Claims

1. A process for purifying a stream comprising 1,4-butanediol comprising the steps of:
   (a) supplying a crude product stream comprising 1,4-butandiol and one or more of γ-butyrolactone, 2-(4-hydroxybutoxy)-tetrahydrofuran, 4-hydroxybuty1(4-hydroxybutyrate), and 3-(4-hydroxybutoxy)-tetrahydrofuran to a first distillation column;
   (b) removing a side-draw comprising 1,4-butanediol, and light components, said light components including at least some of those produced by reaction in the first distillation column;
   (c) passing the stream to a hydrogenation zone;
   (d) subjecting the stream from step (c) to hydrogenation in the hydrogenation zone in the presence of a hydrogenation catalyst, and recovering from the hydrogenation zone a 1,4-butanediol product stream having a reduced content of 2-(4-hydroxybutoxy)-tetrahydrofuran, and optionally additionally including (4-hyroxybutyl)-4-hydroxybutyrate formed by reaction of γ-butyrolactone;
   (e) passing the 1,4-butaendiol product stream from step (d) to a second distillation column operated such that where (4-hyroxybutyl)-4-hydroxybutyrate is present, it is removed as a bottom stream and removing a 1,4-butanediol stream as overhead; and
   (f) passing the overhead stream removed in (e) to a third distillation column and recovering a purified 1,4-butanediol stream.

2. A process according to Claim 1 wherein the side draw from the first distillation column is taken from a point above the point at which the feed is added to the column.

3. A process according to Claim 1 or 2 wherein the process additionally includes the step of:

   (b1) passing the side draw to the hydrogenation zone via a further distillation column in which at least some of the light components are stripped from the stream before it is passed to the hydrogenation zone.

4. A process according to Claim 3 wherein the first and further distillation columns are combined into a single vessel.

5. A process according to Claim 4 wherein the vessel includes a separating baffle.

6. A process according to any one of Claims 1 to 5 wherein the second and third distillation columns are combined into a single vessel.

7. A process according to Claim 6 wherein the vessel includes a separating baffle

8. A process according to any one of Claims 1 to 7 wherein a recycle from the second and/or third distillation column is fed to the first distillation column.

9. A process according to any one of Claims 1 to 8 wherein the hydrogenation is carried out at a temperature of from ~~about~~ 30°C to ~~about~~ 170°C, preferably from ~~about~~ 50°C to ~~about~~ 125°C.

10. A process according to any one of Claims 1 to 9 wherein the hydrogenation is carried out at a pressure of from ~~about~~ 50 psia (~~about~~ 3.45 bar) to ~~about~~ 2000 psia (~~about~~ 137.90 bar), preferably from ~~about~~ 150 psia (~~about~~ 10.34 bar) to ~~about~~ 1000 psia (~~about~~ 68.95 bar).

11. A process according to any one of Claims 1 to 10 wherein the feed to the hydrogenation zone is supplied at a liquid hourly space velocity of from ~~about~~ 0.1 h^{-1} to ~~about~~ 4.0 h^{-1}, preferably from ~~about~~ 0.5 h^{-1} to ~~about~~ 1.5 h^{-1}.

12. A process according to any one of Claims 1 to 11 wherein the distillation columns are operated at pressures of from ~~about~~ 0.1 to ~~about~~ 1 bar abs, preferably from ~~about~~ 0.1 to ~~about~~ 0.3 bar abs.

13. A process according to any one of Claims 1 to 12 wherein the distillation columns are operated at temperatures of from ~~about~~ 100°C to ~~about~~ 250°C, preferably from ~~about~~ 120°C to ~~about~~ 220°C.

14. A process according to any one of Claims 1 to 13 wherein the distillation columns contain from ~~about~~ 10 to ~~about~~ 100 theoretical stages, preferably from ~~about~~ 15 to ~~about~~ 80 theoretical stages.

PROCESS FOR PURIFYING A STREAM COMPRISING 1,4- BUTANEDIOL

The present invention relates to a process for separating 1,4-butanediol. In particular, it relates to a process for separating 1,4-butanediol from a product stream from a reactor in which a hydrocarbon feedstock comprising maleic acid, maleic anhydride, mono- or di-(C_1 to C_4) alkyl maleate or mixtures thereof is reacted with a hydrogen rich stream.

Whilst several synthetic routes to 1,4-butanediol are known, one process for the production of 1,4-butanediol uses maleic anhydride as a starting material. This is esterified with an alkanol, usually a C_1 to C_4 alkanol, such as methanol or ethanol, to yield the corresponding dialkyl maleate which is then subjected to hydrogenolysis to yield 1,4-butanediol and the alkanol. The alkanol may be recycled to the esterification reaction to produce further dialkyl maleate. Processes and plant for the production of dialkyl maleates from maleic anhydride are described in, for example, US4795824 and WO90/08127 ~~which are incorporated herein by reference~~. The hydrogenolysis of dialkyl maleates to yield 1,4-butanediol is discussed in, for example, US4584419, US4751334 and WO88/00937 ~~the disclosures of which are incorporated herein by reference~~.

The hydrogenolysis of the dialkyl maleate, such as dimethyl maleate or diethyl maleate, may also lead to the production of amounts of the valuable co-products, γ-butyrolactone and tetrahydrofuran. Since there is a ready market for these by-products, their co-production with 1,4-butanediol may not be disadvantageous. However, they must be separated from the 1,4-butanediol. These co-products may also be present in product streams from other processes used to produce 1,4-butanediol.

The product mixture will normally also contain other components. For example, it will normally contain minor amounts of the dialkyl succinate corresponding to the dialkyl maleate where the diester is used as the starting material, succinic acid, where maleic acid is used as the starting material etc. In addition, the alkanol used in the esterification will be present together with n-butanol, the corresponding dialkyl alkoxysuccinate, water and other impurities such as 2-(4-hydroxybutoxy)-tetrahydrofuran.

The various components and products are normally separated and purified by a number of distillation steps using conventional distillation arrangements. Where the process relates to

the production of 1,4-butanediol with tetrahydrofuran and γ-butyrolactone from a feed comprising dialkylmaleate, the tetrahydrofuran is generally removed first as described in, for example, US 5310954, ~~which is incorporated herein by reference~~.

Lighter components such as alkanols and water are then removed by conventional distillation. The remaining mixture can then be further distilled to recover the 1,4-butanediol product and the γ-butyrolactone. Again this can be carried out by conventional distillation means which can include top, bottom and side draw arrangements.

Other arrangements, for example the use of a divided wall column, can be used. One example of the use of a divided wall column for this separation can be found in EP1280787 ~~which is incorporated herein by reference~~.

As discussed above, 2-(4-hydroxybutoxy)-tetrahydrofuran is a by-product of the reaction to form 1,4-butanediol. This is a major contaminant of butanediol and is difficult to remove by distillation. It is therefore generally removed by reactive means such as those described in, for example, US6137016 and EP1794109.

The inventors have found that mixtures of some or all of 1,4-butanediol, tetrahydrofuran, γ-butyrolactone, alkanols and water are reactive at the conditions at which conventional distillations are carried out. Without wishing to be bound by any theory, it is believed that this reactivity increases the problems associated with separating the components of the mixture by the distillation means described in the prior art. It is therefore difficult to obtain the desired 1,4-butanediol in high purity. In this connection, "high purity" is generally considered to be purities in the region of about 99 wt% and above, preferably above 99.5 wt% and may be of the order of about 99.8 wt% and above.

Specifically, in prior art arrangements, reactions can occur in both the hydrogenation steps and in the distillation steps. These reactions can produce a range of heavy and light components. Examples of heavy components formed include transesters, such as hydroxybutylmethyl succinate, and heavy ethers, for example bis(4-hydroxy)dibutyl ether.

In addition, of particular importance is the formation of 4-hydroxybutyl (4-hydroxybutyrate) from butanediol and γ-butyrolactone. The formation of 4-hydroxybutyl (4-hydroxybutyrate) is an equilibrium reaction in which the 4-hydroxybutyl (4-hydroxybutyrate) can revert to 1,4-butanediol and γ-butyrolactone under certain conditions.

Similarly, the second and third distillation columns may be combined into a single vessel. This may be achieved by any suitable means. In one arrangement, a separating baffle will divide the vessel into two columns for at least a portion of the length of the vessel. The baffle, where present, will extend to the bottom of the vessel and will generally be sealed thereto. In this arrangement, the side draw from the first distillation column, will be achieved via any suitable means including overflow over the baffle. In an alternative arrangement a draw may be taken from the first column, i.e. the first side of the column and fed back on the other side of the baffle. A purge will generally be taken from the bottom of the first distillation column to remove heavies.

A recycle from the second and/or third distillation column may be fed to the first distillation column. Where recycle streams are present they may be fed directly to the first distillation column or may be mixed with the crude feed stream prior to addition to the first distillation column. In one arrangement, at least some of the recycle stream may be fed directly to the first distillation column with the remainder being added to the feed stream.

The recycle from the third distillation column may be taken from any suitable point. In one arrangement, a recycle stream may be taken from the bottom of the third distillation column. A second recycle stream may be taken from the top of the third distillation column. These recycle streams may be combined before being returned to the first distillation column and they may be supplied separately and optionally to different parts of the distillation column.

At least some of the light components present in the side draw taken from the first distillation column will be separated in the further distillation column, where present, and may be returned to the first distillation column. They may be returned to any suitable point and will generally be returned to a point in the first distillation column where the side draw is taken.

The step of carrying out hydrogenation in step (c) may be carried out by any suitable means. In one arrangement, it may be carried out in accordance with the process described in US6137016 ~~which is incorporated herein by reference~~. In one arrangement, the hydrogenation is carried out in the presence of from about 0.5 wt% up to about 15 wt%, based upon the weight of 1,4-butanediol to the hydrogenation zone, of water.

Any suitable hydrogenation catalyst may be used. The hydrogenation catalyst is preferably a Group VIII metal-containing hydrogenation catalyst. Suitable Group VIII metal-containing