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The present invention provides in a second embodiment a process for the preparation of glycolic acid, comprising

(A) feeding carbon monoxide, methylene dipropionate, a homogeneous acid catalyst, propionic acid, and water to a hydrocarboxylation reaction zone to produce an effluent comprising the homogeneous catalyst and esters of glycolic and propionic acids;

(B) recovering the homogeneous acid catalyst from the effluent by extracting the effluent with a hydrophilic solvent comprising 15 weight percent to 100 weight percent water and 0 weight percent to 85 weight percent of glycolic acid, each on a total hydrophilic solvent weight basis, and with a first hydrophobic solvent selected from at least one of the group consisting of n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, s-butyl acetate, methyl propionate, ethyl propionate, i-propyl propionate, methyl tertiary-butyl ether, methyl i-butyl ketone, methyl i-propyl ketone, methyl propyl ketone, hexane, heptane, and toluene to form a first aqueous extract phase comprising a major amount of the homogeneous acid catalyst contained in the effluent and a first organic raffinate phase comprising a major amount of the esters of glycolic and propionic acids contained in the effluent;

(C) separating the first organic raffinate phase and the first aqueous extract phase; and

(D) recycling the first aqueous extract phase to step (A).

The examples of the first embodiment regarding methylene dipropionate, homogeneous acid catalyst, propionic acid, molar ratio of propionic acid to methylene dipropionate, molar ratio of homogeneous acid catalyst to methylene dipropionate, molar ratio of water to methylene dipropionate, carbon monoxide, hydrocarboxylation reaction zone process conditions, esters of glycolic and propionic acids, hydrolyzing and hydrolyzed mixture composition, extraction, first and second hydrophobic solvent and first and second hydrophilic solvent, as well as feed ratios of each solvent to the effluent and hydrolyzed mixture on a weight basis, separation of the first and second extracts and first and second raffinates, separation of the homogenous acid catalyst from the effluent and recycle of the homogeneous acid catalyst to the hydrocarboxylation reaction zone, separation and recycle of the propionic acid and second hydrophobic solvent, esterification of the glycolic acid and hydrogenation of the glycolate ester oligomers and glycolic acid oligomers to produce ethylene glycol apply to the second embodiment.

For example, the process of the invention includes an aspect wherein the feeding of the propionic acid, homogeneous acid catalyst, methylene dipropionate in step (A) occurs at a molar ratio of propionic acid:methylene dipropionate of from 0.5:1 to 4:1 or 0.5:1 to 2.5:1, a molar ratio of homogenous acid catalyst:methylene dipropionate of from 0.01:1 to 0.07:1, and a molar ratio of water:methylene dipropionate of from 0.25:1 to 2:1 or 0.5:1 to 1.5:1. In another example the extraction occurs with a first hydrophobic solvent selected from at least one of the group consisting of hexane, heptane, toluene, xylene, and methyl tertiary-butyl ether.

In another example, greater than 90 weight percent of the esters of glycolic and propionic acids are recovered in the first organic raffinate phase and greater than 95 weight percent of

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the homogenous acid catalyst is recovered in the first aqueous extract phase. In another example, the extracting of step (B) occurs in a continuous counter-current extractor, wherein the first aqueous extract phase exits the bottom of the extractor and the first organic raffinate phase exits the top of the extractor, the first hydrophilic solvent is fed to the extractor above the effluent, and the feed ratio of the first hydrophilic solvent to the effluent ranges from 0.5:1 to 4:1 on a weight basis. Additionally, a first hydrophobic solvent can be fed to the extractor below the effluent, wherein the feed ratio of the first hydrophobic solvent to the effluent ranges from 0.01:1 to 5:1 on a weight basis, and the feed ratio of the first hydrophilic solvent to the effluent ranges from 0.5:1 to 4:1 on a weight basis.

In another example of the process of the present invention, the molar ratio of carbon monoxide to methylene dipropionate ranges from 1:1 to 10:1, and the hydrocarboxylation reaction zone is operated at a pressure of from 35 bar gauge to 200 bar gauge and a temperature of from 80° C. to 220° C.

In yet another example, the above process further comprises (E) hydrolyzing the first organic raffinate phase to produce a hydrolyzed mixture comprising glycolic acid and propionic acid; (F) recovering the propionic acid from the hydrolyzed mixture by extracting the hydrolyzed mixture with a second hydrophobic solvent selected from at least one of the group consisting of n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, s-butyl acetate, methyl propionate, ethyl propionate, i-propyl propionate, methyl tertiary-butyl ether, methyl i-butyl ketone, methyl i-propyl ketone, methyl propyl ketone, and toluene to form a second aqueous raffinate phase comprising a major amount of the glycolic acid contained in said hydrolyzed mixture and a second organic extract phase comprising a major amount of the propionic acid contained in the hydrolyzed mixture; (G) separating the second aqueous raffinate phase and the second organic extract phase; and (H) separating the second organic extract phase into the second hydrophobic solvent and the propionic acid, recycling the second hydrophobic solvent to step (F), and recycling the propionic acid to step (A).

In yet another example, the above process further comprises (I) reacting a first ethylene glycol with the second aqueous raffinate phase while simultaneously removing water to produce an esterification effluent comprising glycolate ester oligomers and glycolic acid oligomers and an overhead stream comprising water; and (J) reacting hydrogen with the esterification effluent to produce a second ethylene glycol, separating the second ethylene glycol into a product ethylene glycol and the first ethylene glycol, recycling the first ethylene glycol to step (I).

The invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention.

EXAMPLES

The compounds and abbreviations given in Table 1 are used throughout the Examples section. Structures for each compound are also given.