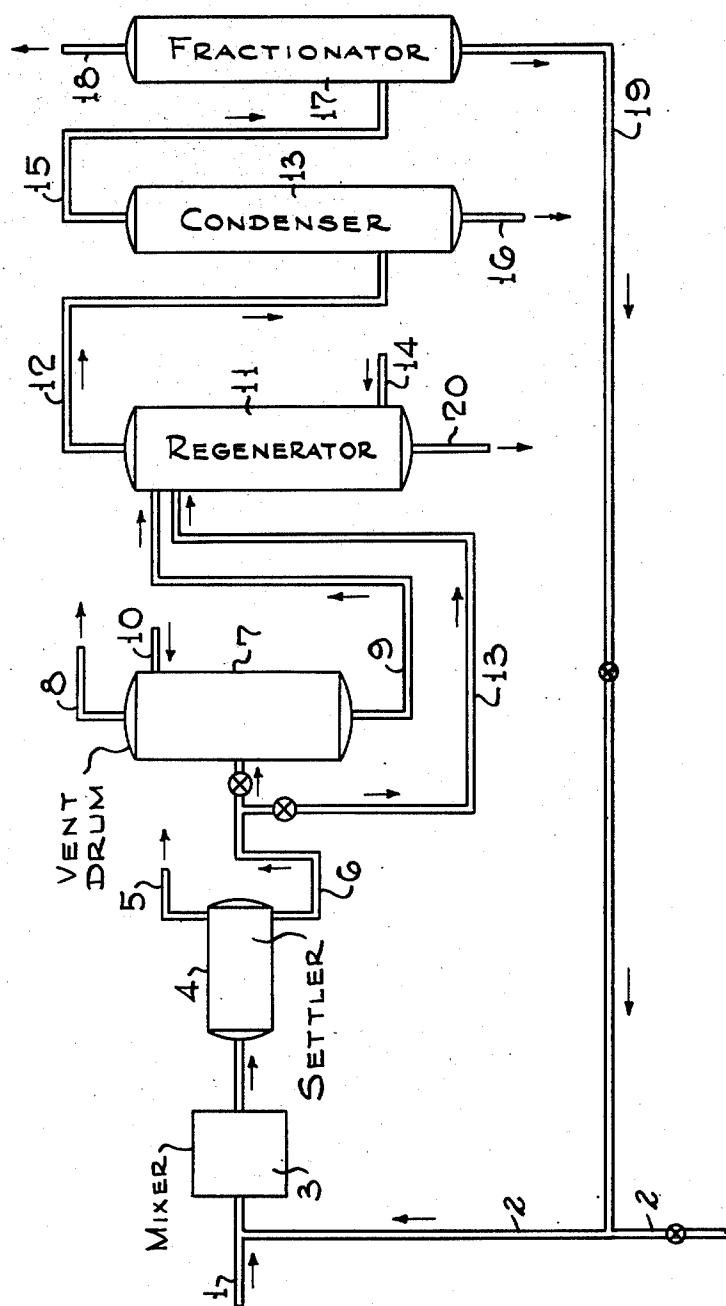


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ISOBUTYLENE PURIFICATION SYSTEM

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ISOBUTYLENE PURIFICATION SYSTEM

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This invention relates to the production of isobutylene, and particularly to the production of isobutylene free of butene-1. The invention is adapted to the production of isobutylene by absorption of C₄-hydrocarbon fractions in acid to form an extract and subsequent regeneration of isobutylene therefrom.

Isobutylene is most satisfactorily separated from C₄-hydrocarbon fractions derived from petroleum or other sources by absorption of the C₄-hydrocarbon stream in acid of 55-70 wt. percent strength, such as polybasic mineral acids, particularly sulfuric acid. An isobutylene-sulfuric acid extract may be produced by extracting a C₄ cut containing isobutylene, butene-1, butene-2, isobutane, normal butane, butadiene, and small percentages of C₃ and C₅-hydrocarbons, with 55-70 wt. percent 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 C₄-hydrocarbons and mechanically entrains a portion of all hydrocarbons coming in contact with the acid. These hydrocarbons include C₄-paraffins and also the normal butenes. This physical solubility and entrainment are especially high when operating to produce extracts of high saturations, for example, 1.0 to 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 C₄-paraffins and normal butenes be removed as thoroughly as possible therefrom.

It is an object, therefore, of this invention to provide a method for producing isobutylene free of hydrocarbon contaminants particularly butene-1, butene-2, isobutane and n-butane.

Removal of the above-mentioned contaminants from the acid extract has been carried out in the past by vacuum venting of the extract before regeneration. This is accomplished by subjecting the extract to a flashing operation under a vacuum of 1 to 14 lbs./sq. in. absolute,

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preferably 10 p. s. i. absolute. 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 dissolved and entrained normal butenes and butanes particularly when dealing with extracts of high saturation. Hence, a more complete removal process has been sought.

According to the terms of this invention substantially complete removal of undesirable C₄-hydrocarbon contaminants from a C₄-acid extract is accomplished by washing the acid extract with a substantially saturated liquid hydrocarbon. This hydrocarbon may be a saturated C₄ cut, an isopentane cut, a normal pentane cut, a hexane cut etc., or any of these pure hydrocarbons preferably of C₄ to C₆ mol wt. range. When hydrocarbon cuts are employed they should be substantially free of unsaturates particularly butene-1. That is, the n-butene-1 content should be below 10%, preferably below 3% by liquid volume. The hydrocarbon wash is preferably carried out in the liquid phase and preferably at about 100° F. In such a contacting operation the mechanically entrained and physically dissolved isobutane and n-butene-1 are substantially completely removed from the extract by solution in the hydrocarbon wash solvent.

The washing operation is particularly effective in removing isobutane and butene-1 from the extract. This is highly important because it is known that n-butane and butene-2 present in the regenerated isobutylene can be removed by subsequent distillation of the crude isobutylene product. However, isobutane and butene-1 cannot be so removed due to the closeness of their boiling points to the boiling point of isobutylene. Hence, they would appear in the final isobutylene product. This contamination cannot be tolerated since the isobutylene is to be employed in polymerization processes which are sensitive to such impurities.

By the process of this invention the amount of isobutane and butene-1 contaminant in the mechanically entrained and dissolved state in the extract can be reduced to as low as $\frac{1}{16}$ of its original amount. In general this will reduce the percentage of isobutane and butene-1 in the final rerun isobutylene product from about 0.6-1.5% to 0.3 to 0.8% (wt.).

In one embodiment of the invention the wash hydrocarbon is mixed with the acid extract in an orifice mixer at a temperature of 60-120° F., pref-

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erably about 100° F. and about 100–150 lbs. pressure, settled, and the effluent hydrocarbon is either sent to the extraction section (if recycle is employed) or to a separate distillation unit for removal of C₄ contaminants (if iso-C₅, n-C₅, etc. is used).

The purified extract may then be sent to a vacuum vent drum held under about 1–14 p. s. i. pressure in order to remove more completely entrained C₄-hydrocarbons as a precautionary measure. This vent drum is optional, of course, and can be by-passed if desired, and the purified extract sent directly to the extract regenerator where the isobutylene is removed from the sulfuric acid extract. This is usually accomplished by dilution followed by steam stripping. However, other inert stripping agents such as hydrocarbons, particularly the higher liquid saturated hydrocarbons. Also the isobutylene may be recovered from the acid extract by solvent extraction, however, this is not preferred over recovery by stripping.

The washing operation may be carried out on the acid extract after it emerges from the acid absorption zone, i. e., while still under pressure of 80–150 lbs. p. s. i. g. or it may be carried out on the acid extract after it has been subjected to the vacuum venting operation. However, processing under pressure is preferred in order to avoid foaming of the extract. In either event liquid phase washing of the extract is preferred. The wash hydrocarbon is easily separated from the acid extract due to phase separation. After separation the hydrocarbon may be disposed of in any manner, although it is preferred to recycle it to the acid extraction stage of the process for the removal of any isobutylene therefrom.

The washing operation may be carried out in a mixer-settler system or by countercurrently washing the extract with the hydrocarbon in a column of sufficient size to provide adequate residence time for settling and separation of the acid and hydrocarbon phases. Likewise a series of contact zones may be employed.

The following description with reference to the drawing discloses one embodiment of the invention. The drawing represents in elevational view one type of apparatus for carrying out the process. Referring to the drawing a contaminated isobutylene-acid extract prepared as previously described and still under pressure is led via line 1 to an orifice-type mixer 3 where it is thoroughly mixed with a light, substantially saturated hydrocarbon fed through line 2. The amount of light hydrocarbon employed is about 3 to 10 volumes per volume of mechanically entrained and physically dissolved contaminating hydrocarbons. As an example, about 50 barrels per stream day of entrained C₄ cut containing 30% butene-1 required 150–200 barrels per stream day of a substantially saturated C₄ cut (containing 3% butene-1) to reduce the butene-1 content of the final isobutylene product from 0.6 to 0.3 wt. per cent butene-1 based on isobutylene. The solvent hydrocarbon is mixed with the extract at about 60–120° F., preferably 100° F. and a pressure of about 100–150 p. s. i. and transferred to settler 4. From the settler the effluent hydrocarbon containing the dissolved contaminants and small amounts of isobutylene is removed via line 5 and preferably returned to the acid-absorption unit of the system for recovery of isobutylene therefrom. If the latter process is not employed the effluent is sent to a separate distillation unit for removal of the C₄-contaminants,

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particularly butene-1 and isobutane therefrom, after which it is re-employed in the washing operation. The purified acid extract is pumped from the settler via line 6 to vent drum 7 (operated as previously described) as a precautionary measure. In the vent drum a pressure of about 10 p. s. i. absolute is maintained in order to more completely remove any entrained C₄-contaminants escaping removal by the wash solvent. This vent drum can, of course, be by-passed, if desired, and the purified extract pumped directly via lines 8 and 13 to the extract regenerator 11. Water or tertiary butyl alcohol recovered from the system, as will be later described, may be introduced into vent drum 7 via line 10, preferably in the form of a spray to reduce foaming of the extract. Entrained hydrocarbons released in the venting operation are removed via line 8 as vent gas. The purified extract is pumped from the vent drum via line 9 to the regenerator 11. In the regenerator the extract is diluted and subjected to a process for the recovery of isobutylene therefrom. The preferred recovery method is a steam stripping operation, steam being introduced through line 14. In place of steam other inert gases such as nitrogen or pentane etc. may be employed or heavier normally liquid hydrocarbons may be successfully employed. The product taken overhead from the regenerator via line 12 contains isobutylene, water, tertiary butyl alcohol, trace of sec-butyl alcohol and some hydrocarbon polymers. Spent acid is removed via line 20 for reconcentration and recycle to the absorption stage of the process. The overhead product is led via line 12 to a partial condenser 13 in which the gaseous isobutylene product is separated from the water, tertiary butyl alcohol and polymers which are removed via line 16 for further separation and re-use. For example, the t-butyl alcohol may be recovered therefrom and recycled through line 10 to the vent drum to prevent foaming as previously described. The isobutylene stream is allowed to pass overhead from partial condenser 13 via line 15 to a fractionator 17. The fractionator is operated so as to separate substantially pure isobutylene which passes overhead via line 18 from final traces of n-butane, n-butene-2 and hydrocarbon polymers which are removed as bottoms via line 19. The latter stream which contains but small amounts of unsaturates in the form of n-butene-1 is known as the recycle C₄ stream and is preferably employed as the wash solvent for the extract being recycled via line 19 to the solvent line 2. If desired, other wash streams such as saturated C₄ cut, isopentane cut, normal pentane cut, hexane cut etc. can be used and introduced through line 21.

In the acid absorption stage of the process sulfuric acid is usually employed in the preparation of the acid extract. However, any polybasic mineral acid-acting substance may be employed e.g. phosphoric acid, benzenesulfonic acid, toluene sulfonic acid etc. or mixtures of these acids, or salts of these acids which in aqueous solution behave as acids. The invention is not to be considered limited to any manner in which the acid extract is prepared as the invention is equally applicable to the purification of any contaminated isobutylene-acid extract regardless of its previous history.

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

1. In the preparation of isobutylene comprising absorption of a mixture of C₄ hydrocarbons

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containing isobutylene, butene-1, butene-2, butadiene, isobutane and n-butane in an acid to form an isobutylene-acid extract and subsequent regeneration of the isobutylene from the acid extract, the improvement which comprises contacting the acid extract with a saturated aliphatic hydrocarbon of 4 to 8 carbon atoms per molecule substantially free of unsaturates and separating a liquid hydrocarbon phase from the acid extract prior to the isobutylene regeneration step.

2. In the preparation of isobutylene comprising absorption of a mixture of C₄ hydrocarbons containing isobutylene, butene-1, butene-2, butadiene, isobutane and n-butane in sulfuric acid to form an isobutylene-sulfuric acid extract and subsequent regeneration of the isobutylene from the sulfuric acid extract, the improvement which comprises contacting the sulfuric acid extract with a saturated aliphatic hydrocarbon of 4 to 8 carbon atoms per molecule substantially free of unsaturates and separating a liquid hydrocarbon phase from the sulfuric acid extract prior to the isobutylene regeneration step.

3. A process according to claim 2 in which the saturated aliphatic hydrocarbon is a C₄ cut substantially free of butene-1.

4. A process according to claim 2 in which the saturated aliphatic hydrocarbon is a C₄ cut containing less than 10 vol. per cent of butene-1.

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5. In the regeneration of isobutylene from an isobutylene-sulfuric acid extract contaminated with other mechanically entrained and dissolved C₄ hydrocarbons, the improvement which comprises contacting the contaminated isobutylene-sulfuric acid extract with a saturated aliphatic hydrocarbon of 4 to 8 carbon atoms per molecule substantially free of unsaturates, separating a liquid hydrocarbon phase from the sulfuric acid extract and recovering isobutylene from the thus purified sulfuric acid extract.

6. A process according to claim 5 in which the contaminated extract is contacted with the saturated aliphatic hydrocarbon at a temperature between 60° F. and 120° F. and at a pressure of 80-150 p. s. i. g.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,380,350	Willauer et al.	July 10, 1945
2,431,005	Willauer et al.	Nov. 18, 1947
2,433,030	Cone	Dec. 23, 1947