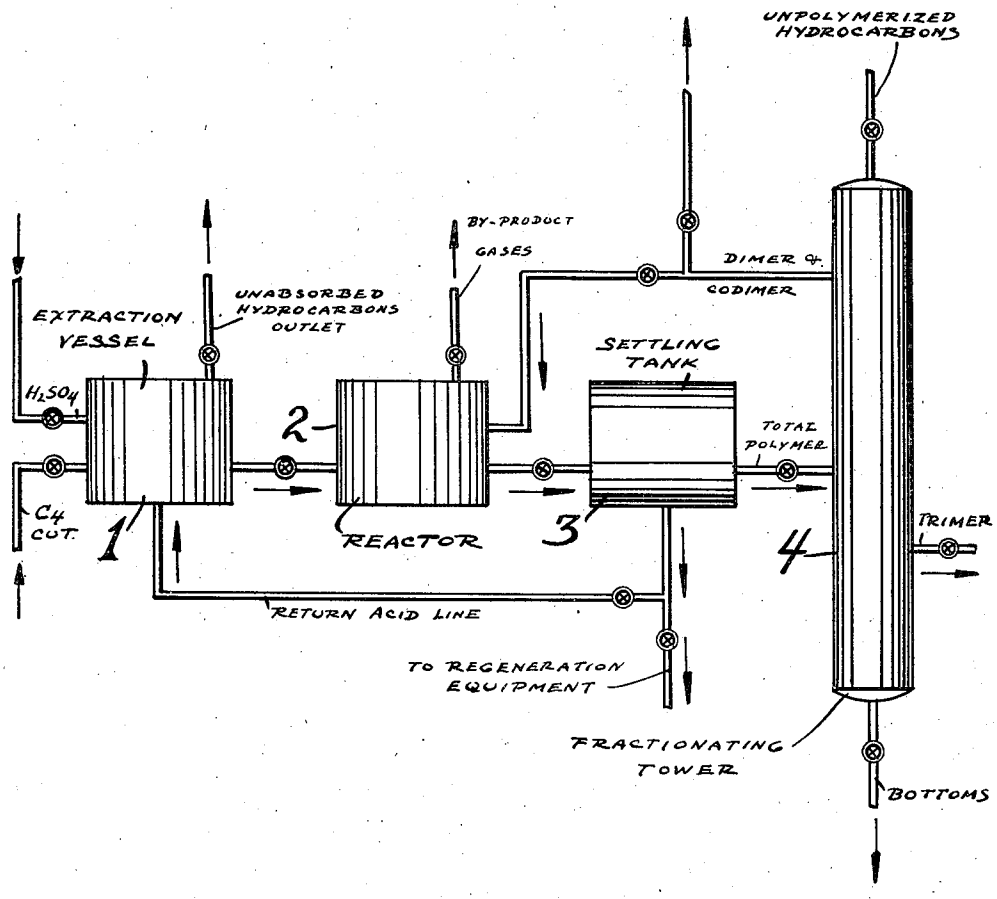
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POLYMERIZATION OF HYDROCARBONS

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POLYMERIZATION OF HYDROCARBONS

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This invention relates to the manufacture of olefin polymers, especially those of the type which are suitable for use in the manufacture of motor fuels and hydrocarbon products of similar boiling range.

The invention is particularly concerned with a practical method for the production of "safety" fuels for aviation purposes, that is, fuels having low vapor pressures. The manufacture of such fuels has become of great importance in recent years, more particularly because of the tendency toward flying at very high altitudes, where the rapid vaporization of fuels presents a serious problem. This vaporization means the loss of the fractions of the fuel having the highest octane number. There is also the great danger of vapor lock, involving loss of power, increased consumption of fuel and sometimes even actual engine stoppage. It is an object of the invention to provide a means for converting readily available petroleum products into fuels suitable for operating airplane engines and having a distinctly higher boiling range than gasoline as well as a high flash point.

Methods have been proposed for the manufacture of diisobutylene from petroleum refinery C_4 cuts containing isobutylene. Hydrogenated diisobutylene is a product having a high octane rating and is used for blending with motor fuels of the gasoline range to improve their octane number. Such fuels have a relatively high volatility and low flash point and create a fire hazard when used under conditions where sparks may be encountered. It has been found, however, that hydrogenated triisobutylene has a boiling range of 170°–200° C., which is within the range required for "safety" fuels and has a remarkably high octane number, i. e., of the order of 98 to 99 (A. S. T. M. clear) or even higher. It is therefore well suited for use alone as a "safety" fuel or in blends of such fuels. The present invention provides a simple and direct means for producing triisobutylene from a refinery C_4 cut and for converting the same into the hydrogenated product.

The present invention is a modification of the known process of preparing isobutylene polymers from isobutylene or hydrocarbon mixtures containing isobutylene by absorption in sulfuric acid and heating the extract so formed. Previous processes of this kind have resulted in the formation of a major proportion of diisobutylene, as in the Rosen and Thomas U. S. Patent 2,178,808. The present invention provides a process which makes possible the production of the highest percentages of trimer in the polymerized product and a quality of trimer product which gives the hydrogenated polymer the highest possible octane rating. These results are accomplished by employing a novel selection and combination of polymerization factors, such as acid strength, temperature, time of contact, etc. By the process of this invention yields of trimer as high as 90% by weight, or higher, based on the isobutylene content of the feed, may be obtained, and the hydrogenated polymer product will have an A. S. T. M. octane number of 98 or higher. The various reaction conditions required for producing the best results will be discussed in turn below.

Suitable initial materials for the process of the invention are mainly hydrocarbon mixtures comprising chiefly C_4 hydrocarbons, such as the C_4 refinery cuts obtained in the distillation and cracking of petroleum, which contain at least 5%, preferably 10% to 20%, of isobutylene as well as substantial quantities of n-butylenes and butanes. Isobutylene itself may of course be used.

The effect of various strengths of acid on the proportion of trimer in the final polymer product was determined for the polymerization of pure isobutylene and a refinery C_4 cut. It was found that the most suitable acid strength was an aqueous sulfuric acid of about 75–80% by weight of pure acid, preferably 75%. In all of the investigations of other factors of the process acids of such strength were used.

A most important condition for the production of the highest grade and quantity of trimer, in cases where the polymer was to be produced from a C_4 hydrocarbon mixture containing both n-butylenes and isobutylene, was found to be the temperature at which the hydrocarbon mixture was contacted with the acid for the purpose of selectively absorbing the isobutylene. It was found that a quite low temperature, i. e., at least as low as about 0° C., but above the freezing point of the acid used, was required to give the most satisfactory selective absorption. At higher temperatures large proportions of n-butylene are absorbed along with the isobutylene, resulting in the formation of a considerable amount of copolymers of isobutylene and n-butylene. This product is not desired for the purpose of making the highest octane number "safety" fuels and their blends, because of the fact that the trimer fraction of such copolymerization product, after hydrogenation, shows a poorer octane rating than that of a product obtained under conditions where only a comparatively small amount of copolymer results.

The following table shows results obtained by

absorbing a C_4 refinery cut containing about 40–50% of total olefins and 10–15% of isobutylene. The acid used was of 75% strength, and the amount of the C_4 cut used in each case was approximately 80% by weight of the acid present. The hydrocarbon mixture was gradually introduced into the acid held at the temperatures indicated, with stirring, during a period of about one hour. After the absorption was completed, the temperature was allowed to rise, the unabsorbed hydrocarbons were removed as gases, and the acid extract was heated gradually, with stirring, over a period of about one hour, from room temperature to about 100° C. The polymer product was separated, washed and fractionated and the amounts of total polymer and of its trimer content determined. The trimer was hydrogenated in the presence of a finely divided active nickel catalyst, and the A. S. T. M. octane number of the hydrotrimer determined. The results are as follows:

TABLE

Test No.	Absorption temp., °C.	Weight per cent of polymer based on i-C_4H_8 in feed	Weight percent trimer fraction based on i-C_4H_8 in feed	O. N. (A. S. T. M.) of hydrotrimer
1	—3–0	132	95	98
2	15–20	152	85	96
3	40	204	50	94

It is seen that at temperatures above 0° C. the polymer produced is considerably greater in amount than that which would be expected from an extract containing only isobutylene, and the excess is largely due to the formation of copolymers of isobutylene and n-butylene. However, the percentage of the trimer fraction as well as the quality of the final hydrotrimer product is shown to be adversely affected by the presence of such large amounts of copolymer in the polymer product. The employment of low absorption temperatures is therefore an important factor in the production of the most desirable products.

Further investigation showed that the best results are obtained by heating the acid extract of olefins for a period of one-half to two hours and at a temperature between about 20° and 100° C., the temperature throughout the heating step averaging 60° to 80° C. It was also found that somewhat better yields of trimer are obtained when the extract is heated gradually over this temperature range, with stirring, than when the heating is conducted at a constant temperature intermediate between these limits, e. g., at 60° C. Satisfactory results are, however, obtained by constant temperature heating.

The time of contact of the acid with the isobutylene extract has been found to be a very important factor in the production of the highest yield of trimer. This factor, taken with the strength of the acid used and the temperature of absorption, is a fundamental feature of novelty of the present invention. Experience has shown that for any specified strength of sulfuric acid which is used there is a definite range of contact time which gives an optimum yields of the trimer, when the heating is conducted over a temperature range of 20° to 100° C. and preferably at 60° to 80° C. For example, when 65% acid is used, the best time of contact is 4 to 5 hours, and with 70% acid, the best time is 2 to 3 hours. However, the best results are secured by using 75–80% acid, and for this strength the preferred time of contact at the polymerization temperature is one-half to 2 hours. If the heating is conducted for periods shorter or longer than those falling within the preferred ranges shown, the yields of trimer are substantially less than those obtained when the preferred times are used.

It has been found that the yields of trimer may be increased somewhat further by returning to the reaction mixture a portion of the dimer or dimer-codimer mixture obtained on fractionation of the polymer product. In a continuous process based upon this invention, a portion of such lighter polymers may be continuously recycled to the polymerization reactor.

A suitable method for carrying out the present invention as a batch process will now be described for the case in which a C_4 refinery cut is used as the raw material. A suitable mixing and reaction vessel is a Turbo mixer which is equipped with a jacket for cooling and heating and with the necessary fittings for introducing the reactants and discharging the reaction products. The C_4 refinery cut, which is a gas at normal temperatures, is liquefied under pressure and passed into a well-agitated sulfuric acid solution of the proper strength. When the amount of the C_4 cut is from 1 to 1.5 times that of the sulfuric acid in the reactor, a suitable time for passing the hydrocarbon feed into the acid is one to two hours. Provision is made for the release of unabsorbed hydrocarbons which evaporate during the absorption process or on subsequent heating. The temperature of the acid during the absorption step is maintained at 0° C. or lower by means of a suitable cooling medium, such as alcohol, which is passed through the cooling jacket after passing in contact with a cooling medium, such as dry ice. The evaporation of the liquid butane in the mixture assists in maintaining low temperatures. After all of the charge has been passed in contact with the acid, steam is admitted to the heating jacket at such a rate that the rise of the temperature of the agitated acid extract is approximately 1° to 2° C. per minute until the final polymerization temperature is reached. Moderate superatmospheric pressures, of the order of 25 lbs. per sq. in., are preferably maintained during the reaction. At the end of the polymerization step, the agitation is discontinued and the polymer allowed to separate as a layer above the acid layer. The polymer is then removed therefrom and washed with an equal volume of 10% aqueous sodium bicarbonate solution and finally with water. In order to prevent the formation of emulsions in some cases, especially when a more concentrated acid (75–80%) is used, the polymer may be washed with a small quantity, say about 25% of an aqueous 50% (by volume) solution of isopropyl alcohol prior to the sodium bicarbonate treatment to remove sulfonation products. After drying the purified polymer by contacting with calcium chloride, it may then be passed to a fractionating column to segregate the trimer fraction from the total polymer.

In operations where the initial material is substantially pure isobutylene, the hydrocarbon may be introduced into the acid under conditions, such as room temperature and atmospheric pressure, which will not cause premature polymerization or otherwise interfere with the subsequent progress of the reaction.

The method of the present invention may also be utilized in a continuous process for the pro-

duction of triisobutylene from a C_4 refinery cut. Such a process is shown in schematic form in the accompanying drawing, which consists of a flow diagram. The hydrocarbon feed gas and a sufficient quantity of sulfuric acid of proper strength to maintain the acid in the extraction vessel at a constant level are introduced into the extraction vessel 1, which is maintained at the desired absorption temperature. The extraction vessel is of sufficient size to permit sufficient contact between the acid and hydrocarbon before passing to the reactor, and efficient agitation is maintained in this vessel. Unabsorbed hydrocarbons may be removed from the extract by raising the temperature sufficiently to vaporize such hydrocarbons and allowing the vapors to escape, or by passing the entire mixture to a separating vessel (not shown) and allowing the unabsorbed hydrocarbons to separate as an upper liquid layer, which may be drawn off. The acid extract passes next to the reactor 2, where the proper polymerization temperature is maintained, and the reaction mixture is continuously agitated. The size of the reaction vessel and rate of flow into and out of the same are regulated to permit the extract to receive the heat treatment for the required period of time. Any gaseous unreacted hydrocarbons or products of decomposition may be removed through a release valve. The reaction product, consisting of a mixture of acid and polymers, is passed to a settling tank 3, where the product separates into an acid layer and a polymer layer. The acid layer is continuously drawn off from the bottom of the settling tank and returned to the extraction vessel 1, where it is reused for further absorption of hydrocarbons. A portion of the used acid may be drawn off continuously or from time to time in order that it may be purified or fortified, for example, by the addition of sulfur trioxide, and it may then be returned to the extraction vessel. The polymer layer is continuously passed to a fractionating tower 4, which separates the product into (1) unpolymerized hydrocarbons, (2) dimer and codimer, (3) trimer and cotrimer, and (4) heavier polymers. A portion of the dimer and codimer fraction may be returned to the reactor for further treatment, since the dimer may be converted to trimer by longer contact with the acid. The reactor for this continuous process may consist of a heating vessel of any convenient form for maintaining a constant temperature, such as a Turbo mixer surrounded by a steam jacket, when a constant polymerization temperature is desired. If it is preferred to provide for gradual heating of the extract from room temperature to a considerably higher temperature, say 100° C., the reactor may consist of a long reaction tube, which is heated to gradually increasing temperatures throughout its length, so that the incoming acid extract first receives mild heating treatment and then treatment of increasing intensity; or there may be a series of heating vessels, each of which is maintained at a constant temperature, but with the temperature increasing from vessel to vessel until the highest temperature desired is reached in the last reaction vessel.

The trimer fraction produced as in the above-described process may be hydrogenated to form a "safety" fuel by the use of a suitable hydrogenation catalyst, e. g., a finely divided active nickel catalyst. This catalyst is quite susceptible to poisoning by impurities, especially sulfur, and the trimer may be purified, for example, by refluxing in the presence of a caustic solution prior to the hydrogenation step. The hydrogenation with the nickel catalyst may be carried out in a hydrogenation bomb at 1500–2000 lbs. per sq. in. hydrogen pressure and at a temperature of 150° C. during a period of 12–36 hours, using 20 grams of the nickel catalyst for each 600 cubic centimeters of polymer. Other effective catalysts may be used, but it is important to choose the catalyst and the conditions of hydrogenation so that hydrogenation takes place with a minimum of depolymerization.

One method of carrying out the present invention may be illustrated by the following example, which is not to be considered as limitative:

EXAMPLE

A C_4 refinery cut was treated according to the above-described method for a batch process to form an isobutylene polymer product. The complete data of the run are as follows:

Absorption step

Charge:		
Refinery C_4 cut	parts by weight	3,000
H_2SO_4 (75%)	do	2,467
Olefin content of C_4 cut	weight percent	41.3
Isobutylene content of C_4 cut	weight percent	14.3
Time of C_4 cut addition	hours	1.5
Temperature during absorption	° C	−3 to 0
Recovery:		
Spent C_4 cut	parts by weight	2,470
Isobutylene	do	16.5
Acid extract	do	2,942
Material balance	weight percent	99

Polymerization step

Contact time	hours	1
Temperature	° C	20–100
Recovery:		
Polymer	parts by weight	526
Acid	do	2,366
Material balance	weight percent	98
Total polymer yield (on isobutylene charged)	weight percent	122.5
Dimer yield (on isobutylene charged)	weight percent	3.2
Codimer yield (on isobutylene charged)	weight percent	17.5
Trimer (plus cotrimer) yield (on isobutylene charged)	weight percent	90.0
Octane number (A. S. T. M.) of hydrogenated trimer		99.4

In the above example, the polymerization step is carried out by heating the acid extract gradually from 20° C. to 100° C. during a period of one hour.

The present invention is not to be considered as being limited in any way by the examples, which are given by way of illustration only, but should be considered as being limited only by the terms of the appended claims.

We claim:

1. The method of preparing a hydrocarbon product containing a major proportion of triisobutylene which comprises contacting a C_4 petroleum refinery cut, containing a substantial proportion of isobutylene, with a 75% to 80% aqueous sulfuric acid solution, heating the acid extract so formed at a temperature between 20° and 100° C. and averaging 60° to 80° C. for a period of one-half to two hours in the presence of a substantial proportion of added diisobutyl-

ene, and separating the polymer formed from the acid.

2. A continuous process for preparing a hydrocarbon product containing a major proportion of triisobutylene which comprises continuously passing a C_4 petroleum refinery cut, containing a substantial proportion of isobutylene, into a 75% to 80% aqueous sulfuric acid solution in an extraction zone at a temperature at least as low as about 0° C., but above the freezing point of said acid solution, removing unabsorbed gases and continuously passing the extract so formed to a heating zone while the temperature is maintained at 60° to 80° C., continuously passing the product from said heating zone to a settling zone, where the acid and the polymer formed in said heating zone separate into layers, continuously removing the polymer from the acid layer, continuously returning the acid from said settling zone to said extraction zone, continuously passing said polymer to a fractionating zone, where it is fractionated into a triisobutylene fraction, a fraction containing diisobutylene and other fractions, and continuously returning a portion of said fraction containing diisobutylene to the said heating zone.

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