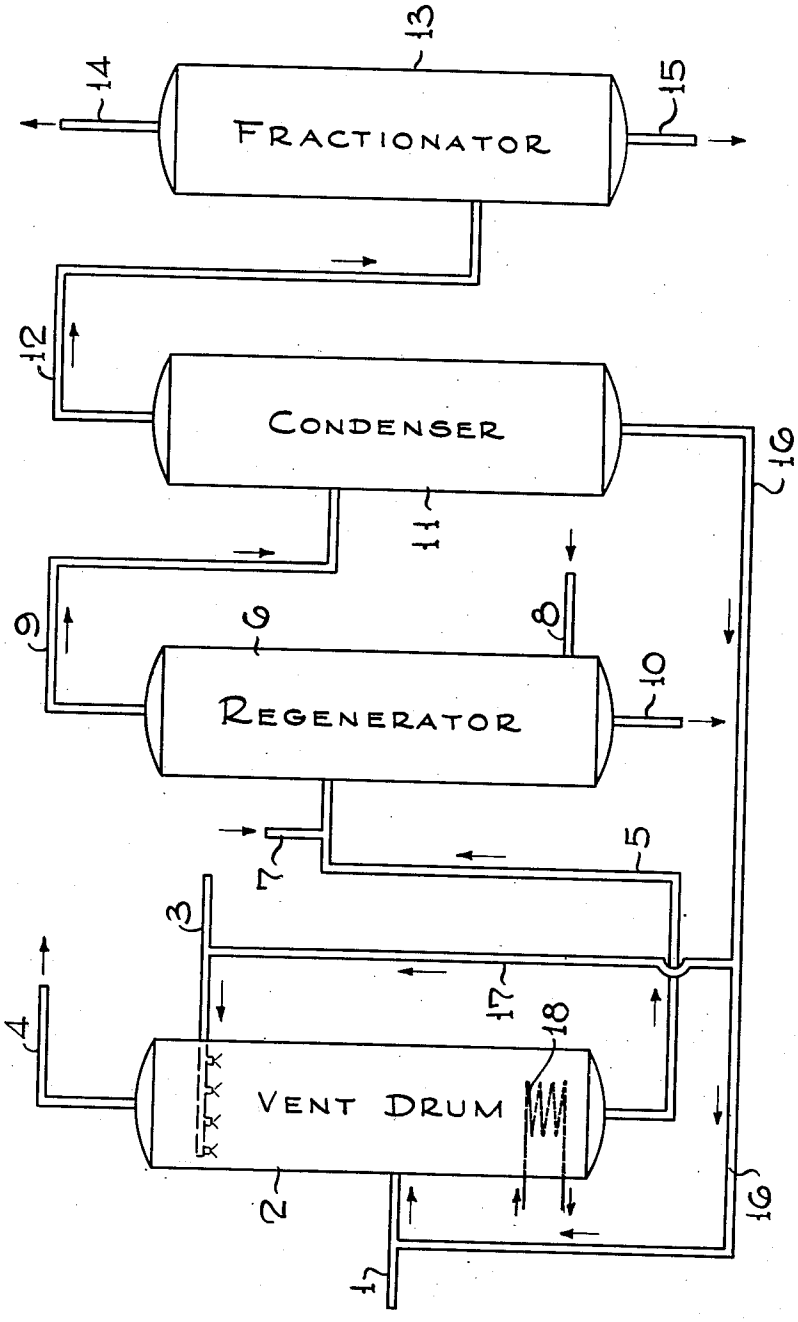
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METHOD OF PURIFYING ISOBUTYLENE
BY SULFURIC ACID EXTRACTION
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METHOD OF PURIFYING ISOBUTYLENE BY SULFURIC ACID EXTRACTION

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This invention relates to the production of isobutylene and particularly to the production of isobutylene free of other C_4 hydrocarbons, particularly, butene-1. The invention is adapted to the production of isobutylene by absorption of C_4-hydrocarbon fractions in acid to form an extract and subseqent regeneration of isobutylene therefrom.

Isobutylene is most satisfactorily separated from C_4-hydrocarbon fractions derived by cracking petroleum or from other sources by absorption of the C_4-hydrocarbon stream in acid of 55 to 70 weight per cent strength, such as the polybasic mineral acids, for example, sulfuric acid, phosphoric acid, or the polybasic mineral acid-acting acids, such as benzenesulfonic acid, toluenesulfonic acid etc.

An isobutylene-sulfuric acid extract may be produced by extracting a C_4-hydrocarbon cut containing isobutylene, butene-1, butene-2, isobutane, normal butane, butadiene and small percentages of C_3 and C_5-hydrocarbons with 55 to 70 weight per cent sulfuric acid at temperatures in the range of approximately 60 to 120° F. and pressures of 80 to 150 p. s. i. g. Under these conditions the sulfuric acid extracts the isobutylene fairly selectively. When an extract, prepared in this manner, is subjected to heating under controlled conditions, such as by stripping with steam, inert gases, such as nitrogen, light hydrocarbons, such as pentane etc., or with heavier inert hydrocarbons which are normally liquid, the isobutylene may be regenerated from the extract in relatively pure form. In the extraction operation, however, small percentages of butene-1 and butene-2 also react with the acid and are present in the final extract. Also, the acid extract exhibits some solubility for other C_4-hydrocarbons and mechanically entrains a portion of all hydrocarbons coming into contact with the acid. These hydrocarbons include the C_4-paraffins and also the normal butenes. This physical solubility and entrainment is especially high when operating to produce extracts of high saturation, for example, 1.0–1.5 mols of olefin per mol of acid.

Since it is the object of the isobutylene production process to produce an isobutylene stream of maximum purity, it is imperative that the C_4-paraffins and normal butenes be removed as thoroughly as possible therefrom. Removal of these contaminants has been carried out in the past by vacuum venting the extract before regeneration. This is accomplished by subjecting the extract to a flashing operation to a vacuum of 1 to 14 p. s. i. absolute, preferably 10 p. s. i. absolute.

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The means of inducing this vacuum is to pass the extract through an efficient flash zone, having a vapor outlet connection to the suction of a compressor, steam jet etc. However, it has been found that vacuum venting produces only a partial removal of physically dissolved and entrained hydrocarbons, particularly, when the extract is one of high saturation as indicated. Hence, a process which will permit more complete removal of these hydrocarbons has been sought. Another disadvantage, occurring in the operation of the vacuum vent drum, is the tendency of the extract to produce considerable foam, which causes carry-over of large amounts of the extract into the hydrocarbon vent stream.

It is an object of this invention, therefore, to eliminate foaming and to reduce solubility of the dissolved gases when an isobutylene sulfuric extract of high saturation is subjected to pressure reduction in a vent drum to remove contaminants, such as the C_4-paraffins, butadiene, the normal butenes and hydrocarbon polymers thereof.

According to this invention, foaming is eliminated and more complete removal of physically dissolved and mechanically entrained hydrocarbons is accomplished during the vacuum venting of an isobutylene acid extract by adding to the extract, prior to or during the vacuum venting operation, tertiary butyl alcohol or an aqueous solution of tertiary butyl alcohol. The tertiary butyl alcohol may be added to the extract feed to the vent drum, or more preferably, the tertiary butyl alcohol may be added in the form of a spray to the top of the vent drum.

According to the invention, therefore, an isobutylene extract is produced by extracting a C_4 cut containing isobutylene, butene-1, butene-2, saturated butanes and butadiene and small percentages of C_3 and C_5-hydrocarbons with an acid, such as sulfuric acid of about 55 to 70 weight per cent concentration, and preferably, sulfuric acid of 60 to 70 weight per cent concentration. The acid at temperatures of 60° F. to 120° F. and pressures of approximately 80 to 150 p. s. i. g. extracts the desired isobutylene fairly selectively. However, other hydrocarbons become physically dissolved or mechanically entrained in the extract as previously recited. The acid extract leaves the absorber at about 100 p. s. i. g. and is allowed to settle into two layers. A spent hydrocarbon layer, which is removed, and an acid extract layer. The settling operation takes place at approximately 70 to 80 p. s. i. g.; hence, considerable gas is dissolved in the resulting extract. The settled extract is then passed to a vacuum vent drum.

The invention will now be described with reference to the drawing which discloses one embodiment of the invention. The drawing represents an elevational view of one type of apparatus for carrying out the isobutylene regeneration process. Referring to the drawing, a contaminated isobutylene acid extract prepared as previously described, and still under pressure, is led via line 1 into vent drum 2. Prior to introduction of the extract into the vent drum, tertiary butyl alcohol or an aqueous solution thereof, may be added to the extract via line 16. In the vent drum the pressure on the extract is reduced from 70 to 80 lbs. to pressures of 1 to 14 p. s. i. absolute, preferably, 10 p. s. i. absolute. This sudden reduction in pressure, plus the fact that steam is added to the vent drum via coil 18 to raise the temperature from approximately 100° F. to 110 to 112° F., cause physically dissolved and mechanically entrained gases to disengage. In the disengaging operation, as normally carried out in the absence of tertiary butyl alcohol, the extract is caused to foam up, often to the extent that it will pass overhead with the vented gases, causing loss of the valuable extract and contaminating the hydrocarbon stream with acid. However, in the presence of the tertiary butyl alcohol, the foaming is suppressed so that gases disengage rapidly without the formation of a stable foam. The tertiary butyl alcohol also reduces the solubility of the gases in the extract so that they will more readily disengage therefrom. When the tertiary butyl alcohol is added to the vent drum through line 3 in the form of a spray, the alcohol additionally assists in the physical destruction of any foam which may form, although the alcohol itself serves as an agent to reduce surface tension and to minimize foam formation regardless of its point of addition. Vent gases, including the saturated C_4-hydrocarbons, the normal butenes and butadiene, together with some light polymers thereof, pass overhead from the vent drum via line 4. The vented extract is then led via line 5 to regenerator 10. Prior to introduction of the extract into the regenerator, it is diluted with water added via line 7 until the sulfuric acid is reduced to approximately 45 to 48 weight per cent concentration. In the regenerator a stripping operation occurs by means of steam or other inert gas added through line 8. The product taken overhead from the regenerator via line 9 contains isobutylene, water, tertiary butyl alcohol, traces of secondary butyl alcohol and some hydrocarbon polymers. Weak spent acid is removed from the regenerator via line 10. The overhead vapor product from the regenerator is condensed in partial condenser 11 in which gaseous isobutylene is separated from the water, tertiary butyl alcohol, secondary butyl alcohol and polymers, which are removed via line 16. The tertiary butyl alcohol formed in the regeneration process is an excellent source of material to be added to the vent drum according to this invention. However, the recycle product obtained as bottoms from the condenser should be substantially purified of large amounts of secondary butyl alcohol and hydrocarbon polymer before being recycled to the acid extract via line 16. Secondary butyl alcohol is not desirable in the tertiary butyl alcohol because it decomposes to butene-1 and butene-2 during the venting operation, thus causing possible contamination of the desired isobutylene product. The isobutylene stream is allowed to pass overhead from partial condenser 11 via line 12 to fractionator 13. The fractionator is operated so as to separate substantially pure isobutylene which passes overhead via line 14 from final traces of other hydrocarbons, such as normal butanes, butene-2 and hydrocarbon polymers, which are removed as bottoms via line 15. Recycle tertiary butyl alcohol can, of course, be added to the vent drum via line 17 and line 3 where it enters the vent drum in the form of a spray.

The tertiary butyl alcohol employed in the vent drum according to the terms of this invention may be pure tertiary butyl alcohol or an aqueous solution of tertiary butyl alcohol containing small amounts of water and other impurities, such as secondary butyl alcohol and hydrocarbon polymers. However, these impurities, as previously related, should be held to a very small amount. The amount of tertiary butyl alcohol employed in the vent drum may vary approximately between 5 and 20 weight per cent, preferably, 8 to 12 weight per cent based on the weight of acid extract.

Example I

The efficiency of the isobutylene regeneration process, when carried out according to the terms of the present invention, can be realized from the following data.

Upon the addition of tertiary butyl alcohol to the vent drum in a commercial plant size isobutylene production process, it was possible to increase the C_4-hydrocarbon feed to the absorber from about 400,000 to about 600,000 lbs. per day. This increase is, of course, possible because of the more rapid and complete removal of the vent gases from the vent drum and also because of the elimination of substantial foaming in the vent drum. At the same time, the production of isobutylene was increased from 13 tons per day to a figure between 23 and 44 tons per day. These results were produced by employing approximately 11,000 to 15,000 lbs. per hour of recycle tertiary butyl alcohol, containing approximately 80 vol. percent tertiary butyl alcohol, 10% water and the balance impurities, chiefly, C_4 polymers and secondary butyl alcohol. The acid extract feed rate to the vent drum, to produce the above improved conditions, was increased to about 12,100 lbs. of extract per hour. The extract saturation was approximately 0.7 to 1.5 or more mols of isobutylene per mol of sulfuric acid in sulfuric acid of 65 weight percent strength on a hydrocarbon free basis.

Having described the invention in a manner so that it may be practiced by those skilled in the art, what is claimed is:

1. A process for the production of isobutylene which comprises contacting a C_4-hydrocarbon stream containing isobutylene, normal butenes, butanes and butadiene at a temperature of 60 to 120° F. and at a pressure of 80 to 150 p. s. i. g. with an acid to form an isobutylene acid extract, adding tertiary butyl alcohol to the extract in a vent drum while still under pressure, reducing the pressure on the extract to approximately 1 to 14 p. s. i. absolute, whereby physically dissolved and mechanically entrained hydrocarbons, including normal butenes, butanes and butadiene, are released from the extract, and thereafter recovering isobutylene from the acid extract.

2. A process according to claim 1 in which the acid is sulfuric acid of 55 to 70 weight percent concentration.

3. A process according to claim 1 in which the acid is sulfuric acid of 65 weight percent concentration.

4. A process according to claim 1 in which the tertiary butyl alcohol is added to the vent drum in the form of a spray.

5. A process according to claim 1 in which the tertiary butyl alcohol is added in amounts of 5 to 20 weight percent based on the weight of acid extract in the vent drum.

6. A process according to claim 1 in which the tertiary butyl alcohol is added in amounts of 8 to 12 weight percent based on the weight of acid extract in the vent drum.

7. A process according to claim 1 in which the tertiary butyl alcohol added to the vent drum is an aqueous solution of tertiary butyl alcohol, containing approximately 80 volume percent tertiary butyl alcohol.

8. A process for purifying an isobutylene-acid extract contaminated with physically dissolved and mechanically entrained normal butenes, butanes and butadiene, which comprises adding tertiary butyl alcohol to the extract while under pressure of 80 to 150 p. s. i. g., and thereafter reducing the pressure on the extract to approximately 1 to 14 p. s. i. absolute, whereby the physically dissolved and mechanically entrained normal butenes, butanes and butadiene are removed from the isobutylene-acid extract.

9. A process according to claim 8 in which the isobutylene-acid extract is an isobutylene-sulfuric acid extract.

10. A process according to claim 8 in which the tertiary butyl alcohol added to the extract is an aqueous solution of tertiary butyl alcohol, containing approximately 80 volume percent tertiary butyl alcohol.

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