PROCESS FOR THE PRODUCTION OF 1,4-BUTANEDIOL, GAMMA-BUTYROLACTONE AND TETRAHYDROFURAN

This invention relates to the production of butane-1,4-diol, γ-butyrolactone and tetrahydrofuran.

Butane-1,4-diol, together with variable amounts of γ-butyrolactone and tetrahydrofuran, can be produced by hydrogenolysis of diesters of maleic acid, fumaric acid and mixtures thereof. A major use of butane-1,4-diol is as a feedstock for the plastics industry, particularly for the production of polybutylene terephthalate. It is also used as an intermediate for the production of γ-butyrolactone and of the important solvent, tetrahydrofuran.

The maleate and fumarate diesters used as feedstock for the production of butane-1,4-diol by such a hydrogenolysis route are conveniently prepared from maleic anhydride, which is itself produced by vapour phase oxidation of a hydrocarbon feedstock, such as benzene, mixed C_4 olefins, or n-butane, in the presence of a partial oxidation catalyst. In the partial oxidation of benzene there is typically used a supported vanadium pentoxide catalyst promoted with MoO_3 and possibly other promoters. The reaction temperature is from about 400°C to about 455°C and the reaction pressure is from about 1 bar to about 3 bar, while about 4 times the theoretical amount of air is used in order to stay outside the explosive limits. The contact time is about 0.1 s. When the feedstock is a mixed C_4 olefin feedstock, i.e. a mixed butenes feedstock, then the partial oxidation catalyst may be vanadium pentoxide supported on alumina. Typical reaction conditions include use of a temperature of from about 425°C to about 485°C and a pressure of from about 1.70 bar to about 2.05 bar. The volume ratio of air to butenes may be about 75:1 in order to stay below explosive limits. Alternatively it is possible, according to more modern practice, to design the plant so that satisfactory safe operation can be

achieved, despite the fact that the feed mixture of air and butenes is within the flammable limits. In the case of n-butane as feedstock, the catalyst is typically vanadium pentoxide and the reaction conditions include use of a temperature of from about 350°C to about 450°C and a pressure of from about 1 bar to about 3 bar. The air:n-butane volume ratio may be about 20:1, even though this may be within the flammable limits. One design of reactor for such partial oxidation reactions comprises vertical tubes surrounded by a jacket through which a molten salt is circulated in order to control the reaction temperature.

In each case a hot vaporous reaction mixture is recovered from the exit end of the reactor which comprises maleic anhydride vapour, water vapour, carbon oxides, oxygen, nitrogen, and other inert gases, besides organic impurities such as formic acid, acetic acid, acrylic acid, and unconverted hydrocarbon feedstock.

One way of recovering maleic anhydride from such a reaction mixture is to cool it to about 150°C using a steam-producing stream and then to cool it further to about 60°C by cooling it against water in order to condense part of the maleic anhydride, typically about 30% to about 60% of the maleic anhydride present. The remainder of the stream is then scrubbed with water.

Scrubbing with water or with an aqueous solution or slurry is described, for example, in US-A-2638481. Such scrubbing results in production of a solution of maleic acid which is then dehydrated, by distilling with xylene, for example, so as to remove the water and re-form the anhydride. A disadvantage of such a procedure, however, is that an unacceptable proportion of the product remains in the vapour phase. In addition, some of the maleic acid is inevitably isomerised to fumaric acid. The byproduct fumaric acid

represents a loss of valuable maleic anhydride and is difficult to recover from the process system since it tends to form crystalline masses which give rise to process problems.

Because of this isomerisation problem a variety of other anhydrous scrubbing liquids have been proposed. For example, dibutyl phthalate has been proposed as scrubbing liquid in GB-A-727828, GB-A-763339, and GB-A-768551. Use of dibutyl phthalate containing up to 10 weight % phthalic anhydride is suggested in US-A-4118403. US-A-3818680 teaches use of a normally liquid intramolecular carboxylic acid anhydride, such as a branched chain C_{12-15}-alkenyl substituted succinic anhydride, for absorption of maleic anhydride from the reaction mixture exiting the partial oxidation reactor. Tricresyl phosphate has been proposed for this purpose in FR-A-1125014. Dimethyl terephthalate is suggested for this duty in JP-A-32-8408 and dibutyl maleate in JP-A-35-7460. A high molecular weight wax as scrubbing solvent is taught in US-A-3040059, while US-A-2893924 proposes scrubbing with diphenylpentachloride. Use of an aromatic hydrocarbon solvent having a molecular weight between 150 and 400 and a boiling point above 140°C at a temperature above the dew point of water in the vaporous reaction mixture, for example dibenzylbenzene, is suggested in FR-A-2285386. Absorption of maleic anhydride from the vaporous partial oxidation reaction mixture in dimethylbenzophenone followed by distillation is described in US-A-3850758. Polymethylbenzophenones, at least a portion of which contain at least 3 methyl groups, can be used as liquid absorbent for maleic anhydride according to US-A-4071540. Dialkyl phthalate esters having C_4 to C_8 alkyl groups and a total of 10 to 14 carbon atoms in both alkyl groups are proposed for absorption of maleic anhydride from the reaction mixture in US-A-3891680. An ester of a

cycloaliphatic acid, for example dibutyl hexahydrophthalate, is suggested as absorption solvent for maleic anhydride in ZA-A-80/1247.

It has also been proposed to effect direct condensation of maleic anhydride from the reaction mixture exiting the partial oxidation reactor. However, this procedure is inefficient because an unacceptable proportion of the maleic anhydride remains in the vapour phase.

The maleic anhydride product recovered following condensation or by scrubbing or absorption and distillation is then reacted with a suitable C_1 to C_4 alkanol, such as methanol or ethanol, to yield the corresponding di-(C_1 to C_4 alkyl maleate. This di-(C_1 to C_4 alkyl) maleate may contain a minor amount of the corresponding di-(C_1 to C_4 alkyl) fumarate, besides traces of the corresponding mono-(C_1 to C_4 alkyl) maleate and/or fumarate. It is then subjected to hydrogenolysis to yield a mixture of butane-1,4-diol, together with variable amounts of γ-butyrolactone and tetrahydrofuran, depending upon the hydrogenolysis conditions that are selected, and of the C_1 to C_4 alkanol which can be recycled to produce further di-(C_1 to C_4 alkyl) maleate.

Processes and plant for the production of dialkyl maleates from maleic anhydride are described, for example, in US-A-4795824 and in WO-A-90/08127. This last mentioned document describes a column reactor containing a plurality of esterification trays each having a predetermined liquid hold-up and containing a charge of a solid esterification catalyst, such as an ion exchange resin containing pendant sulphonic acid groups. A liquid phase containing, for example, a carboxylic acid component flows down the column from one esterification tray to the next lower one against an upflowing stream of vapour of the lower boiling component of the esterification reagents, typically the C_1 to C_4 alkanol.

Water of esterification is removed from the top of the column reactor in a vapour stream, while ester product is recovered from the sump of the reactor. As the liquid flows down the trays it encounters progressively drier reaction conditions and the esterification reaction is driven further towards 100% ester formation. This column reactor may be followed by a polishing reactor operating under liquid phase reaction conditions, the ester-containing stream from the bottom of the column reactor being admixed with further C_1 to C_4 alkanol prior to admission to the polishing reactor. When used for the production of a di-(C_1 to C_4 alkyl) maleate, the column reactor can be preceded by a non-catalytic monoesterification reactor in which maleic anhydride is reacted with the C_1 to C_4 alkanol in the absence of an added catalyst to form the mono-(C_1 to C_4 alkyl) maleate.

The hydrogenation of dialkyl maleates to yield butane-1,4-diol is discussed further in US-A-4584419, US-A-4751334, and WO-A-88/00937, the disclosures of all of which are herein incorporated by reference.

It would be desirable to simplify the production of butane-1,4,-diol, γ-butyrolactone and tetrahydrofuran, from maleic anhydride by the di-(C_1 to C_4 alkyl) maleate hydrogenolysis route. In particular it would be desirable to reduce the capital cost of construction of such a plant and also to reduce its running costs, thereby making butane-1,4-diol, γ-butyrolactone and tetrahydrofuran more readily available.

It is accordingly an object of the present invention to simplify the production of butane-1,4,-diol, γ-butyrolactone and tetrahydrofuran from maleic anhydride by the di-(C_1 to C_4 alkyl) maleate hydrogenolysis route. A further object is to reduce the capital cost of construction of such a plant by reducing significantly the numbers of distillation columns

and the amount of other equipment required. It further seeks to reduce the running costs of a butane-1,4-diol production plant, thereby making butane-1,4-diol, γ-butyrolactone and tetrahydrofuran more readily available.

According to the present invention there is provided a process for the production of at least one C_4 compound selected from butane-1,4-diol, γ-butyrolactone and tetrahydrofuran, which includes the step of hydrogenation in the vapour phase of a di-(C_1 to C_4 alkyl) maleate in the presence of a particulate ester hydrogenation catalyst, which process comprises:

(a) contacting a vaporous stream containing maleic anhydride vapour, water vapour, and carbon oxides in an absorption zone with a high boiling organic solvent having a boiling point at atmospheric pressure which is at least about 30°C higher than that of the di-(C_1 to C_4 alkyl) maleate thereby to form a solution of maleic anhydride in the high boiling organic solvent;

(b) recovering from the absorption zone a waste gas stream;

(c) reacting maleic anhydride in the solution of maleic anhydride of step (a) under esterification conditions in an esterification zone with a C_1 to C_4 alkanol to form the corresponding di-(C_1 to C_4 alkyl) maleate;

(d) recovering from the esterification zone a solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent;

(e) contacting the solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent with a gaseous stream containing hydrogen thereby to strip di-(C_1 to C_4 alkyl) maleate therefrom and to form a vaporous stream comprising hydrogen and di-(C_1 to C_4 alkyl) maleate;

(f) contacting material of the vaporous stream of step (e) in a hydrogenation zone under ester hydrogenation conditions in the presence of a heterogeneous ester hydrogenation

catalyst thereby to convert di-(C_1 to C_4 alkyl) maleate to at least one C_4 compound selected from butane-1,4-diol, γ-butyrolactone and tetrahydrofuran; and

(g) recovering from the hydrogenation zone a product stream containing said at least one C_4 compound.

Preferably in such a process the C_1 to C_4 alkanol is methanol or ethanol and the di-(C_1 to C_4 alkyl) maleate is dimethyl maleate or diethyl maleate. The use of methanol as the C_1 to C_4 alkanol and of dimethyl maleate as the di-(C_1 to C_4 alkyl) maleate is especially preferred.

The vaporous stream of step (a) of the process of the invention is preferably produced by partial oxidation of a hydrocarbon feedstock in the presence of a partial oxidation catalyst using molecular oxygen, typically in the form of air. The hydrocarbon feedstock can be benzene, or a mixed C_4 olefin stream, but is most preferably n-butane. The use of n-butane as hydrocarbon feedstock is currently preferred upon the grounds of cost since it is a cheaper feedstock than benzene or butenes. Hence in the process of the invention the feedstock used for production of the maleic anhydride containing vaporous stream of step (a) is most preferably n-butane and the catalyst is preferably vanadium pentoxide. Typical partial oxidation conditions in this case include use of a temperature of from about 350°C to about 450°C and a pressure of from about 1 bar to about 3 bar, an air to n-butane ratio of from about 15:1 to about 50:1, e.g. about 20:1 and a partial oxidation catalyst comprising vanadium pentoxide; the contact time is typically from about 0.01 s to about 0.5 s, e.g. about 0.1 s.

Partial oxidation of the hydrocarbon feedstock is conveniently conducted in a reactor which comprises vertical tubes surrounded by a jacket through which a molten salt is circulated in order to control the reaction temperature. The

vaporous stream from the partial oxidation reactor can then be cooled by external cooling with boiler feed water to raise steam, and possibly also by further external cooling with cooling water to a temperature in the range of from about 60°C to about 160°C.

In step (a) of the process of the invention the vaporous maleic anhydride stream is preferably contacted with the high boiling solvent at a temperature in the range of from about 60°C to about 160°C, preferably from about 80°C to about 120°C, and at a pressure of from about 1 bar to about 3 bar so as to form a solution comprising maleic anhydride in the high boiling solvent. The contacting can be carried out by bubbling the vaporous stream through a body of the solvent. Alternatively the solvent can be sprayed into the vaporous stream. Countercurrent contacting devices can also be employed wherein the ascending vaporous stream is contacted by a descending stream of solvent in a gas-liquid contacting device, such as a packed scrubber tower or a scrubber tower provided with trays. In this step the solvent will typically be at a lower temperature than the vaporous stream so that the latter is cooled.

In the resulting solution of maleic anhydride in the high boiling solvent the concentration of maleic anhydride in the high boiling solvent may range from about 100 g/l to about 400 g/l.

The high boiling solvent has a boiling point at atmospheric pressure that is at least about 30°C higher than that of the di-(C_1 to C_4 alkyl) maleate. The solvent should be selected so that it does not react significantly with maleic anhydride under conditions used in the contacting step (a) or the esterification step (c). Hence it is preferably inert under the scrubbing conditions of step (a) as well as under the esterification conditions used in step (c). It

should also be substantially inert under the hydrogenation conditions of step (f).

As examples of suitable high boiling solvents there can be mentioned dibutyl phthalate; tricresyl phosphate; dibutyl maleate; a high molecular weight wax; an aromatic hydrocarbon solvent having a molecular weight between 150 and 400 and a boiling point above 140°C, such as dibenzylbenzene; and dialkyl phthalate esters having C_4 to C_8 alkyl groups and a total of 10 to 14 carbon atoms in both alkyl groups. When the solvent used is an ester it is preferred that the alkyl moiety in such an ester shall be derived from the same alkanol as the C_1 to C_4 alkanol used in the esterification step (c). In this way any transesterification reactions that may occur do not give rise to additional esters. Thus when the alkanol used is methanol and the dialkyl maleate is dimethyl maleate, any ester used as the high boiling solvent is preferably also a methyl ester. Examples of such methyl esters which can be used as the high boiling solvent include dimethyl phthalate, dimethyl esters of other aromatic acids, such as dimethyl 2,3-naphthalenedicarboxylate, diesters of cyclic aliphatic diacids, such as dimethyl 1,4-cyclohexanedicarboxylate, and methyl esters of long chain fatty acids containing, for example, from 14 to 30 carbon atoms. Other solvents that can be used include high boiling ethers such as dimethyl ethers of polyethylene glycols of appropriate molecular weight, such as tetraethyleneglycol dimethyl ether.

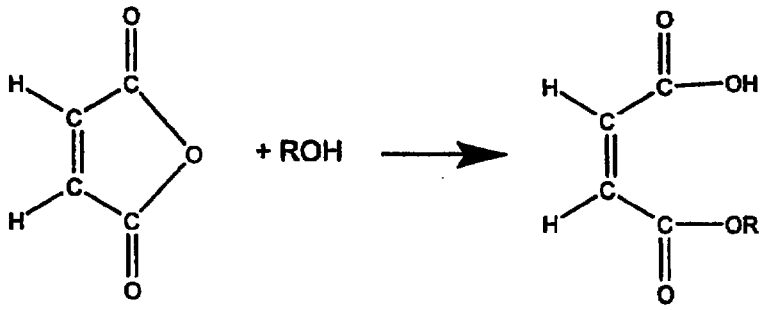
Another desirable quality of the high boiling solvent is that it should be essentially water insoluble and/or essentially incapable of dissolving water.

The high boiling solvent used in step (a) conveniently comprises material resulting from the hydrogen stripping step (e). Hence it may contain already some di-(C_1 to C_4 alkyl)

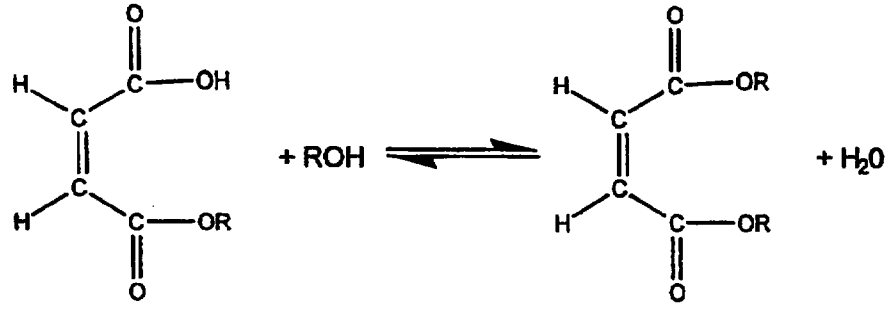
maleate.

Provided that appropriate conditions are adopted in step (a), the gas stream recovered in step (b) of the process of the invention can be essentially free from maleic anhydride.

Esterification of the maleic anhydride with the C_1 to C_4 alkanol is effected in step (c) in an esterification zone. This may comprise a non-catalytic reactor in which the maleic anhydride in the solution in the high boiling solvent undergoes reaction in the absence of added catalyst with the C_1 to C_4 alkanol to form the corresponding mono-(C_1 to C_4 alkyl) maleate. The reaction is:-



where R is a C_1 to C_4 alkyl radical. Some conversion of the mono-(C_1 to C_4 alkyl) maleate to the corresponding di-(C_1 to C_4 alkyl) maleate may also occur. The reaction concerned is:-



where R is as defined above.

Such a non-catalytic reactor can be operated under monoesterification conditions which typically comprise use of a temperature of from about 65°C to about 260°C and a pressure of from about 1 bar to about 50 bar. This can be followed by

a catalytic esterification stage. For example, the catalytic esterification stage may comprise a plurality of stirred tank reactors such as is disclosed in US-A-4795824. Preferably, however, the catalytic esterification stage comprises a column reactor of the type disclosed in WO-A-90/03127. In this case the non-catalytic monoesterification stage may comprise a stirred tank reactor or a column reactor containing one or more trays which do not contain any esterification catalyst and which is fed from the bottom with methanol or other C_1 to C_4 alkanol vapour, while the maleic anhydride solution from step (a) is fed downward through the column reactor.

If the catalytic esterification stage comprises a column reactor of the type disclosed in WO-A-90/03127, then the solution of maleic anhydride (or a solution comprising the corresponding mono-(C_1 to C_4 alkyl) maleate, if a separate monoesterification stage is used) in the high boiling liquid is fed to the top esterification tray of the column reactor, while an excess of C_1 to C_4 alkanol vapour is fed to the bottom of the reactor.

In the column reactor the esterification trays each hold a charge of a solid esterification catalyst. Each tray has a vapour upcomer means to permit vapour to enter the tray from below and to agitate the mixture of liquid and solid esterification catalyst in a zone of turbulence on the tray and to keep the catalyst particles in suspension. In order avoid the danger of "hot spots" forming on the tray through formation of pockets of settled catalyst particles, the floor of each tray is preferably designed so as to slope towards the zone of turbulence at a slope which exceeds the angle of repose of the catalyst particles under the liquid. In addition each esterification tray has a downcomer means which permits liquid, but not catalyst particles, to flow down from

that tray to the next lower one. Such a downcomer means will usually be provided with a screen to prevent catalyst particles passing downwardly therethrough.

Typical reaction conditions in the column reactor include use of a temperature and pressure under which the C_1 to C_4 alkanol distils. Such temperature and pressure conditions will vary in dependence upon the C_1 to C_4 alkanol selected but will typically include use of a temperature of from about 65°C to about 135°C and a pressure of from about 1 bar to about 3 bar. A typical solid esterification catalyst is the ion exchange resin sold under the designation Amberlyst™ 16 by Rohm and Haas (U.K.) Limited of Lennig House, 2 Mason's Avenue, Croydon CR9 3NB.

In passing up the column from one esterification tray to the next higher one, the upflowing C_1 to C_4 alkanol vapour carries with it water of esterification. Thus the di-(C_1 to C_4 alkyl) maleate-containing liquid passing down the column reactor from one esterification tray to the next lower one encounters drier and drier conditions as it proceeds down the column. In this way the esterification reaction leading to formation of the di-(C_1 to C_4 alkyl) maleate is driven further and further towards 100% conversion to the di-(C_1 to C_4 alkyl) maleate.

Any byproduct acid, such as acetic acid or acrylic acid, that is also present in the vaporous stream from the partial oxidation reactor, together with any maleic acid or fumaric acid present in the solution supplied to the esterification zone, will undergo conversion to the corresponding C_1 to C_4 alkyl ester or diester, as the case may be.

The vapour phase stream emerging from the topmost esterification tray comprises C_1 to C_4 alkanol vapour and water vapour; it may further include traces of minor byproducts such as the di-(C_1 to C_4 alkyl) ether, besides

traces of the di-(C_1 to C_4 alkyl) maleate and of the C_1 to C_4 alkyl acrylate. A further additional tray or trays may be provided above the uppermost esterification tray to act as a form of washing column in order to return di-(C_1 to C_4 alkyl) maleate to the esterification trays. The resulting vapour stream, which is now essentially free from di-(C_1 to C_4 alkyl) maleate, exits the top of the column.

From the bottom of the column reactor there is recovered a liquid stream comprising a solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent. This is essentially acid free. If desired this liquid can be admixed with additional C_1 to C_4 alkanol and passed through a polishing reactor containing a bed of solid esterification catalyst operating under liquid phase operating conditions. Such conditions typically include use of a temperature of from about 65°C to about 135°C and a pressure of from about 1 bar to about 3 bar. A typical solid esterification catalyst is the ion exchange resin sold under the designation Amberlyst™ 16 by Rohm and Haas (U.K.) Limited of Lennig House, 2 Mason's Avenue, Croydon CR9 3NB.

In step (e) of the process of the invention, a gas stream comprising hydrogen is passed through the solution of the di-(C_1 to C_4 alkyl) maleate.

The hydrogen stripping step is preferably conducted substantially at or at a pressure slightly higher than the inlet pressure to the ester hydrogenation zone. The hydrogen stripping step is similarly preferably conducted at substantially the desired inlet temperature to the hydrogenation step or a little below this temperature, for example from about 5°C to about 20°C below this temperature. Then the temperature can be raised to the desired inlet temperature by admixture of further hot hydrogen-containing gas which has the additional benefit of diluting the vaporous

ester-containing stream and thereby ensuring that it is at a temperature above its dew point, preferably at least about 5°C higher than its dew point.

The hydrogenation step is advantageously conducted in the vapour phase, using a heterogeneous ester hydrogenation catalyst. Typical ester hydrogenation catalysts include reduced promoted copper catalysts, for example reduced copper chromite catalysts such as that sold under the designation PG 85/1 by Davy Process Technology Limited of 30 Eastbourne Terrace, London W2 6LE.

The catalyst particles preferably have a particle size in the range of from about 0.5 mm to about 5 mm. The particles may be of any convenient shape, e.g. spheres, pellets, rings or saddles. When using a fixed bed of catalyst the reactor can be a shell-and-tube reactor, which can be operated substantially isothermally; however, it is preferably an adiabatic reactor. The use of an adiabatic reactor is advantageous since its capital cost is much lower than that of a shell-and-tube reactor and it is generally much easier to charge the reactor with the chosen catalyst.

Hydrogenation is conducted at an elevated temperature of, for example, from about 150°C to about 240°C and at a pressure of from about 5 bar to about 100 bar, preferably from about 50 bar to about 70 bar.

From the hydrogenation zone there is recovered a hydrogenation product mixture which contains, in addition to the C_1 to C_4 alkanol, also butane-1,4-diol, and some tetrahydrofuran and γ-butyrolactone. Even if the primary product of interest is butane-1,4-diol, the presence of these minor amounts of tetrahydrofuran and γ-butyrolactone is not disadvantageous since these compounds are important chemicals of commerce and it is accordingly economic to recover them in pure form. If desired, γ-butyrolactone can be recycled to

the hydrogenation zone to produce additional butane-1,4-diol. In addition the hydrogenolysis product mixture will normally contain minor amounts of the corresponding di-(C_1 to C_4 alkyl) succinate, n-butanol, the corresponding dialkyl alkoxysuccinate, e.g. dimethyl methoxysuccinate if the C_1 to C_4 alkanol is methanol, and water.

For further details regarding hydrogenation of a di-(C_1 to C_4 alkyl) maleate and subsequent purification of the resultant crude hydrogenation product mixture, reference may be made to US-A-4584419, WO-A-86/03189, WO-A-88/0937, US-A-4767869, US-A-4945173, US-A-4919765, US-A-5254758, US-A-5310954, and WO-A-91/01960.

In order that the invention may be clearly understood and readily carried into effect a plant for the production of butane-1,4-diol, as well as some γ-butyrolactone and tetrahydrofuran, using a preferred process in accordance with the present invention will now be described, by way of example only, with reference to the accompanying drawing which is a flow diagram of the plant.

Referring to the drawing, n-butane is supplied in line 1 at a pressure of from 1 to 3 bar and at a temperature of 400°C to a partial oxidation plant 2 which is also supplied with air in line 3. Partial oxidation plant 2 is of conventional design and includes a partial oxidation reactor comprising tubes packed with a partial oxidation catalyst consisting of vanadium pentoxide packed into tubes provided with a jacket through which molten salt can be circulated for the purpose of temperature control. The partial oxidation reactor is operated at an air:n-butane feed ratio of 20:1.

A hot vaporous partial oxidation product stream is cooled by external cooling against boiler feed water to raise steam and then against cooling water to reduce its temperature to 138°C. It is recovered from plant 2 in line

4. This contains 2.9% w/w maleic anhydride, 5.8% w/w water, 1.3% w/w carbon dioxide, 1.0% w/w carbon monoxide, 0.01% w/w acetic acid, 0.01% w/w acrylic acid, 15.7% w/w oxygen, and the balance essentially comprising nitrogen and other inert gases. It is fed to the bottom of a scrubbing tower 5, up which it passes against a downflowing spray of dimethyl phthalate which is supplied at a temperature of about 68°C from line 6. The scrubbed waste gas stream which contains 0.03% w/w maleic anhydride exits the top of scrubbing tower 5 in vent gas line 7 and is passed to a waste gas burner.

From the bottom of scrubbing tower 5 there is recovered a liquid stream in line 8 which comprises a solution of approximately 22% w/w maleic anhydride and 0.04% w/w acrylic acid in dimethyl phthalate. This is supplied to the top of a column reactor of the type described in WO-A-90/08127. This comprises a number of esterification trays mounted one above the other, each containing a charge of a solid esterification catalyst, such as Amberlyst™ 16 resin, and each having a vapour upcomer for upflowing vapour and a liquid downcomer to permit liquid to flow down the column from one esterification tray to the next lower one. Methanol vapour is supplied to the bottom of column reactor by way of line 10. Water of esterification is removed in the vapour stream exiting the column reactor in line 11. Column reactor 9 is operated at a temperature of from about 110°C to about 125°C and at a pressure of from about 1 bar to about 3 bar. The residence time in the column reactor is about 3 hours. Normally the temperature on the top tray will be somewhat higher (e.g. about 125°C) than that on the lowermost tray (e.g. about 115°C).

A solution containing about 250 g/l dimethyl maleate in dimethyl phthalate is withdrawn from the bottom of column reactor 9 in line 12 and pumped to near the top of a

stripping column 13 which is operated at a temperature of 170°C and a pressure of 885 psia (61.02 bar). Column 13 has a number of distillation trays above the point of injection of the dimethyl maleate solution into column 13 so as to reduce carryover of the high boiling solvent dimethyl phthalate in the overhead stream from column 13. The solution of dimethyl maleate in dimethyl phthalate flows down stripping column 13 against an upflowing stream of hydrogen from line 14. The stripped dimethyl phthalate is recycled from the bottom of stripping column 13 by way of line 6 to the top of scrubbing tower 5. From the top of stripping column 13 there emerges in line 15 a near saturated vapour mixture stream comprising dimethyl maleate in hydrogen, with a hydrogen:dimethyl maleate molar ratio of about 320:1. This vapour mixture stream is at a temperature of from about 180°C to about 195°C and at a pressure of 62 bar. It is diluted with further hot hydrogen at a temperature of from about 180°C to about 195°C to yield a vaporous stream with a hydrogen:dimethyl maleate molar ratio of about 350:1 and is at least about 5°C above its dew point.

This vaporous mixture passes onwards in line 17 to hydrogenation plant 18 which includes an adiabatic reactor packed with a reduced copper chromite catalyst and operated at an inlet temperature of 173°C, an inlet pressure of 885 psia (61.02 bar), and an exit temperature of 190°C. The dimethyl maleate feed rate corresponds to a liquid hourly space velocity of 0.5 h^{-1}. The plant also includes a purification section in which the crude hydrogenation product mixture is distilled in several stages to yield pure butane-1,4-diol in line 19. Lines for separate recovery of γ-butyrolactone and tetrahydrofuran are indicated at 20 and 21 respectively.

CLAIMS:

1. A process for the production of at least one C_4 compound selected from butane-1,4-diol, γ-butyrolactone and tetrahydrofuran, which includes the step of hydrogenation in the vapour phase of a di-(C_1 to C_4 alkyl) maleate in the presence of a particulate ester hydrogenation catalyst, which process comprises:

(a) contacting a vaporous stream containing maleic anhydride vapour, water vapour, and carbon oxides in an absorption zone with a high boiling organic solvent having a boiling point at atmospheric pressure which is at least about 30°C higher than that of the di-(C_1 to C_4 alkyl) maleate thereby to form a solution of maleic anhydride in the high boiling organic solvent;

(b) recovering from the absorption zone a waste gas stream;

(c) reacting maleic anhydride in the solution of maleic anhydride of step (a) under esterification conditions in an esterification zone with a C_1 to C_4 alkanol to form the corresponding di-(C_1 to C_4 alkyl) maleate;

(d) recovering from the esterification zone a solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent;

(e) contacting the solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent with a gaseous stream containing hydrogen thereby to strip di-(C_1 to C_4 alkyl) maleate therefrom and to form a vaporous stream comprising hydrogen and di-(C_1 to C_4 alkyl) maleate;

(f) contacting material of the vaporous stream of step (e) in a hydrogenation zone under ester hydrogenation conditions in the presence of a heterogeneous ester hydrogenation catalyst thereby to convert di-(C_1 to C_4 alkyl) maleate to at least one C_4 compound selected from butane-1,4-diol, γ-butyrolactone and tetrahydrofuran; and

(g) recovering from the hydrogenation zone a product stream

containing said at least one C_4 compound.

2. A process according to claim 1, in which the C_1 to C_4 alkanol is methanol and the di-(C_1 to C_4 alkyl) maleate is dimethyl maleate.

3. A process according to claim 1 or claim 2, in which the vaporous stream of step (a) is produced by partial oxidation of a hydrocarbon feedstock in the presence of a partial oxidation catalyst using molecular oxygen.

4. A process according to claim 3, in which the hydrocarbon feedstock is n-butane.

5. A process according to claim 4, in which the partial oxidation catalyst comprises vanadium pentoxide and in which the partial oxidation conditions include use of a temperature of from about 350°C to about 450°C, a pressure of from about 1 bar to about 3 bar, an air to n-butane ratio of from about 15:1 to about 50:1 and a contact time of from about 0.01 s to about 0.5 s.

6. A process according to any one of claims 1 to 5, in which in step (a) the vaporous maleic anhydride stream is contacted with the high boiling solvent at a temperature in the range of from about 60°C to about 160°C and at a pressure of from about 1 bar to about 3 bar so as to form a solution comprising maleic anhydride in the high boiling solvent.

7. A process according to claim 6, in which the contacting step is carried out in a countercurrent contacting device wherein the ascending vaporous stream is contacted by a descending stream of solvent in a gas-liquid contacting device.

8. A process according to any one of claims 1 to 7, in which the solvent is an alkyl ester whose alkyl moiety is derived from the same alkanol as the C_1 to C_4 alkanol used in the esterification step (c).

9. A process according to any one of claims 1 to 8, in

which the C_1 to C_4 alkanol is methanol, the di-(C_1 to C_4 alkyl) maleate is dimethyl maleate, and the high boiling solvent is also a methyl ester.

10. A process according to claim 9, in which the methyl ester is dimethyl phthalate.

11. A process according to claim 9, in which the methyl ester is a methyl ester or mixture of methyl esters of a long chain fatty acid or acids containing from 14 to 30 carbon atoms.

12. A process according to any one of claims 1 to 8, in which the high boiling solvent is a dimethyl ether of a polyethylene glycol.

13. A process according to any one of claims 1 to 12, in which the high boiling solvent used in step (a) comprises recycled material resulting from the hydrogen stripping step (e).

14. A process according to any one of claims 1 to 13, in which the esterification zone comprises a non-catalytic reactor in which the maleic anhydride in the solution in the high boiling solvent undergoes reaction in the absence of added catalyst with the C_1 to C_4 alkanol to form the corresponding mono-(C_1 to C_4 alkyl) maleate.

15. A process according to any one of claims 1 to 14, in which the catalytic esterification stage comprises a column reactor provided with a plurality of esterification trays each of which holds a charge of a solid esterification catalyst, has a vapour upcomer means to permit vapour to enter the tray from below and to agitate the mixture of liquid and solid esterification catalyst in a zone of turbulence on the tray and to keep the catalyst particles in suspension, and a downcomer means which permits liquid, but not catalyst particles, to flow down from that tray to the next lower one, the column reactor being supplied beneath the

lowermost esterification tray with a stream of C_1 to C_4 alkanol vapour and to an upper esterification tray with a solution in the high boiling solvent comprising a material selected from maleic anhydride, a mono-(C_1 to C_4 alkyl) maleate wherein the C_1 to C_4 alkyl group is derived from the C_1 to C_4 alkanol, and a mixture thereof.

16. A process according to claim 15, in which the floor of each tray slopes towards the zone of turbulence at a slope which exceeds the angle of repose of the catalyst particles under the liquid.

17. A process according to any one of claims 1 to 16, in which the esterification zone comprises an autocatalytic esterification zone wherein the esterification conditions include use of a temperature of from about 70°C to about 250°C, a pressure of from about 1 bar to about 50 bar and wherein maleic anhydride is converted by reaction with C_1 to C_4 alkanol at least in part to the corresponding mono-(C_1 to C_4 alkyl) maleate.

18. A process according to any one of claims 1 to 17, wherein the esterification zone includes a catalytic esterification zone wherein the esterification conditions include use of a temperature of from about 65°C to about 135°C and of a solid esterification catalyst comprising an ion exchange resin containing pendant sulphonic acid groups.

19. A process according to any one of claims 1 to 18, in which the hydrogen stripping step is conducted at substantially the inlet pressure to the ester hydrogenation zone.

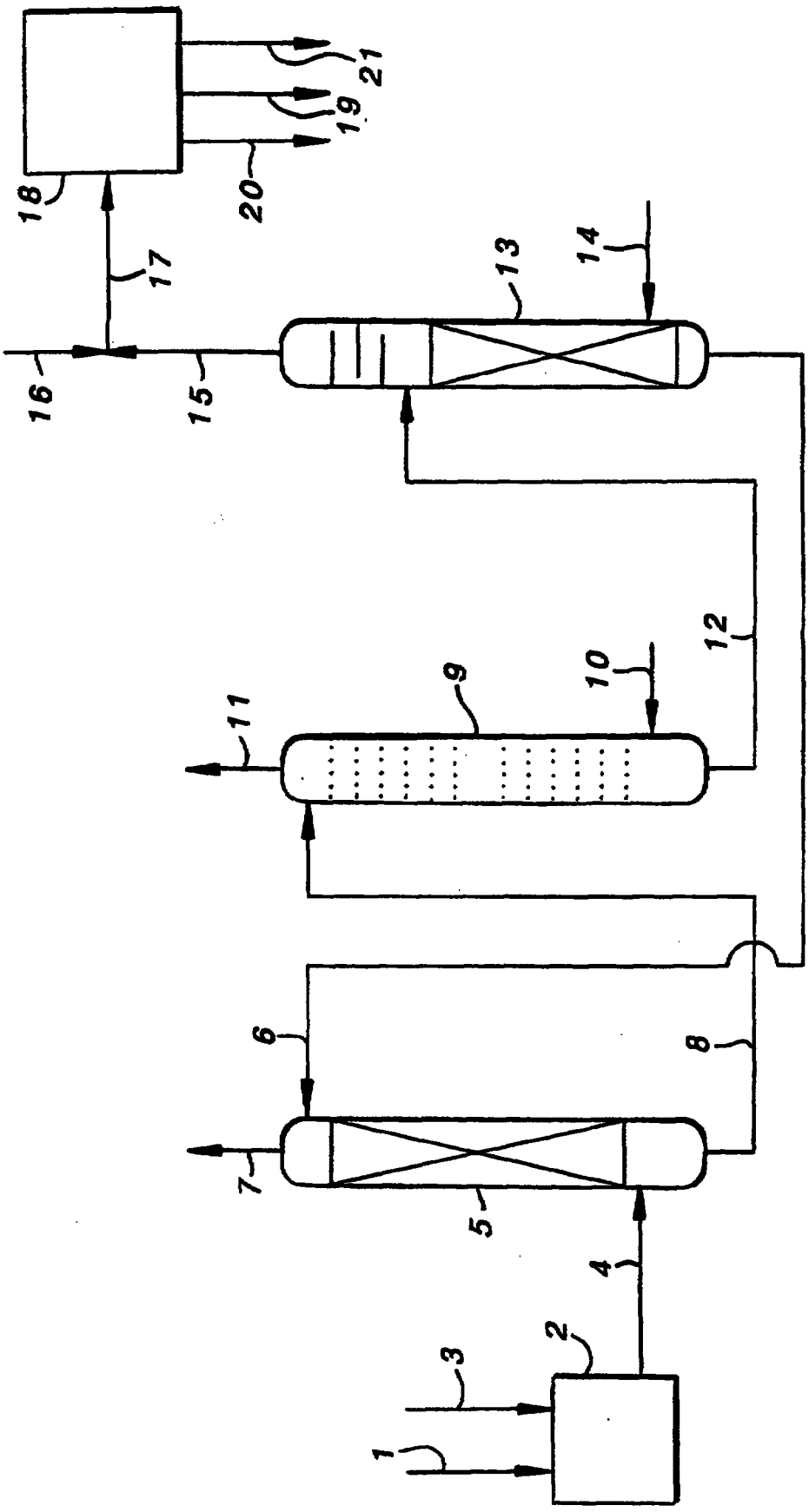
20. A process according to any one of claims 1 to 19, in which the hydrogen stripping step is conducted at a temperature in the range of from the inlet temperature to the hydrogenation zone to about 20°C below the inlet temperature to the hydrogenation zone.

21. A process according to any one of claims 1 to 20, in which the hydrogenation step is conducted in the vapour phase using a reduced promoted copper catalyst at a temperature of from about 150°C to about 240°C and at a pressure of from about 5 bar to about 100 bar.

22. A process according to any one of claims 1 to 21, in which there is recovered from the hydrogenation zone a hydrogenation product mixture which contains, in addition to butane-1,4-diol and the C_1 to C_4 alkanol, also minor amounts of tetrahydrofuran and γ-butyrolactone.

23. A process according to claim 22, in which the hydrogenation product mixture is purified by distillation in one or more stages, including distillation in a "light ends" column to separate overhead the volatile components of the mixture including tetrahydrofuran, the C_1 to C_4 alkanol, water, and n-butanol.

24. A process according to claim 23, in which the bottoms product from the "light ends" column is further purified by distillation in one or more stages to yield pure butane-1,4-diol.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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C07C 67/08, 69/60, 29/149, 29/17, 33/035, C07D 307/33, 307/08 — A1

(11) International Publication Number: WO 97/43242

(43) International Publication Date: 20 November 1997 (20.11.97)

(21) International Application Number: PCT/GB97/01285

(22) International Filing Date: 12 May 1997 (12.05.97)

(30) Priority Data:
96303390.7 14 May 1996 (14.05.96) EP
(34) Countries for which the regional or international application was filed: GB et al.

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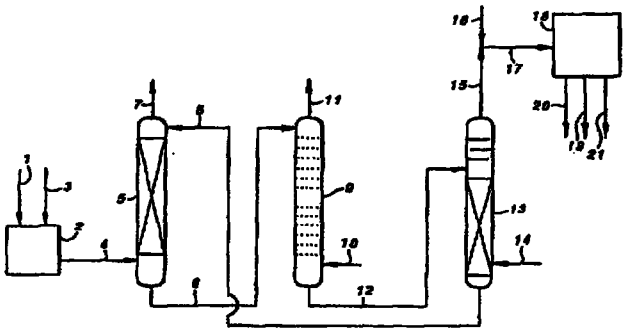
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR THE PRODUCTION OF 1,4-BUTANEDIOL, GAMMA-BUTYROLACTONE AND TETRAHYDROFURAN



(57) Abstract

A process is described for the production of at least one C_4 compound selected from butane-1,4-diol, γ-butyrolactone and tetrahydrofuran, which includes the step of hydrogenation in the vapour phase of a di-(C_1 to C_4 alkyl) maleate in the presence of a particulate ester hydrogenation catalyst, which process comprises: (a) contacting a vaporous stream containing maleic anhydride vapour, water vapour, and carbon oxides in an absorption zone with a high boiling organic solvent having a boiling point at atmospheric pressure which is at least about 30 °C higher than that of the di-(C_1 to C_4 alkyl) maleate thereby to form a solution of maleic anhydride in the high boiling organic solvent; (b) recovering from the absorption zone a waste gas stream; (c) reacting maleic anhydride in the solution of maleic anhydride of step (a) under esterification conditions in an esterification zone with a C_1 to C_4 alkanol to form the corresponding di-(C_1 to C_4 alkyl) maleate; (d) recovering from the esterfication zone a solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent; (e) contacting the solution of the di-(C_1 to C_4 alkyl) maleate in the high boiling solvent with a gaseous stream containing hydrogen thereby to strip di-(C_1 to C_4 alkyl) maleate therefrom and to form a vaporous stream comprising hydrogen and di-(C_1 to C_4 alkyl) maleate; (f) contacting material of the vaporous stream of step (e) in a hydrogenation zone under ester hydrogenation conditions in the presence of a heterogeneous ester hydrogenation catalyst thereby to convert di-(C_1 to C_4 alkyl) maleate to at least one C_4 compound selected from butane-1,4-diol, γ-butyrolactone and tetrahydrofuran; and (g) recovering from the hydrogenenation zone a product stream containing said at least one C_4 compound.