobutylene is subjected to sulfuric acid under polymerizing conditions tetra-isobutylene would be obtained.

However and in accordance with this invention, it has been found that contrary to normal expectations the dimer, di-isobutylene, can be subjected to the action of sulfuric acid so as to effect conversion of the dimer to the trimer without substantial production of the tetramer.

More specifically the invention involves treating di-isobutylene or a hydrocarbon feed consisting essentially of di-isobutylene with sulfuric acid of about 60 to 85% H_2SO_4 and preferably about 70% H_2SO_4 . The treatment is effected at a temperature in the range about 100 to 250° F. and preferably within the range about 150 to 200° F., employing a time of contact between hydrocarbons and acid ranging from about 1 to 20 minutes. The acid may be employed in the proportion of about 0.3 to 3.0 volumes of acid per volume of dimer in the reaction zone, the preferred ratio being about equal volumes of acid and hydrocarbon.

The treated hydrocarbons are separated from the acid and will comprise a mixture of the dimer and trimer. The dimer may be separated from the trimer by fractional distillation and returned to the polymerization reaction while the trimer product is accumulated for further disposition as desired.

The trimer product may be hydrogenated, and advantageously employed in the manufacture of safety fuel. For safety fuel it is usually considered desirable to employ hydrocarbons boiling

within the range about 285 to 400° F. so that the fuel product will have an open-cup flash of not more than about 105° F. Tri-isobutylene, since it has a boiling point of about 354° F., therefore, provides a desirable hydrocarbon component for safety fuel whereas the dimer and tetramer compounds cannot be used in substantial amounts since they have boiling points outside this preferred range for safety fuel.

According to a modification of the invention iso-butylene or a C_4 hydrocarbon fraction containing isobutylene may be treated with sulfuric acid under polymerizing conditions so as to obtain a product comprising the dimer and trimer as well as some other material including higher molecular weight polymers and unreacted hydrocarbons. This product may be fractionated to separate therefrom a fraction consisting essentially of the dimer and this dimer fraction then subjected to further treatment with sulfuric acid in a separate treating zone in accordance with the procedure set forth above for conversion to the trimer. This preliminary treatment of the C_4 fraction with sulfuric acid may involve the so-called cold sulfuric acid process for polymerization or the so-called hot acid polymerization process as will be described in more detail later.

In order to describe the invention further reference will now be made to the accompanying drawing.

As indicated in the drawing a hydrocarbon feed consisting essentially of C_4 hydrocarbons including isobutylene is conducted from a source not shown through a pipe 1 to an absorber 2 wherein the feed hydrocarbons are subjected to countercurrent contact with sulfuric acid introduced through a pipe 3. The conditions of operation maintained in the absorber 2 correspond substantially to those employed in the conventional cold sulfuric acid process. Thus the acid introduced through the pipe 3 contains about 60 to 70% H_2SO_4 and the temperature maintained within the absorber 2 is in the range about 60 to 100° F.

The acid and hydrocarbons are introduced in the ratio of about 1 part of acid per part of hydrocarbon by volume.

Under these conditions about 90% of the isobutylene contained in the feed hydrocarbon mixture is absorbed in the acid. The unabsorbed hydrocarbons which may comprise normal paraffins as well as some normal butylenes are discharged through a pipe 4.

The solution of isobutylene in sulfuric acid is

continuously drawn off from the absorber through a pipe 5 and passed through a heater 6 wherein polymerization is effected. The temperature in the heater 6 is in the range about 140 to 200° F. and the reaction time is usually about 1 minute so that the polymer product may comprise about 75% dimer and 25% trimer. This product is continuously drawn off to a separator 7 wherein the mixture separates into phases. The acid phase is continuously withdrawn and recycled all or in part through a pipe 8 to the previously mentioned pipe 3. The hydrocarbon phase is continuously drawn off through a pipe 9 to a fractionating still 10 wherein the hydrocarbons are subjected to fractionation to segregate a fraction rich in the dimer. It will be understood, of course, that prior to fractionation the hydrocarbons may be subjected to treatment with a neutralizing agent such as caustic soda or other suitable alkaline material for the purpose of removing remaining acid.

In the fractionation, a light fraction comprising isobutylene (monomer) may be removed through a pipe 11 and this material may be recycled all or in part to the absorber 2.

An intermediate fraction consisting essentially of the dimer is removed through a pipe 12 while the higher boiling fraction comprising the trimer is removed through a pipe 13.

The dimer fraction is conducted through the pipe 12 to a polymerizer 14 wherein the fraction is subjected to further treatment with sulfuric acid to effect conversion to the trimer. The acid employed at this stage may contain from 60 to 85% H_2SO_4 and preferably about 70% H_2SO_4 . The acid may be fresh, regenerated or used acid. The reaction is effected at a temperature in the range about 100 to 250° F. and preferably in the range between 150 to 200° F. employing a contact time between acid and hydrocarbon undergoing treatment of 5 to 20 minutes. The ratio of acid to dimer undergoing treatment is maintained within the range about 0.3 to 3.0 volumes of acid per volume of dimer.

The resulting polymer product is conducted through a pipe 15 to a separator 16 wherein phase separation occurs. The acid phase is drawn off from a pipe 17 and may be recycled all or in part to the polymerizing unit 14.

The hydrocarbon phase is drawn off through a pipe 18 to a fractionating still 19, wherein the hydrocarbons are fractionated so as to separately recover the trimer and unreacted dimer. The unreacted dimer is advantageously returned through a pipe 20 to the polymerizer 14 for further treatment. The small amount of lower molecular weight material may be removed as a separate fraction through a pipe 21 while any higher boiling residue is separated as another fraction and removed through a pipe 22, the trimer or trimer fraction being discharged through a pipe 23.

As already indicated the primary stage may involve the so-called hot acid polymerization process in which type of operation absorption and polymerization of isobutylene is effected in a single step. In this type of operation acid of about 63 to 70% H_2SO_4 is employed at a temperature in the range about 160 to 220° F. with a time of contact about 10 to 15 minutes.

By way of specific example a feed consisting of di-isobutylene is treated in a continuous reactor with 80% H_2SO_4 acid, the reaction products being discharged to an acid settler wherein acid is sepa-

rated from the hydrocarbon. The hydrocarbon is fed continuously to the reactor in which an acid to hydrocarbon volume ratio of 1.5:1 is maintained by acid recycle from the settler. The contact time for the hydrocarbons is fifteen minutes at a temperature of 120° F.

Thereafter the treated hydrocarbons are separated from the catalyst and fractionally distilled into three liquid fractions, namely, a dimer fraction boiling up to about 329° F., a trimer fraction boiling in the range 329 to 365° F. and a residual fraction boiling above 365° F. The volume per cent of each fraction obtained is as follows:

	Per cent
Dimer fraction.....	31.1
Trimer fraction.....	62.2
Residual fraction.....	6.7

Thus, it is seen that the feed hydrocarbon is converted into a product of which 62.2% by volume consists mainly of the trimer, the amount of higher molecular weight polymer material being relatively small, being substantially less than 10% of the product.

In the specific example the treatment of a feed consisting of the dimer has been described, but it will be understood that the process is not necessarily confined to the treatment of the pure compound. In the case of the two stage operation either substantially pure isobutylene or a normally gaseous hydrocarbon mixture comprising isobutylene may be used as the initial feed.

Obviously many modifications and variations of the invention, as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of producing tri-isobutylene which comprises subjecting a feed hydrocarbon consisting essentially of di-isobutylene to the action of sulfuric acid having a concentration of about 60 to 85% H_2SO_4 at a temperature in the range about 100 to 250° F. for a relatively short period of time such that di-isobutylene undergoes substantial conversion to tri-isobutylene with relatively small production of polymer material of higher molecular weight than tri-isobutylene, separating the treated hydrocarbons from the acid and removing tri-isobutylene from the treated hydrocarbon product.

2. The method of producing tri-isobutylene which comprises subjecting a feed hydrocarbon consisting essentially of di-isobutylene to the action of sulfuric acid having a concentration of about 70 to 80% H_2SO_4 at a temperature in the range about 150 to 200° F. for a relatively short period of time such that di-isobutylene undergoes substantial conversion to tri-isobutylene with relatively small production of polymeric material of higher molecular weight than tri-isobutylene, separating the treated hydrocarbons from the acid and removing tri-isobutylene from the treated hydrocarbon product.

3. The method of producing tri-isobutylene which comprises subjecting a normally gaseous hydrocarbon feed comprising isobutylene to the action of a polymerization catalyst under conditions such that a hydrocarbon mixture is obtained which contains di-isobutylene and tri-isobutylene, separating di-isobutylene from the hydrocarbon mixture, subjecting the di-isobutylene so obtained to the action of sulfuric acid having a concentration of about 60 to 85% H_2SO_4 at a

temperature in the range about 100 to 250° F. for a relatively short period of time such that di-isobutylene undergoes substantial conversion to tri-isobutylene with relatively small production of polymer material of higher molecular weight than tri-isobutylene, separating the treated hydrocarbons from the acid and removing tri-isobutylene from the treated hydrocarbon product.

4. The method of producing tri-isobutylene which comprises subjecting a normally gaseous hydrocarbon feed comprising isobutylene to the action of a polymerization catalyst under conditions such that a hydrocarbon mixture is obtained which contains di-isobutylene and tri-isobutylene, separating di-isobutylene from the hydrocarbon mixture, subjecting the di-isobutylene so obtained to the action of sulfuric acid having

a concentration of about 70 to 80% H_2SO_4 at a temperature in the range about 150 to 200° F. for a relatively short period of time such that di-isobutylene undergoes substantial conversion to tri-isobutylene with relatively small production of polymer material of higher molecular weight than tri-isobutylene, separating the treated hydrocarbons from the acid and removing tri-isobutylene from the treated hydrocarbon product.

5. The method according to claim 3 in which the isobutylene feed is polymerized by the action of sulfuric acid containing about 60 to 70% H_2SO_4 and at a temperature in the range 40 to 200° F.

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