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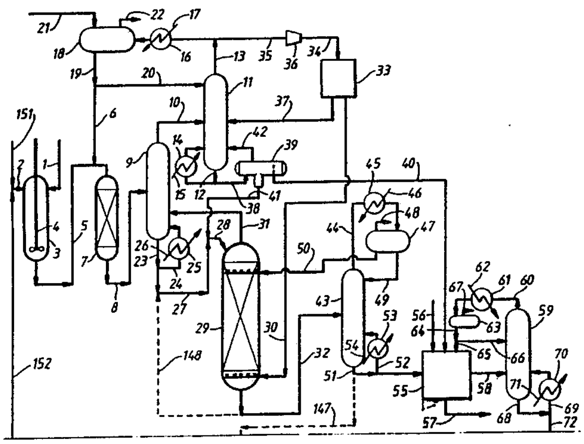
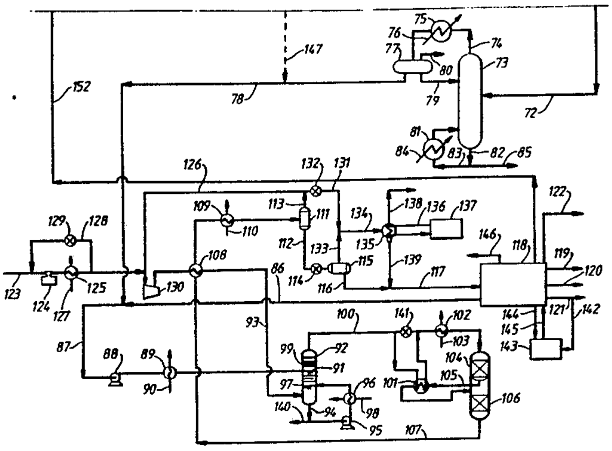




(57) Abstract

A process for the co-production of butane-1,4-diol and *gamma*-butyrolactone which comprises: (a) esterifying maleic anhydride by reaction with an alkyl alcohol to form the corresponding dialkyl maleate; (b) hydrogenating resulting dialkyl maleate to yield a reaction product mixture comprising said alkyl alcohol, butane-1,4-diol and *gamma*-butyrolactone; (c) recovering alkyl alcohol from said reaction product mixture; (d) recycling recovered alkyl alcohol to step (a); and (e) recovering butane-1,4-diol and *gamma*-butyrolactone from the reaction product mixture of step (c); wherein said process comprises: (i) continuously supplying maleic anhydride and a molar excess of an alkyl alcohol to a monoesterification zone maintained at an elevated temperature thereby to form the corresponding mono-alkyl maleate; (ii) continuously supplying resulting mono-alkyl maleate in admixture with a molar excess of said alkyl alcohol to a primary catalytic esterification zone containing a charge of a solid esterification catalyst and maintained under esterification conditions thereby to form an intermediate ester-containing mixture containing a major amount of the corresponding dialkyl maleate and a minor amount of said mono-alkyl maleate; (iii) continuously supplying a first liquid feed comprising said monoalkyl maleate to a secondary esterification zone containing a charge of a solid esterification catalyst; (iv) continuously supplying a second feed stream comprising said alkyl alcohol to said secondary esterification zone; (v) maintaining said secondary esterification zone at an elevated temperature sufficient to form or maintain therein a vaporous stream containing said alkyl alcohol; (vi) intimately contacting said first liquid feed in said secondary esterification zone in the presence of said catalyst with said vaporous stream; (vii) recovering from said secondary esterification zone a vaporous effluent stream containing, in addition to alkyl alcohol vapour, also water in vapour form, said water being produced in said secondary esterification zone by esterification of said monoalkyl maleate with said alkyl alcohol; (viii) recovering from said secondary esterification zone a liquid product containing said dialkyl maleate; (ix) vaporising dialkyl maleate produced in said secondary esterification zone in a stream of a hydrogen-containing gas; (x) passing resulting vaporous dialkyl maleate containing stream through a plurality of hydrogenation zones connected in series, each containing a charge of a solid esterification catalyst and each maintained under ester hydrogenation conditions; (xi) controlling the reaction conditions in each of the plurality of hydrogenation zones so as to produce a predetermined butane-1,4-diol:*gamma*-butyrolactone molar ration in the reaction product mixture; and (xii) recovering from the reaction product mixture (1) an alkyl alcohol fraction, (2) a butane-1,4-diol fraction, and (3) a *gamma*-butyrolactone fraction.

PROCESS FOR THE CO-PRODUCTION OF BUTANE-1,4-DIOL AND GAMMA-BUTYROLACTONE.

This invention relates to a process for the co-production of butane-1,4-diol and gamma-butyrolactone.

Butane-1,4-diol is used as a monomer in the production of plastics such as polybutylene terephthalate. It is also used as an intermediate for manufacture of gamma-butyrolactone and of the important solvent, tetrahydrofuran.

The most commonly adopted present method of manufacturing butane-1,4-diol involves reacting acetylene and formaldehyde by the Reppe reaction to give but-2-yne-1,4-diol which is then hydrogenated to form butane-1,4-diol.

Alternatively it has been proposed in EP-B-0018161 to react allyl alcohol, which can be produced from propylene, with iso-butylene to form allyl t-butyl ether. This compound is then hydroformylated using, for example a rhodium complex hydroformylation catalyst, to give 4-t-butoxybutyraldehyde. According to EP-A-0018162 this aldehyde can be oxidised to 4-t-butoxybutyric acid and then subjected to ether cleavage to yield gamma-butyrolactone, whilst EP-B-0018163 teaches how the aldehyde is hydrogenated and cleaved under mild conditions with the aid of an acid catalyst to give butane-1,4-diol. In either case iso-butylene is a co-product which is recycled for reaction with further allyl alcohol.

There have also been a number of proposals to produce butane-1,4-diol from maleic anhydride. According to these proposals maleic anhydride, which is produced by oxidation of butane or benzene, is esterified to give a diester of maleic acid which is then hydrogenated in one or more stages to give butane-1,4-diol. Alternatively it is proposed that, maleic acid or anhydride should be directly hydrogenated. In some of these proposals gamma-butyrolactone is an intermediate product.

US-A-4001282 describes a process for production of butyrolactone by passing vaporised maleic acid, maleic anhydride, or a mixture thereof together with water and hydrogen over a metallic catalyst capable of hydrogenolysing a carboxylic group to a hydroxymethyl group. Typical catalysts include copper-zinc catalysts (such as Girdler G-66 ARS and G-66-BRS) and copper chromite catalysts (such as Girdler G-13). Besides gamma-butyrolactone the reported products include succinic acid anhydride, propionic acid, butyric acid, propanol and n-butanol, but no mention is made of butane-1,4-diol.

US-A-4048196 teaches production of butane-1,4-diol and/or tetrahydrofuran by multi-stage catalytic hydrogenation of maleic anhydride or succinic anhydride. In a first liquid phase hydrogenation step maleic anhydride or succinic anhydride is hydrogenated over a nickel catalyst to give butyrolactone. This is then hydrogenated in the liquid phase over a copper/zinc oxide or hydroxide catalyst to give butane-1,4-diol and tetrahydrofuran.

In US-A-4083809, US-A-4105674 and GB-A-1534136 there is described a process for producing butyrolactone using a Cu-Pd catalyst for vapour phase hydrogenation of maleic acid, succinic acid, their anhydrides, and mixtures of two or more thereof.

US-A-2079414 describes use of copper chromite as a catalyst for effecting hydrogenation of esters. It is recommended that, in operating in the vapour phase, temperatures within the range of 300°C to 400°C should be used. Example 12 describes hydrogenation of diethyl succinate at a hydrogen:ester molar ratio of about 10:1 in the vapour phase over a mixed Cd-Cu-Zn chromite catalyst at 367°C and 2500 p.s.i. (about 173 bar) to yield a mixture of tetramethylene glycol (butane-1,4-diol) and tetrahydrofuran.

US-A-2040944 recommends use of temperatures of 230°C to 400°C for hydrogenation of esters of non-aromatic polybasic acids with a monohydric aliphatic alcohol containing at least four carbon atoms. It recommends copper chromite as catalyst and teaches that the catalyst can be prepared by ignition of a copper ammonium chromate precipitate and used without further treatment or after reduction by hydrogen at a temperature of 500°C or higher. It goes on to mention that either the liquid phase or vapour phase can be used, depending largely upon the ester to be hydrogenated. Pressures of 100 to 250 bar are recommended, as well as use of about 5 to 20 moles of hydrogen per mole of ester. Example 1 describes a liquid phase batch reaction in which crude butyl succinate is hydrogenated at 3000 p.s.i.g. (207 bar) at 255°C using a copper chromite catalyst.

A discussion of the use of copper chromite as a catalyst for hydrogenation of esters is to be found in "Organic Reactions", Vol. 8, published in 1954 by J. Wiley and Sons, Inc. Chapter 1 of this reference book is by Homer Adkins and is entitled "Catalytic Hydrogenation of Esters to Alcohols". Table II on page 15 lists two experiments in which diethyl succinate is reacted at 5000 p.s.i. (345 bar) and 150°C for 4 hours and at 3300 p.s.i. (227.5 bar) and 250°C for 6.5 hours respectively. This reference suggests that the "copper chromite" catalyst is more correctly described as an approximately equimolecular combination of cupric oxide and cupric chromite, i.e. CuO, $CuCr_2O_4$.

Production of copper chromite catalysts for use in hydrogenation of esters is described in FR-A-1276722. This recommends use of ester hydrogenation conditions including use of temperatures of between 100°C and 350°C, preferably between 200°C and 300°C, and hydrogen pressures between "50 hpz and 500 hpz" (by which is presumably meant between 50 bar and 500 bar).

Production of butane-1,4-diol and tetrahydrofuran by a process in which a dialkyl maleate is subjected to hydrogenolysis in the liquid phase in the presence of a copper chromite catalyst is described in GB-A-1454440 and GB-A-1464263. A similar liquid phase process using nickel-based catalysts is described in GB-A-1587198.

Hydrogenation of a di-(C_1 to C_7 alkyl) succinate at 100 to 300 atmospheres and 200°C to 260°C over a copper chromite catalyst to produce butane-1,4-diol is described in DE-A-2719867.

Production of butane-1,4-diol by hydrogenation of a (C_1- to C_4-alkyl) ester of succinic acid using a Cu - Cr oxide system is also described in JP-A-68/26605.

WO-A-82/03854 proposes, <u>inter alia</u>, a process for the production of butane-1,4-diol and/or tetrahydrofuran by vapour phase hydrogenation of a dialkyl ester of maleic acid, fumaric acid, acetylenedicarboxylic acid or succinic acid at 75°C to 300°C and at a pressure of 0.1 kg/cm^2 absolute (approximately 0.1 bar) to about 100 kg/cm^2 absolute (approximately 100 bar) over a catalyst comprising a reduced mixture of copper oxide and zinc oxide. Improved catalyst activity can be obtained in such a process, according to GB-A-2150560, by including a minor amount of CO_2 in the hydrogen-containing gas used to effect hydrogenation.

US-A-4172961 describes in Example 1 experiments in which a mixture of dibutyl butoxysuccinate, dibutyl maleate and dibutyl fumarate is hydrogenated using a copper chromite catalyst at 2000 p.s.i.g. to 4000 p.s.i.g. (141.65 bar to 282.26 bar) and at a temperature of 250°C to yield butane-1,4-diol.

A two stage hydrogenation procedure in which a dialkyl maleate is hydrogenated first to the corresponding dialkyl succinate in a first hydrogenation zone and then the resulting dialkyl succinate is hydrogenated to yield butane-1,4-diol in a second hydrogenation zone is described in US-A-4032458. Copper chromite is suggested as the catalyst for use in both hydrogenation zones; use of temperatures of about 100°C to about 200°C and hydrogen pressures of about 2000 p.s.i.g. to about 3500 p.s.i.g. (about 141.65 bar to about 247.11 bar) in the first hydrogenation zone is recommended, whilst use of temperatures of about 225°C to about 300°C and pressures of about 3000 p.s.i.g. to about 4000 p.s.i.g. (about 241.95 bar to 282.26 bar) in the second hydrogenation zone is said to provide the necessary severity of operating conditions required to convert substantially all of the dialkyl esters to a product comprising butane-1,4-diol and monohydric alkanol.

Butyrolactone is produced, according to GB-A-1168220, by vapour phase hydrogenation of maleic anhydride, succinic acid, an ester of maleic acid, an ester of succinic acid, or an ester of fumaric acid in the presence of a copper-zinc catalyst to which may be added small amounts of one or more promoters other than chromium. This specification mentions that the preparation of butyrolactone by hydrogenation of the chosen starting materials was already known and states (see page 1, lines 23 to 25):

> "It is also possible to carry out the hydrogenation in the vapour phase when the preferred catalyst is copper chromite."

GB-A-1168220 continues (see page 1, lines 29 to 39):

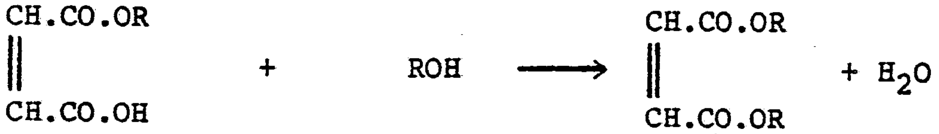
> "Furthermore hitherto known hydrogenation processes in the vapour phase suffer from

> the disadvantage of having to be carried out at a relatively high temperature, for example, about 300°C, and moreover in order to obtain a good conversion rate, the reaction material should be fed to the catalyst at low speed. It is also difficult to reactivate the copper-chromite catalyst, when the activity has been lowered by use for a period of time."

Vapour phase hydrogenation of a di-(C_1 to C_3 alkyl) ester of a C_4 dicarboxylic acid, such as diethyl maleate, using a copper chromite catalyst, in two stages, to yield butane-1,4-diol as major product is described in EP-A-0143634 and in WO-A-86/03189. A related process for the production of gamma-butyrolactone as major product is described in WO-A-86/07358.

The production of dialkyl maleates by esterification of maleic anhydride, of maleic acid or of a mixture containing both maleic anhydride and maleic acid has been described on many occasions in the literature. As maleic acid is dibasic, esterification proceeds stepwise via the monoalkyl maleate. In the case of maleic anhydride this stepwise esterification can be described by the equations:

$$\begin{array}{l}\mathrm{CH.CO}\\ \| \quad >\mathrm{O}\\ \mathrm{CH.CO}\end{array} + \mathrm{ROH} \longrightarrow \begin{array}{l}\mathrm{CH.CO.OR}\\ \|\\ \mathrm{CH.CO.OH}\end{array} \quad (1);\ \text{and}$$



$$\begin{array}{l}\mathrm{CH.CO.OR}\\ \|\\ \mathrm{CH.CO.OH}\end{array} + \mathrm{ROH} \longrightarrow \begin{array}{l}\mathrm{CH.CO.OR}\\ \|\\ \mathrm{CH.CO.OR}\end{array} + H_2O \quad (2),$$

where R is an alkyl group. These reactions can be carried out in two substantially separate steps in separate reactors or simultaneously in a single reactor. The monoesterification step of equation (1) can be effected non-catalytically, conveniently by use of elevated temperatures. The diesterification step of equation (2) can likewise be carried out non-catalytically; however, it is usually preferred to use an esterification catalyst in the diesterification step of equation (2), such as an acid catalyst (e.g. sulphuric acid).

Diethyl maleate is produced as a fine chemical on a commercial scale, usually by a batch reaction process. In this known process maleic anhydride or a mixture of maleic anhydride and maleic acid, in either case possibly containing a minor amount of fumaric acid, is reacted with excess ethanol in the presence of a homogeneous liquid phase esterification catalyst, such as sulphuric acid or a derivative thereof. The reaction conditions are generally selected so as to cause substantially all of the maleic anhydride to react. However, as the diesterification reaction of equation (2) above is reversible, the reaction product does not yield solely the desired diethyl maleate; usually the reaction yields at most about 95 mole % diethyl maleate, the balance comprising mainly monoethyl maleate, besides smaller amounts of monoethyl fumarate, diethyl fumarate, maleic acid and fumaric acid. The reaction mixture also contains excess ethanol and water produced by the esterification of the mono-esters formed as intermediates, i.e. monoethyl maleate and monoethyl fumarate.

In order to recover the dialkyl maleate product the catalyst must first be removed, prior to attempting purification by distillation techniques, by neutralisation with alkali and then washing with water. These neutralisation steps produce significant quantities of aqueous liquors and remove not only the catalyst but also any monoalkyl maleate and any other acid materials present, such as traces of unreacted maleic anhydride or maleic acid.

In addition, as diethyl maleate is somewhat soluble in water, some of the desired diethyl maleate product is lost, together with the acidic materials, in the wash liquor. Although it would be theoretically possible to recover the monoalkyl maleate from the resulting aqueous liquors and to recycle this to the process for the production of further dialkyl maleate, this is not economically feasible. Hence the monoalkyl maleate is lost to the process in these aqueous liquors which are a potential pollution hazard. Moreover the loss of monoalkyl maleate and disposal of these waste liquors represent a significant operating cost. Similar procedures can be used for batch production of other dialkyl maleates using other alkyl alcohols in place of ethanol.

Although it would be possible to adapt this known process for continuous operation with relatively simple modifications thereof, the resulting process would still suffer from the drawback of significant loss of potential product, in the form of monoalkyl maleate and of the other organic acid materials present in the reaction product mixture. Moreover, as the acid catalyst is destroyed in the product recovery steps, the consumption of sulphuric acid or derivative thereof would add to the cost of operation of a large scale continuously operating plant.

A further disadvantage of the known process is the risk of contamination of the dialkyl maleate product with sulphur-containing impurities, which may rule out its use for some purposes, for example as a feedstock for hydrogenation to yield butane-1,4-diol, tetrahydrofuran and/or _gamma_-butyrolactone. Further teaching regarding use of dialkyl maleates for this purpose can be obtained, for example, from EP-A-0143634, WO-A-86/03189 or

WO-A-86/07358. As the catalysts used for such duty are poisoned by the presence of sulphur-containing compounds in the feedstock ester (or in the hydrogen-containing gas), stringent purification measures may be required in order to reduce the sulphur content of the ester to an acceptably low level. Such additional purification steps add significantly to production costs.

Various proposals which avoid the use of catalysts have been described. Thus US-A-4361710 proposes washing a gaseous mixture containing maleic anhydride with a monohydric or polyhydric alcohol boiling above 180°C (e.g. 2-ethylhexanol or dodecan-1-ol) to form a solution of the corresponding maleic acid half-ester in the alcohol followed by heating the solution to remove water and to form a solution of maleic acid diester in the alcohol. As water boils at a temperature well below that of the alcohol it is readily removed from the reaction mixture, thus enabling the diesterification reaction to be driven to completion.

US-A-4032458 describes a process for the production of 1,4-butanediol in which maleic acid is esterified at elevated temperature and pressure and then subjected to a two step hydrogenation procedure. According to the description of the drawing it is preferred to use for esterification a monohydric alcohol which forms a heterogeneous azeotrope with water, such as n-butanol. The esterification step is carried out in a distillation zone from which an n-butanol-water azeotrope is removed overhead. According to column 11, lines 23 to 27, this azeotrope is condensed and allowed to separate into two layers. The n-butanol layer is decanted, redistilled, and recycled to the distillation zone. The n-butanol-water azeotrope has a boiling point (92.7°C at atmospheric pressure) which is appreciably lower than the boiling point of the alcohol itself (117.4°C at atmospheric pressure), thus permitting the water to be removed readily from the esterification mixture. In addition the process can only operate as described because the condensed azeotrope is heterogeneous and separates into two layers, thus permitting ready recovery of n-butanol for recycle to the process.

Although it is stated at column 8, lines 45 to 47 of US-A-4032458 that:

> "Other suitable monohydric alcohols useful in the process of their invention include ethanol, propanol, butanol, amylalcohol and the like",

the illustrated form of plant will not operate with ethanol in place of n-butanol because ethanol is fully miscible with water and forms therewith a homogeneous azeotrope comprising a single liquid phase. It requires much energy to produce substantially dry ethanol from this azeotrope for recycle to the process. Moreover, because the boiling point of the ethanol-water azeotrope is extremely close (78.17°C at atmospheric pressure) to that of ethanol itself (78.32°C at atmospheric pressure) all the ethanol must be distilled out of the esterification mixture in order to remove all the water. n-propanol gives rise to similar problems. Because of these factors it is extremely costly in energy requirements, when using ethanol or propanol in the distillation-esterification step of the process of US-A-4032458, to remove the water of esterification completely and hence drive the esterification reaction towards production of a 100% yield of dialkyl maleate.

US-A-4562283 discloses a method of separating maleic anhydride from gaseous reaction mixtures by contact in the bottom of a column with butanol and then washing the treated gases in the column with a countercurrent stream of butyl maleate. According to column 2, lines 33 to 36 of US-A-4562283, any water formed is removed from the column above the feed point for the butanol. Again, this procedure can be used for removal of the water of esterification only because the butanol-water azeotrope boils appreciably below butanol itself and because the azeotrope separates into two liquid phases upon condensation.

When a dialkyl maleate, such as diethyl maleate, is used as starting material for hydrogenation for the production of butane-1,4-diol and/or gamma-butyrolactone, the resulting crude reaction mixture may contain, in addition to butane-1,4-diol and gamma-butyrolactone, possibly also a small amount of unconverted dialkyl maleate, as well as minor amounts of other components including tetrahydrofuran, the corresponding dialkyl succinate, water and n-butanol. The recovery of the desired products, in particular butane-1,4-diol and gamma-butyrolactone, from such mixtures can be difficult since conventional distillation methods may result in production of azeotropic mixtures of other components of the crude reaction mixture with the desired products.

In US-A-4032583 there is described a process for recovering butane-1,4-diol in high purity from a crude reaction mixture which contains, inter alia, gamma-butyrolactone. This process involves adding water and then subjecting the resulting aqueous mixture to solvent extraction with a hydrocarbon solvent followed by distillation of the resulting raffinate. In this way most of the co-products and only a trace of the butane-1,4-diol are extracted into the hydrocarbon solvent, while the aqueous layer contains essentially pure butane-1,4-diol. Before extraction sufficient water is added to produce an aqueous layer preferably containing from about 20 wt% to about 50 wt% water. The water is recovered as an overhead product in the subsequent distillation step and butane-1,4-diol is recovered as a bottom product. As the process involves use of two additional components, namely water and a hydrocarbon solvent, it is somewhat complex to carry out. Moreover as water has a high latent heat of vaporisation and has to be removed in considerable quantity during the distillation step, the process requires considerable energy input for its performance. In addition, although distillation of the hydrocarbon extract phase for solvent recovery is proposed in US-A-4032583, as well as recycle of unconverted ester, no procedure is described for recovery of other potentially useful products from this hydrocarbon extract.

It is an object of the present invention to provide a novel improved process for the co-production of butane-1,4-diol and gamma-butyrolactone using as a starting material a precursor that can be produced from maleic anhydride and hence ultimately from butane or benzene as feedstock. The invention further seeks to provide an improved process for the co-production of butane-1,4-diol and gamma-butyrolactone from maleic anhydride in which the risk of contamination of the dialkyl maleate intermediate with sulphorous impurities is substantially obviated. It further seeks to provide a continuous process for the co-production of butane-1,4-diol and gamma-butyrolactone in which a predetermined butane-1,4-diol:gamma-butyrolactone molar ratio in the reaction product mixture can be accomplished by appropriate selection of the hydrogenation conditions. Moreover it further seeks to provide a process in which efficient recovery of gamma-butyrolactone can be achieved.

According to the present invention there is provided a process for the co-production of butane-1,4-diol and gamma-butyrolactone which comprises:

(a) esterifying maleic anhydride by reaction with an alkyl alcohol to form the corresponding dialkyl maleate;

(b) hydrogenating resulting dialkyl maleate to yield a reaction product mixture comprising said alkyl alcohol, butane-1,4-diol and gamma-butyrolactone;

(c) recovering alkyl alcohol from said reaction product mixture;

(d) recycling recovered alkyl alcohol to step (a); and

(e) recovering butane-1,4-diol and gamma-butyrolactone from the reaction product mixture of step (c);

wherein said process comprising:

(i) continuously supplying maleic anhydride and a molar excess of an alkyl alcohol to a monoesterification zone maintained at an elevated temperature thereby to form the corresponding mono-alkyl maleate;

(ii) continuously supplying resulting mono-alkyl maleate in admixture with a molar excess of said alkyl alcohol to a primary esterification zone containing a charge of a solid esterification catalyst and maintained under esterification conditions thereby to form a primary ester-containing mixture containing a major amount of the corresponding dialkyl maleate and a minor amount of said mono-alkyl maleate;

(iii) continuously supplying a first liquid feed comprising said monoalkyl maleate to a secondary esterification zone containing a charge of a solid esterification catalyst;

(iv) continuously supplying a second feed stream comprising said alkyl alcohol to said secondary esterification zone;

(v) maintaining said secondary esterification zone at an elevated temperature sufficient to form or maintain therein a vaporous stream containing said alkyl alcohol;

(vi) intimately contacting said first liquid feed in said secondary esterification zone in the presence of said catalyst with said vaporous stream;

(vii) recovering from said secondary esterification zone a vaporous effluent stream containing, in addition to alkyl alcohol vapour, also water in vapour form, said water being produced in said secondary esterification zone by esterification of said monoalkyl maleate with said alkyl alcohol;

(viii) recovering from said secondary esterification zone a liquid product containing said dialkyl maleate;

(ix) vaporising resulting dialkyl maleate produced in said secondary esterification zone in a stream of a hydrogen-containing gas;

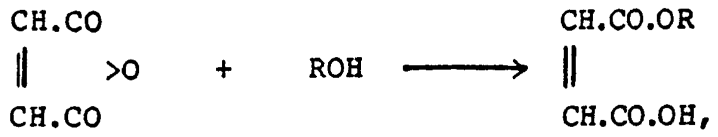
(x) passing resulting vaporous dialkyl maleate containing stream through a plurality of hydrogenation zones connected in series, each containing a charge of a solid hydrogenation catalyst and each maintained under ester hydrogenation conditions;

(xi) controlling the reaction conditions in each of the plurality of hydrogenation zones so as to produce a predetermined butane-1,4-diol:gamma-butyrolactone molar ratio in the reaction product mixture; and

(xii) recovering from the reaction product mixture (1) an alkyl alcohol fraction, (2) a butane-1,4-diol fraction, and (3) a gamma-butyrolactone fraction.

The process may include use of a single secondary esterification zone; often, however, it will be preferred to operate using a plurality of secondary esterification zones connected in series.

In step (i) of the process of the invention maleic anhydride is reacted with an alkyl alcohol to form the corresponding mono-alkyl maleate according to the following equation:



$$\begin{array}{l} \mathrm{CH.CO} \\ \| \quad >\mathrm{O} \\ \mathrm{CH.CO} \end{array} + \mathrm{ROH} \longrightarrow \begin{array}{l} \mathrm{CH.CO.OR} \\ \| \\ \mathrm{CH.CO.OH}, \end{array}$$

where R is an alkyl radical containing, for example, 1 to 4 carbon atoms. This reaction does not require the presence of a catalyst. Although an equimolar mixture of maleic anhydride and alkyl alcohol can be used, a molar excess of alkyl alcohol is used in the process of the present invention. Thus the maleic anhydride:alkyl alcohol molar ratio may vary within wide limits, but is typically from about 1:1 to about 1:10. Usually, however, it will be preferred to operate with such a molar ratio in the range of from about 1:1.5 to about 1:5, e.g. about 1:2.

The maleic anhydride used in the process of the invention may be a substantially pure grade of maleic anhydride. Alternatively it may comprise a mixture of maleic anhydride and maleic acid, containing preferably a major molar amount of maleic anhydride and a minor molar amount of maleic acid. Typically, if a mixture of maleic anhydride and maleic acid is used, this contains at least about 80 mole % of maleic anhydride and not more than about 20 mole % of maleic acid. It may further contain a minor amount, usually from about 0.001 mole % up to about 5 mole %, of fumaric acid. The higher that the content of maleic acid or of fumaric acid is, the larger is the amount of water that will be produced in the monoesterification zone.

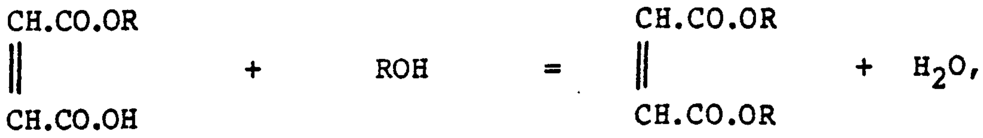
The alkyl alcohol fed to the monoesterification zone may contain water recycled from a downstream stage of the process.

It is preferred to use an alkyl alcohol containing from 1 to 4 carbon atoms. Examples of suitable alkyl alcohols include methanol, n-propanol, iso-propanol, n-butanol, and iso-butanol. Especially preferred for use in the process of the invention is ethanol. Hence the monoalkyl maleate may be monomethyl maleate, mono-n- or iso-propyl maleate, or mono-n- or iso-butyl maleate, but is preferably monoethyl maleate.

In the monoesterification step (i) of the process the temperature is typically from about 50°C to about 150°C, e.g. about 60°C to about 100°C, while the pressure is sufficient to maintain the alkyl alcohol in the liquid phase. Typically this is in the range of from about 1 bar up to about 5 bar absolute.

The monoesterification zone may comprise any convenient form of reactor, e.g. a stirred tank reactor. The reaction mixture is generally retained in the monoesterification zone for a predetermined time, typically of the order of from about 15 minutes to about 300 minutes or more, e.g. about 30 minutes. The residence time is selected to permit substantially complete reaction of maleic anhydride and the alkyl alcohol under the chosen reaction conditions to form the corresponding monoalkyl maleate. Hence the reaction mixture from the monoesterification zone comprises monoalkyl maleate, usually also excess alkyl alcohol, and a minor amount only of unreacted maleic anhydride (usually about 0.5 mole % or less), besides possibly also some water, dialkyl maleate, monoalkyl fumarate, dialkyl fumarate, maleic acid and/or fumaric acid.

This monoesterification mixture is then subjected, possibly after addition of further alkyl alcohol, to further esterification in the primary and secondary catalytic esterification zones of the process so as to yield, ultimately, the corresponding dialkyl maleate according to the equation:



$$\begin{array}{l}\mathrm{CH.CO.OR}\\ \|\\ \mathrm{CH.CO.OH}\end{array} + \mathrm{ROH} = \begin{array}{l}\mathrm{CH.CO.OR}\\ \|\\ \mathrm{CH.CO.OR}\end{array} + H_2O,$$

where R is as defined above. This reaction is an equilibrium reaction. Hence, in order to maximise production of dialkyl maleate, it is necessary to remove the water formed in the esterification reaction.

In step (ii) of the process of the invention a mixture of mono-alkyl maleate and alkyl alcohol in molar excess of that required to effect esterification of the monoalkyl maleate is passed through a primary esterification zone which contains a charge of a solid esterification catalyst and is maintained under esterification conditions. Such esterification conditions will normally include use of an elevated temperature in the primary esterification zone, as well as use of a pressure sufficient to maintain the alkyl alcohol in the liquid phase. The esterification catalyst may be, for example, an ion exchange resin containing acidic substituents selected from sulphonic acid groups and carboxylic acid groups. By passage of a mixture of monoalkyl maleate and alkyl alcohol through the primary esterification zone in co-current, at least a proportion of the monoalkyl maleate is converted to dialkyl maleate. The resulting primary esterification product mixture contains a mixture of mono- and dialkyl maleates, typically in a mole ratio of from about 70:30 to about 20:80, in addition to excess alkyl alcohol and water produced in the esterification reaction and minor amounts of by-products, such as maleic acid, fumaric acid, and mono- and dialkyl fumarates. Preferably the residence time in the primary esterification zone is so selected in relation to the temperature and pressure conditions therein that the primary esterification product mixture is substantially an equilibrium mixture.

Examples of suitable solid esterification catalysts include ion exchange resins, preferably macroreticular ion exchange resins, containing sulphonic acid groups and/or carboxylic acid groups.

Typical reaction conditions in the primary esterification zone include use of a temperature in the range of from about 80°C to about 140°C, preferably about 100°C to about 125°C and of a pressure in the range of from about 1 bar absolute to about 20 bar absolute, preferably from about 5 bar absolute to about 15 bar absolute. The liquid hourly space velocity through the primary catalytic esterification zone preferably ranges from about 0.25 hr^{-1} to about 5 hr^{-1}, typically about 1 hr^{-1} to about 2 hr^{-1}.

The primary esterification product mixture is free from added catalyst and hence can be distilled without disturbing significantly the reaction equilibrium under normal, reduced or increased pressure, in order to separate alkyl alcohol and water, which are recovered overhead, from an ester-containing mixture containing both mono- and dialkyl maleates. The alkyl alcohol distillate can possibly, after treatment to remove water therefrom, be used to form the second feed stream to the secondary esterification zone, if there is only one such zone, or to one or more of the secondary esterification zones, if there are two or more such zones. It can also serve as a source of alkyl alcohol for use in the monoesterification zone or in the primary esterification zone.

The ester-containing mixture resulting from distillation of the primary esterification product mixture can be used as such as the feed stream to the secondary catalytic esterification zone of the process of the invention or can be admixed first with alkyl alcohol, with an inert diluent and/or with material recycled from downstream in the process.

Distillation of the primary esterification product mixture is preferably effected so as to separate therefrom at least a major part of the water of esterification produced in the primary catalytic esterification zone so as to produce the first liquid feed to the secondary esterification zone.

The final product mixture from the secondary esterification zone, if there is only one secondary esterification zone, or from the final secondary esterification zone, if there is more than one such zone, contains predominantly dialkyl maleate. The proportion of dialkyl maleate is, as already mentioned, dependent on the water content of the second feed stream. When a stream comprising "dry" alkyl alcohol containing, for example, less than about 1 mole % water is used as the second feed stream, then the liquid product stream from the secondary esterification zone, if there is only one such zone, or from the final secondary esterification zone, if there is more than one such zone, typically contains dialkyl maleate in an amount of at least about 97 mole % up to about 99 mole % or more, as well as alkyl alcohol, and small amounts of water, maleic acid, and monoalkyl maleate. In some cases traces of fumaric acid and of monoalkyl fumarate can be detected. This final product mixture can be further purified, e.g. by subjection one or more times to the process of copending European patent application No. (Case 86079) filed simultaneously herewith. If desired, the purification steps may include washing with aqueous alkali or, preferably, with an aqueous wash liquor which contains an alkali metal hydroxide, carbonate, bicarbonate, or a mixture of two or more thereof dissolved in an aqueous solution of the corresponding di-(alkali metal) salt of maleic acid according to the teachings of copending British patent application No. 8618893 filed 1st August

1986 and then with water, followed by one or more distillation steps.

The preferred alkyl alcohol is ethanol and the preferred dialkyl maleate is diethyl maleate.

The cost of producing "dry" ethanol from a "wet" ethanol stream is appreciable. Moreover, it will usually be desirable upon economic grounds to recycle ethanol present in the vaporous effluent stream from the, or from each, secondary esterification zone and in other available streams, for example from a downstream hydrogenation step utilising the process of EP-A-0143634, of WO-A-86/03189 or of WO-A-86/07358, for production of further diethyl maleate. Hence in some cases it may be decided that it is uneconomic to produce "dry" ethanol, e.g. with a water content of no more than about 1 mole %. In this case available ethanol-containing streams may contain from about 2 mole % up to about 10 mole % or more, e.g. up to about 15 mole % of water. Such ethanol containing streams can be utilised as the second feed stream but in this case it will usually suffice to utilise a single secondary esterification zone, e.g. a stirred tank reactor, containing a charge of an ion exchange resin containing sulphonic acid and/or carboxylic acid groups. The diethyl maleate content of the liquid product stream will in this case usually be significantly lower than in the case that "dry" ethanol is used, either in a single reactor with an immobilised ion exchange resin or in a plurality of stirred tank reactors connected in series. Hence, under these circumstances, the diethyl maleate content of the liquid product may be from about 75 mole %, usually at least about 80 mole%, up to about 85 mole % or so, and typically not more than about 90 mole %.

When a stream comprising "wet" ethanol is used as the second feed stream, for example a stream containing from 2 mole % up to about 10 mole % water, then the final product mixture may contain, for example, from about 75 mole % up to about 90 mole %, e.g. about 80 mole % to about 85 mole %, dialyl maleate with the balance comprising monoalkyl maleate, water, maleic acid, fumaric acid, monoalkyl fumarate and dialkyl fumarate. Advantageously such a liquid product stream is further purified by the process of copending European patent application No.   (Case 86079) filed simultaneously herewith.

In a preferred process for the production of diethyl maleate, maleic anhydride and ethanol, preferably in molar excess, are reacted in the monoesterification zone to yield a mixture of monoethyl maleate and ethanol. This is preferably admixed with a further quantity of ethanol and passed to a primary esterification zone, which contains a charge of a solid esterification catalyst, such as an ion exchange resin of the type mentioned above. The primary esterification zone can take the form of a trickle bed reactor or a stirred tank reactor or a resin packed column.

In a preferred process, using ethanol as the alkyl alcohol, the primary esterification product mixture is a mixture of monoethyl maleate, diethyl maleate, ethanol and water (and possibly also minor amounts of impurities). This can be distilled in a first distillation zone to yield an ethanol/water mixture, containing also a minor amount of diethyl maleate, as overhead product, and an ester-containing product containing, typically, an approximately 70:30 molar mixture of diethyl maleate and monoethyl maleate plus a small amount of "light ends", such as ethanol and water, as a bottom product. Distillation can be effected under a reduced pressure of, for example, about 0.5 bar or at an elevated pressure of up to about 5 bar; however, it is conveniently effected at, or just above, atmospheric pressure, e.g. at about 1.05 bar. As it is not necessary to remove all of the "light ends" from the bottom product, the bottom of the first distillation zone can be kept relatively cool thus reducing the risk of thermal decomposition at this stage. The overhead product from the first distillation zone is, as already noted, a mixture of water and ethanol (plus a minor amount of diethyl maleate); preferably the monoethyl maleate:ethanol molar ratio of the reactant mixture fed to the primary esterification zone is so controlled that the water content of the overhead product from this distillation step is higher than that of the water/ethanol azeotrope obtained upon distillation of water/ethanol mixtures at the pressure of distillation. The mixture obtained as overhead product from the first distillation zone can then be redistilled in a second distillation zone, again conveniently at or just above atmospheric pressure, to yield a "wet" ethanol overhead product which is drier than the feed to the second distillation zone but is still wetter than the water/ethanol azeotrope obtainable upon distillation of water/ethanol mixtures at the pressure of the second distillation zone. The "wet" ethanol overhead product from the second distillation zone typically contains about 15 mole % of water. Part of this "wet" ethanol overhead product from the second distillation column can be recycled to the primary esterification zone while part is returned to the second distillation column as a reflux stream, and the remainder is passed to an ethanol dehydration unit to produce "dry" ethanol to form the vaporous feed stream in the secondary catalytic esterification zone, if there is only one such zone, or in one of the secondary catalytic esterification zones, if there is more than one secondary esterification zone of step (iii) of the process of the invention. The bottom product from the second distillation zone is mainly water but contains any diethyl maleate that distils from the first distillation zone.

The ethanol dehydration unit may be of any suitable design capable of producing from a "wet" ethanol stream containing up to about 20 mole % water a sufficient stream of "dry" ethanol with a water content less than about 1 mole % for use as the source of the vaporous feed stream in step (v) of the process of the invention. Membrane separation techniques can be used for the production of "dry" ethanol; alternatively molecular sieves can be used.

In one preferred form of the process a single secondary esterification zone is used which may comprise a stirred tank reactor containing a charge of a macroreticular ion exchange resin containing sulphonic acid groups, such as Amberlyst 16, through which ethanol vapour is bubbled.

In a further preferred process the second esterification zone comprises a reactor containing an immobilised charge of a macroreticular ion exchange resin containing sulphonic acid groups, such as Amberlyst 16, through which ethanol vapour, preferably "dry" ethanol vapour, is passed in countercurrent to a liquid phase containing monoethyl maleate flowing down through the charge of ion exchange resin; in such a process the reactor is operated as a flooded bubble reactor. To ensure immobilisation of the resin catalyst this can be in the form of packages wrapped in wire mesh, each containing a quantity of beads of the resin. Alternatively the resin may be trapped as beads in wire baskets. It is also envisaged that the resin may be woven into appropriate form or interwoven with wire mesh.

In a further preferred process a plurality of secondary esterification zones connected in series are used, each comprising a reactor containing as catalyst a charge of an ion exchange resin containing sulphonic acid groups and/or carboxylic acid groups, such as Amberlyst 16. Although such a process can involve use of only two such reactors, or five or more, there are conveniently used three or four such reactors in series. Each reactor is provided with a suitable screen to retain its respective charge of resin beads in the reactor. The monoethyl maleate feed stream (e.g. an approximately 70:30 molar ratio diethyl maleate:monoethyl maleate mixture) is fed through the reactors in turn in cuntercurrent flow to a stream of ethanol vapour. "Dry" ethanol is passed through the last reactor in the series, the vaporous effluent from which is then passed through the penultimate reactor, while the vaporous effluent from the penultimate reactor is passed through the ante-penultimate reactor (and so on, if more than three reactors are used). In this way substantially all of the water of esterification produced in each reactor is removed in the vaporous ethanol stream. The liquid phase encounters progressively drier ethanol vapour as it passes from one reactor to the next.

In a modification of this alternative preferred process the vaporous effluent stream from the final reactor is condensed prior to introduction into the penultimate reactor, while the vaporous effluent stream from the penultimate reactor is also condensed prior to introduction to the ante-penultimate reactor (and so on, if more than three reactors are used). In this form of the process an ethanol containing stream is supplied in liquid form to all the reactors, except the final reactor, and is vaporised in the respective reactor to form the respective vaporous stream.

In yet another modification of this alternative preferred process the vaporous effluent stream from the final reactor is compressed prior to introduction into the penultimate reactor, while the vaporous effluent stream from the penultimate reactor is also compressed prior to introduction to the ante-penultimate reactor (and so on, if more than three reactors are used.

The reaction conditions in the, or in each, secondary catalytic esterification zone preferably include use of a temperature in the range of from about 100 to about 125°C and a pressure of from about 1 to about 3 bar. The total residence time in the secondary catalytic esterification zone or zones is typically in the range from about 2 to about 10 hours.

As mentioned above, the bottom product from the second distillation zone contains diethyl maleate in addition to water. Conveniently this mixture is allowed to settle out in a decanter. The aqueous layer can either be discarded or, if an aqueous neutralisation stage is used for final product purification, this aqueous phase can be used to provide make up water for this aqueous neutralisation stage. The organic layer can be returned to the plant, conveniently upstream from the secondary catalytic esterification zone or zones.

The reaction mixture from the secondary catalytic esterification zone if only one such zone is used, or from the final secondary catalytic esterification zone, if more than one such zone is used, contains predominantly dialkyl maleate, typically in an amount of at least about 75 mole % up to about 99 mole % or more, as well as alkyl alcohol, and small amounts of water, maleic acid, and mono-alkyl maleate. In some cases traces of fumaric acid, and mono-alkyl fumarate, and/or dialkyl fumarate can be detected. This reaction mixture is free from added catalyst. It can be used in certain circumstances in the as obtained state without any purification, as the feedstock for the hydrogenation step of the process of the invention. Alternatively, it can first be purified, e.g. by washing with aqueous alkali and then with water or by passage preferably in the presence of a minor amount of water through an ion exchange resin containing amine groups or ammonium groups or through a bed of solid alkali, e.g. sodium hydroxide or sodium carbonate, followed possibly by a water wash and then by one or more distillation steps.

It will thus be seen that in the process of the invention, water of esterification is removed as vapour from the or each secondary catalytic esterification zone by stripping with a stream of alkyl alcohol vapour. The alkyl alcohol can be supplied in liquid form to said secondary catalytic esterification zone and vaporised therein. More conveniently, however, it is supplied thereto in vapour form.

The rate of supply of alkyl alcohol as, or to form, the vaporous feed stream to said secondary catalytic esterification zone (or to the final secondary catalytic esterification zone, if more than one such zone is used) should be sufficient to establish and maintain a sufficient concentration of alkyl alcohol in the liquid phase to drive the mono- to dialkyl maleate esterification reaction to equilibrium and to strip a major part, preferably substantially all, of the water of esterification released in this reaction from the liquid phase.

As a heterogeneous esterification catalyst is used, the catalyst remains in the secondary catalytic esterification zone or zones. Thus the dialkyl maleate product stream of step (viii) is essentially free from sulphurous impurities introduced as a result of interaction with the catalyst. It is preferably subjected to a purification procedure, such as that described in copending European Patent Application No. (Case 86079) filed simultaneously herewith, prior to hydrogenation. This describes and claims a continuous process for the production of a substantially acid free dialkyl maleate from a feed stream containing a major amount of dialkyl maleate and a minor amount of monoalkyl maleate which comprises:

(a) continuously supplying the feed stream to a primary distillation zone;

(b) continuously distilling the feed stream in the primary distillation zone under temperature and pressure conditions conducive to thermal decomposition of monoalkyl maleate to yield maleic anhydride and alkanol;

(c) recovering from the primary distillation zone (i) a bottom fraction containing monoalkyl maleate and dialkyl maleate in admixture, (ii) a vaporous fraction comprising alkanol, and (iii) an intermediate fraction which is substantially free from alkanol and which comprises a major proportion of dialkyl maleate and a minor proportion of maleic anhydride;

(d) continuously redistilling the intermediate fraction (iii) from step (c) in a secondary distillation zone to yield (i) an overhead fraction contaning maleic anhydride and (ii) a bottom fraction containing substantially acid free dialkyl maleate; and

(e) recovering the bottom fraction (ii) or step (d). For further teaching regarding this process the attention of the reader is directed to that copending European patent application, the disclosure of which is herein incorporated by reference.

Step (x) of the process of the invention requires that the dialkyl maleate and any other condensible component present be in the vapour phase in the hydrogenation zones. This means that the composition of the vaporous mixture must be controlled so that, under the selected operating conditions, the temperature of the mixture in contact with the hydrogenation catalyst is always above the dew point of the ester and of any other condensible component present. The temperature of the mixture in contact with the hydrogenation catalyst is at all times preferably at least about 5°C, more preferably at least about 10°C, and even more preferably at least about 15°C, higher than the dew point of the mixture. This can normally be achieved by selecting an appropriate gas:ester ratio in the vaporous stream. A convenient method of forming a vaporous mixture in step (ix) of the process of the invention is to spray the liquid dialkyl maleate or a solution thereof into a stream of hot hydrogen-containing gas so as to form a saturated or partially saturated vaporous stream. Alternatively such a vaporous stream can be obtained by bubbling a hot hydrogen-containing gas through a body of the liquid dialkyl maleate or a solution thereof. If a saturated vapour mixture is formed it should then be heated further or diluted with more gas so as to produce a partially saturated vaporous mixture prior to contact with the hydrogenation catalyst.

The vaporous mixture contains excess hydrogen. It may additionally contain a minor amount of carbon oxides. The vaporous mixture may further include vaporised inert solvent (if used) and one or more inert gases (e.g. N_2, Ar, CH_4 etc) which may be present in the hydrogen supply in a major or minor amount. It may also include vaporous material recycled from the product recovery section. Preferably the hydrogen supply is substantially free from sulphur compounds, from halogens such as Cl_2, and from halogen-containing compounds such as HCl.

In the vaporous mixture supplied to the first hydrogenation zone the H_2:dialkyl maleate molar ratio is typically at least about 50:1 up to about 1000:1 or more. Preferably it is at least about 150:1 up to about 500:1. The presence of the excess hydrogen and of any inert gases that may be present helps to moderate the temperature rise in the first hydrogenation zone.

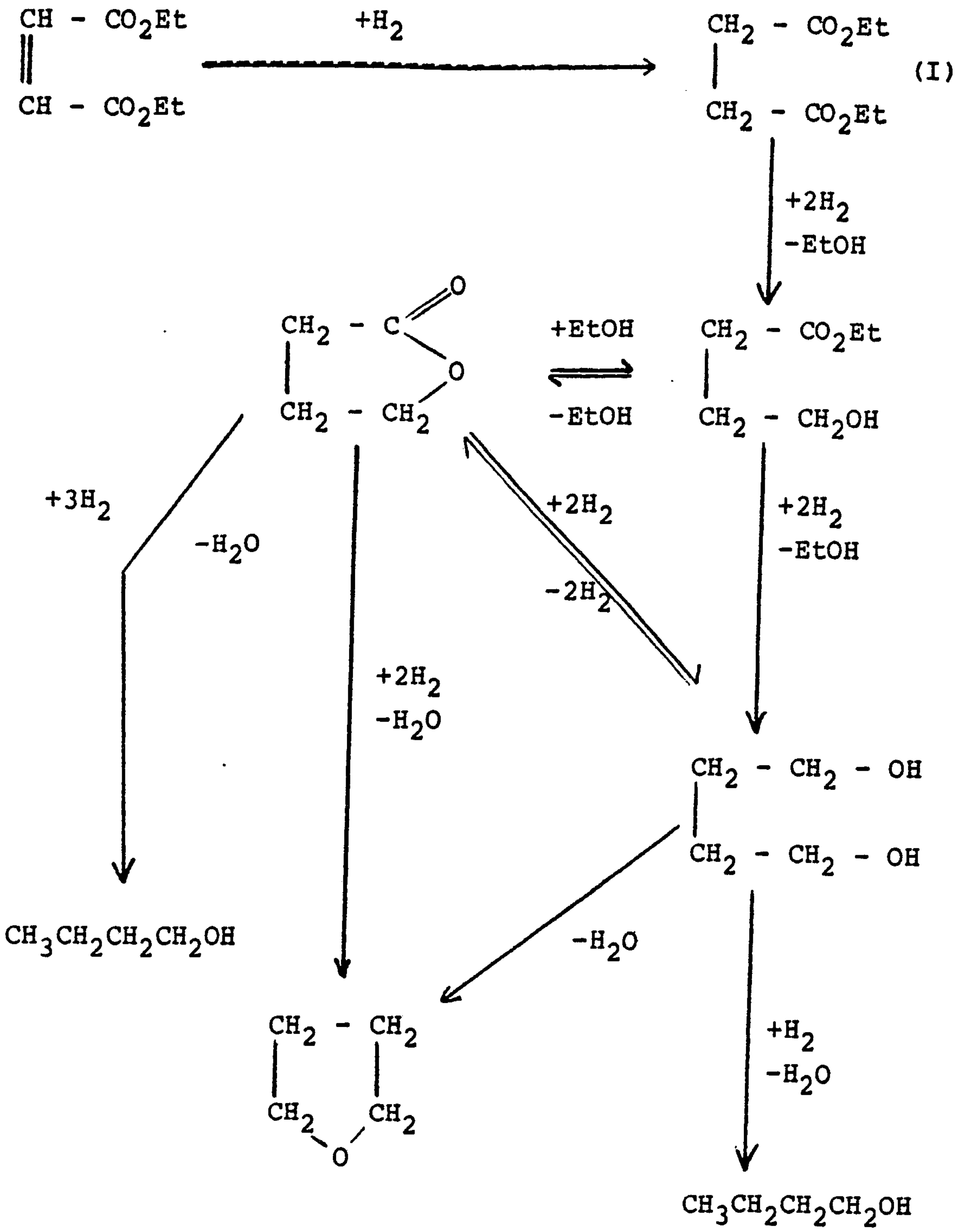
In step (x) of the process of the invention dialkyl maleate produced in the preceding steps is hydrogenated in the vapour phase in a plurality of hydrogenation zones connected in series. Such zones may each comprise a separate reactor vessel; alternatively two or more zones may comprise separate beds of catalysts in the same reactor vessel. Further teaching regarding choice of hydrogenation conditions can be obtained from US-A-4584419, from WO-A-86/03189, or from WO-A-86/07358.

As hydrogenation catalyst there can be mentioned reduced copper chromite catalysts and reduced barium promoted copper chromite catalysts, as well as reduced copper oxide/zinc oxide catalysts of the type disclosed in WO-A-82/03854. Preferably the hydrogenation catalyst comprises copper chromite. It is especially preferred to use a reduced copper chromite catalyst containing, before reduction, from about 25% by weight to about 45% by weight of copper and from about 20% by weight to about 35% by weight of chromium.

The preferred hydrogenation catalyst is a reduced copper chromite catalyst. This should be prepared by careful reduction of copper chromite prior to use. Preferably the catalyst is reduced at a temperature of not more than about 200°C, for an extended period using a mixture of H_2 and an inert gas, such as nitrogen, methane or argon. A typical gas used for reduction of the catalyst is an H_2 in N_2 mixture containing, for example, from about 1% up to about 15% by volume of H_2. Usually the catalyst is reduced for at least about 24 hours prior to use. Best results are obtained when reduction is effected for several days at a temperature of from about 120°C to about 180°C prior to use in the process of the invention. It will usually be unnecessary to exceed about 10 days reduction pretreatment. If the catalyst is reduced at a temperature in excess of about 200°C, the activity is noticeably inferior to the activity obtained by reduction at lower temperatures. If the catalyst is supplied in pre-reduced form then the period of reduction can be shorter. In the later stages of pretreatment high H_2 concentrations can be used; thus H_2 can replace the H_2/N_2 mixture towards the end of the reduction pretreatment. It is best to use an elevated pressure during this pretreatment period; for example, pressures of from 1 bar up to about 50 bar or higher can be used. After the reduction treatment the catalyst should be maintained under an inert gas, a hydrogen/inert gas mixture or hydrogen until use.

The formula of copper chromite may be written as $CuCr_2O_4$. However, it is known that copper chromite is non-stoichiometric and some authors have, for example, described a copper chromite catalyst as copper chromium oxide of the formula $CuO.CuCr_2O_4$. Thus the catalyst may contain an excess of copper oxide. It may further or alternatively contain a minor amount of at least one stabilizer, such as barium or manganese. The catalyst preferably contains, before reduction, from about 25 to about 45% by weight of copper and from about 20 to about 35% by weight of chromium. The most preferred catalysts are those containing from about 32 to about 38% by weight of copper and from about 22 to about 30% by weight of chromium. Such catalysts preferably contain no more than about 15% by weight of a stabilizer or stabilizers, if present. The catalyst may be supported on a suitable inert carrier. Desirably the catalyst is in finely divided form having an internal surface area, as measured by the well-known BET method, of at least about 30 sq. m. per gram and preferably at least about 60 sq. m. per gram. Preferably it is formed into cylindrical pellets or into other conventional catalyst shapes, such as rings, saddles, or the like.

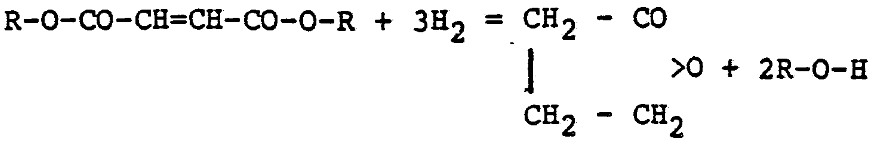
Hydrogenation of a dialkyl maleate in the vapour phase typically yields a mixture of butane-1,4-diol and _gamma_-butyrolactone and variable amounts of byproducts such as tetrahydrofuran and _n_-butanol. Although the reaction mechanism has not been fully elucidated yet, the currently available evidence is consistent with the following sequence in the case of diethyl maleate:-



It will be seen that hydrogenation of one mole of dialkyl maleate to one mole of butane-1,4-diol consumes 5 moles of H_2, according to the following equation:

$$R\text{-}O\text{-}CO\text{-}CH{=}CH\text{-}CO\text{-}O\text{-}R + 5H_2 = 2ROH + HO(CH_2)_4OH \quad (II)$$

On the other hand production of 1 mole of _gamma_-butyrolactone consumes 3 moles of H_2 per mole of dialkyl maleate, according to the equation:



$$\mathrm{R{-}O{-}CO{-}CH{=}CH{-}CO{-}O{-}R} + 3\mathrm{H_2} = \begin{array}{l} \mathrm{CH_2 - CO} \\ \big| \qquad \quad > \mathrm{O} + 2\mathrm{R{-}O{-}H} \\ \mathrm{CH_2 - CH_2} \end{array} \qquad \text{(III)}$$

(R in equations (II) and (III) has the meaning ascribed to it above).

As pointed out above, there are a number of competing reactions which may take place in the hydrogenation zones. Close control of the conditions in the hydrogenation zone must accordingly be exercised in order to achieve a desired product mix in the reaction product mixture exiting the final hydrogenation zone.

Hydrogenation of a dialkyl maleate to the corresponding dialkyl succinate, according to equation (I) above, is a fairly strongly exothermic reaction. Hence, in one preferred process according to the present invention, steps are taken with a view to limiting reaction, so far as is practicable, in the first hydrogenation zone to hydrogenation of the ethylenic unsaturation in the dialkyl maleate, and reserving the subsequent reactions for the subsequent hydrogenation zone or zones. According to this proposal the first hydrogenation zone contains a hydrogenation catalyst that either has little or no ester hydrogenation activity or is maintained under hydrogenation conditions such that hydrogenation of the ester groups and formation of butane-1,4-diol are minimised in this zone.

In this form of the process there can be mentioned as catalysts for use in the first hydrogenation zone, besides the hydrogenation catalysts already mentioned, supported nickel, palladium, ruthenium and cobalt hydrogenation catalysts, zinc oxide, and copper chromite catalysts which have been deliberately deactivated to reduce their ester hydrogenation characteristics.

In order to limit the extent of subsequent hydrogenation of the dialkyl succinate intermediate and the further reactions postulated above in the first hydrogenation zone, it will usually be expedient to supply the dialkyl maleate to the first hydrogenation zone in this case at a relatively high rate, for example at a rate corresponding to a liquid hourly space velocity of at least about 1 hr^{-1}, preferably from about 3.0 hr^{-1} to about 6.0 hr^{-1}. By the term "liquid hourly space velocity" we mean the number of unit volumes of the liquid ester supplied to the vaporization zone per unit volume of catalyst per hour. This normally corresponds to a gaseous hourly space velocity in the range of from about 2500 hr^{-1} up to about 16000 hr^{-1}, for example up to about 85000 hr^{-1}, most preferably in the range of from about 8000 hr^{-1} to about 3000 hr^{-1}. By the term "gaseous hourly space velocity" we mean the number of unit volumes of vaporous mixture measured at 1 bar and 0°C passed over a unit volume of catalyst per hour.

Hence the volume of catalyst in this first hydrogenation zone is selected to provide this relatively high rate of dialkyl maleate throughput. Moreover it will usually be desirable to maintain the inlet temperature to the first hydrogenation zone in this case as low as is practicable, consistent with use of vapour phase conditions; typically this inlet temperature lies in the range of from about 160°C to about 180°C.

The intermediate hydrogenation reaction mixture exiting the first hydrogenation zone is, in this case, substantially free from dialkyl maleate and contains dialkyl succinate besides butane-1,4-diol, gamma-butyrolactone and tetrahydrofuran. Typically this mixture is at a temperature of from about 185°C to about 200°C. Normally this mixture is cooled somewhat prior to entry to the next hydrogenation zone but without cooling below the dew point temperature of the mixture. Preferably the inlet temperature to the second hydrogenation zone is less than about 200°C, and lies in the range of from about 150°C to about 200°C, and even more preferably in the range of from about 170°C to about 190°C. In passage through the second hydrogenation zone substantially all of any dialkyl succinate is hydrogenated and there is recovered from the exit end of the second hydrogenation zone a mixture containing butane-1,4-diol and gamma-butyrolactone, besides minor amounts of tetrahydrofuran, n-butanol, water, and traces of unreacted dialkyl succinate.

By operating according to this preferred form of the process of the invention, the yield of tetrahydrofuran can be minimised. According to our experience the yield of tetrahydrofuran appears to be dependent upon the value of the maximum temperature to which the reactant stream is exposed in contact with the catalyst as well as upon the residence time at such maximum temperature in contact with the catalyst. By operating according to this preferred process, the maximum "hot spot" temperature in the first hydrogenation zone is kept as low as possible and the residence time at such high temperature is minimised. This form of the process is accordingly preferred if tetrahydrofuran is not considered to be a particularly desirable product by the plant operator.

On the other hand, if a market exists for the tetrahydrofuran byproduct of the process, then it becomes less important to limit its production.

The reaction mixture exiting the second hydrogenation zone, in this preferred process, contains butane-1,4-diol and gamma-butyrolactone in a molar ratio which, in our experience, is determined by the maximum temperature and by the residence time at maximum temperature in the second hydrogenation zone. If this molar ratio is not in accordance with the plant operator's product requirements, then adjustment of this ratio can be achieved by cooling or by heating the reaction mixture exiting the second hydrogenation zone and passage through a third hydrogenation zone. As will be apparent to the skilled reader, the extent of cooling should not be so great as to lower the temperature below the dew point temperature of the mixture nor should the extent of heating be sufficient to raise its temperature above about 200°C. Usually the mixture will be heated or cooled by between about 5°C and about 25°C, typically between about 10°C and about 15°C (subject always to the dew point considerations and the upper temperature limitation already mentioned) prior to entry to the third hydrogenation zone.

If the reaction mixture exiting the second hydrogenation zone is cooled, preferably by at least about 5°C, then the butane-1,4-diol:gamma-butyrolactone molar ratio in the product mixture exiting the third hydrogenation zone is higher than the corresponding molar ratio in the reaction mixture exiting the second hydrogenation zone. In this way more butane-1,4-diol is produced at the expense of gamma-butyrolactone.

On the other hand, if the reaction mixture exiting the second hydrogenation zone is heated somewhat, e.g. by at least about 5°C, prior to entry to the third hydrogenation zone, then the butane-1,4-diol:gamma-butyrolactone molar ratio in the product mixture exiting the third hydrogenation zone is lower than the corresponding ratio in the reaction mixture exiting the second hydrogenation zone. In this way more gamma-butyrolactone can be produced at the expense of butane-1,4-diol.

It will thus be seen that by careful control of the reaction conditions in the various hydrogenation zones, the plant operator can exercise a considerable amount of control over the product distribution in the reaction mixture exiting the final hydrogenation zone.

Although it is possible to operate the hydrogenation zones under quasi-isothermal conditions using tube-and-shell type reactors, it will usually be more practical to operate the hydrogenation zone adiabatically since this allows cheaper forms of reactor to be used.

The operating pressure in each of the hydrogenation zones is preferably at least about 25 bar but will not usually exceed about 70 bar, and is most preferably in the range of from about 35 bar to about 45 bar. Usually it is at least about 30 bar.

The liquid hourly space velocity through each of the second and third hydrogenation zones is typically in the range of from about 0.1 hr^{-1} up to about 3.0 hr^{-1}, more usually in the range of from about 0.6 hr^{-1} up to about 1.5 hr^{-1}.

As described above, it is possible to design the plant with the aim of completing hydrogenation of the dialkyl maleate to dialkyl succinate before any significant hydrogenation of dialkyl succinate occurs. It is alternatively possible, particularly if formation of tetrahydrofuran is not considered disadvantageous by the plant operator, to operate the hydrogenation zones, preferably under adiabatic conditions, so that essentially complete hydrogenation of all the ester material (i.e. dialkyl maleate and dialkyl succinate formed as intermediate) takes place in the first hydrogenation zone. (In this case the first hydrogenation zone essentially combines the functions of the first and second hydrogenation zones of the first preferred process described above). The second hydrogenation zone can then be used to adjust the butane-1,4-diol:gamma-butyrolactone molar ratio in the same way as the third hydrogenation zone is used in the first preferred process.

Temperature adjustment can be carried out between successive hydrogenation zones and can be effected by external heating or cooling in a heat exchanger. Alternatively, or in addition, further hydrogen-containing gas and/or dialkyl maleate can be admixed with the appropriate reaction mixture, prior to admission to the next succeeding zone, for the purpose of temperature adjustment and/or to adjust the composition of the vaporous stream.

The reaction product mixture exiting the final hydrogenation zone contains butane-1,4-diol, gamma-butyrolactone, and minor amounts of tetrahydrofuran, water, n-butanol and dialkyl succinate. Separation of this mixture can be achieved by a multi-stage distillation process, the first stage of which involves distillation to yield a "light ends" fraction containing tetrahydrofuran, water and n-butanol, and a "heavy ends" fraction containing butane-1,4-diol, gamma-butyrolactone and dialkyl succinate. The "light ends" fraction can be separated into its components by distillation in three columns operating conveniently at or just above atmospheric pressure, at an elevated pressure of from about 5 bar to about 10 bar, and at or just above atmospheric pressure respectively. In the first of these columns a first water/tetrahydrofuran azeotrope is produced as overhead product, which is then redistilled in the second column at higher pressure to yield as overhead product a second water/tetrahydrofuran azeotrope, that is richer in water than the first such azeotrope and which is recycled to the first column, and as bottom product a substantially dry tetrahydrofuran stream. The bottom product from the first column is a wet mixture of ethanol and n-butanol which is separated in the third column to yield an overhead "wet" ethanol stream, which can be recycled for use in the process, and a bottom product comprising substantially dry n-butanol.

The "heavy ends" fraction contains, besides a minor amount of "heavies" byproducts (such as dialkyl alkoxysuccinate), butane-1,4-diol, gamma-butyrolactone, and dialkyl succinate (such as diethyl succinate). It is not always possible to achieve satisfactory separation of such a mixture by fractional distillation because it may include materials which form binary azeotropes with one or more other components of the mixture. In particular gamma-butyrolactone forms a binary azeotrope with diethyl succinate. It has, however, surprisingly been found that distillation in the presence of water enables a satisfactory distillation procedure to be adopted using a water flooded distillation column as a first water distillation zone and a further distillation column as a second water distillation zone for distillation of the bottom product from the first water distillation zone.

Hence, according to one preferred procedure the "heavy ends" fraction obtained upon distillation of the reaction product mixture from the final hydrogenation zone can be separated by the following steps:

(A) distilling the "heavy ends" fraction in one or more steps to yield a butyrolactone-rich fraction containing, in addition to gamma-butyrolactone, a minor amount of said dialkyl succinate;

(B) distilling the gamma-butyrolactone-rich fraction in a first water distillation zone in the presence of water;

(C) recovering as an overhead product from the first water distillation zone of step (B) a vaporous stream comprising an azeotropic mixture of water and dialkyl succinate;

(D) condensing said azeotropic mixture;

(E) allowing said azeotropic mixture to separate, after condensation, into a water rich layer and an ester rich layer;

(F) returning the water rich layer of step (E) to the first water distillation zone of step (B);

(G) recovering from step (B) a bottom product that contains water and gamma-butyrolactone and is substantially free from dialkyl succinate;

(H) distilling the bottom product of step (G) in a second water distillation zone;

(I) recovering from the second water distillation zone of step (H) a water-containing overhead product; and

(J) recovering as a bottom product from the second water distillation zone of step (H) a gamma-butyrolactone rich product stream.

The first water distillation zone of step (B) is preferably operated at or neat atmospheric pressure or under reduced pressure, for example, at a pressure in the range of from about 0.5 bar to about 1.2 bar. The second water distillation zone of step (H) is preferably maintained under reduced pressure, for example, at a pressure in the range of from about 0.25 bar to about 0.75 bar.

Preferably the water-containing overhead product of step (I) is returned to the first water distillation zone of step (B).

Recovered dialkyl succinate can be recycled to one of the hydrogenation zones for formation of further product. Recovered alkyl alcohol (e.g. ethanol) can be recycled for formation of further dialkyl maleate.

In an alternative preferred procedure the "heavy ends" fraction obtained upon distillation of the reaction product from the final hydrogenation zone is separated by the following steps:-

(AA) distilling the "heavy ends" fraction in one or more stages to yield a gamma-butyrolactone-rich fraction containing, in addition to gamma-butyrolactone, a minor amount of diethyl succinate;

(BB) providing a stream of substantially acid free diethyl maleate;

(CC) supplying substantially acid free diethyl maleate of step (BB) and gamma-butyrolactone rich fraction of step (AA) to a fractionation zone;

(DD) fractionally distilling the gamma-butyrolactone rich fraction of step (AA) in the fractionation zone in the presence of said substantially acid free diethyl maleate;

(EE) recovering as an overhead fraction from the fractionation zone a product stream that is substantially free from diethyl succinate and consists essentially of pure gamma-butyrolactone; and

(FF) recovering from the fractionation zone a liquid bottom product comprising diethyl maleate and diethyl succinate in admixture one with another.

The material of the liquid bottom product of step (FF) can be recycled to the hydrogenation step of the process.

The fractionation zone of step (CC) may comprise a single fractionation column, in which case a stream of the gamma-butyrolactone rich fraction of step (AA) may be fed to an intermediate part of the fractionation column while diethyl maleate is fed to a part of the distillation column above said intermediate part.

The invention also contemplates a form of plant in which the fractionation zone of step (CC) comprises first and second fractionation columns connected in series, in which a stream of the gamma-butyrolactone rich fraction of step (AA) is fed to an intermediate part of the first fractionation column, in which diethyl maleate is fed to a part of the first fractionation column above said intermediate part, in which a first top fraction is recovered from the top of the first distillation column, said first top fraction being substantially free from diethyl succinate and comprising a mixture of diethyl maleate and gamma-butyrolactone, in which said first top fraction is supplied to the second fractionation column, in which said overhead fraction comprises the top fraction from the second fractionation column, in which a bottom fraction comprising diethyl maleate is recycled from the bottom of the second fractionation column to said first fractionation column, and in which said liquid bottom product comprises the bottom product from the first fractionation column.

The fractionation zone is conveniently operated at a pressure in the range of from about 0.01 bar to about 0.75 bar absolute.

The fractional distillation step (DD) is carried out in the presence of added diethyl maleate. Desirably the added diethyl maleate is acid free. Such diethyl maleate can be added as substantially pure diethyl maleate. Preferably the diethyl maleate is substantially free from diethyl fumarate, and preferably contains not more than about 0.1 mole %, and even more preferably less than about 0.01 mole %, of diethyl fumarate.

Typically the gamma-butyrolactone rich fraction of step (AA), contains from about 99 mole % to about 75 mole % gamma-butyrolactone and from about 1 mole % to about 25 mole % diethyl succinate.

It will usually be preferred to add diethyl maleate to the fractionation zone of step (CC) in a molar ratio with respect to the diethyl succinate in the feed mixture of from about 4:1 to about 200:1.

In order that the invention may be clearly understood and readly carried into effect six preferred forms of plant for the continuous co-production of butane-

1,4-diol and gamma-butyrolactone, each using a preferred process according to the invention, will now be described, by way of example only, with reference to the accompanying drawings, wherein:-

Figures 1 to 4 of which are each a flow diagram of a corresponding plant;

Figures 5 and 6 are each a flow diagram of a preferred form of product recovery section; and

Figures 7 and 8 are flow diagrams of further forms of plant.

It will be appreciated by those skilled in the art that, since the drawings are diagrammatic, some conventional items of equipment such as heat exchangers, pumps, valves, vacuum equipment, temperature sensors, pressure sensors, pressure controllers, condensers, reboilers, and the like, have been omitted from the drawings for the sake of simplicity. It will be readly apparent to the skilled reader that such additional items of equipment may be necessary for the successful operation of the illustrated plants, and the provision and positioning of such ancillary items of equipment form no part of the present invention and will be provided in accordance with standard chemical engineering practice.

Figure 1 of the drawings illustrates a continuously operable plant for the co-production of butane-1,4-diol and gamma-butyrolactone and tetrahydrofuran, the primary product of interest being butane-1,4-diol. This plant is supplied in line 1 with liquid maleic anhydride and in line 2 with ethanol in a mole ratio of about 1:2. The liquid maleic anhydride may contain a minor amount of maleic acid, typically not more than about 5 mole % of maleic acid, and a lower amount, typically less than about 1 mole %, of fumaric acid. Ethanol supplied in line 2 may contain a small amount of water, e.g. about 3.5 mole % of water. This ethanol comprises a mixture of make up ethanol supplied in line 151 and wet ethanol recycled in line 152 from an ester hydrogenation plant which is further described below. The streams from lines 1 and 2 are mixed in monoesterification reactor 3 by means of stirrer 4. The reaction mixture is held in reactor 3 for a residence time of about 60 minutes, the temperature in reactor 3 being maintained at 95°C.

Essentially quantitative formation of monoethyl maleate occurs in monoesterification reactor 3. A liquid reaction mixture is discharged from reactor 3 in line 5 which contains an approximately equimolar mixture of monoethyl maleate and ethanol, plus a small amount of water.

This mixture is admixed with a further mole of ethanol, supplied as a "wet" ethanol stream containing about 15 mole % of water in line 6. The resulting mixture contains monoethyl maleate, ethanol and water in a mole ratio of about 1 : 2 : 0.25 and is then fed into a primary esterification reactor 7 which contains a bed of an ion exchange resin containing $-SO_3H$ groups, such as Amberlyst 16. (The word "Amberlyst" is a Registered Trade Mark). It is maintained at 115°C under pressure.

The liquid hourly space velocity through the resin bed of primary esterification reactor 7 is approximately 1.75 hr^{-1}. About 70 mole % of the monoethyl maleate is esterified to diethyl maleate in passage through reactor 7. The liquid effluent stream in line 8 accordingly contains diethyl maleate, monoethyl maleate, water, and excess ethanol in a molar ratio of approximately 0.7 : 0.3 : 0.95 : 1.3, and possibly also minor amounts of maleic anhydride, maleic acid, fumaric acid, monoethyl fumarate and diethyl fumarate.

This mixture is passed by way of line 8 to a first distillation column 9 which operates at substantially atmospheric pressure. An ethanol/water mixture, in a molar ratio of about 2 : 1.25, which contains also a minor amount of diethyl maleate, is recovered overhead in line 10 and is fed into a second distillation column 11, also operating at substantially atmospheric pressure. The overhead product in line 10 is a mixture that is wetter than the ethanol/water azeotrope which could be obtained at the pressure of operation of column 9, i.e. substantially atmospheric pressure. Column 11 effects separation of the components of the overhead mixture from column 9 into a bottom product containing water and any diethyl maleate, which bottom product is recovered in line 12, and an ethanol/water overhead product, which is recovered in line 13, that contains about 15 mole % water. Reference numeral 14 indicates a reboiler for column 11 which is fed with steam in line 15.

Part of the ethanol/water mixture in line 13 is condensed in condenser 16 against cooling water supplied in line 17; a proportion of the resulting condensate which is collected in drum 18 is returned to column 11 by way of lines 19 and 20, whilst the remainder is recycled to reactor 7 by way of lines 19 and 6.

The contents of drum 18 can be blanketed with nitrogen supplied in line 21, whilst a vent line 22 is provided to vent non-condensible materials from the plant.

The bottom product from column 9 in line 23 is a mixture of diethyl maleate, monoethyl maleate, and minor amounts of "lights" (e.g. water and ethanol), in a mole ratio of approximately 0.7 : 0.3 : 0.2. Part of this mixture is recycled to column 9 by way of line 24 and reboiler 25 whose steam heating line is indicated at 26, and the remainder is passed through lines 27 and 28 to the top end of a secondary esterification reactor 29 containing a charge of a macroreticular ion exchange resin containing -SO_3H groups, such as Amberlyst 16. In order to immobilise the resin within the reactor 29 it is preferably loaded into the reactor as small packages wrapped in wire mesh, each containing a small quantity of beads of the resin. The reactor may include a number of internal trays (not shown) each carrying a layer of the resin, whether in the form of wrapped packages or in the form of free resin beads. "Dry" ethanol vapour is introduced by means of line 30 into the bottom end of reactor 29 and is maintained in the vapour phase by contact with the downflowing hot liquid mixture from line 28. Further esterification occurs in secondary esterification reactor 29 by reaction of residual monoethyl maleate in the downflowing liquid mixture with ethanol. Water produced in the esterification reaction is stripped by the upflowing ethanol vapour and the resulting "wet" ethanol vapour is fed by way of line 31 to an intermediate part of first distillation column 9. The liquid product stream, which now contains a minor amount only of monoester, i.e. monoethyl maleate and possibly also monoethyl fumarate, and mainly comprises diester, i.e. diethyl maleate and possibly also diethyl fumarate, besides traces of ethanol and water, exits reactor 29 in line 32.

Typical reaction conditions in reactor 29 include use of a temperature of about 115°C and a pressure of about 2 bar. The residence time in secondary esterification reactor 29 is at least 4 hours.

"Dry" ethanol for supply in line 30 is provided by means of a suitable ethanol dehydration unit 33. This can utilise a membrane to separate "dry" ethanol from the wet ethanol fed thereto in line 34; alternatively it can utilise a molecular sieve to achieve the same end. The feed stream to dehydration unit 33 is supplied by way of line 35 and compressor 36 from the overhead stream in line 13 from second distillation column 11. Water is recovered from ethanol dehydration unit 33 in the form of a "wet" ethanol stream which is recycled in line 37 from dehydration unit 33 to an intermediate part of second distillation column 11. Typically the "dry" ethanol in line 30 has a water content of less than 2 mole %, e.g. about 1.5 mole % or less.

Part of the mixture of water and diethyl maleate which is recovered as a bottom product from second distillation column 11 in line 12 is fed in line 38 to a decanter 39 in which it settles out to form two phases. The water-rich upper layer is rejected as effluent or is supplied in line 40 for use as make-up water to a downstream aqueous neutralisation stage, described in more detail hereafter, if such is included in the plant. The lower layer in decanter 39, which consists mainly of diethyl maleate, is passed in line 41 for admixture with the liquid stream in line 27 and subsequent treatment in reactor 29. Reference numeral 42 indicates a vent line from decanter 39 connected to an intermediate part of column 11.

The liquid product stream from reactor 29 in line 32 is passed to a third distillation column 43 which is operated under vacuum (0.8 bar). Ethanol and any water present are recovered overhead in line 44 and condensed in condenser 45 whose chilled water supply line is indicated at 46. The resulting condensate is collected in drum 47. Reference numeral 48 indicates a connection to a vacuum pump or steam ejector (not shown). Part of the condensate from drum 47 is recycled to the top of column 43 in line 49 to form a reflux stream, whilst the remainder is returned to an upper part of reactor 29 in line 50.

The bottom product from third distillation column 43 is recovered by way of line 51 and consists essentially of diester, i.e. diethyl maleate or a mixture of diethyl maleate with a minor amount of diethyl fumarate, and contains a small amount only, e.g. about 2 mole % or less, of monoethyl maleate and other minor impurities including maleic acid, monoethyl fumarate, and fumaric acid. The content of monoethyl maleate depends on the water content in the ethanol vapour stream in line 30; the lower the water content in this ethanol vapour stream is, the lower is the monoethyl maleate content of the diethyl maleate product stream in line 51.

Part of the stream in line 51 is recycled to column 43 by way of line 52 and a reboiler 53 which is fed with steam in line 54.

The diester stream in line 51 can be used for some purposes without further purification. However, it will often be preferred to purify this by removing the final traces of monoester therefrom. This can be achieved by washing with aqueous alkali, e.g. aqueous sodium carbonate, possibly followed by a subsequent water wash, in neutralisation stage 55. Make up water for washing can be supplied to neutralisation stage 55 in line 40 whilst solid sodium carbonate or sodium carbonate solution is supplied as necessary as indicated at 56. A small amount of alkaline waste aqueous wash liquor containing a minor amount of the sodium salt of monoethyl maleate is discarded in line 57.

The washed diester is then fed in line 58 to a further distillation column 59 operated at 0.75 bar. Water is recovered overhead in line 60 and is condensed in condenser 61 whose cooling water supply line is indicated at 62. A part of the condensate is recycled from drum 63 to neutralisation stage 55 by way of lines 64 and 65, the remainder being returned to column 59 as a reflux stream in line 66. Reference numeral 67 represents a connection to a vacuum pump or steam ejector (not shown).

Part of the diester bottom product from column 59 in line 68 is fed in line 69 to a reboiler 70 fed with steam in line 71 for recycle to column 59. The remainder is fed in line 72 to a final purification column 73 in which it is redistilled at a pressure of 0.6 bar. The overhead product in line 74 is condensed in condenser 75 against cooling water in line 76; part of the condensate from drum 77 is removed in line 78 as pure diester. Such diester is predominantly diethyl maleate but contains also a minor amount of diethyl fumarate resulting either from isomerisation in the course of the esterification reactions or as a result of the fact that the maleic anhydride supplied in line 1 contains a minor amount of fumaric acid. The remainder of the condensate is returned from drum 77 to column 73 as a reflux stream in line 79. A connection to a vacuum pump or steam ejector (not shown) is indicated at 80. A reboiler 81 fed by lines 82 and 83 is provided for column 73; this reboiler is supplied with steam in line 84. Any build up of "heavies" is controlled by taking a purge stream in line 85. The diethyl maleate in line 78 is admixed with a liquid recycle stream in line

86 containing diethyl succinate, and possibly also gamma-butyrolactone and/or butane-1,4-diol. The resulting combined liquid stream in line 87 is fed by pump 88 to feed heater 89 in which it is heated to 210°C by steam supplied in line 90. The resulting hot liquid stream is passed to a spray nozzle 91 in feed saturator 92, in which the resulting spray encounters an ascending stream of hot hydrogen-containing gas supplied in line 93 at 42 bar. Liquid is withdrawn from the bottom of feed saturator 92 in line 94 and is pumped by a feed saturator pump 95 to circulation heater 96 before being sprayed back into feed saturator 92 through nozzle 97. Reference numeral 98 indicates the steam heating line for circulation heater 96, whilst reference numeral 99 indicates a spray eliminator pad in the top of feed saturator 92. The ester vapour laden stream exits feed saturator 92 in line 100 at a temperature of 166°C and passes via heat exchanger 101 to a steam heater 102 in which its temperature is raised to 170°C by means of superheated steam applied in line 103. The H_2:ester molar ratio is approximately 300:1. This mixture is then passed under substantially adiabatic reaction conditions through a first bed 104 of copper chromite catalyst containing 25% by weight of copper and 35% by weight of chromium and having a surface area of 85 m^2/g. The vaporous reaction mixture exits first bed 104 at an exit temperature of about 185°C. Analysis of this first reaction mixture indicates the absence of diethyl maleate and shows that, besides hydrogen and inert gases (e.g. CO, CO_2, methane, propane, nitrogen, argon and any other inert gases which may be present in the hydrogen supply to the plant), it contains also significant amounts of diethyl succinate, ethanol, tetrahydrofuran, n-butanol, gamma-butyrolactone, and butane-1,4-diol. In passage through first bed 104 under the substantially adiabatic reaction conditions employed in the process, diethyl

maleate is converted smoothly and substantially quantitatively to diethyl succinate, 95.5 mole % of which is then converted to products with a selectivity to ethanol of substantially 100%, a selectivity to tetrahydrofuran of 4.3 mole %, a selectivity to n-butanol of 0.2 mole %, a selectivity to gamma-butyrolactone of 16.0 mole %, and a selectivity to butane-1,4-diol of 79.3 mole %, the balance being minor byproducts. Hence the butane-1,4-diol:gamma-butyrolactone molar ratio in this first product mixture from the first hydrogenation zone 104 is 4.96:1. The size of the catalyst charge in first bed 104 is preferably selected in relation to the rate of supply of vaporous diethyl maleate thereto so that reaction can proceed substantially to equilibrium in bed 104. The rate of supply of vaporous diethyl maleate to bed 104 corresponds to a liquid hourly space velocity of about 0.45 hr^{-1}.

The vaporous first reaction mixture exits first bed 104 at about 185°C and is passed by way of line 105 to heat exchanger 101, in which it is cooled to 170°C, and is then passed to a second bed 106 of the same copper chromite catalyst. In passage through bed 106 further hydrogenation reactions take place and the reaction mixture re-equilibriates to yield a second reaction mixture which exits the second hydrogenation zone formed by catalyst bed 106 at a temperature of 171-172°C. The butane-1,4-diol:gamma-butyrolactone molar ratio in this second reaction mixture is 9:1. The volume of catalyst in the second bed 106 is approximately twice that in the first bed 104; hence the rate at which vaporous diethyl maleate is supplied to bed 104 corresponds to a liquid hourly space velocity, taken over both beds 104 and 106, of about 0.15 hr^{-1}.

The second reaction mixture passes in line 107 to a heat exchanger 108 and then to a product cooler 109, in which it is cooled by means of cooling water supplied in line 110, to product catchpot 111. The liquid condensate is recovered in line 112, whilst the gases exit in line 113. The liquid condensate is passed through a pressure letdown valve 114 to a pressure let-down catchpot 115 and thence by lines 116 and 117 to a product recovery section 118 in which butane-1,4-diol is separated from gamma-butyrolactone, from tetrahydrofuran, from ethanol, from n-butanol, from diethyl succinate, and from any other minor components present in the condensate. Further details of product recovery section 118 appear from Figure 5 which is described in more detail below.

Tetrahydrofuran is recovered in line 119, gamma-butyrolactone in line 120, and butane-1,4-diol in line 121. Diethyl succinate, and possibly also some gamma-butyrolactone and/or butane-1,4-diol, is recycled in line 86. Ethanol is recovered and recycled in line 152 for production of further diethyl maleate, while a minor amount of n-butanol is recovered in line 122.

Fresh hydrogen is supplied to the plant in line 123 and is fed by way of compressor 124 and cooler 125 for admixture with the recycled gas in line 126. Cooling water is supplied to cooler 125 in line 127. A by-pass line 128 fitted with a pressure relief valve 129 is fitted around compressor 124. The combined gas stream from lines 123 and 126 is compressed by recycle compressor 130 and fed through heat exchanger 108 to line 93.

A gas purge stream is taken from line 113 in line 131 after passage through pressure let-down valve 132 and is combined with the vent gas in line 133 from catchpot 115; the combined stream in line 134 passes to gas purge condenser 135 which is fed with refrigerant in line 136 from refrigeration unit 137. The purge gas exits in line 138 whilst any condensate is recovered in line 139 and fed to product recovery section 118 in line 117. A purge can be taken from the bottom of feed saturator 92 in line 140 as necessary.

Reference numeral 141 indicates a normally closed valve which can be opened at start up of the plant so as to cause the vaporous mixture in line 100 to bypass heat exchanger 101.

If desired, butane-1,4-diol can be passed from the purified butane-1,4-diol product line 121 via line 142 to a dehydration zone 143 which contains a charge of a dehydration catalyst such as gamma-alumina, aluminium phosphate, silica-alumina, a molecular sieve, an acidic clay or similar dehydration catalyst so as to convert at least a proportion of the butane-1,4-diol to tetrahydrofuran. This zone is maintained at a temperature in the range of from about 200°C to about 300°C. (Alternatively dehydration zone 143 can be supplied with a crude butane-1,4-diol stream from product recovery section 118 in line 144). The tetrahydrofuran-containing product stream from dehydration section 143 is passed to product recovery section 118 in line 145, thereby increasing the amount of tetrahydrofuran appearing in line 119.

A small amount of "heavies" is recovered from product recovery section 118 in line 146.

In a modification of the plant of Figure 1 line 40 is used for disposal of the aqueous layer from decanter 39, and items 55 to 77 and 79 to 85 are omitted. Instead crude diethyl maleate, containing typically less than about 2 mole % of monoethyl maleate (e.g. about 0.5 mole % of monoethyl maleate) is fed from the bottom of column 43 by way of line 147 to line 78. In this way the capital expense of the crude diethyl maleate purification section is avoided, as well as the running expenses associated therewith and the difficulties associated with disposal of the waste aqueous salt wash liquor in line 57.

As described above reactor 29 is operated as a single pass reactor. If desired, part of the liquid product stream from reactor 29 can be recycled to the inlet end of reactor 29 in line 148.

The plant of Figure 2 is similar to that of Figure 1 and like reference numerals have been used in both Figures to indicate like parts. However, it is designed so as to produce gamma-butyrolactone as the major product rather than butane-1,4-diol as in the case of the plant of Figure 1. In the plant of Figure 2 the single stage reactor 29 of the plant of Figure 1 is replaced by a series of three continuously stirred tank reactors 201, 202 and 203, each containing a charge of Amberlyst 16 ion exchange resin beads. The stirrers for reactors 201, 202 and 203 are indicated at 204, 205 and 206. Typical reaction conditions in each of reactors 201, 202 and 203 are similar to those mentioned for reactor 29 of the plant of Figure 1. Liquid phase is led from the first of the stirred reactors 201 to the second reactor 202 in the series by way of line 207, whilst liquid is fed from reactor 202 to the third of the series, i.e. reactor 203, in line 208. "Dry" ethanol vapour in line 30 is fed to the bottom of reactor 203. A mixture of ethanol vapour and water vapour resulting from the esterification occurring in reactor 203 exits the top of reactor 203 in line 209 and is fed to the bottom of reactor 202, in which it picks up further water vapour. The resulting ethanol/water vapour mixture exits the top of reactor 202 in line 210, is admixed with recycled ethanol vapour in line 211 from line 44 and is fed to the bottom of reactor 201 in line 212. The vaporous effluent from reactor 201 is a wet ethanol vapour and is passed by way of line 31 to distillation column 9.

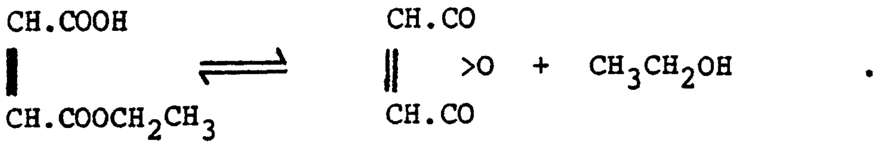
The liquid feed to reactor 201 is an approximately 70:30 molar ratio diethyl maleate:monoethyl maleate mixture; in line 207 the corresponding molar ratio is about 85:15, while in line 208 it is about 92:8. The corresponding mixture in line 32 is an approximately 99:1 molar mixture of diethyl and monoethyl maleates. The precise values of these ratios will depend, inter alia, upon the water content and rate of supply of the "dry" ethanol supplied in line 30, and upon the temperature and residence time of the liquid reaction mixture in each of reactors 201, 202 and 203.

Another difference between the plants of Figures 1 and 2 is that heat exchanger 101 is replaced by a heater 221 which is heated by means of superheated steam supplied in line 222. In addition valve 141 is omitted, as also is dehydration zone 143 and lines 142, 144 and 145.

In operation of the plant of Figure 2 the temperature of the ester vapour laden stream in line 100 is raised to 190°C in passage through steam heater 102. The vaporous first reaction mixture exiting copper chromite catalyst bed 104 is at a temperature of 205°C; its temperature is raised to 215°C in passage through heater 221. In this case the gamma-butyrolactone:butane-1,4-diol molar ratio in line 107 is higher than the corresponding ratio in line 105. It is also significantly higher than the corresponding molar ratio in line 107 of the plant of Figure 1.

The plant of Figure 3 is generally similar to that of Figure 2, except that condensers 231 and 232 are provided in lines 209 and 210 respectively and that the condensate from condenser 210 is admixed with condensate in line 50 for supply to line 212. Thus ethanol is fed as a liquid to each of reactors 202 and 201 and is vaporised therein by contact with the downflowing hot ester-containing liquid stream.

Another difference between the plants of Figures 2 and 3 is that, in the latter plant, items 55 to 77 and 79 to 85 are omitted. Instead some of the bottom product from column 43 is fed in line 241 to a first diester purification column 242 which is operated at a pressure of 0.066 bar. An overhead stream containing ethanol and minor amounts of water, maleic anhydride, monoethyl maleate, and diethyl maleate, is recovered overhead in line 243 at a temperature of 140°C. The presence of maleic anhydride in the overhead product in line 243 results, it is thought, from the reversible decomposition of monoethyl maleate in column 242 according to the equation:



$$\begin{array}{l} \mathrm{CH.COOH} \\ | \\ \mathrm{CH.COOCH_2CH_3} \end{array} \rightleftharpoons \begin{array}{l} \mathrm{CH.CO} \\ \| \\ \mathrm{CH.CO} \end{array} \!\!>\mathrm{O} + \mathrm{CH_3CH_2OH} \quad .$$

The vapours in line 243 are led through a condenser 244 which is supplied in line 245 with water under pressure at a temperature of 130°C. A major part of the condensable components of the vapours in line 243 with boiling points above that of ethanol are thereby condensed in first condenser 244. Part of the resulting condensate in line 246 is returned to primary distillation column 242 in line 247 to form a reflux stream therefor. This condensate consists of a mixture of maleic anhydride, diethyl maleate and monoethyl maleate. A minor part of these higher boiling components in the vapours in line 243 and a major part of the ethanol and water contained therein pass on, still in the vapour form, in line 248 to a second condenser 249 which is supplied in line 250 with chilled cooling medium (e.g. chilled water) so as to cool the vapours to a temperature below 20°C. In this way the residual condensable components present in the vapour stream in line 248 are in large part condensed and losses in the vapour purge are minimised. The resulting condensate contains mainly ethanol and water besides traces of monoethyl maleate, diethyl maleate and maleic anhydride and is recovered in line 251 for recycle to the monoesterification reactor by way of line 152. Line 252 indicates a connection to a vacuum pump or steam ejector (not shown).

A bottom product containing a mixture of diethyl maleate and monoethyl maleate is recovered from column 242 in line 253. Part of this bottom product is recycled in line 254 to column reboiler 255 which is supplied with steam in line 256, while the remainder is recycled to the esterification plant in line 257. A purge stream can be taken from line 257 in line 258. The remainder of the condensate in line 246 is fed in line 259 to an intermediate point of a second diester purification column 260. The maleic anhydride present in the stream in line 259 appears overhead in line 261 and is passed to condenser 262 which is fed in line 263 with water at 60°C. The resulting condensate is returned as a reflux stream to column 260 in line 264. Uncondensed maleic anhydride vapour passes on in line 265 and is combined with the stream in line 248 before being condensed in condenser 249 and recycled to the esterification plant in line 251. The bottom product from column 260 is recovered in line 265 and contains substantially pure diethyl maleate and, at most, only traces (typically about 0.3 mole % or less in total) of acidic materials, such as monoethyl maleate, maleic anhydride and/or maleic acid. Part of this bottom product is recycled in line 266 to column reboiler 267 which is fed with steam in line 268. The remainder is passed in line 269 to neutralisation reactor 270 where final traces of acid are removed by washing with an aqueous solution of sodium carbonate and di-sodium maleate according to the teachings of copending British patent application No. 8618893 filed 1st August 1986. Make up water can be supplied to reactor 270 in line 271 from line 40, whilst make up sodium carbonate is supplied in line 272. The contents of reactor 270 are stirred by means of stirrer 273. A small amount of spent aqueous alkaline wash liquor is removed in line 274, whilst acid free diethyl maleate passes on in line 275 to a drying column 276 which is operated at 0.3 bar. A small amount of water is recovered overhead in line 277, is condensed in condenser 278 which is supplied with cooling water in line 279, and is colllected in drum 280. Part of the condensate is returned as reflux stream in line 281 to the top of column 276, whilst the remainder is recycled in line 282 to line 40. Reference numeral 283 indicates a purge line for water from the plant. A vacuum pump or steam ejector (not shown) is connected to line 284 in order to produce the desired reduced operating pressure in column 276.

Dry diethyl maleate vapour is recovered from column 276 in line 285, and is condensed in condenser 286, whose cooling line is indicated at 287. The resulting condensate passes on to line 78.

Part of the bottom product from column 276 is recycled by way of line 288 and column reboiler 289, whose steam line is shown at 290, whilst a small purge stream containing sodium values is withdrawn in line 291.

In the plant of Figure 4 the single secondary esterification reactor 29 of Figure 1 is replaced by four stirred tank reactors 301, 302, 303 and 304 connected in series; each of these reactors contains a charge of Amberlyst 16. Reference numerals 305, 306, 307 and 308 indicate their respective stirrers. "Dry" ethanol vapour is fed from ethanol dehydration unit 33 in line 30 under the influence of compressor 309 (which replaces compressor 36 of the plant of Figure 1). The compressed vapour passes on in line 310, a part being condensed and fed to monoesterification reactor 3 by way of line 311, whilst the remainder is fed by way of line 312 to a sparger fitted at the lower end of the fourth reactor 304.

The bottom product from column 9 is fed by way of lines 23 and 27 to the top of the first reactor 301. A liquid stream is taken from the bottom of reactor 301 in line 313 and is passed to the top of reactor 302. In a similar manner line 314 feeds liquid from the bottom of reactor 302 to the top of reactor 303, whilst liquid is taken from reactor 303 to reactor 304 in line 315.

Ethanol vapour containing water of esterification from reactor 304 entrained therein is fed by means of line 316 and blower 317 to a sparger in the bottom of reactor 303. In similar manner line 318 and blower 319 are used to pass ethanol vapour and entrained water vapour to a sparger in the bottom of reactor 302. The vapours exiting reactor 302 are fed by means of lines 320 and blower 321 to a sparger in the bottom of reactor 301.

Wet ethanol vapour is recovered from the top of reactor 301 in line 322 and is combined with the vapours in line 35 to form a combined stream which is fed in line 34 to ethanol dehydration unit 33.

The ethanol recycle stream in line 50 and ester stream from decanter 39 in line 41 are combined and fed to the top of reactor 301 in line 323.

Instead of recycling "wet" ethanol from line 19 by way of line 6 to line 5, as occurs in the plant of Figure 1, a corresponding amount of make up ethanol is supplied to line 5 from line 2 by way of line 325.

The diethyl maleate purification section of the plant of Figure 4 is similar to that of the plant of Figure 3, except that reactor 270 is replaced by a column contactor 350 which is provided with a suitable packing (not shown) or with a series of sieve trays and downcomers (not shown). This contains a charge of an aqueous alkaline wash liquor and has a liquid distributor 351 near its base to which line 269 is connected. Distributor 351 serves to break the ester stream up into small droplets, typically with a droplet diameter of from about 1 mm to about 2.5 mm. The alkaline wash liquor contains 10% w/w Na_2CO_3 and 35% w/w di-sodium maleate and is circulated by means of line 352, pump 353, and line 354 to the top of column contactor 350. A purge stream is taken in line 355 in order to control the composition of the circulating liquor. Make up sodium carbonate solution is supplied in line 356, such solution being formed by admixing sodium carbonate, supplied in line 357 with water from lines 358 and 40. Further details of the operation of contactor 350 can be found in copending British patent application No. 8618893 filed 1st August 1986.

Coalesced diethyl maleate collects at the top of column contactor 350 above the interface 359 with the aqueous alkaline wash liquor and is passed to column 276 in line 275.

Acid free diethyl maleate from condenser 286 is passed by way of line 370 to product recovery section 371 which is operated according to the general teachings of European patent application No. (Case 86040) filed simultaneously herewith. Product recovery section 371 is described in more detail below in relation to Figure 6 of the drawings.

A stream containing diethyl maleate in admixture with a minor amount of by-product diethyl succinate, and possibly also gamma-butyrolactone, is passed from product recovery section 371 in line 372 to pump 88. Hence line 372 replaces lines 86 and 87 of the plants of Figures 1 to 3.

In a modification of the plant of Figure 1 diethyl maleate supplied in line 76 is hydrogenated in the vapour phase to diethyl succinate in a further hydrogenation zone (not shown) in line 76 upstream from the first hydrogenation zone 79. Such further upstream hydrogenation zone contains, for example, a relatively small charge of copper chromite catalyst and the rate of passage of ester therethrough preferably corresponds to a liquid hourly space velocity of at least about 3.0 hr^{-1}. Prior to entry to hydrogenation zone 79 the resulting hydrogenated ester containing reaction mixture, which now contains a minor amount only each of diethyl maleate and butane-1,4-diol and a major amount of diethyl succinate, is cooled to remove the heat of hydrogenation of the C:C bond of the unsaturated ester starting material.

Figure 5 illustrates one form of product recovery section 118 for use in any of the plants of Figures 1 to 3. This is a simplified flow diagram and omits condensers, condensate drums, reflux lines, pumps, reboilers and the like. Further details of this product recovery section can be found in GB-A-2175894. The crude product in line 117 is fed to a first product distillation column 501, which is operated under vacuum at a pressure of 0.27 bar with a head temperature of 48°C. The "light ends", i.e. a mixture of tetrahydrofuran, ethanol, water, and n-butanol, are stripped off in column 151, recovered overhead in line 502, and passed to a second product distillation column 503. Column 503 is operated at 1.2 bar at a head temperature of 58°C. A first tetrahydrofuran/water azeotrope is recovered overhead in line 504 and is passed to a third product distillation column 505 which is operated at 7.0 bar with a head temperature at 126°C. Essentially pure tetrahydrofuran is recovered as a bottom product from third product distillation column 505 in line 119. The overhead product in line 506 from column 505 is a second tetrahydrofuran/water azeotrope which is markedly richer in water than the first tetrahydrofuran/water azeotrope from column 503. This second azeotrope is recycled from line 506 by way of line 502 to column 503.

The bottom product in line 507 from column 503 is a wet mixture of ethanol and n-butanol. This is fed to a fourth product distillation column 508 which is operated at 1.2 bar with a head temperature of 85°C. The overhead product in line 152 from this column is a slightly wet ethanol. The bottom product in line 121 from column 508 is dry n-butanol.

It will thus be seen that separation of the "light ends" mixture of tetrahydrofuran, ethanol, water, and n-butanol from first product distillation column 501 can be effected in the three further product distillation columns 503, 505 and 508, operating at 1.2 bar, 7.0 bar and 1.2 bar respectively.

The "heavy ends" fraction in line 509 from first product distillation column 501 is a mixture containing, in addition to butane-1,4-diol and gamma-butyrolactone, a minor amount of diethyl succinate, as well as a minor amount of "heavies", such as diethyl ethoxysuccinate. This is fed to a fifth product distillation column 510, which is operated under vacuum at a pressure of 0.12 bar with a head temperature of 134°C. The overhead product from column 510 is a mixture of diethyl succinate, gamma-butyrolactone and a minor amount of butane-1,4-diol; this is passed by way of line 511 to a sixth product distillation column 512. Column 512 is operated under vacuum at a pressure of 0.05 bar and at a head temperature of 110°C. The bottom product from column 512 in line 86 is mainly diethyl succinate and is recycled. The overhead product from column 512 is an azeotropic mixture of gamma-butyrolactone and diethyl succinate; it is then taken by way of line 513 to a seventh product distillation column 514 which is operated at a pressure of 0.65 bar and at a head temperature of 80°C. The azeotropic mixture from line 513 is distilled in column 514 in the presence of water. The overhead product in line 515 from column 514 is an azeotropic mixture of diethyl succinate and water, containing a small amount of gamma-butyrolactone. This is condensed and allowed to separate in drum 516 into two layers; the upper water layer 517, which contains a minor amount of organic material, is recycled to the top of column 514 in line 518. Make up water is added in line 519. The lower layer 520, which separates in drum 516, comprises mainly diethyl succinate and is recycled to line 86 via line 521.

The bottom product in line 522 from column 514 is essentially a mixture of water and butyrolactone. This is separated in an eighth product distillation column 523 which is operated at 0.5 bar and a head temperature of 82°C. The overhead product in line 524 is mainly water and is recycled to column 514. The bottom product in line 525 is substantially dry, pure gamma-butyrolactone but still contains trace amounts of "heavies", such as diethyl ethoxysuccinate, and of butane-1,4-diol; this is fed to ninth product distillation column 526 from which pure gamma-butyrolactone is recovered overhead in line 120. The bottom product from column 526 is a mixture of gamma-butyrolactone, "heavies" and butane-1,4-diol and is recycled by way of line 527 to column 512.

It will thus be seen that recovery of pure gamma-butyrolactone from the crude butyrolactone stream in line 511 is effected in four distillation columns, i.e. sixth, seventh, eighth, and ninth product distillation columns 512, 514, 523 and 526 respectively. The diethyl succinate/gamma-butyrolactone azeotrope which would otherwise prevent effective separation of the crude mixture by distillation methods is broken by addition of water in column 514.

Reverting to column 510, the bottom product therefrom in line 527 is a mixture of butane-1,4-diol and "heavies". This is distilled in tenth product distillation column 528 at a pressure of 0.24 bar and a head temperature of 134°C to give an overhead product, which is substantially pure butane-1,4-diol, in line 121 and a bottom "heavies" product in line 529. This "heavies" product is stripped in column 530 of remaining traces of butane-1,4-diol, which are recycled to column 510 in line 531. The stripped "heavies" stream in line 146 is exported beyond battery limits or is used as boiler fuel in the plant.

Figure 6 illustrates diagrammatically the design of product recovery section 371 of the plant of Figure 4; this operates according to the teachings of European patent application No. (Case 86040) filed simultaneously herewith. As its design is, in many respects, similar to the design of the product recovery section 118 of Figure 5, like reference numerals have been used to indicate like parts. In particular the separation of the crude product in line 117 by means of first product distillation column 501 into a "light ends" fraction in line 502, which is subsequently distilled in columns 503 and 505 to yield tetrahydrofuran in line 119, ethanol in line 152, and n-butanol in line 122, and into a "heavy ends" fracton in line 509 is conducted in the same way as in the plant of Figure 5. Moreover, operation of columns 510, 528, and 530 is exactly the same in the plant of Figure 6 as for that of Figure 5. However, column 512 is omitted and the overhead product in line 511 from column 510 is taken to a distillation column 601 which is operated at a head pressure of 0.12 bar and at a head temperature of 140°C. Column 601 is supplied by way of line 602, at a point above the point of connection of line 601, with diethyl maleate from line 370. Condenser 603 ensures a reflux stream for column 601. The overhead product in line 604 from column 601 is substantially free from diethyl succinate but is predominantly a mixture of gamma-butyrolactone and diethyl maleate and is passed to a further column 605 which is operated at a head pressure of 0.067 bar and a head temperature of 117°C. The bottom product from column 605 is diethyl maleate and is recycled by way of line 606 to column 601.

The bottom product from column 601 in line 607 comprises a mixture of diethyl succinate, diethyl maleate, a minor amount of butane-1,4-diol, and trace amounts of "heavies", such as diethyl ethoxysuccinate. This is admixed with diethyl maleate in line 608 to form the stream in line 372. Hence the diethyl succinate and diethyl maleate are passed in line 372 to hydrogenation.

The top product from column 605 in line 120 is substantially pure gamma-butyrolactone.

In the plants illustrated in Figures 1 and 2 it is proposed that the neutralisation stage 55 shall involve use of an aqueous alkali, followed by a subsequent water wash; alternatively neutralisation can be achieved using an aqueous alkaline wash liquor comprising an alkali metal (e.g. sodium) hydroxide, carbonate, bicarbonate, or a mixture of two or more thereof dissolved in an aqueous solution of the corresponding di-(alkali metal) salt of maleic acid (e.g. disodium maleate), as taught by copending British patent application No. 8618893 filed 1st August 1986, followed by distillation in column 59.

Alternatively the neutralisation stage 55 of the plants illustrated in Figures 1 and 2 can be replaced by a purification stage using the distillative process of copending European Patent Application No. (Case 86079) filed simultaneously herewith.

Figure 7 of the drawings illustrates a continuously operable plant for production of diethyl maleate which is then used for the co-production of butane-1,4-diol, gamma-butyrolactone and tetrahydrofuran.

This plant is supplied in line 701 with liquid maleic anhydride and in line 702 with make up ethanol. A mixture of maleic anhydride and ethanol is supplied to a monoesterification reactor 703 which is also supplied with a wet ethanol stream in line 704 in an ethanol:maleic anhydride molar ratio of about 2:1. The ethanol supplied in line 704 contains about 15 to 20 mole % of water. Reactor 703 is fitted with a jacket 705 by means of which it can be cooled, as necessary, by admission of cooling water thereto. The contents of monoesterification reactor can be mixed by means of stirrer 706. The reaction mixture is held in reactor 703 for a residence time of about 60 minutes, the temperature in reactor 703 being maintained at about 100°C.

Essentially quantitative formation of monoethyl maleate occurs in monoesterification reactor 703. A liquid reaction mixture is discharged from reactor 703 in line 707 which contains an approximately equimolar mixture of monoethyl maleate and ethanol, plus a corresponding amount of water.

This mixture is passed forward in line 708 and is admixed with a further mole of ethanol, supplied as a "wet" ethanol stream containing about 15 to 20 mole % of water in line 709. The resulting mixture contains monoethyl maleate, ethanol and water in a mole ratio of about 1 : 2 : 0.25 and is then pumped by means of pump 710 through heater 711, which is supplied with steam in line 712, to a primary esterification reactor 713 which contains a bed of an ion exchange resin containing $-SO_3H$ groups, such as Amberlyst 16. (The word "Amberlyst" is a Registered Trade Mark). It is maintained at about 105°C under pressure.

The liquid hourly space velocity through the resin bed of primary esterification reactor 713 is approximately 1.75 hr^{-1}. About 70 mole % of the monoethyl maleate is esterified to diethyl maleate in passage through reactor 713. The liquid effluent stream in line 714 accordingly contains diethyl maleate, monoethyl maleate, water, and excess ethanol in a molar ratio of approximately 0.7 : 0.3 : 0.95 : 1.3, and possibly also minor amounts of maleic anhydride, maleic acid, fumaric acid, monoethyl fumarate and diethyl fumarate.

This mixture is passed by way of line 714 to a first distillation column 715 which operates at substantially atmospheric pressure. An ethanol/water mixture, in a molar ratio of about 2 : 1.25, which contains also minor amounts of diethyl maleate, of tetrahydrofuran and of diethyl ether, is recovered overhead in line 716.

The overhead product in line 716 is a mixture that is wetter than the ethanol/water azeotrope which could be obtained at the pressure of operation of column 715, i.e. substantially atmospheric pressure. Part of the vapours in line 716 are condensed in condenser 717 which is supplied in line 718 with cooling water. The resulting condensate passes on to condensate drum 719 and is recycled in line 720 by pump 721 to form a reflux stream for column 715. The uncondensed vapours pass on in line 722 to an ethanol recovery column 723, from which a bottom product containing water and any diethyl maleate is recovered in line 724; part of this bottom product is recycled by means of pump 725 through heater 726, whose steam line is indicated at 727, to column 723 whilst the remainder is passed in line 728 to cooler 729 and then to a water treatment section (not shown).

An overhead product is recovered from column 723 in line 730, that contains about 15 to 20 mole % water. It also contains any light boiling materials present such as diethyl ether and tetrahydrofuran.

The ethanol/water mixture in line 730 is condensed in condenser 731 against cooling water supplied in line 732; part of the resulting condensate which is collected in drum 733 is returned to column 723 by way of line 734 and pump 735 to form a reflux stream for column 723. Reference numeral 802 indicates a vent line for drum 733.

The rest of the condensate from drum 733 is passed in line 736 to an ether recovery column 737 from which any diethyl ether and other "lights", e.g. tetrahydrofuran, are recovered overhead in line 738 and are condensed in condenser 739 whose coolant supply line is indicated at 740. Condensate is returned as a reflux stream to column 737 from condensate drum 741 by means of line 742 and pump 743. Vapours are vented to a flare stack in line 744 while diethyl ether is passed to storage in line 745 via cooler 746 which is supplied with chilled water in line 747. Such diethyl ether also contains some of the tetrahydrofuran present in the material in line 722.

The bottom product from column 737 in line 748 is a wet ethanol stream containing about 15 to 20 mole % of water. Part is recycled to column 737 by pump 749 through reboiler 750, which is heated with steam supplied in line 751, whilst the remainder is recycled to monoesterification reactor 703 in lines 752 and 704.

The bottom product from column 715 in line 753 is a mixture of diethyl maleate, monoethyl maleate, and minor amounts of "lights" (e.g. water and ethanol), in a mole ratio of approximately 0.7 : 0.3 : 0.2. Part of this mixture is recycled to column 715 by way of pump 754 and reboiler 755 whose steam heating line is indicated at 756, and the remainder is passed through line 757 and then through lines 758 and 759 to the respective top end of a pair of secondary esterification reactors 760, 761, each containing a charge of a macroreticular ion exchange resin containing $-SO_3H$ groups, such as Amberlyst 16.

Each reactor 760, 761 is provided with a stirrer 762, 763 and is fitted at its lower end with a respective vapour distributor 764, 765. Ethanol vapour is introduced by means of lines 766, 767 and 768 through distributors 764, 765 into the bottom ends of reactors 760, 761.

Further esterification occurs in secondary esterification reactors 760, 761 by reaction of residual monoethyl maleate with ethanol. Water produced in the esterification reaction is stripped by the upflowing ethanol vapour and the resulting "wet" ethanol vapour in lines 769 and 770 is fed by way of line 771 through condenser 772, which is supplied with cooling water in line 773, to drum 774 from which it is recycled by pump 775 and lines 776, 777 and 708 to primary esterification reactor 713.

Reference numeral 778 indicates a vent line.

The liquid product stream from secondary esterification reactors 760, 761, which now contains diethyl maleate and monoethyl maleate in a molar ratio of about 85:15, besides minor amounts of ethanol and water, exits reactors 760, 761 in lines 779 and 780 and is pumped by means of pump 781 through line 782 to a flash column 783 which will be described further below.

Typical reaction conditions in reactors 760, 761 include use of a temperature of about 115°C and a pressure of about 1 bar. The residence time in secondary esterification reactors 760, 761 is about 2½ hours.

The ethanol vapour supplied in line 766 is a mixture of make up ethanol from line 702 and ethanol recycled in line 784 from the product recovery section of a hydrogenation plant 785 (described further below); this ethanol mixture is vaporised in heater 800 which is supplied with steam in line 801.

The liquid product stream from reactors 760, 761 in line 782 is passed to a column 783 which is operated under vacuum (about 0.1 bar). Ethanol and any water present are recovered overhead in line 786 and part of this overhead stream is condensed in condenser 787 which is cooled to about 70°C by tempered water supplied in line 788. The resulting condensate is collected in drum 789. The condensate from drum 789 is recycled to the top of column 783 by pump 790 in line 791 to form a reflux stream. The uncondensed part of the stream from line 786, which consists mainly of ethanol and water, passes on in line 792 and is condensed in a further condenser 793 whose chilled water supply line is indicated at 794. The resulting condensate is collected in drum 795 and is recycled to the secondary esterification reactors 760, 761 by means of line 796 and pump 797. Reference numeral 816 indicates a connection to a vacuum pump (not shown).

The bottom product from column 783 is recovered by way of line 798 and consists essentially of a mixture of diethyl maleate and monoethyl maleate, besides other minor impurities including maleic acid, diethyl fumarate, monoethyl fumarate, and fumaric acid.

The ester stream in line 798 is pumped by a pump 799 to a purification plant 804 which operates according to the teachings of copending European Patent Application No.   (Case 86079) filed simultaneously herewith. For example, purification plant 804 can operate as described in relation to Figure 5 of that copending European patent application, to which reference should be made for further details. This purification plant 804 may further include a distillation section for separation of diethyl maleate from diethyl fumarate. A recycle stream containing a mixture of diethyl maleate and monoethyl maleate is returned from purification plant 804 by way of lines 805 and 806. A purge stream is taken in line 807. A condensate containing maleic anhydride is recycled to monoesterification reactor 703 in line 803. A mixture consisting mainly of ethanol and water is recycled to column 783 in line 808.

Acid free diethyl maleate, possibly containing a minor amount of diethyl fumarate, is recovered from purification plant 804 in line 809 and is passed to a vapour phase hydrogenation plant 785 which is arranged to operate according to the process described in EP-A-0143634, in WO-A-86/03189 or in WO-A-86/07358. Plant 785 is supplied with hydrogen in line 810. Such a plant includes a product recovery section, for example one designed to operate according to the teachings of copending European Patent Application No. (Case 86040) filed simultaneously herewith and as illustrated in Figure 6.

There are recovered from hydrogenation plant 785 a stream of tetrahydrofuran in line 811, a stream of gamma-butyrolactone in line 812, and a stream of butane-1,4-diol in line 313. Minor amounts of n-butanol and of "heavies" are recovered in lines 814 and 815 respectively.

In the plant of Figure 8 maleic anhydride is supplied in line 901 to monoesterification reactor 902, to which is also supplied a stream containing ethanol in line 903. Reactor 902 is also fed by way of line 901 with a recycle stream from line 904 that contains recovered maleic anhydride and diethyl maleate. Monoesterification reactor 902 is provided with a stirrer 905, with a cooling coil 906 (which doubles as a steam heating coil at start up of the plant), and with a vent line 907. Maleic anhydride reacts with ethanol in reactor 902 to produce monoethyl maleate in the absence of a catalyst. The liquid reaction mixture from reactor 902 is discharged in line 908 and pumped by pump 909 to steam heater 910. Upstream from heater 910 it is admixed with two streams comprising further ethanol supplied in lines 911 and 912.

The mixed stream flows on in line 913 to a primary esterification reactor 914 which contains a fixed bed of an acidic ion exchange resin, such as Amberlyst 16. Reaction between monoethyl maleate and ethanol to form diethyl maleate takes place in reactor 914.

An intermediate esterification product mixture is recovered from primary esterification reactor 914 in line 915 and is heated by means of steam heater 916 before entering a flash distillation column 917. A vaporous stream containing mainly ethanol and water, but also a minor amount of diethyl ether (besides tetrahydrofuran and a trace of diethyl maleate, both of which are present in a recycle stream to monoesterification reactor 902 as described further below), is recovered overhead in line 918 which leads to an ethanol recovery column 919. This is also supplied with water in line 920 which has been used in condensers in the plant and which·includes water containing streams recovered from elsewhere in the plant. The overhead product from column 919 in line 921 is condensed by means of condenser 922 and contains mainly ethanol with lesser amounts of water, diethyl ether and tetrahydrofuran. The resulting condensate collects in drum 923; part is returned to column 918 in line 924 by pump 925 to form a reflux stream, whilst the remainder is passed in line 926 to an ether recovery column 927. A part of the bottom product from column 919 in line 928 is recycled by pump 929 to column 919 through column reboiler 930 and line 931. This bottom product in line 928 is mainly water but contains some ethanol and diethyl maleate. The remainder of the bottom product in line 928 is taken in line 932, cooled in cooler 933 and passed on to a water treatment plant (not shown).

From the ether recovery column 927 is recovered overhead in line 934 a vaporous stream comprising diethyl ether, together with minor amounts of ethanol, water and tetrahydrofuran. This is condensed by means of condenser 935. The resulting condensate collects in drum 936; part is recycled as a reflux stream to column 927 in line 937 by pump 938, while the remainder is passed in line 939 to cooler 940 and thence to storage.

Reference numerals 941 and 942 represent vent lines for condensate drums 923 and 936 respectively.

The bottom product from ether recovery column 927 in line 943 is mainly ethanol, but contains a minor amount of water and small amounts of tetrahydrofuran and diethyl ether. Part is returned through reboiler 944 in line 945 to column 927 by means of pump 946, whilst the remainder is recycled in line 947 for admixture with further ethyl alcohol in line 948 to form the stream in line 903.

The bottom product from flash distillation column 917 is taken in line 949 to a secondary esterification reactor 950. This is provided with a stirrer 951 and a sparger 952 which is connected to a line 953 through which ethanol vapour is supplied to reactor 950. Further reaction of monoethyl maleate and ethanol occurs in reactor 950, resulting in formation of additional diethyl maleate. A stream containing recycled ethanol is returned to reactor 950 in line 954.

Water of esterification is stripped by the upflowing ethanol vapour which exits reactor 950 in line 955. This vapour is condensed in condenser 956 and collects in drum 957 from which it is recycled to primary esterification reactor 902 in line 912 by pump 958. Reference numeral 959 represents a vent line for drum 957.

A liquid product mixture containing mainly diethyl maleate but also a lesser amount of monoethyl maleate, together with some ethanol and water and traces of diethyl ether and tetrahydrofuran, is recovered in line 960. This is pumped by pump 961 through a pressure reduction valve 962 to a flash distillation column 963 which is operated under vacuum. The overhead stream in line 964 is recycled to secondary esterification reactor 950 by way of line 954 and contains ethanol and water besides some diethyl maleate and a trace of monoethyl maleate.

The bottom product from column 963 is pumped in line 965 to a diethyl maleate purification plant 966 by pump 967. Plant 966 operates according to the teachings of copending European patent application No. (Case 86079) filed simultaneously herewith. It preferably includes a distillation column for separation of diethyl maleate from diethyl fumarate. Acid free diethyl maleate is recovered in line 968 and is passed to a vapour phase hydrogenation plant 969. This is arranged to operate according to the process described in EP-A-0143634, in WO-A-86/03189 or in WO-A-86/07358 and is supplied with hydrogen in line 970. It includes a product recovery section, for example one designed to operate according to the process of copending European patent application No. (Case 86040) filed simultaneously herewith. There are recovered from plant 969 a stream of tetrahydrofuran in line 971, a stream of gamma-butyrolactone in line 972, and a stream of butane-1,4-diol in line 973. Minor amounts of "heavies" are recovered in line 974.

Instead of providing for recovery of n-butanol by-product within the product recovery section of the hydrogenation plant 969, as in the plant of Figure 7, a column 975 is fed with a mixture of "lights" recovered from plant 969, including ethanol and n-butanol, in line 976 and with make up ethanol in line 977. The mixed stream in line 978 yields upon distillation a vaporous stream in line 979 part of which flows on in line 980 through heater 981 and line 953 to the secondary esterification reactor 950. The rest of the vaporous stream in line 979 passes to a condenser 982. The resulting condensate in line 983 collects in drum 984, part being returned as a reflux stream to column 975 in line 985 by means of pump 986, and the remainder flowing in line 448 to join line 947. Reference numeral 987 indicates a vent line for drum 984. A stream of n-butanol, produced as a by-product in hydrogenation plant 969, is recovered from the bottom of column 975 in line 988. Part of this stream is returned to column 975 in line 989 through reboiler 990. The remainder is passed to storage in line 991.

From diethyl maleate purification plant 966 there is recovered in line 992 a stream containing a mixture of ethanol, diethyl maleate, water, and maleic anhydride, besides traces of tetrahydrofuran, diethyl ether, maleic acid, and fumaric acid. This is admixed with the material in line 964 to form the stream in line 954. Also recovered from diethyl maleate purification plant 966 is a stream containing maleic anhydride and diethyl maleate, besides traces of ethanol and water; this is recycled to monoesterification reactor 902 in line 904. Another stream recovered from plant 966 in line 993 contains a mixture of monoethyl maleate and diethyl maleate and minor amounts of "heavies". Part is purged in line 994, whilst the remainder is recycled to primary esterification reactor 914 in line 995.

The composition of some of the more important streams in the plant of Figure 8 and some typical operating conditions are set out in the Table. (In the Table "THF" means tetrahydrofuran and "DEE" means diethyl ether; in addition the items "Monoethyl maleate" and "Diethyl maleate" include minor amounts of monoethyl fumarate and of diethyl fumarate respectively).

TABLE

LINE NO.	901	903	904	908	913	915	949	953	954	960
Flow rates in kg moles per hour										
Ethanol	-	134.1	0.3	52.2	305.9	238.9	13.5	159.0	39.1	33.0
Water	-	25.5	Trace	23.5	90.5	155.8	14.3	19.6	7.1	8.9
THF	-	1.0	-	1.0	1.7	1.7	Trace	Trace	Trace	Trace
DEE	-	0.5	-	0.5	1.5	2.9	Trace	0.2	Trace	Trace
Maleic anhydride	77.2	-	7.0	-	-	-	-	-	1.6	-
Maleic acid	-	-	Trace	12.5	12.5	-	-	-	Trace	-
Fumaric acid	-	-	-	0.1	0.1	-	-	-	-	-
Monoethyl maleate	-	-	-	61.1	73.5	35.0	35.0	-	Trace	20.9
Diethyl maleate	-	-	2.7	13.2	30.6	81.6	81.5	-	5.6	99.1
"Heavies"	-	-	-	-	1.4	1.7	1.7	-	-	1.9
Temperature (°C)	60	40	91	90	100	119	157	108	10	115
Pressure (bar)	6.0	6.0	6.0		6.5	5.0	1.8	1.8	1.1	1.1

It will be readily apparent to the skilled reader that the illustrated forms of plant can readily be modified to operate using other C_1 to C_4 alkyl alcohols to produce di-(C_1 to C_4 alkyl) maleates other than diethyl maleate. For example, in the case of the plants of Figures 1 to 4, as methanol does not form an azeotrope with water, separation of water from the overhead product in line 10 can be effected by distillation and no separate dehydration unit 33 is required to produce a sufficiently "dry" methanol stream for supply in line 25.

When operating with n-propanol to produce di-n-propyl maleate little or no modification of the illustrated plants will be required as n-propanol forms single phase azeotropes with water in much the same way as ethanol.

n-butanol also forms an azeotrope with water but this separates into two layers upon cooling. Hence, in the case of the plants of Figures 1 to 4, decantation can be used to form a "dry" n-butanol stream in line 30 for production of di-n-butyl maleate.

It will be appreciated by those skilled in the art that as dialkyl maleates and dialkyl fumarates generally have very similar physical properties, any diethyl fumarate formed in the esterification steps, either as a result of isomerisation of diethyl maleate or as a result of the presence of fumaric acid in the maleic anhydride used as feedstock, will report with the diethyl maleate in the illustrated plants. Hence references to diethyl maleate should in many cases be read as referring to a mixture of diethyl maleate and diethyl fumarate. Similarly references to monoethyl maleate should be read as meaning on occasion a mixture of monoethyl maleate and monoethyl fumarate, while references to maleic acid may in some cases mean a mixture of maleic acid and fumaric acid. In the case of the product recovery section of Figure 6 the diethyl maleate supplied in line 602 is desirably free from diethyl fumarate, and preferably contains not more than about 0.1 mole %, and even more preferably less than about 0.01 mole %, of diethyl fumarate. Hence a fractional distillation step for separation of diethyl maleate and diethyl fumarate may be necessary to produce a diethyl maleate stream of sufficient purity for use in the product recovery section of Figure 6.

CLAIMS

1. A continuous process for the co-production of butane-1,4-diol and gamma-butyrolactone which comprises:

(a) esterifying maleic anhydride by reaction with an alkyl alcohol to form the corresponding dialkyl maleate;

(b) hydrogenating resulting dialkyl maleate to yield a reaction product mixture comprising said alkyl alcohol, butane-1,4-diol and gamma-butyrolactone;

(c) recovering alkyl alcohol from said reaction product mixture;

(d) recycling recovered alkyl alcohol to step (a); and

(e) recovering butane-1,4-diol and gamma-butyrolactone from the reaction product mixture of step (c);

characterised in that said process comprises:

(i) continuously supplying maleic anhydride and a molar excess of an alkyl alcohol to a monoesterification zone maintained at an elevated temperature thereby to form the corresponding mono-alkyl maleate;

(ii) continuously supplying resulting mono-alkyl maleate in admixture with a molar excess of said alkyl alcohol to a primary catalytic esterification zone containing a charge of a solid esterification catalyst and maintained under esterification conditions thereby to form an intermediate ester-containing mixture containing a major amount of the corresponding dialkyl maleate and a minor amount of said mono-alkyl maleate;

(iii) continuously supplying a first liquid feed comprising said monoalkyl maleate to a secondary esterification zone containing a charge of a solid esterification catalyst;

(iv) continuously supplying a second feed stream comprising said alkyl alcohol to said secondary esterification zone;

(v) maintaining said secondary esterification zone at an elevated temperature sufficient to form or maintain therein a vaporous stream containing said alkyl alcohol;

(vi) intimately contacting said first liquid feed in said secondary esterification zone in the presence of said catalyst with said vaporous stream;

(vii) recovering from said secondary esterification zone a vaporous effluent stream containing, in addition to alkyl alcohol vapour, also water in vapour form, said water being produced in said secondary esterification zone by esterification of said monoalkyl maleate with said alkyl alcohol;

(viii) recovering from said secondary esterification zone a liquid product containing said dialkyl maleate;

(ix) vaporising dialkyl maleate produced in said secondary esterification zone in a stream of a hydrogen-containing gas;

(x) passing resulting vaporous dialkyl maleate containing stream through a plurality of hydrogenation zones connected in series, each containing a charge of a solid esterification catalyst and each maintained under ester hydrogenation conditions;

(xi) controlling the reaction conditions in each of the plurality of hydrogenation zones so as to produce a predetermined butane-1,4-diol:gamma-butyrolactone molar ratio in the reaction product mixture; and

(xii) recovering from the reaction product mixture (1) an alkyl alcohol fraction, (2) a butane-1,4-diol fraction, and (3) a gamma-butyrolactone fraction.

2. A process according to claim 1, characterised in that the maleic anhydride:alkyl alcohol molar ratio in step (i) is in the range of from about 1:1.5 to about 1:5.

3. A process according to claim 1 or claim 2, characterised in that the monoesterification zone of step (i) is operated at a temperature in the range of from about 60°C to about 100°C and at a pressure in the range of from about 1 bar to about 5 bar absolute.

4. A process according to any one of claims 1 to 3, characterised in that the residence time in the monoesterification zone of step (i) is from about 15 minutes to about 300 minutes.

5. A process according to any one of claims 1 to 4, characterised in that the monoesterification mixture resulting from step (i) is admixed with further alkyl alcohol prior to admission to the primary esterification zone of step (ii).

6. A process according to any one of claims 1 to 5, characterised in that the reaction conditions in the primary esterification zone include use of a temperature in the range of from about 100°C to about 120°C and a pressure in the range of from about 5 bar absolute to about 20 bar absolute.

7. A process according to any one of claims 1 to 6, characterised in that the liquid hourly space velocity through the primary cataytic esterification zone of step (ii) ranges from about 1 hr^{-1} to about 2 hr^{-1}.

8. A process according to any one of claims 1 to 7, characterised in that the primary esterification product mixture is distilled to separate alkyl alcohol and water from an ester-containing mixture containing monoalkyl maleate and dialkyl maleate which is supplied as the first liquid feed in step (iii) to the secondary catalytic

esterification zone, if there is only one such zone, or to the first of the secondary catalytic esterification zones, if there is more than one such zone.

9. A process according to any one of claims 1 to 8, characterised in that said second feed stream is supplied to said secndary esterification zone in vapour form.

10. A process according to any one of claims 1 to 8, characterised in that said second feed stream is supplied to said secondary esterification zone in liquid form.

11. A process according to any one of claims 1 to 10, characterised in that said secondary esterification zone comprises a reactor containing a charge of an immobilised ion exchange resin containing acidic groups selected from sulphonic acid groups and carboxylic acid groups.

12. A process according to claim 11, characterised in that said immobilised ion exchange resin comprises packages wrapped in wire mesh, each containing a quantity of beads of said resin.

13. A process according to any one of claims 1 to 12, characterised in that said vaporous stream is caused to pass through said secondary esterification zone in countercurrent to said first liquid feed.

14. A process accordng to any one of claims 11 to 13, characterised in that the water content of said second feed stream is less than about 1 mole %.

15. A process accordng to any one of claims 1 to 10, characterised in that said secondary esterification zone

comprises a stirred tank reactor containing a charge of an ion exchange resin containing acidic groups selected from sulphonic acid groups and carboxylic acid groups.

16. A process according to claim 15, characterised in that the water content of said second feed stream is less than about 15 mole %.

17. A process according to any one of claims 1 to 10, characterised in that a plurality of said secondary esterification zones connected in series are used, each said secondary esterification zone comprising a reactor containing a charge of an ion exchange resin containing acidic groups selected from sulphonic acid groups and carboxylic acid groups.

18. A process according to claim 17, characterised in that at least one of said reactors is a stirred tank reactor.

19. A process according to claim 17 or claim 18, characterised in that the water content of the second feed stream supplied to the final one of said secondary esterification zones is lower than the corresponding water content of the respective second feed stream spplied to any preceding one of said plurality of secondary esterification zones.

20. A process according to any one of claims 17 to 19, characterised in that the water content of the second feed stream to said fnal secondary esterification zone is less than about 1 mole %.

21. A process according to any one of claims 17 to 20, characterised in that the water content of the

respective second feed stream supplied to each of said plurality of secondary esterification zone decreases progressively from one zone to the next in the series.

22. A process according to any one of claims 17 to 21, <u>characterised in that</u> the second feed stream to the, or to each, said secondary esterification zone preceding said final secondary esterification zone comprises material of the vaporous product stream from the next succeeding secondary esterification zone.

23. A process according to claim 22, <u>characterised in that</u> the second feed stream to the, or to each, said secondary esterification zone preceding said final secondary esterification zone comprises liquid condensate obtained by condensing the vaporous product stream from the next succeeding secondary esterification zone.

24. A process according to claim 22, <u>characterised in that</u> the second feed stream to the, or to each, said secondary esterification zone preceding said final secondary esterification zone comprises a vaporous stream obtained by compressing the vaporous product stream from the next succeeding secondary esterification zone.

25. A process according to any one of claims 1 to 24, <u>characterised in that</u> the first liquid feed contains, in addition to monoalkyl maleate, also at least a minor amount of dialkyl maleate.

26. A process according to claim 25, <u>characterised in that</u> the dialkyl maleate content of the first liquid feed is from about 60 mole % to about 80 mole %.

27. A process according to any one of claims 1 to

26, characterisd in that the alkyl alcohol is ethanol, the monoalkyl maleate is monoethyl maleate, and the dialkyl maleate is diethyl maleate.

28. A process according to claim 27, characterised in that the primary esterification product mixture is distilled in a first distillation step to separate a mixture containing ethanol and water from a mixture containing mono- and di-ethyl maleates, which mixture is used as the first liquid feed to said secondary esterification zone, if there is only one secondary esterification zone, or to the first one of said secondary esterification zones, if there is more than one said esterification zone.

29. A process according to claim 28, characterised in that the monoethyl maleate:ethanol molar ratio of the reaction mixture supplied to said primary esterification zone is selected so that the ethanol/water mixture obtained in the first distillation step is richer in water than the azeotropic mixture which would be produced at the distillation pressure of the first distillation step.

30. A process according to claim 29, characterised in that the ethanol/water mixture from the first distillation step is re-distilled in a second distillation step to yield overhead a mixture of ethanol and water which is drier than the ethanol/water mixture supplied to the second distillation step and as bottom product a mixture of water and a minor amount of diethyl maleate.

31. A process according to claim 30, characterised in that a part of the overhead product from the second distillation step is subjected to dehydration to provide a dried ethanol stream for use as the second feed stream to

said secondary esterification zone, if there is only one secondary esterification zone, or to the final one of said plurality of secondary esterification zones, if there is more than one said secondary esterification zone.

32. A process according to claim 31, <u>characterised in that</u> dehydration is effected using a membrane or molecular sieve.

33. A process according to claim 31 or claim 32, <u>characterised in that</u> a water enriched fraction produced as by-product in the dehydration step is recycled to the second distillation step.

34. A process according to any one of claims 31 to 33, <u>characterised in that</u> the bottom product from the second distillation step is allowed to separate into two liquid layers, and in which the resulting organic layer is recycled to the process upstream from said at least one secondary esterification zone.

35. A process according to claim 34, <u>characterised in that</u> the resulting aqueous layer is used as make up water in an aqueous neutralisation zone through which the diethyl maleate product from the secondary esterification zone is passed.

36. A process according to any one of claims 31 to 35, <u>characterised in that</u> another part of the overhead product from the second distillation step is recycled to said primary esterification stage t provide make up ethanol therefor.

37. A process accordng to claim 28, <u>characterised in that</u> the secondary esterification zone comprises a stirred

tank reactor containing a charge of ion exchange resin containing sulphonic acid groups and in which the water content of the second feed stream is less than about 15 mole %.

38. A process according to claim 37, characterised in that vaporous effluent from the secondary esterification zone is condensed and recycled to the primary esterification zone.

39. A process according to any one of claims 1 to 38, characterised in that step (x) comprises passage of the vaporous dialkyl maleate containing stream through first and second hydrogenation zones, each containing a charge of a heterogeneous ester hydrogenolysis catalyst, in which a vaporous first reaction mixture that is substantially free from the starting ester and contains, in addition to unreacted hydrogen, butane-1,4-diol and gamma-butyrolactone in a first molar ratio is recovered from the first hydrogenation zone and is cooled prior to passage through thesecond hydrogenation zone, and in which a vaporous second reaction mixture that contans, in addition to unreacted hydrogen, butane-1,4-diol and gamma-butyrolactone in a secnd molar ratio that is greater than the first molar ratio, is recovered from the second hydrogenation zone.

40. A process according to claim 39, characterised in that the feed temperature to the first hydrogenation zone ranges from about 170°C to about 190°C.

41. A process according to claim 39 or claim 40, characterised in that the vaporous first reaction mixture is recovered from the first hydrogenation zone at a temperature in the range of from about 170°C to about

200°C.

42. A process according to any one of claims 39 to 41, characterised in that the vaporous first reaction mixture is cooled by at least about 5°C upon exit from the first hydrogenation zone prior to entry to the second hydrogenation zone.

43. A process according to any one of claims 39 to 42, characterised in that the feed temperature to the second hydrogenation zone lies in the range of from about 150°C to about 190°C.

44. A process according to any one of claims 39 to 43, characterised in that the pressure in the hydrogenation zones lies in the range of from about 25 bar to about 70 bar.

45. A process according to any one of claims 39 to 44, characterised in that the dialkyl maleate is fed to the first hydrogenaton zone at a rate corresponding to a liquid hourly space velocity of from about 0.1 hr^{-1} to about 3.0 hr^{-1}.

46. A process according to any one of claims 1 to 38, characterised in that step (x) comprises passage of the vaporous dialkyl maleate containing stream through first and second hydrogenation zones, each containing a charge of e heterogeneous ester hydrogenolysis catalyst, under substantially adiabatic reaction conditions, in which a vaporous first reaction mixture that is substantially free from the starting ester and contains, in addition to unreacted hydrogen, gamma-butyrolactone and butane-1,4-diol in a first molar ratio is recovered from the first hydrogenation zone and is heated prior to

passage through the second hydrogenation zone, and in which a vaporous second reaction mixture that contains, in addition to unreacted hydrogen, gamma-butyrolactone and butane-1,4-diol in a second molar ratio that is greater than the first molar ratio, is recovered from the second hydrogenation zone.

47. A process according to claim 46, characterised in that the feed temperature to the first hydrogenation zone ranges from about 170°C to about 260°C.

48. A process according to claim 47, characterised in that the feed temperature to the first hydrogenation zone is from about 190°C to about 230°C.

49. A process accordng to any one of claims 46 to 48, characterised in that the vaporous first reaction mixture is heated by at least about 5°C upon exit from the first hydrogenation zone prior to entry to the second hydrogenation zone.

50. A process accordng to any one of claims 46 to 49, characterised in that the feed temperature to the second hydrogenation zone is at least about 190°C.

51. A process according to any one of claims 46 to 50, characterised in that the pressure in the hydrogenation zones lies in the range of from about 3 bar to about 30 bar.

52. A process according to any one of claims 46 to 51, characterised in that the dialkyl maleate is fed to the first hydrogenation zone at a rate corresponding to a liquid hourly space velocity of from about 0.1 hr^{-1} to about 0.6 hr^{-1}.

53. A process according to any one of claims 1 to 52, <u>characterised in that</u> the heterogeneous hydrogenation catalyst comprises copper chromite.

54. A process according to claim 53, <u>characterised in that</u> the copper chromite catalyst contains, before reduction, from about 25 to about 45% by weight of copper and from about 20 to about 35% by weight of chromium.

55. A process according to any one of claims 1 to 54, <u>characterised in that</u> the hydrogen:dialkyl maleate molar ratio in the vaporous dialkyl maleate containing stream of step (x) is in the range of from about 50:1 to about 1000:1.

56. A process according to any one of claims 1 to 55, <u>characterised in that</u> the dialkyl maleate is diethyl maleate, and in which step (xii) comprises distilling the reaction product mixture of step (xi) to yield a "light ends" fraction containing tetrahydrofuran, water and <u>n</u>-butanol and a "heavy ends" fraction containing butane-1,4-diol, <u>gamma</u>-butyrolactone and diethyl succinate and thereafter:

(AA) distilling the "heavy ends" fraction in one or more stages to yield a <u>gamma</u>-butyrolactone-rich fraction containing, in addition to <u>gamma</u>-butyrolactone, a minor amount of diethyl succinate;

(BB) providing a stream of substantially acid free diethyl maleate;

(CC) supplying substantially acid free diethyl maleate of step (BB) and <u>gamma</u>-butyrolactone rich fraction of step (AA) to a fractionation zone;

(DD) fractionally distilling the <u>gamma</u>-butyrolactone rich fraction of step (AA) in the fractionation zone in the presence of said substantially acid free dialkyl maleate;

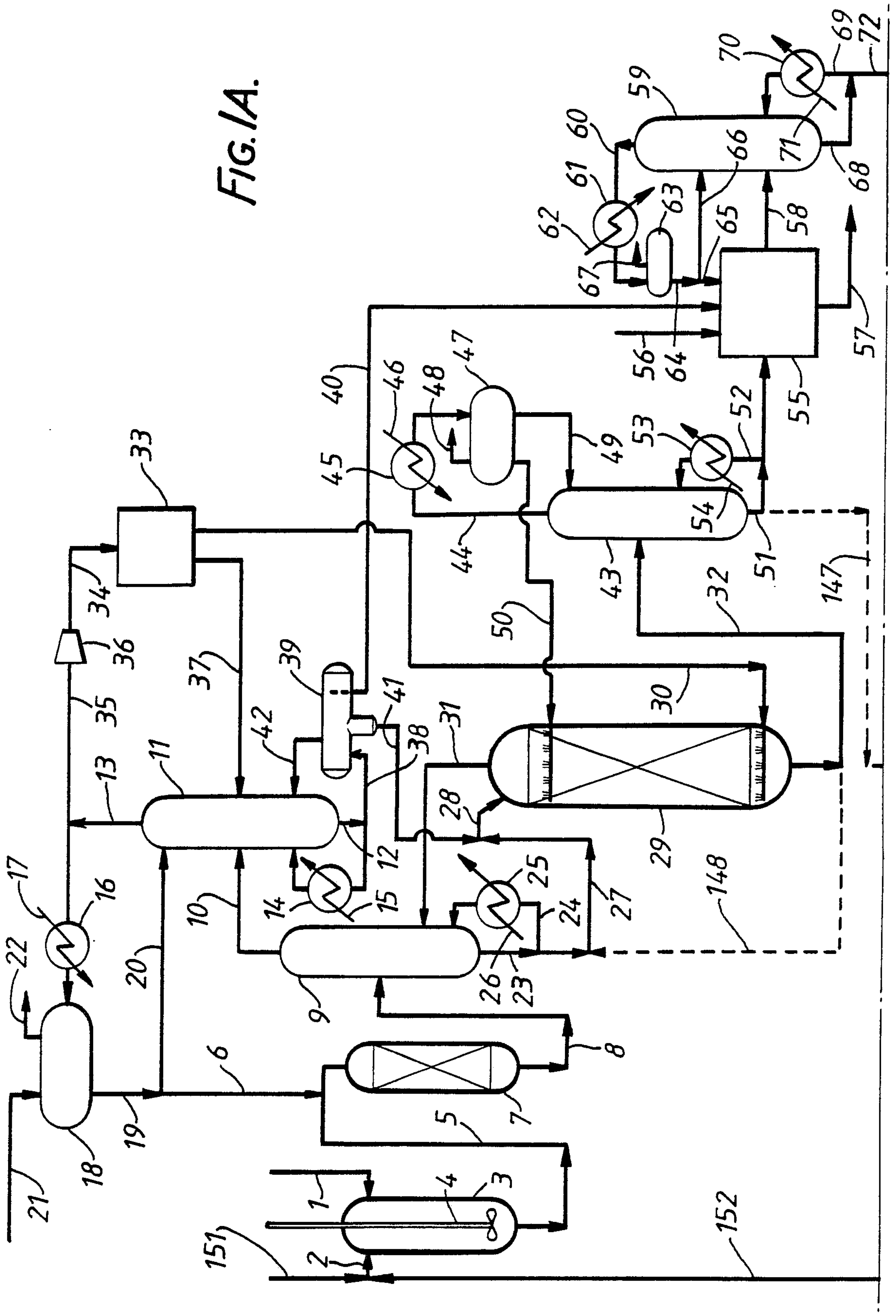
(EE) recovering as an overhead fraction from the fractionation zone a product stream that is substantially free from diethyl succinate and consists essentially of pure gamma-butyrolactone; and

(FF) recovering from the fractionation zone a liquid bottom product comprising diethyl maleate and diethyl succinate in admixture one with another.

57. A process according to claim 56, characterised in that material of the liquid bottom product of step (FF) is recycled to the hydrogenation step of the process.

58. A process according to claim 56 or claim 57, characterised in that the acid free diester of step (BB) is obtained by neutralisation of the liquid product of step (viii).

FIG. 1A.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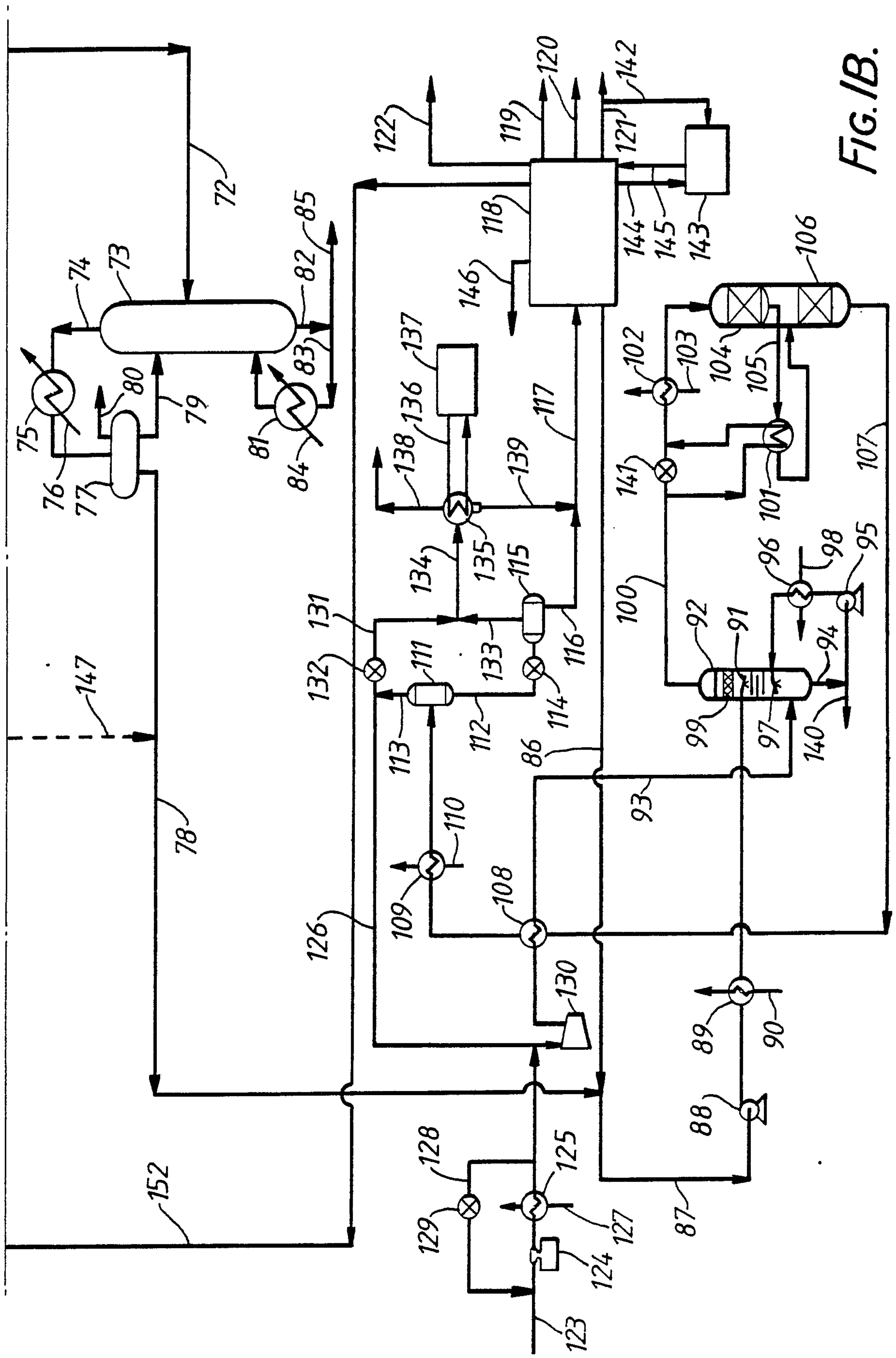
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FIG. 1B.

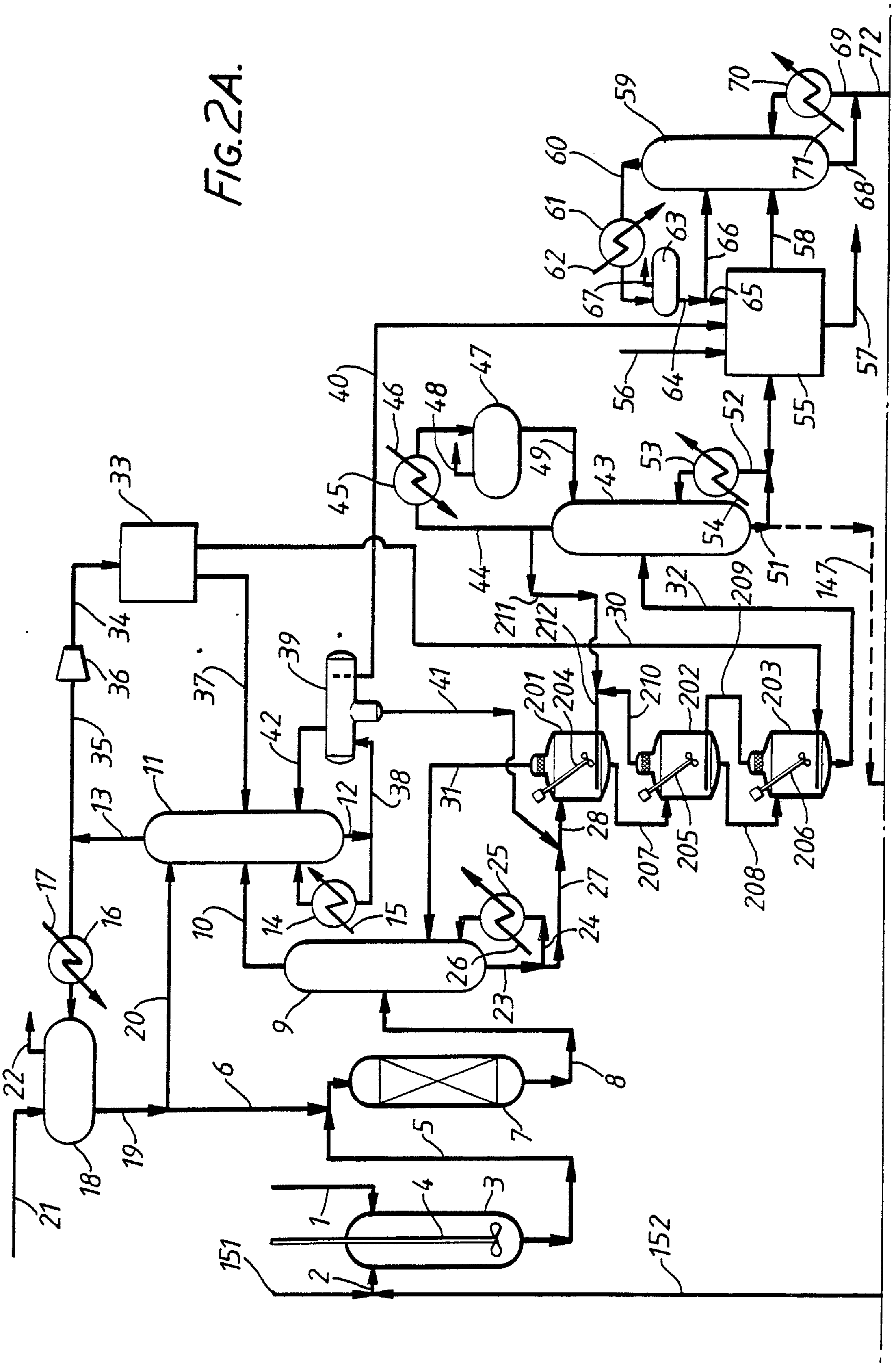
FIG. 2A.
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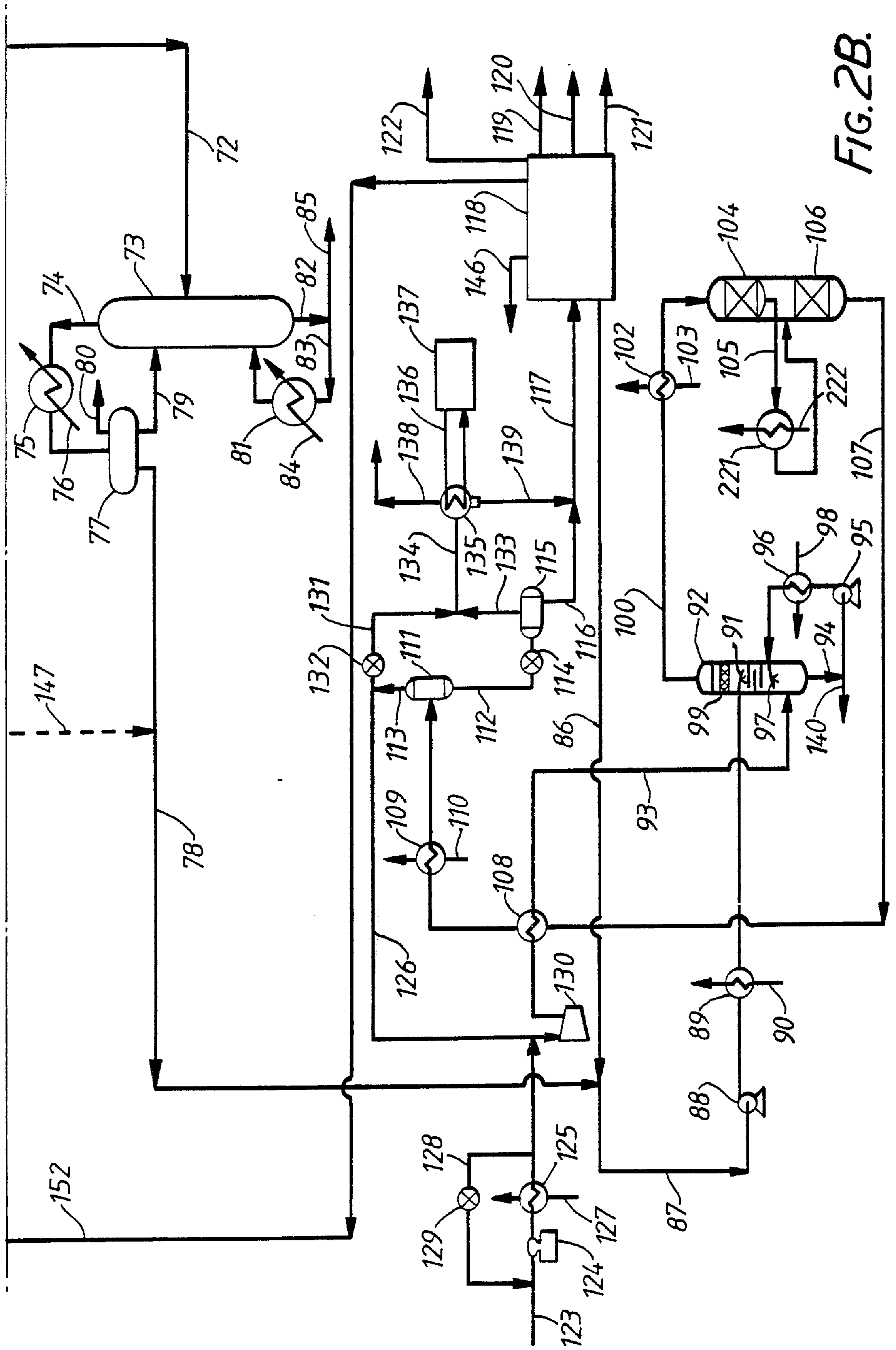
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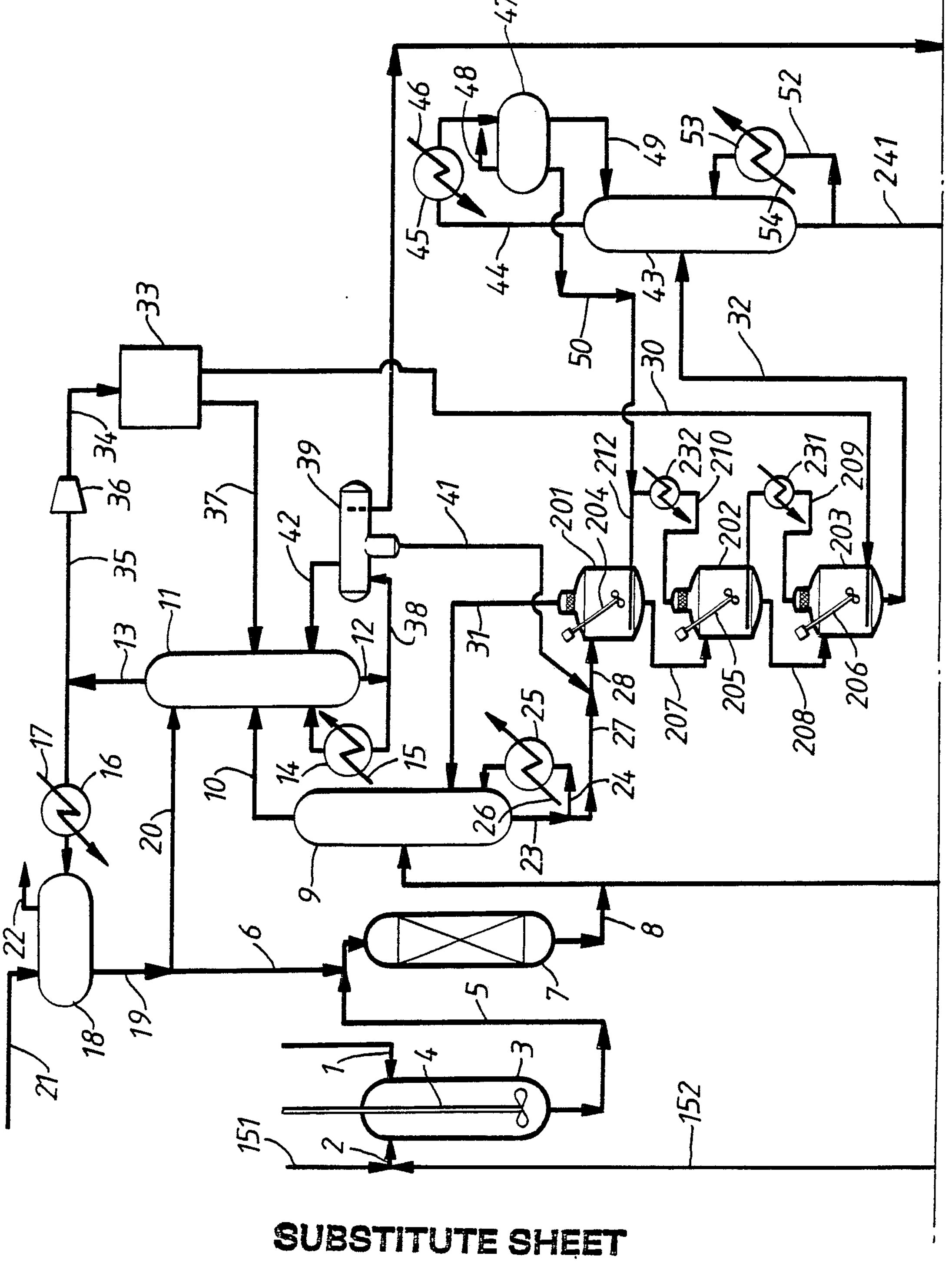
FIG.2B.

FIG. 3A.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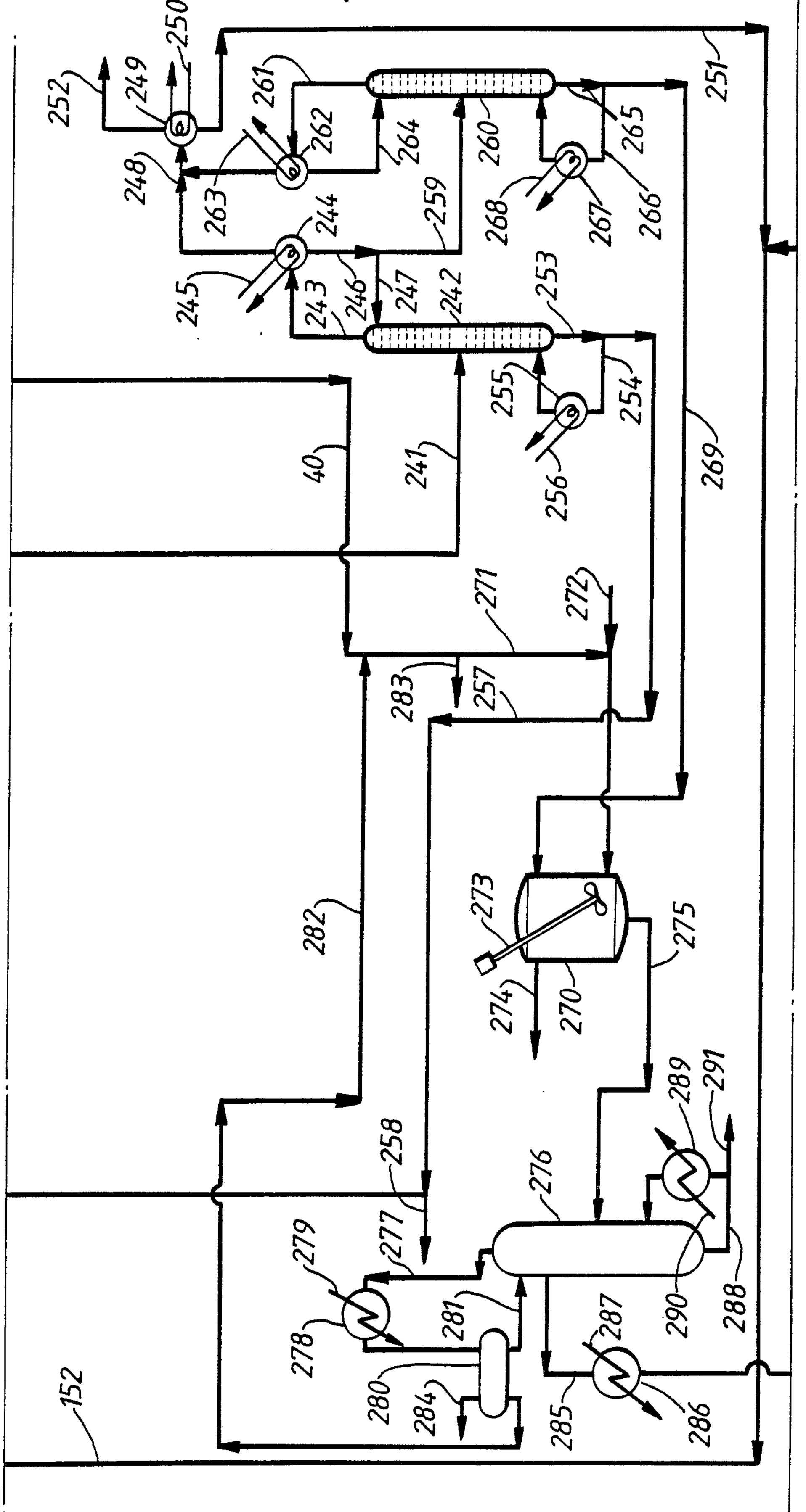

FIG.3B.

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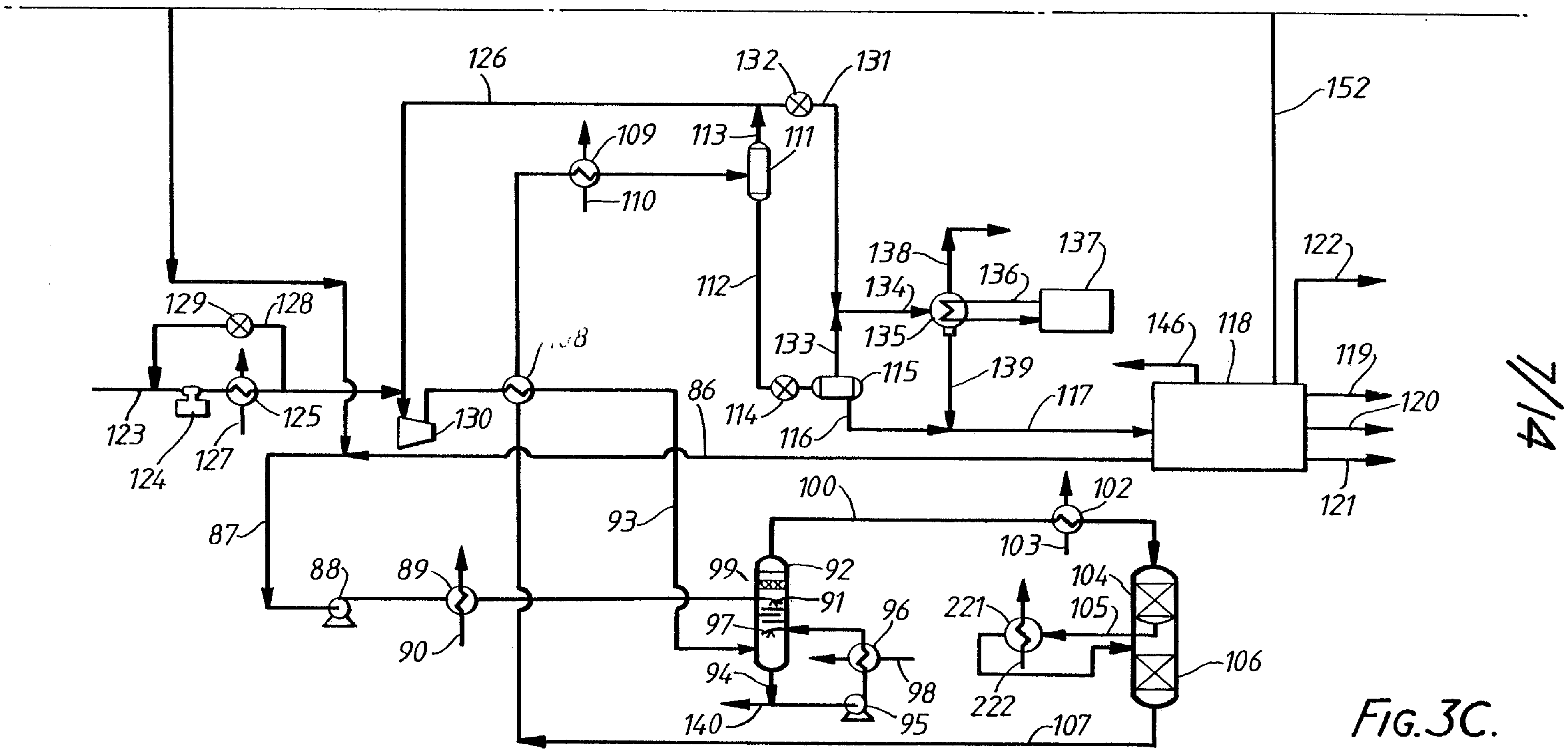
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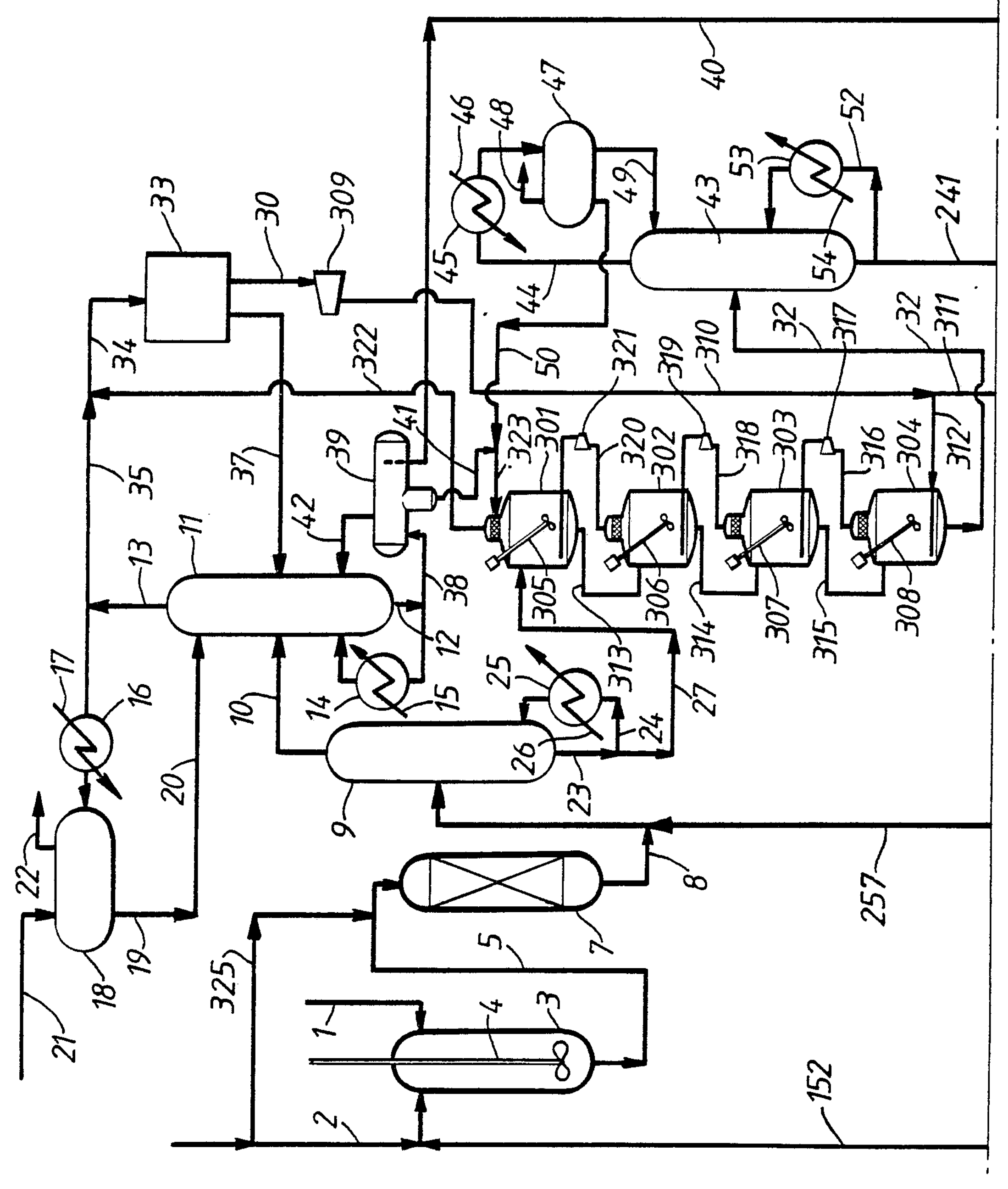
FIG.3C.

FIG. 4A.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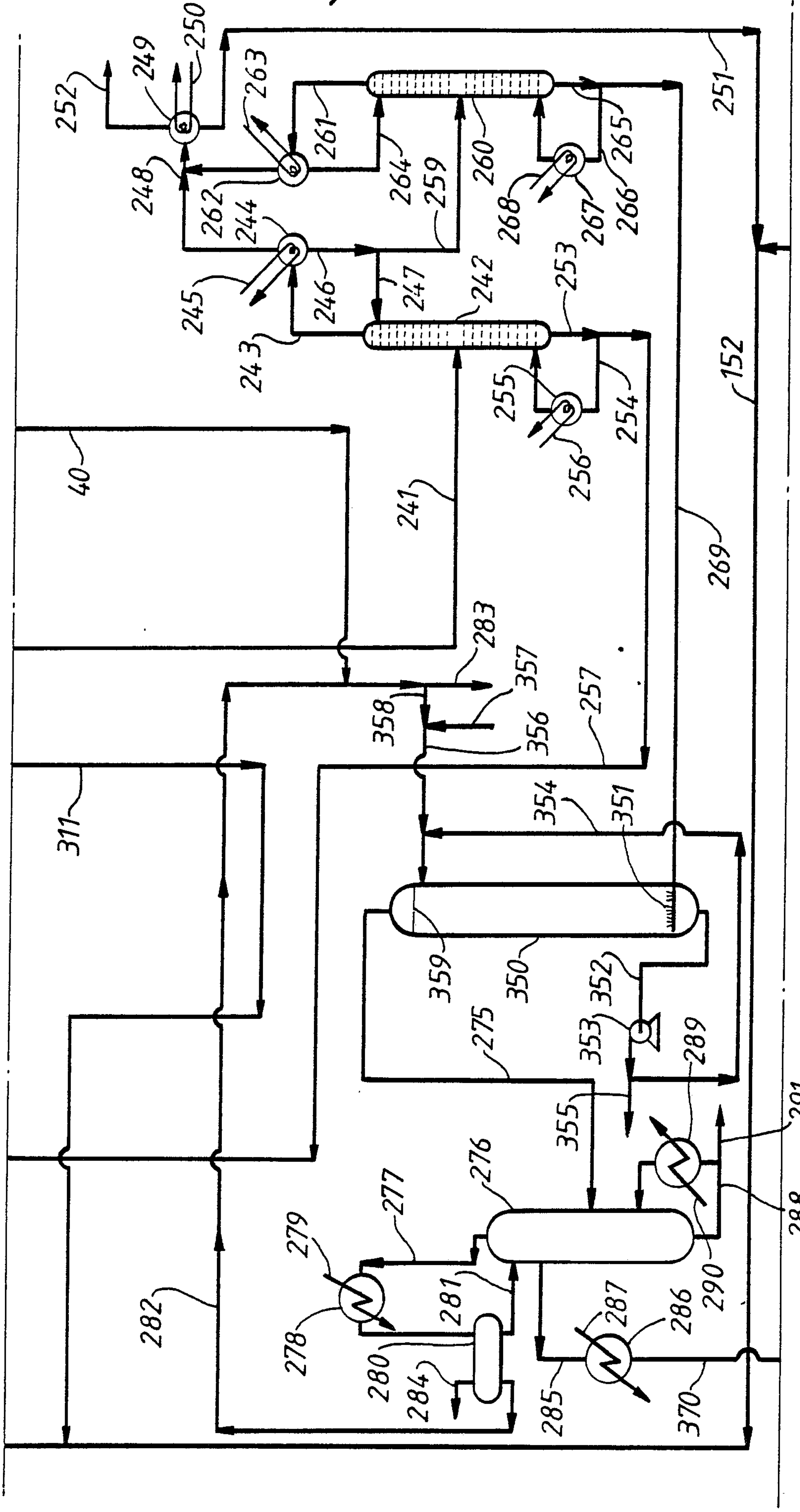
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FIG. 4B.

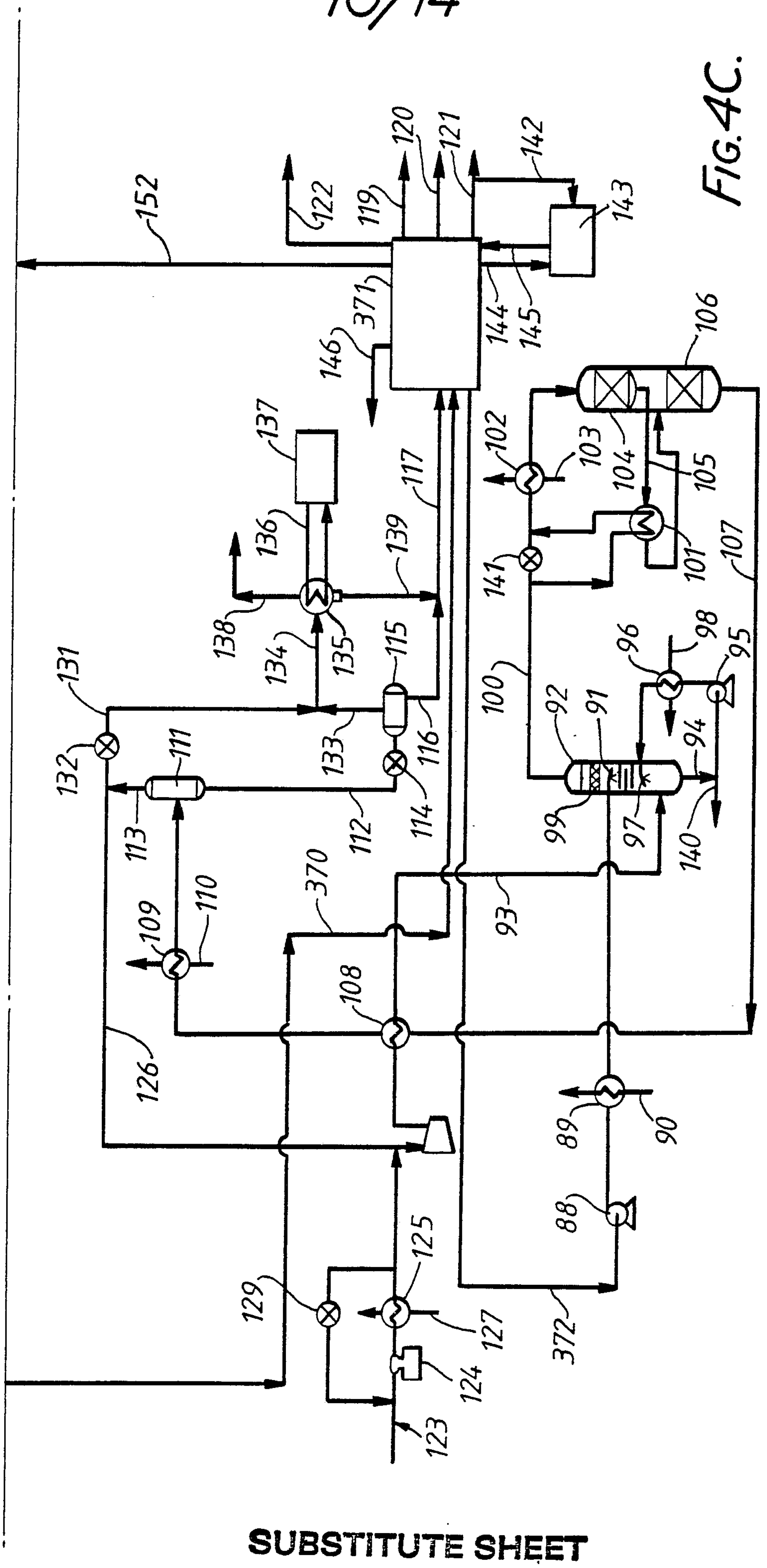
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FIG.4C.

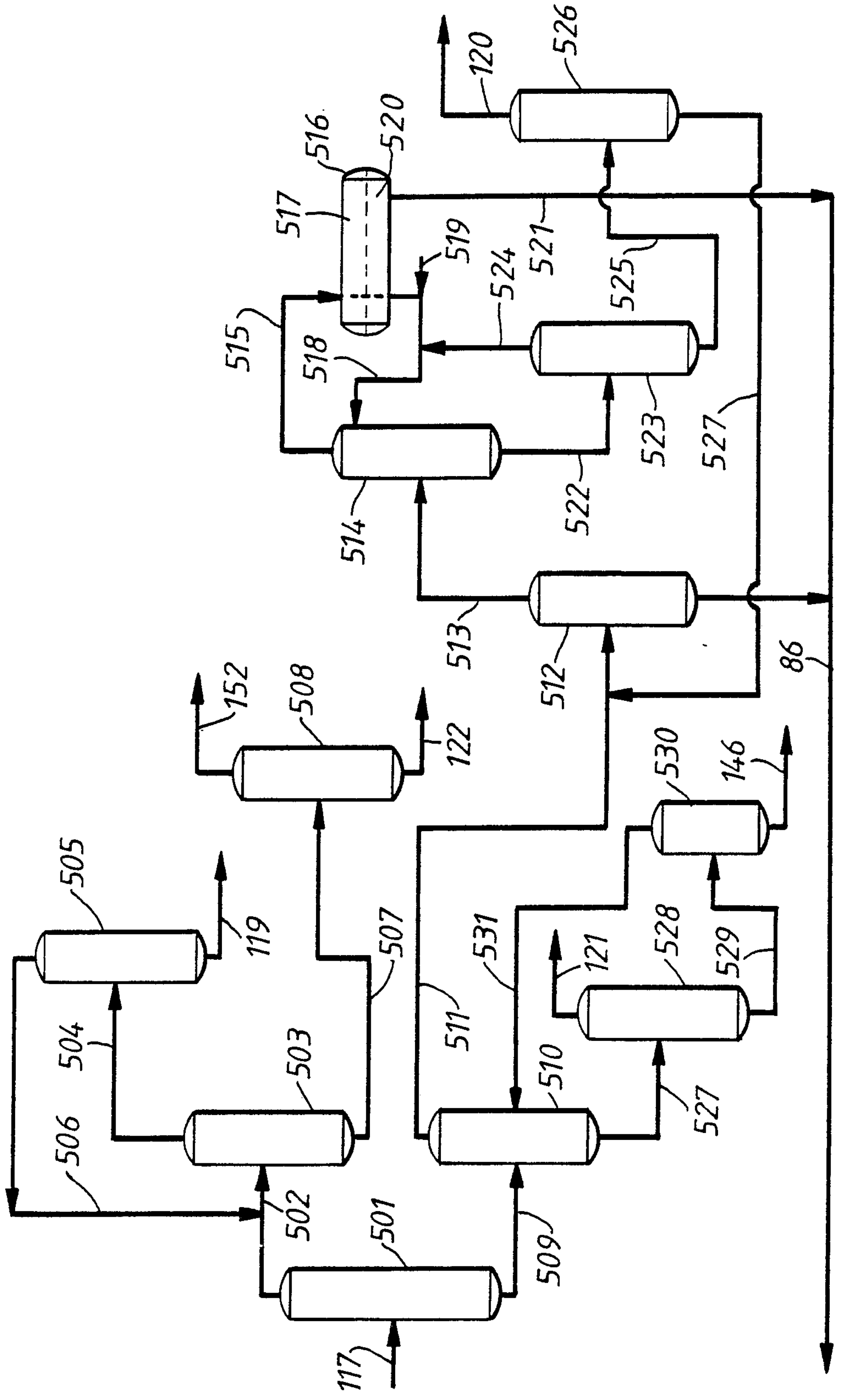
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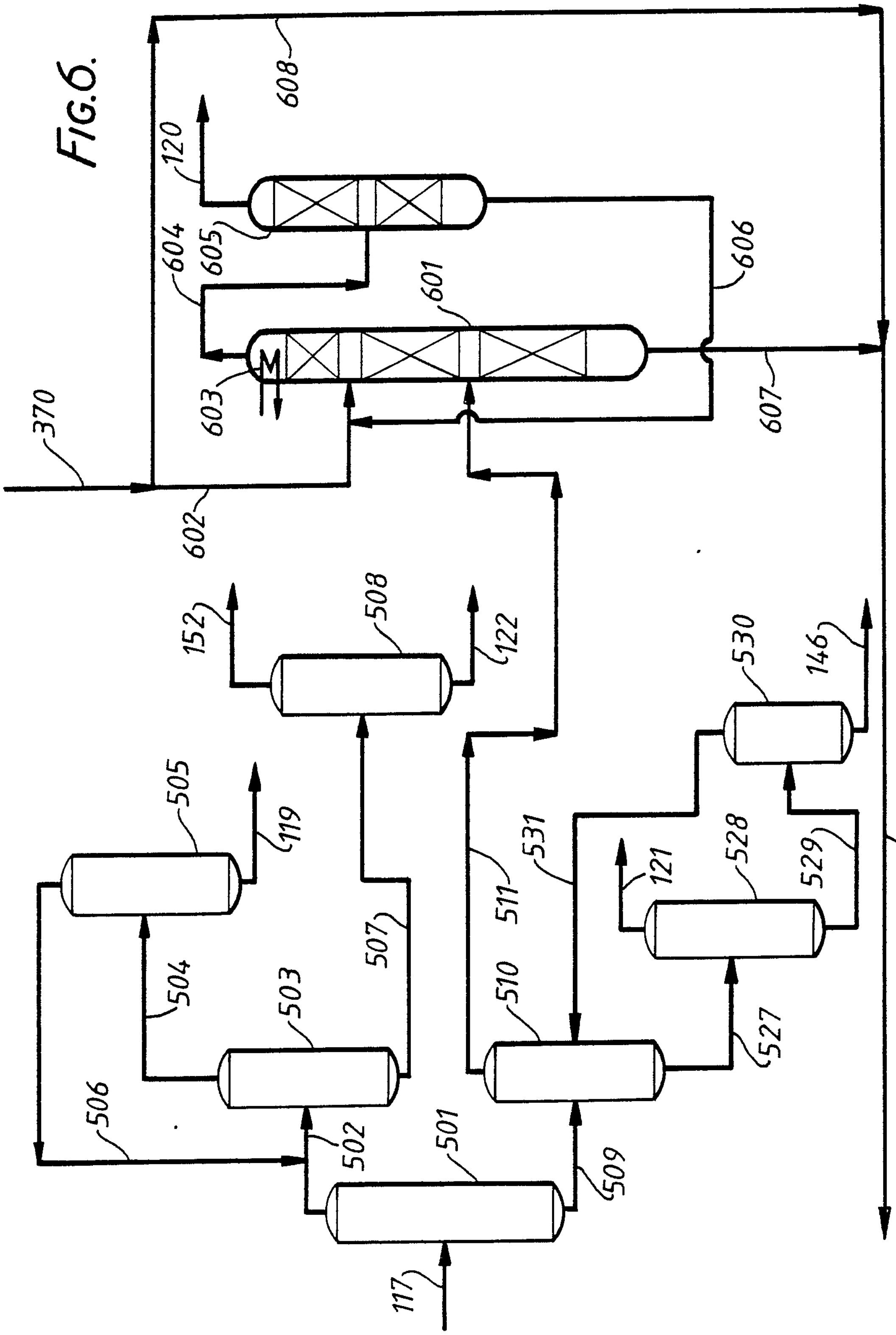
FIG.5.

FIG.6.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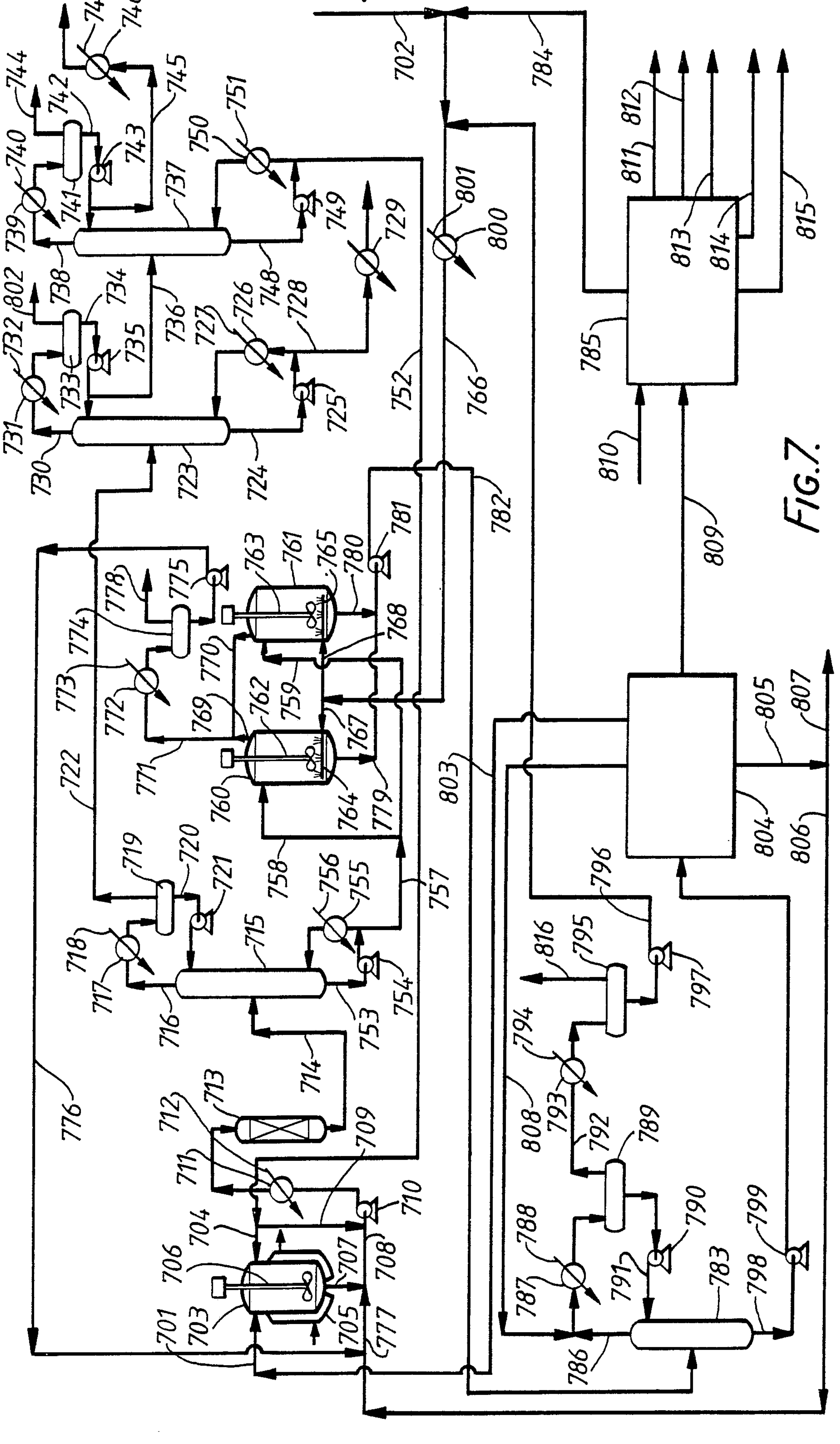
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FIG.7.

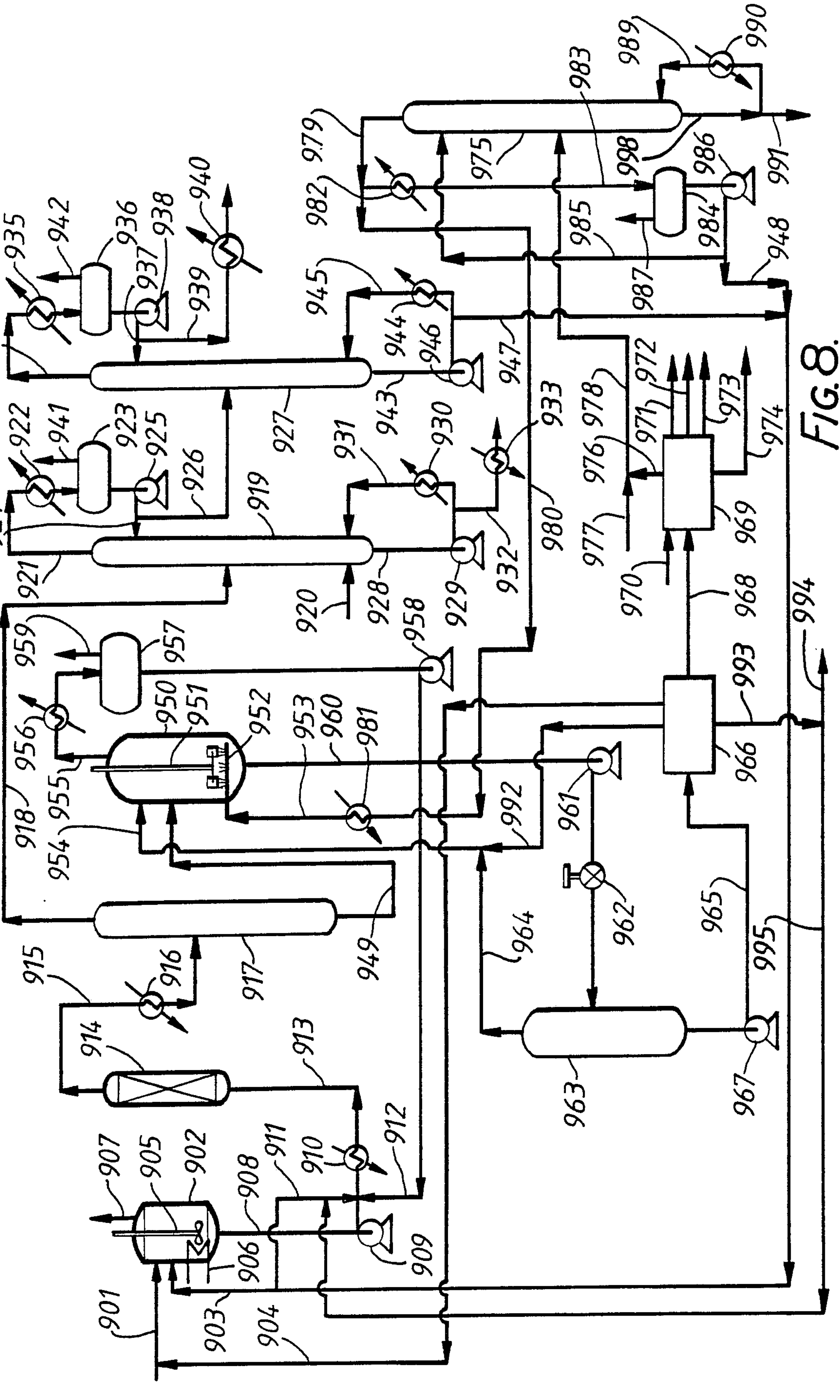
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FIG. 8.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00547

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 07 C 29/136; C 07 C 31/20; C 07 D 307/32

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 07 C 29/00 C 07 C 31/00 C 07 D 307/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	WO, A, 86/03189 (DAVY McKEE) 5 June 1986 see pages 23-24, claims cited in the application	1
A	EP, A, 0143634 (DAVY McKEE) 5 June 1985 see pages 26,27, claims cited in the application	1
A	US, A, 4032458 (S.D. COOLEY) 28 June 1977 see column 11, line 12 - column 13, line 52; figure cited in the application	1

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* Special categories of cited documents: [10]

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 16th November 1987	Date of Mailing of this International Search Report 11 JAN 1988
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 8700547

SA 18135

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The members are as contained in the European Patent Office EDP file on 04/12/87
The European Patent Office is is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A- 8603189	05-06-86	EP-A- 0204730 JP-T- 62501702	17-12-86 09-07-87
EP-A- 0143634	05-06-85	JP-A- 61022035 US-A- 4584419	30-01-86 22-04-86
US-A- 4032458	28-06-77	None	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82