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PROPYLENE OXIDE PURIFICATION

BACKGROUND OF THE INVENTION

ACTION

FIELD OF THE INVENTION

The present invention relates to the separation of propylene oxide and methanol by a liquid/liquid extraction process.

PRIOR ART DESCRIPTION

The separation or removal of methanol from propylene oxide by conventional distillation processes is difficult by reason of the low relative volatility of propylene oxide with respect to methane at higher concentrations such as concentrations above 95 wt.% or so.

Technology has been developed for the production of propylene oxide by oxidative procedures which include the use of a methanol solvent during the oxidation reaction. Illustrative of patents relating to this technology are USP 4,824,976, 4,833,260, 5,252,758 and the like.

Reaction mixtures produced by this technology comprise the product propylene oxide and the methanol solvent and it is important that the propylene oxide and methanol be separated as conveniently and economically as possible.

BRIEF DESCRIPTION

In accordance with the present invention, a propylene oxide and methanol solution is subjected to a liquid/liquid extraction using water and a hydrocarbon such as n-octane in order to separate the propylene oxide and methanol.

DESCRIPTION OF THE DRAWING

The accompanying Figure 1 provides a schematic illustration of a practice of the invention. Figure 2 provides a schematic illustration of a comparative process not according to the invention. Figure 3 and 4 show schematic illustrations of preferred practices of the invention.

DETAILED DESCRIPTION

It has now been found that propylene oxide and methanol can be separated by a relatively straightforward liquid/liquid extraction procedure

using as extractive solvents water and a hydrocarbon such as n-octane. In an especially preferred practice of the invention, as shown in Figure 1, a liquid stream comprised of propylene oxide and methanol is fed to a conventional continuous extraction column 1 via line 2. Water as an extractive solvent is fed to the column at the upper end via line 3, and a hydrocarbon such as n-octane is fed to the column at the lower end via line 4. In the extraction column, water flows downwardly extracting with it methanol contained in the feed. The hydrocarbon, on the other hand, flows upwardly through the column carrying with it propylene oxide. Thus, from the column an upper liquid stream is recovered via line 5 comprised of the hydrocarbon solvent and the extracted propylene oxide substantially reduced in methanol, while from the bottom of the column an aqueous stream, comprised of the extractive water solvent and methanol is removed via line 6. The removed streams can be suitably processed in a conventional manner to recover the components. Thus, the hydrocarbon extractive solvent and propylene oxide stream can be fractionated to separate the hydrocarbon which can be conveniently reused in the extraction step. The separated propylene oxide can be further purified by conventional methods in order to obtain a suitably high purity product propylene oxide. In processes where high purity propylene oxide is accomplished with extractive distillation, the hydrocarbon extractive solvent stream 5 can be fed directly to extractive distillation, making this invention particularly convenient for removal of methanol as shown in Figure 4. As to the aqueous stream, this stream can be treated by conventional distillation to separate methanol and water. Methanol can be conveniently returned to the propylene oxide forming reaction where it functions as an effective solvent, and water can be recycled to the extraction.

In carrying out the present invention, no special conditions of temperature or pressure are necessary for successful separation of propylene oxide and the methanol. Generally speaking temperatures ranging from about 60 to 150°F are suitable and pressures close to normal can be employed.

The feed streams, which are treated in accordance with the present invention, are comprised of propylene oxide and methanol, preferably from a catalyzed hydrogen peroxide oxidation of propylene. Generally it is advisable to subject the feed first to a distillation, especially where methanol concentrations are high, in order to remove methanol before extraction. The feed to the extraction process generally will comprise by weight about 2 to 10% methanol with the remainder essentially propylene oxide.

The extractive hydrocarbon solvent employed accordingly to the present invention is a saturated hydrocarbon, preferably a C_7 –C_9 saturated paraffin hydrocarbon. Octane is preferred because it is not only an effective extraction solvent but frequently in propylene oxide purification procedures n-octane is employed in an extractive distillation whereby trace impurities are removed from propylene oxide. Other saturated hydrocarbons which are useful include n-heptane and n-nonane as well as branched saturated hydrocarbons having 7-9 carbon atoms.

Through practice of the present invention, the separation of methanol from propylene oxide is effectively accomplished. Purities of product propylene oxide with respect to contained methanol achieved through practice of the invention can range from about 99.8 to 99.995 wt.% purity usually 99.9 to 99.95 wt.% purity.

The invention is especially suitable in conjunction with procedures for the manufacture of propylene oxide which involve the oxidation of propylene with hydrogen peroxide carried out in the liquid phase using a methanol containing solvent. The mixtures, which are resolved in accordance with the invention can be mixtures of propylene oxide and methanol as well as propylene oxide and methanol plus water.

In general, commercially available propylene oxide has a purity in excess of 99.95%. Oxygenated hydrocarbons such as acetaldehyde, methanol, and methyl formate are key impurities, along with water and hydrocarbons such as hexenes and hexanes. Several refining schemes are possible to provide propylene oxide at these low impurity levels, including extractive distillation with heavy hydrocarbons such as octanes.

For example, Figure 2 illustrates for comparative purposes a simple distillation to obtain crude propylene oxide with methanol concentrations typical of those encountered in the feed to a commercial propylene oxide refining operation.

The propylene oxide reaction mixture which typically may comprise 10 wt.% propylene oxide, 5 wt.% water and 85 wt.% methanol and impurities is introduced into distillation column 201 via line 202 and fractionally distilled to recover overhead via line 203 a propylene oxide stream of 99+% propylene oxide which is suitable as feed to a commercial propylene oxide refining operation. The methanol and water bottoms stream is separated via line 204.

A disadvantage of such a straight distillation procedure is that a large distillation column having many theoretical stages is required along with high reflux ratios in order to achieve the appropriate separation.

It is possible to economically do a rough distillation of the propylene oxide reaction mixture to substantially concentrate propylene oxide and in an especially advantageous practice of the invention such a rough distillation is performed prior to the liquid/liquid extraction according to the invention. Such a procedure is illustrated in Figure 3.

With reference to Figure 3, a propylene oxide reaction mixture such as described above in connection with Figure 2 is introduced to distillation column 301 via line 302 and therein fractionally distilled to recover an overhead rough crude propylene oxide which is greatly concentrated in propylene oxide with respect to the feed, for example 95 wt.% propylene oxide and 5 wt.% methanol and impurities, and which is removed via line 303.

Far fewer theoretical stages and lower reflux ratios can be employed in column 301 as compared to those needed for the separation in column 201 previously described.

The rough crude propylene oxide stream passes via line 303 to liquid/liquid extractor 304 to which is introduced water extractant via line 305 and octane extractant via line 306. The liquid/liquid extraction is carried out as described in connection with Figure 1, the octane and propylene oxide

stream being removed via line 307 and the water methanol stream being removed via line 308.

Conveniently the water and methanol stream passes back to column 301 via line 308 as shown and from column 301 a methanol and water stream is recovered via line 309.

By the distillation and extraction sequence shown in Figure 3 it is possible to obtain a propylene oxide stream via line 307 which is comparable to that obtained via line 203 of Figure 2 in a much more economic manner.

In certain processes, propylene oxide is refined to commercially acceptable purities by extractive distillation using an extractive solvent such as octane. See, for example, USP 3,843,488.

Figure 4 illustrates especially preferred practice of the invention which integrates the liquid/liquid extraction with extractive distillation using octane solvent.

Referring to Figure 4, the octane and propylene oxide extraction stream passes from extractor 304 via line 307 to extractive distillation column 310 wherein methanol, water and light impurities are separated as overhead vapor along with some octane via line 311. The overhead is condensed in condenser 312 and passed to decanter 313 along with liquid octane via line 314. An aqueous purge with methanol and light impurities is separated via line 315. Octane is returned as reflux via line 316 to column 310.

From column 310 a bottoms octane and propylene oxide stream is removed via line 317 to column 321 wherein refined propylene oxide of high purity is recovered via line 322. Octane is passed via line 314 to decanter 313 with a portion passing via line 306 to extractor 304.

It is worth noting that if the rough crude propylene oxide from column 301 is passed to extractive distillation without the liquid/liquid extraction step, the methanol and light impurities can be removed in an aqueous stream from the overhead decanter. However, the methanol cannot be conveniently be recycled since there is no outlet for the light impurities.

As above described, the process of the invention is especially useful in separating propylene oxide and methanol such are present in the reaction

mixtures resulting from the reaction of propylene and hydrogen peroxide using a methanol solvent.

Example

Referring to Figure 4, the reaction mixture from the catalytic reaction of hydrogen peroxide and propylene in methanol solvent to form propylene oxide is fed via line 302 to distillation column 301 wherein a crude separation of methanol and propylene oxide takes place. An overhead crude propylene oxide stream is removed and passes via line 303 to extraction column 304 wherein it is subjected to the liquid/liquid extraction in accordance with the invention.

Column 304 is a conventional extractor adapted to provide intimate contact of the various liquid streams fed thereto. The water extraction solvent is fed to column 304 via line 305 near the upper end and n-octane extraction solvent is fed via line 306 near the lower end. The water extraction solvent passes downwardly through the column and is removed together with extracted methanol via line 308 and conveniently passed, as shown, to column 301 for separation of minor amounts of n-octane contained therein. An aqueous methanol stream is recovered from column 301 via line 309 and this stream can be treated by conventional means for recovery of methanol which can be reused in the propylene reaction to form propylene oxide.

The n-octane extraction solvent stream containing extracted propylene oxide is recovered from column 304 via line 307 and passes to distillation column 310 wherein light impurities are separated by extractive distillation. Overhead from column 310 passes via line 311 to condenser 312 and decanter 313 and n-octane is fed to decanter 313 via line 314. A small purge stream is removed from decanter 313 via line 315. Reflux n-octane passes via line 316 to column 310 and a bottoms stream is removed therefrom via line 317 and passed to distillation column 321. A propylene oxide product stream from which the great bulk of the methanol has been separated is recovered overhead via line 322, and a bottoms n-octane stream is recovered via line 314.

The accompanying table is provided which gives the flow rates, compositions, and conditions at the various points in the process described above. It can be seen that practice of the invention provides essentially complete separation of methanol from the propylene oxide in an economic and convenient procedure.

Table

Stream ID	302	303	305	306	307	308	309
Temperature F	110	111.2	110	120	109.6	118.3	187
Pressure, PSI	200	20	100	100	30	30	29.6
Vapor Frac	0	0	0	0	0	0	0
Mole Flow, LBMOL/HR	23405	1430	1493	1751	3143	1531	23505
Mass Flow LB/HR	752771	79803	26897	200000	277394	29306	702274
Mass Flow LB/HR							
Propylene Oxide	75861	75786	0	0	75785	1	76
Methanol	636865	3990	0	0	76	3914	636789
Water	40045	16	26897	0	1539	25374	65403
Normal Octane	0	11	0	200000	199994	16	6
Mass Frac							
Propylene Oxide	0.1010	0.9500	0.0000	0.0000	0.2730	0.0000	0.0000
Methanol	0.8460	0.0500	0.0000	0.0000	0.0000	0.1340	0.9070
Water	0.0530	0.0000	1.0000	0.0000	0.0060	0.8660	0.0930
Normal Octane	0.0000	0.0000	0.0000	1.0000	0.7210	0.0010	0.0000

Table continued

Stream ID	311	313	314	315	316	319	322
Temperature F	168.6	120	316.9	100	100	216.4	122.4
Pressure, PSI	30	80	33.6	30	30	42.6	25
Vapor Frac	1	0	0	0	0	0	0
Mole Flow, LBMOL/HR	549	2626	4377	90	3085	5680	1303
Mass Flow LB/HR	30000	300000	499995	1738	328262	575657	75662
Mass Flow LB/HR							
Propylene Oxide	22771	0	1	123	22648	75662	75660
Methanol	421	0	0	76	345	0	0
Water	1794	0	0	1538	256	1	1
Normal Octane	5013	300000	500000	0	305013	500000	0
Mass Frac							
Propylene Oxide	0.7590	0.0000	0.0000	0.0710	0.0690	0.1310	1.0000
Methanol	0.0140	0.0000	0.0000	0.0440	0.0010	0.0000	0.0000
Water	0.0600	0.0000	0.0000	0.8850	0.0010	0.0000	0.0000
Normal Octane	0.1670	1.0000	1.0000	0.0000	0.9290	0.8690	0.0000

I claim:

1. A process for the separation of a mixture of propylene oxide and methanol by liquid/liquid solvent extraction which comprises contacting the said mixture with water and $C_7 - C_9$ hydrocarbon extractive solvents.

2. The process of claim 1 wherein the hydrocarbon extractive solvent is octane.

3. The process of claim 1 wherein extracted propylene oxide and hydrocarbon solvent is subjected to an extractive distillation.