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ACID EXTRACTION OF MIXED OLEFIN HYDROCARBONS

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The present invention relates to an improved process for the recovery of normal and branched-chain olefin components from a hydrocarbon stream containing them. More particularly, the invention is concerned with the recovery of secondary alcohols and the recovery of branched-chain olefins from a mixed hydrocarbon stream containing normal and branched-chain olefins which are difficult to separate by fractionation. By normal olefins is meant those olefins capable of yielding secondary alcohols immediately upon hydration.

The production of aliphatic monohydric alcohols through the absorption of olefinic hydrocarbons in mineral acids such as sulfuric acid, using the cracked gases from a petroleum oil refinery as the source of aliphatic olefins, to form an acid extract which is subsequently hydrolyzed and distilled to recover the alcohol, is a widely used process. Generally speaking, cracked gases, produced by thermal, catalytic or steam cracking of hydrocarbon oils, are a heterogeneous mixture of saturated hydrocarbons, normal olefins, tertiary olefins, some hydrogen and smaller quantities or traces of other unsaturated hydrocarbons such as diolefins and acetylenes. For the purpose of this invention, the tertiary olefins are best described as those mono- or diolefins which have in the molecule a double bonded carbon atom attached to three other carbon atoms. Thus, the four valences of a tertiary carbon atom are occupied by three other carbon atoms.

The first step toward economic utilization of cracked refinery gases is the separation of the gases by close fractionation into isomeric groups or fractions in which substantially all of the hydrocarbons present have the same number of carbon atoms. The next step in the refinery process, according to the present best practice, is the separation of the various hydrocarbons within an isomeric group. This is accomplished by methods relying upon a marked difference in the reactivity of the various hydrocarbons. The diolefins, acetylenes, and other hydrocarbons of higher unsaturation than mono-olefins may be first removed by reaction with copper salts or other known means. Of the major remaining constituents, it is known that the tertiary mono-olefins are the most reactive to sulfuric acid; next come the normal mono-olefins. The saturated hydrocarbons are inert for all practical purposes. For instance, isobutylene is removed from a mixture of hydrocarbons containing isobutylene and normal butenes by reacting the mixture with sulfuric acid of 60–65% acid strength on a hydrocarbon-free basis, or with other strong acids of equivalent strength, under conditions such that little if any of the normal butenes react, or an amylene fraction may be contacted with 65–75% sulfuric acid or with 80–85% benzene sulfonic acid to remove the tertiary amylenes. The normal olefins may then be converted to secondary alcohols and other valuable derivatives. However, the sulfuric acid method for separating tertiary olefins from normal olefins may leave varying quantities of tertiary olefins behind with these normal olefins. The preliminary removal of tertiary olefins represents an added expense and, in many instances, it is preferably avoided if the tertiary olefin concentration of the feed is not too high. In practice, the tertiary olefin present in such a fraction is usually 2–25% of the total hydrocarbon. When such fractions are mixed with fresh or lean acid of sufficient strength, e. g., 75–92% H_2SO_4 under ordinary conditions, i. e., 0°–30° C., and atmospheric pressure or higher, to react with the normal olefin to give an acid extract, large amounts of polymer are formed due to the polymerization of the tertiary olefins and copolymerization of the tertiary olefins with normal olefins. Also contamination of the ultimate secondary alcohol with tertiary alcohol results. Alternatively, the fraction may be brought into prior contact with sulfuric acid of 60–70% concentration or with phosphoric acid at elevated temperatures to remove the tertiary olefins by copolymerization with the normal olefins, before being brought into contact with 75–92% acid. However, little normal olefin remains to be converted to alcohol.

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Recently processes have been developed, e. g., steam cracking of petroleum fractions in which hydrocarbons are cracked at temperatures in the neighborhood of 1200° F. in the presence of steam. This process produces cracked products containing a higher percentage of olefin, averaging 80–95% total olefin as compared to 30–50%, found in the cracked gases produced by former cracking processes. In the fractions obtained from steam-cracked gases which contain isomeric groups of olefins, it has been found that from 10–25% of the total hydrocarbons are tertiary olefins. Products containing a high percentage of olefins suitable for extraction by the process of this invention have been also produced by the synthesis of hydrocarbons by reaction of hydrogen and carbon oxides in the presence of catalysts, particularly iron catalysts. The olefin products resulting from the process in the presence of the iron catalyst have been found to contain the

proper ratio of tertiary to normal olefins as is required for the extraction described in this invention. Some fractions, particularly the C_5 fraction, containing say 50–70% normal olefins and 15–25% tertiary olefins, respectively, are not amenable to the method of removing the tertiary olefins by contact with H_2SO_4 of 60–75% concentration. In hydrocarbon mixtures of such high concentration of normal and tertiary olefins, the weak acid method removes only about 50% of the tertiary olefins present. This is objectionable because it leaves too high a percentage of tertiary olefin in the hydrocarbon causing polymerization, copolymerization, and contamination in the subsequent alcohol process as previously described. The use of hot weak acid converts the tertiary olefin to polymers which remain in solution in the hydrocarbon and, in addition, consume large amounts of the valuable olefins to produce products other than the desired alcohol. Unless the hydrocarbon is redistilled to remove the polymers, they are carried over into the alcohol process where, in contact with the stronger acid of the alcohol process, they enter into further polymerization and copolymerization reactions causing loss in alcohol yield.

It is an object of this invention to utilize normal and tertiary olefin components of a mono-olefin hydrocarbon stream without appreciable loss of tertiary olefin due to polymerization or to copolymerization with the normal olefin.

It is another object of this invention to recover normal and tertiary olefin components from a strong acid extract containing the same.

These and other objects of the invention will be apparent to those skilled in the art from the following description.

The first step in the process of this invention is to prepare an acid extract containing dissolved therein normal olefins and tertiary olefins. Such extracts may be prepared in a number of ways simply by mixing the hydrocarbon material with fresh acid of appropriate strength, as mentioned above, but preferably as follows:

1. A hydrocarbon stream containing normal and tertiary isomeric mono-olefins in which the ratio of normal olefins to tertiary olefins is at least 2.5 to 1 may be contacted with the reaction product of olefins of the type present in the hydrocarbon feed (or its equivalent in alcohol), and strong acid of a concentration adapted to esterifying olefins, e. g., 82–92% H_2SO_4 (hydrocarbon free basis) for n-butenes; 75–85% H_2SO_4 for n-amylenes, etc., in which the mol ratio of olefin to acid is at least 1:1, and preferably 1.2:1 for amylenes and higher olefins. In other words, the isomeric olefin hydrocarbon stream is not brought into contact with fresh acid but with an acid extract of at least unit saturation. In this manner polymerization and copolymerization of the tertiary olefin is minimized when temperature is about 25° C. This process is the subject matter of U. S. Patent No. 2,497,959, in the name of Richard F. Robey and Salvatore G. Gallo.

2. The normal olefin may be absorbed in a suitable medium such as a relatively strong acid, e. g., H_2SO_4 of about 80–95 weight percent of strength. The resulting extract is thereafter diluted with water to an acid concentration of about 60–75 weight percent on a hydrocarbon free basis, and employed to absorb the more reactive tertiary olefin. The finished extract will then contain both normal and tertiary olefin components in solution.

3. The normal and tertiary olefin extracts may be separately prepared, e. g., by treating the corresponding alcohols with acid, and thereafter mixed.

In any event, the acid extract, by whichever method prepared, consists of an acid solution containing dissolved therein normal and tertiary olefins either in the form of the corresponding ester or alcoholic bodies. Having the normal and tertiary olefins in acid solution this invention is concerned with their removal from the acid extract in such a manner that they can be recovered in relatively pure form. For this purpose a two-stage regeneration process is employed. In the first stage, the tertiary olefin is regenerated as such from the the acid phase under selective stripping conditions after which the remaining acid solution free of tertiary olefins is treated in a second stage for recovery of normal olefins and/or derivatives thereof.

The separation of the tertiary olefin is effected by selective stripping of the acid phase under a preferred set of conditions of temperature, pressure, and acid concentration. The stripping agent employed may be an inert gas such as nitrogen, flue gas, etc., hydrocarbons of appropriate boiling point range, or steam. The quantity of stripping agent used is quite critical for these purposes. Ordinarily it is limited in amount so that the most readily removable material in the extract, namely, the tertiary olefins, are removed without appreciable removal of the normal olefins or of the secondary alcohols derived therefrom. Basically, the invention recognizes the fact that tertiary olefins are relatively more volatile from such acid mixtures than are the normal olefins and their reaction products. Hence, the necessity for controlling the amount of stripping agent employed. Only that amount of steam is added to supply the heat necessary for vaporization of the tertiary olefin. Once stripping is begun, dilution of the acid below the desired concentration is to be avoided. As regards other operating conditions they can be varied depending upon the particular results desired. In the first place, it is necessary to dilute the acid before feeding to the stripping zone by addition of water to a strength of 50–70 weight percent acid (hydrocarbon-free basis), preferably 50–60%. When predilution of this sort is used, the actual stripping operation may be carried out at atmospheric pressure or even at superatmospheric pressures. The effect of increase of pressure is ordinarily to decrease the amount of tertiary olefins relative to the amount of tertiary alcohols recovered. Hence, it is within the scope of this invention not to use predilution, but simply to employ low stripping pressures. The temperature of stripping, of course, depends on the acid strength and the pressure employed in the stripping zone. The amount of polymer formed in such an operation increases with temperature, acid strength and the pressure employed in the stripping zone. While this invention is not specifically limited to conditions which completely avoid olefin polymer formation, it is preferred, within the above limits, to operate under such conditions that polymer formation is minimized.

Following the recovery of tertiary olefins as described above, the normal olefins may be removed in a variety of manners and forms. If it is desired to recover them primarily as the alcohol, then the substantially tertiary olefin-free acid may be subjected to stripping with additional quantities of stripping agent to remove therefrom the secondary alcohol. The acid strength may be adjusted by further dilution with

water or may be raised by addition of stronger acid. In case it is desired to recover the normal olefins as such rather than as the alcohol, it is desirable to add acid, or reconcentrate the acid, to bring the acid strength up to approximately the range employed in the extraction operation proper. In the case of sulfuric acid, this is in the range of 60–80% by weight sulfuric acid. If alcohol is the desired product, then the acid strength should be altered to the range of 30–60% by weight, preferably about 40 weight percent. The pressure employed may be varied. This factor, together with the acid strength, determines the relative amounts of olefin and alcohol obtained. Qualitatively the effects of changes in variables are the same as in the case of tertiary olefins described above. In certain cases it may be desirable to preheat the extract after removal of the olefins for a short period of time to hydrolyze the secondary esters in the acid phase. This is most conveniently conducted at temperatures of 70–210° C. and the acid strengths of 30–50% by weight. Alternatively, the acid containing dissolved normal olefins may be employed as such as a reactive acid liquor, e. g., in the preparation of organic ester.

Basically, then this invention involves the use of a two-stage process for removal of olefins from sulfuric or similar acids with especial emphasis on selective methods for the recovery of the two different types of compounds. The type of stripping zone may be varied according to conventional engineering concepts. Preferably, the operation consists of countercurrent flow of the acid phase and the stripping agent. While sulfuric acid has been employed as a specific example here, it is intended that other acids of the types described above are also within the scope of this invention, e. g., phosphoric acid, benzenesulfonic acid, etc.

Specific examples illustrating the operability of this invention are given below:

Example 1

An acid extract of amylenes in 80% sulfuric acid was prepared containing a total of 1.5 moles of olefin per mole of H_2SO_4. Of the amylenes in solution, 17% were tertiary and the remainder normal. This extract was diluted to 50% acid strength on a hydrocarbon-free basis and subjected without previous hydrolysis to countercurrent steam in a column packed with small Raschig rings. Only amylenes were taken overhead. 217 g. of extract containing 75 g. of amylenes were fed. Of the overhead taken, 12.6 g. was amylenes comprising 84.3% tertiary type. During this period 48 g. of steam were fed. No significant amount of polymer was formed.

Example 2

An acid extract of amylenes was prepared containing 0.20 mol of total C_5 olefin per mole of sulfuric acid. Of the amylenes in solution, 20% were tertiary and the remainder normal. The extract was diluted to 60% acid strength on a hydrocarbon free basis, and then subjected without previous hydrolysis to countercurrent steam in a packed column as in Example 1. 81% of the tertiary amylenes introduced were recovered overhead as monomer. The amylenes recoverd ovrhead comprised 95% tertiary amylene. Almost all of the normal amylenes were found in the residual acid in the form of secondary alcohols and ethers.

Example 3

An acid extract of amylenes in 80% sulfuric acid was prepared containing a total of 1.5 moles of olefin per mole of sulfuric acid. Of the amylenes in solution, 17% were tertiary amylene, and the remainder normal. This extract was diluted to 70% acid strength on a hydrocarbon free basis and subjected to steam stripping as in the previous examples. 51 grams of steam were employed. 220 grams of diluted extract containing 95 grams of amylenes were fed. 20.8 grams of amylenes were taken overhead comprising 75% of the tertiary type in monomer form.

During the first stage of the stripping, according to the terms of this invention, any small amounts of tertiary alcohol obtained as overhead with the tertiary olefin, may be recovered and recycled to the regeneration or absorption stage for further conversion to tertiary olefins.

After the recovery of the tertiary olefin component in each of the examples cited, the remaining extract is ready for treatment for the recovery of the normal olefin component. At this point it is possible to employ conditions conducive to the recovery of the normal olefin as such, or in the form of secondary alcohol. When secondary alcohol is desired, the extract is further diluted with additional quantities of stripping agent, whereas, if the normal olefin recovery is desired, the extract acid strength is increased by the addition of more acid or reconcentration of the extract, and then stripped.

The nature and objects of the present invention having been thus fully set forth and specific examples of the same given, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A process for the recovery of isomeric tertiary and normal mono-olefin components from acid extracts containing both dissolved isomeric tertiary and normal mono-olefins, which comprises diluting the acid extract to an acid concentration of 50–70 wt. per cent on a hydrocarbon free basis, recovering tertiary olefins from the extract by contacting the diluted acid extract in a stripping zone with a stripping agent without further dilution of the acid extract, and subsequently recovering normal olefin components from the stripped tertiary olefin-free acid extract.

2. A process according to claim 1 in which the stripping agent is steam.

3. A process according to claim 1 in which the acid extract is a sulfuric acid extract.

4. A process for the recovery of isomeric tertiary and normal mono-olefins from acid extracts containing both dissolved isomeric tertiary and normal mono-olefin, which comprises diluting the acid extract to an acid concentration of 50–70 weight per cent on a hydrocarbon free basis, recovering tertiary olefins from the diluted extract by contacting the diluted extract in a stripping zone with a stripping agent without further dilution of the acid extract, adding stronger acid to the stripped acid extract to restore the acid concentration to a concentration above 60 weight per cent, and stripping the restored concentrated acid extract with a stripping agent to recover normal olefins therefrom.

5. A process according to claim 4 in which the stripping agent is steam.

6. A process according to claim 4 in which the acid extract is a sulfuric acid extract.

7. A process for the recovery of tertiary mono-

olefins and normal monohydric alcohol from an acid extract containing both dissolved isomeric tertiary and normal mono-olefins, which comprises diluting the acid extract to an acid concentration of 50–70 weight per cent on a hydrocarbon free basis, recovering tertiary mono-olefins from the diluted extract by contacting the diluted extract in a stripping zone with a stripping agent without further dilution of the acid extract, further diluting the tertiary mono-olefin free acid extract to a concentration of 30–60 weight per cent on a hydrocarbon free basis, hydrolyzing the diluted tertiary olefin-free extract and recovering secondary monohydric alcohol from the hydrolyzed extract by contacting the extract with a stripping agent.

8. A process according to claim 7 in which the stripping agent is steam.

9. A process according to claim 7 in which the acid extract is a sulfuric acid extract.

10. A process for the production of tertiary amylene and normal amyl alcohol from a sulfuric acid extract containing both dissolved tertiary and normal amylenes, which comprises diluting the extract to a sulfuric acid concentration of 50–70 weight per cent on a hydrocarbon free basis, recovering tertiary amylene from the diluted extract by contacting the diluted extract in a stripping zone with steam without further dilution of the extract, diluting the tertiary amylene-free acid extract to an acid concentration of 30–60 weight per cent, hydrolyzing the diluted tertiary amylene-free acid extract, and recovering secondary amyl alcohol from the hydrolyzed extract by stripping the hydrolyzed extract with steam.

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