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(54) **Title:** PROCESS OF SEPARATION AND PURIFICATION OF GLYCEROL DERIVATIVES

(57) Abstract: The present patent application discloses a new and innovative method for purification of glycerol derivatives, by simu¬ lated moving bed chromatography. The method of the present patent application allows the separation of at least one glycerol derivative present in a feed solution. The glycerol derivatives purified by the method disclosed herein include dihydroxyacetone (DHA), hydroxypyruvic acid (HPA), glycolic acid (GCO), oxalic acid (OXA), mesoxalic acid (MEO), tartronic acid (TTA), glyceric acid (GCA), glyceraldehyde (GLA), glyoxalic acid (GOX) and umeacted glycerol. The presently disclosed method may be used with any simulated moving bed chromatographic apparatus, including but not limited to moving port and moving column systems.

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DESCRIPTION

"PROCESS OF SEPARATION AND PURIFICATION OF GLYCEROL DERIVATIVES"

Technical field

The present patent application relates to a novel method for the purification of glycerol derivatives, including dihydroxyacetone (DHA), hydroxypyruvic acid (HPA), glycolic acid (GCO), oxalic acid (OXA), mesoxalic acid (MEO), tartronic acid (TTA), glyceric acid (GCA), glyceraldehyde (GLA), glyoxalic acid (GOX) and unreacted glycerol by simulated moving bed chromatography.

Background art

One of the main alternatives in the search for new sources of energy to replace fossil fuels are biofuels, such as biodiesel. Its production generates a byproduct, Glycerol, which represents around 10% in weight of the total biodiesel produced. Even though there are industrial uses for it, the increasing production of biodiesel has led Glycerol to be treated as an industrial waste. Then, besides its low price, problems like the environmental impact have also become relevant .

Crude Glycerol has very low commercial value due to its impurities, but as it can be converted in products of added value the feasibility of the biodiesel industry can be enhanced .

Many researchers are focusing in this conversion through selective catalytic reactions such as selective oxidation, selective hydrogenolysis , catalytic dehydration, pyrolysis

and gasification, among others, in order to convert Glycerol into chemicals and fuels of interest for the Chemical, Fine Chemical, Comestic and Pharmaceutical industries (Fan, Burton, and Zhou 2010) .

Despite the advances on the development of processes to produce valuable compounds from bioglycerol, some challenges still persist on the purification step. Moreover, it is known that the purification step can determine the commercial viability of an industrial process. This means that, one route or an entire industrial process can be discarded if the purification is not energetically and commercially favorable. The difficulty is even greater in those cases in which the compounds of interest are produced at low concentrations or are chemically similar, as it is the case of DHA, HPA, GCO, OXA, MEO, TTA, GCA, GLA and GOX separation.

So far, there are no reports on the production, by catalytic oxidation, of DHA, HPA, GCO, OXA, MEO, TTA, GCA, GLA and GOX, or even any compound, including other glycerol derivatives, from glycerol and their purification by simulated moving bed.

At laboratory scale, (Cai et al. 2014) have described the glycerol oxidation to tartronic acid over a gold catalyst supported in HY zeolites, and the purification step is not included. Probably, the first industrial process to obtain TTA was described in 1981 in (Hurley 1982) . In that document, a chemical process is described comprising the following steps :

- converting a starting material (maleic acid, fumaric acid, tartaric acid, maleic acid anhydride, tartaric acid anhydride, or any of the water soluble esters of

maleic acid, fumaric acid, or tartaric acid) into a salt (the resulting salt must have pH between 10 and 14) ;

- oxidizing the salt solution with aqueous potassium permanganate (KMn04);
- removing a first precipitate from the oxidized salt solution;
- adding a water soluble salt to the solution in which oxalates are insoluble in acid and tartronates are soluble in acid;
- separating a second precipitate resulting from the addition of the metal salt;
- dissolving the tartronate by adding a mineral acid to the second precipitate.

In this case, the production process as well as the purification method are different from the disclosed in the present application.

(Habe et al. 2009) have disclosed a microbial production of GCA and DHA from glycerol during 4 days of incubation in a batch fermentor with pH control. Besides the fact that the process is totally different from the one proposed in this document, the work is still in laboratory scale and needs improvements .

Nowadays, the OXA can be usually obtained through four methods :

- a glucose solution obtained by hydrolysis of starch is placed in a reactor with sulfuric acid, vanadium pentoxide, iron (III) sulfate and nitric acid (65%) under vigorous stirring; Crude oxalic acid is obtained after cooling and centrifugation of the reaction mixture; The crude acid is

again dissolved in hot water, passed through a grease separator and recrystallized; After a second centrifugation and drying, oxalic acid dihydrate is obtained;

- an ethylene glycol solution is oxidized by an oxidizing mixture of sulfuric acid and nitric acid, in the presence of vanadium pentoxide and iron (III) salts. Crude oxalic acid is obtained after a crystallizer and separator steps. The final product is obtained after more steps, including: a dissolve with steam, crystallizer, separator and then a dryer;

- a propene solution is introduced into a solution of nitric acid to produce water soluble intermediates of α-nitratolactic acid and lactic acid. In a second step, the solution of these partially oxidized products is treated with oxygen in the presence of a catalyst. Oxalic acid is formed, crystallized, filtered and dried;

- carbon monoxide (CO) and a lower alcohol are reacted under pressure and in the presence of a catalyst to form the corresponding diester of oxalic acid. Palladium on charcoal and alkyl nitrites are employed as catalysts and the reaction is carried out at 10 - llMPa. The diester is hydrolyzed in the second step to oxalic acid, which is crystallized and dried .

GCO acid is usually produced by hydrolysis of molten monochloroacetic acid with aqueous sodium hydroxide (Zhang and Meng 2013) . The resulting glycolic salt may be removed by evaporative concentration, followed by extraction of the acid with acetone (LEUPOLD et al., 1979) . Another process, which is commercially used in the United States produces GCO from the treatment of formaldehyde or trioxymethylene with carbon monoxide and water in the presence of acid catalysts at high pressure (>30MPa) and high temperature (140-220 oC)

(Shattuck 1948; Larson 1939) (John 1939) . Then, the glycolic acid can be recovered from the concentrated solution by crystallization or separated from this crude mixture by distillation. But this new residue may be neutralized, e.g., with calcium carbonate, to convert the glycolic acid into a readily separable salt, or the residue may be sterilized with a suitable alcohol for removal of the glycolic acid as an ester. None of these use a production step followed by purification step, as does the process disclosed in the present application.

Similarly to GCA, the DHA production process involves a microbial procedure (Green 1960; Charney 1978) . Although it is an industrial process, the fermentation is complete in up to 48 hours, numerous reagents are needed for the microbial growth and the whole process has low yields and low productivities. Moreover, it presents the common problems of industrial biotechnology: discontinuous processing, difficulties to maintain the microbial growth, contaminations by other microorganisms, high sterilization costs and high product recovery cost (Chen 2012) . At the end, the product is isolated by known methods in the art, such as, filtration of the broth, removal of inorganic cations and/or anions (when present) via ion exchange resin adsorption, concentration of the resin effluent and crystallization of DHA from the concentrate. Again, it relates to a totally different process design from the one described in the present patent application.

On the other hand, the literature reports many processes for purification of Organic Acids, which include compounds similar to DHA, HPA, GCO, OXA, MEO, TTA, GCA, GLA and GOX,

but through very different methods of the one proposed in this document:

US 4621153A (Hatch 1986) describes a method of recovering phenylalanine from an aqueous mixture comprising: providing calcium salt in the aqueous mixture; precipitating a complex of phenylalanine and Ca2+; separating the precipitated complex from the aqueous mixture; dissolving the precipitated complex in an aqueous solution at pH below 8.5; and separating the phenylalanine from the Ca2+.

The patent US5254729A (FUJIWARA et al., 1993) reports a method for obtaining substantially colorless glycine from an aqueous glycine solution. The method comprises the following steps: reacting glycolonitrile, carbon dioxide (gas) and ammonia in the presence of water to obtain a solution containing glycine; removing most of carbon dioxide and ammonia by adjusting the pH of the remaining alkaline aqueous glycine solution to 3.5-6 with an acid cation exchange resin; decoloring the aqueous glycine solution by contacting the solution with active carbon and; evaporating water from the solution to crystallize pure glycine crystals.

The work of JP2003221359A (HIROYUKI and AKIHIRO 2003) describes a method for manufacturing dicarboxylic acid from the reaction mixture obtained by bringing a cycloalkane into contact with oxygen in the presence of an imide group compound. An ion-exchange resin treatment is used to separate the dicarboxylic acid. This ion-exchange resin treatment can be performed by supplying the liquid to be treated to a container filled with ion exchange resin (ion exchange resin treatment bath) . The ion exchange resin treatment tank may be a tower type. In addition, a fixed bed, a fluidized bed

system or any other continuous treatment can be used. The work discloses the separation of compounds containing an imide group or it's decomposition products from dicarboxylic acids obtained through the oxidation of a cycloalkane which comprise a completely different set of compounds to be separated comparing with those focused on the present patent application, which are obtained from different raw material, namely, glycerol. Moreover, it does not specify which continuous treatment is better in the reported invention.

The patent EP1441823B1 (Herman 2013) contemplates methods for the isolation of one or more specific components from a more complex material, but using a centrifugal chromatography device (CCD) described in the document.

The patent WO201 6083455A1 (KOLFSCHOTEN and Sanders 2016) describes a process for the precipitation of one or more amino and/or organic acids from a liquid feed comprising a plurality of amino and/or organic acids. In a precipitation vessel, a solution of amino and/or organic acids from a feed in a mixture of a solvent and an anti-solvent passes through a zone capable of selectively removing solvent and/or adding anti-solvent from an external source to the mixture. A mixture depleted in solvent and enriched in anti-solvent is obtained, consequently increasing the concentration of the amino and/or organic acids in the new solvent/anti-solvent mixture, allowing solid particles of the amino and/or organic acids to precipitate from the solvent/anti-solvent mixture in the precipitation vessel at a precipitation temperature. In other words, a crystallization procedure. A process very different from the one described in this document.

Finally, the patent US5245078A (Maeda and Nakazawa 1993) describes a non-continuous chromatographic process for separating tartaric acid, citric acid, lactic acid, gluconic acid and GCO acid from an organic acid-containing solution. The solution is obtained by a fermentation method in which glucose is used as starting material, which comprises:
contacting said organic acid-containing solution with a cation exchange resin of a divinylbenzene cross-linked polystyrene sulfonic acid type, to have the organic acid or acids adsorbed on the cation exchange resin;
contacting the cation exchange resin with a dilute aqueous sulfuric acid eluent solution, to have the organic acid or acids desorbed and then;
separating from the eluate a solution containing the organic acid or acids, wherein said organic acid-containing solution is contacted to a second cation exchange resin under such a condition that the pH or the organic acid-containing solution is maintained at a pH level lower than pKa .

This is a discontinuous process and different from the one described in this document.

The simulated moving bed (SMB) chromatography has been applied to a variety of industrial processes, as an alternative to discontinuous processes.

Originally, the SMB was developed for the petroleum refining and petrochemicals industries, generating the so-called SORBEX process (BROUGHTON; GERHOLD, 1961) . Alternative processes using the SMB technology for the production of p-xylene (PAREX) , for the separation of n-paraffins from branched and cyclic hydrocarbons (MOLEX) , for the separation

of olefins from paraffins and for the separation of fructose from glucose (SAREX) were developed later on.

The purification of amino acids, as phenylalanine from a fermentation broth (MCCULLOCH; GOODMAN, 1991) and the development of large-scale hydrocarbon and carbohydrate separations, started a new approach where the SMB technology has found applications in biotechnology, pharmaceuticals, and fine chemistry areas.

Conventionally, an SMB has two inlet streams (Figure 1), eluent (Figure 1 - 5) and feed (Figure 1 - 6), and two outlet streams, extract (Figure 1 - 7) and raffinate (Figure 1 - 8). These streams divide the unit into four sections or zones, each of which is responsible for a different function. In Section 1 (Figure 1 - 1) the more-retained compound must move with the liquid to be collected in the extract port in order to regenerate the solid while in Section 4 (Figure 1 - 4) the less-retained compound must move with the solid to be collected in the raffinate in order to regenerate the liquid. In Sections 2 (Figure 1 - 2) and 3 (Figure 1 - 3) the more-retained compound must move with the solid to be collected in the extract port and the less-retained one must move with the liquid in the direction of the raffinate collecting point.

From Figure 1, it is possible to see that in Section 1 both species must move upward, in Sections 2 and 3 the less-retained compound must move upward, while the more-retained component must move downward, and finally in Section 4 the net flux of both species has to go downward. In the usual operating mode of an SMB, the inlet and outlet streams move forward to the next column in the direction of the fluid

flow at regular time intervals, called the switching time, t*, and this is how the movement of the solid is simulated. One cycle is completed when the initial location of injection/collection of all the streams is obtained. It can be concluded that, during one cycle, the same column assumes different roles in the separation process depending on the section it is located in.

The patent US6875349B2 (HEIKKILÄ et al., 2005) first described a simulated moving bed process comprising the separation of organic acids, among other compounds. The document describes a method for fractionating a solution in two or more fractions enriched with different components, by SMB. In that time, the method was different from the prior art SMB methods wherein only one profile moved through the loop of chromatographic system. In the new method described, two or more profiles of dissolved material (dry solids profiles) were moving in the entire resin bed (all columns of the loop) . But, in this process the feedstock selected is from different groups as in the present application (e.g. consisting of molasses, vinasse, sulphite cooking liquid, fructose/glucose syrups, beet-derived juices, sugar beet molasses, xylitol run-off, invert sugar mixtures, starch hydrolysates, wood hydrolysates, milk whey solutions, lactose-containing solutions, solutions containing amino acids, fermentation broths containing organic acids, bagasse hydrolysates, inositol-containing solutions, mannitol-containing solutions, sorbitol-containing solutions, xylitol-containing solutions, erythritol-containing solutions, glutamic acid-containing solutions, and glycerol-containing solutions) .

Later, (PAANANEN et al., 2012) disclosed the invention of EP2316551B1, which relates to a system and a process for fractionating a solution into two or more fractions. Although, the products to be recovered can include one or more of the following: glucose, fructose, sucrose, betaine, rhamnose, arabinose, mannose, raffiose, lactose, lactulose, maltose, maltiol, inositol, mannitol, glycerol, xylitol, xylose, sorbitol, erythritol, ribose, 6-O-ci-D-glucopyranosido-D-Sorbitol (1,6-GPS) and 1-O-ci-D-glucopyranosido-D-Mannitol (1,1-GPM), organic acids or amino acids, such as glutamic acid, the document limits them to the following original solutions: sulphite cooking liquors, molasses, especially B-Molasses and/or C-Molasses, vinasse, fructose and/or glucose syrups, beet-derived juices, invert sugar mixtures, starch hydrolysates, wood hydrolysates, milk whey solutions and other lactose-containing solutions, lactulose-containing solutions, maltose-containing solutions, maltitol-containing solutions or solutions containing amino acids. This process is different from our process which is focused on the recovery of organic acids from a solution of glycerol derivatives.

The patent document FR2900654A1 (THEOLEYRE; BAUDOUIN, 2007) provides a process for separating an organic acid by passing this solution through a chromatographic bed filled with an anionic resin. The method is also characterized in that the organic acid is the citric acid and the aqueous solution is a culture broth obtained by fermentation generating said organic acid.

In the work EP2212004B1 (LANG; SIMPKINS, 2015), a process to produce bioactive compounds is described, in which a plurality of these substances contacts with a polymer

adsorbent. The polymer adsorbent has a selective affinity for at least one of the bioactive compounds present in the mixture. The document still suggests gravity fed columns and flash chromatography columns as suitable arrangements or moving bed chromatography apparatus. However, it also describes that the polymer adsorbent may be non-ionic, such as the suitable Alimentech P495 Inert Adsorbent Polymer supplied by Bucher Foodtech.

The document US8951416B2 (SARMALA et al., 2015) is based on the use of a combination of strong acid cation exchange resins (SAC) and weak acid cation exchange resins (WAC) in a specific order and in specified proportions in a chromatographic SMB separation system. Specifically, US8951416B2 relates to a method of separating betaine and at least one other component from a sugar beet based fermentation solution, in which the other compound to be separated can be glycerol, an organic acid or inositol.

Finally, the US20130345473A1 patent (ARCHER et al., 2013) disclosures a process for the separation of at least one di-carboxylic acid compound from a mixture comprising at least one mono-carboxylic acid compound and at least one di-carboxylic acid compound by a chromatography process. Although the above-mentioned document describes that ion-exchange chromatography is carried out using simulated moving bed (SMB) chromatography, it also restrict that the ion exchange chromatographic medium is an anion exchange chosen among specific commercial examples and the feed mixture is specific derived from the oxidation of glucose.

There is still a need for the development of a separation process that is able to efficiently purify glycerol

derivatives obtained from the catalytic chemical conversion of glycerol, such as dihydroxyacetone, hydroxypyruvic acid, glycolic acid, oxalic acid, mesoxalic acid (MEO), tartronic acid, glyceric acid, glyceraldehyde or glyoxalic acid , for instance, generating less chemicals waste, producing high purity compounds and providing high productivities.

Summary

In one embodiment the simulated moving bed chromatography method for separating a glycerol derivative from a feed solution comprising said glycerol derivative and one or more other glycerol derivatives, or impurities, comprises:

(a) selecting a simulated moving bed chromatographic apparatus comprising at least two chromatographic columns interconnected in series; wherein said columns contain a separation media or a mixture of a variety of separation media, comprising ion exchange materials; sequentially comprising first a desorbent port, an extract port, a feed port and a raffinate port; and simultaneously,

(b) contacting, through said feed port, said feed solution with the separation media equilibrated with an acid or basic solution or water-organics mixture or water;

(c) contacting, through said desorbent port, an acid or basic eluent with said separation material, wherein the eluent may also be a water-organics mixture or water; and

(d) withdrawing, through said raffinate or extract port, a raffinate or extract stream, respectively, comprising the fluid mobile phase and mainly one of said glycerol derivatives, and a lower percentage of said other glycerol derivatives, and/or unreacted glycerol, and/or impurity present in said feed solution.

In one embodiment, the simulated moving bed chromatographic apparatus may further comprise additional raffinate or extract streams allowing to perform ternary, pseudo-ternary or higher order separations; withdrawing, through said outlet ports, a raffinate or extract stream comprising the fluid mobile phase, an acid solution or basic solution or water-organics mixture or water itself and mainly one of said glycerol derivative, and a lower percentage of said other glycerol derivative or any impurity present in said feed solution.

In another embodiment, the simulated moving bed chromatographic apparatus may also comprise a second desorbent port to perform solvent gradients inside the unit; contacting, through said second desorbent port, an acid solution or basic solution or water-organics mixture or water itself with said separation material.

In one embodiment, said glycerol derivative is selected from dihydroxyacetone (DHA), hydroxypyruvic acid (HPA), glycolic acid (GCO), oxalic acid (OXA), mesoxalic acid (MEO), tartronic acid (TTA), glyceric acid (GCA), glyceraldehyde (GLA), glyoxalic acid (GOX), unreacted glycerol or any glycerol derivatives.

In another embodiment, the feed solution is product of a chemical conversion of glycerol by a range of process such as selective oxidation, selective hydrogenolysis , catalyst dehydration, pyrolysis, gasification, selective glycerol transesterification and esterification, selective etherification and carboxylation .

In one embodiment the pH of said feed solution is between 1 and 13 by the addition of an acid or a basic species. In a preferred embodiment the pH of said feed solution is between 1 and 7 by the addition of an acid or a basic species. In a more preferential embodiment the pH of said feed solution is between 1 and 5 by the addition of an acid or a basic species.

In one embodiment the feed solution is pretreated by any process suitable to obtain a solution of two or more glycerol derivatives with or without unreacted glycerol without impurities from the process of chemical conversion of glycerol including, but not limited to, ion exchange, distillation, centrifugation and filtration.

In one embodiment the chromatographic material is a cation or anion exchange chromatographic material, wherein said cation exchange chromatographic material is selected from alumina, magnesium silicates, silica, glass, controlled pore glass, carbon, porous graphitic carbon, zirconium phosphate, hydroxyapatite, calcium phosphate, magnesium carbonate, and polymers or resins. In a particular embodiment said polymers or resins for the cation exchange chromatography are selected from hydroxyalkylmethacrolate, polyacrylamine, polymacrolate, poly (hydroxyethylmacrolate), polystyrene, styrene-divinylbenzine polymers, poly (ethyleneglycoldimethacrolate), poly (vinylalcohol), Poly (vinylacetate) , and poly (vinylpyridine)

In another embodiment the cation exchange chromatographic material within each of chromatographic columns is equilibrated with an aqueous acid solution.

In one embodiment the anion exchange chromatographic material is selected from polymers, resins, silica, zirconia, carbon and alumina, wherein said polymers or resins for the anion exchange chromatography are selected from sulfonic acid, alkylsulfonic acid, phenylsulfonic acid, alkylphenylsulfonic acid, and salts thereof, poly (vinylalcohol), poly (methacrylates), hypercross-linked polystyrene and poly (ethylene oxide) and styrene or ethylvinylbenzene polymers or copolymers cross-linked with divinylbenzene (e.g., ethylvinylbenzene-divinylbenzene (EVB-DVB) and styrene or polystyrene-divinylbenzene (DVB or PS-DVB) copolymer) of acrylonitrile, acrylic acid, or methacrylic acid, trimethylamine (TMA), trihexylamine (THA) , diethylenetriamine, diethylenetriamine, unsymmetrical dimethylhydrazine (UDMH) , dimethylethanolamine (DMEA) , methylamine (MA) , dimethylamine (DMA) , methyldiethanolamine (MDEA) or triethanolamine (TEA) .

In one embodiment the said anion exchange chromatographic material within each of chromatographic columns is equilibrated with an aqueous basic solution.

In one embodiment the eluent is an acid or basic solution or water .

The simulated moving bed chromatography may be practiced with any simulated moving bed chromatographic apparatus, including but not limited to moving port and moving column systems .

Detailed Description

A new and innovative method for purification of glycerol derivatives obtained from glycerol, by simulated moving bed chromatography has been discovered.

The present patent application describes a simulated moving bed chromatographic method for separating a glycerol derivative, from a mixture feed solution, containing the glycerol derivative and at least another compound, such as other organic compound and/or other glycerol derivatives and/or unreacted glycerol and/or impurities, comprising:

(a) selecting a simulated moving bed chromatographic apparatus comprising at least two chromatographic columns interconnected in series; wherein said columns contain a separation media or a mixture of a variety of separation media, comprising ion exchange materials; sequentially comprising first a desorbent port, an extract port, a feed port and a raffinate port; and simultaneously,

(b) contacting, through said feed port, said feed solution with the separation media equilibrated with an acid or basic solution or water-organics mixture or water;

(c) contacting, through said desorbent port, an acid or basic eluent with said separation material, wherein the eluent may also be a water-organics mixture or water; and

(d) withdrawing, through said raffinate or extract port, a raffinate or extract stream, respectively, comprising the fluid mobile phase and mainly one of said glycerol derivatives, and a lower percentage of said other glycerol derivatives, and/or unreacted glycerol, and/or impurity present in said feed solution.

The feed solution may be the stream containing glycerol (or the so called crude glycerol) from biodiesel production, which can be from multiple feedstocks or a solution of refined glycerol in any concentration, wherein the feed solution may also contain impurities.

The chromatographic material may be silicas, functionalized silicas, aluminas, carbons, zeolites functionalized and non-functionalized polystyrene, polyacrylamide, cross-linked polystyrenes, polyacrylates or other resins and the aqueous eluent may be water or an acid or basic solution.

Separation Processes

The present patent application relates to a simulated moving bed chromatography method for separating one or more glycerol derivatives from a feed solution of chemically conversion processes of glycerol into said glycerol derivatives, comprising :

(a) selecting a simulated moving bed chromatographic apparatus comprising at least two chromatographic columns interconnected in series; wherein Said columns contain a separation media or a mixture of a variety of separation media, comprising ion exchange materials; sequentially comprising first a desorbent port, an extract port, a feed port and a raffinate port; and simultaneously,

(b) contacting, through said feed port, said feed solution with the separation media equilibrated with an acid or basic solution or water-organics mixture or water;

(c) contacting, through said desorbent port, an acid or basic eluent with said separation material, wherein the eluent may also be a water-organics mixture or water; and

(d) withdrawing, through said raffinate or extract port, a raffinate or extract stream, respectively, comprising the

fluid mobile phase and mainly one of said glycerol derivatives, and a lower percentage of said other glycerol derivatives, and/or unreacted glycerol, and/or impurity present in said feed solution.

The simulated moving bed chromatographic apparatus may further comprise additional raffinate or extract streams allowing to perform ternary, pseudo-ternary or higher order separations; withdrawing, through said outlet ports, a raffinate or extract stream comprising the fluid mobile phase, an acid solution or basic solution or water-organics mixture or water itself and mainly one of said glycerol derivative, and a lower percentage of said other glycerol derivative or any impurity present in said feed solution. It may also comprise a second desorbent port to perform solvent gradients inside the unit; contacting, through said second desorbent port, an acid solution or basic solution or water-organics mixture or water itself with said separation material .

Also, although the previously description refers to feed mixtures containing various glycerol derivatives, as mono-carboxylic acids or dicarboxylic acids, it includes the salt form of these acids, such as sodium, potassium, calcium, and magnesium salts (e.g., tartronate, glycerate, oxalate, glycolate, dihydroxyacetonate) , or ketones or aldehydes or esters or ethers, among others.

Prior to contacting at (b) , the pH of said feed solution may be adjusted to a pH between 1 and 13, which may be between 1 and 7 or between 1 and 5, by the addition of an acid or a basic material. The pH of the feed solution may be adjusted by the addition of any compound suitable to the production of an edible product. Suitable acid compounds include, but

are not limited to, hydrochloric acid, sulfuric acid and phosphoric acid. Preferable is sulfuric acid. Suitable basic compounds include, but are not limited to, sodium hydroxide, potassium hydroxide, ammonium hydroxide and ammonia.

Separation Media

The second aspect of the present patent application is directed to a chromatographic separation process for separating a glycerol derivative, from a mixture containing the glycerol derivative, and one or more other component, which may be another glycerol derivatives and/or unreacted glycerol and/or impurities wherein the eluent can be an acid solution or basic solution or water-organics mixture or water itself and the stationary phase can be a chromatographic material .

As stated above, the eluent may be an acid solution or basic solution or water-organics mixture or water itself . Any of these solutions must be prepared in order to have a pH between 1 and 13, ideally between 1 to 7 or between 1 and 3. A chromatographic separation process that uses slightly acidified water as eluent is advantageous because it reduces the environment impacts and because additional equipment for separation of the glycerol derivative from the eluent may not be required.

The said column or columns may contain a cation exchange chromatographic material comprising a functional group selected from the group consisting of sulfonates, alkylsulfonates, phenylsulfonates, alkylphenylsulfonates and mixtures thereof.

a. The cation exchange chromatographic material may be a strong cation exchange resin. The strong cation

exchange chromatographic material may comprise a sulfonate .

b . The cation exchange chromatography material of the present patent application preferably comprises one or more chromatographic support materials (i.e., stationary phases) .

c . Suitable chromatographic support materials for the cation exchange chromatography include, but are not limited to, alumina, magnesium silicates, silica, glass, controlled pore glass, carbon, porous graphitic carbon, zirconium phosphate, hydroxylapatite, calcium phosphate, magnesium carbonate, and polymers or resins.

d . Suitable polymers or resins for the cation exchange chromatography include, but are not limited to, hydroxyalkylmethacrolate, polyacrylamine, polymacrolate, poly (hydroxyethylmacrolate), polystyrene, styrene-divinylbenzine polymers, poly (ethyleneglycoldimethacrolate), poly (vinylalcohol), Poly (vinylacetate) , and poly (vinylpyridine). Preferable are polymers or resins. More preferable are styrene-divinylbenzine polymers.

e . The cation exchange chromatographic material of the present patent application further comprises a plurality of ligands, selected from one or more functional groups suitable for ion exchange. These functional groups include but are not limited to sulfonic acid, alkylsulfonic acid, phenylsulfonic acid, alkylphenylsulfonic acid, and salts thereof. Preferred

are sulfonic acid functional groups and the salts thereof .

f . Specific examples of cation exchange silica-based chromatographic materials include ADSORBOSPHERE SCX, BAKERBOND SCX, PARTISIL SCX, SPHERISORB S SCX, SUPELCOSIL LC-3SCX, ULTRASILCX, and ZORBAX 300 SCX.

g . Specific examples of cation exchange polymers or resins that may be used include: AMBERLITE 200, AMBERLITE IR-118H, AMBERLITE IR-120PLUS, AMBERLITE IR-122, AMBERLITE IR-130C, AMBERLITE 16641, AMBERLITE IRP-69, DOWEX 50X1-100, DOWEX 50X2-100, DOWEX 50X2-200, DOWEX 50X2-400, DOWEX 50X4-100, DOWEX 50X4-200, DOWEX 50X4-200R, DOWEX 50X4-400, DOWEX 18880, DOWEX 50X8-100, DOWEX 50X8-200, DOWEX 50X8-400, DIAION 1-3561, DIAION 1-3565, DIAION 1-3570, DIAION 1-3573, DIAION 1-3577, DIAION 1-3581, DUOLITE D 5427, and DUOLITE D 5552, which are available from Sigma -Aldrich, St. Louis Missouri, U.S.A.; DIAION HPK25, DIAION PK208, DIAION PK228, DIAION SK1B, DIAION SK1BS, DIAION SK104, DIAION SK112, DIAION SKI 16, DOWEX HCR-S, DOWEX HCR-W2 , DOWEX MSC-1, DOWEX 650C, DOWEX G-26, DOWEX 88, DOWEX MONOSPHERE 88, DOWEX MONOSPHERE 99K/320, DOWEX MONOSPHERE 99K/350, DOWEX MONOSPHERE 99Ca/320, DOWEX MONOSPHERE 99Ca/350, DOWEX Marathon C , DOWEX -032, DOWEX -406, DOWEX -437, DUOLITE C-280, and DUOLITE C-291, which are available from Supelco, Inc., Bellefonte, Pennsylvania, U.S.A.; AMBERLITE IR-120, AMBERLITE IR-120B, AMBERLITE IR-200C, AMBERLITE CG 6000, DIAION SK-1B, DOWEX XUS 40406.00, DOWEX XUS 43518, and DOWEX C500ES. Preferable are AMBERLITE IR-120, AMBERLITE IR-120B, AMBERLITE IR-200C,

DOWEX C500ES, DOWEX XUS 43518, and DOWEX XUS 40406.00. Most preferable is DOWEX XUS 40406.00.

h. The said cation exchange chromatographic material within each of chromatographic columns may be equilibrated (conditioned) with an aqueous acid solution .

The anion exchange chromatography material of the present patent application preferably comprises one or more chromatographic support materials (i.e., stationary phases) .

i. Suitable chromatographic support materials for the anion exchange chromatography include, but are not limited to, polymers, resins, silica, zirconia, carbon and alumina.

j. Suitable polymers or resins for the anion exchange chromatography include, but are not limited to: poly (vinylalcohol), poly (methacrylates), hypercross-linked polystyrene and poly (ethylene oxide) and styrene or ethylvinylbenzene polymers or copolymers cross-linked with divinylbenzene (e.g., ethylvinylbenzene-divinylbenzene (EVB-DVB) and styrene or polystyrene-divinylbenzene (DVB or PS-DVB) copolymer) of acrylonitrile, acrylic acid, or methacrylic acid. For example: acrylate-divinylbenzene (DVB) copolymer, methyl acrylate-divinylbenzene (DVB) copolymer, polyacrylonitrile polymer, polyacrylate polymer, or polymethacrylate polymer.

k. The anion exchange chromatographic material of the present patent application further comprises a plurality of ligands, selected from one or more

functional groups suitable for ion exchange. These functional groups are obtained through an amination procedure during the anion exchange chromatographic production process. These amination process can use, but are not limited to, trimethylamine (TMA), trihexylamine (THA), diethylenetriamine, diethylenetriamine, unsymmetrical dimethylhydrazine (UDMH), dimethylethanolamine (DMEA), methylamine (MA), dimethylamine (DMA), methyldiethanolamine (MDEA) or triethanolamine (TEA).

1. Specific examples of anion exchange chromatographic materials include, but are not limited to, PRP-X100/"Hamilton", USA; PRP-X110/"Hamilton", USA; LCA01/"Sykam", Germany; Gelpack GL-IC-A23/"Hitachi", Japan; ICSep ANl/"Transgenomic", USA; ICSep AN1-SC/"Transgenomic", USA; ICSep AN300/"Transgenomic", USA; ICSep AN300B/"Transgenomic", USA; Star Ion A300/"Phenomenex", USA; Metrosep A Supp l/"Metrohm", Switzerland; Metrosep A Supp 1 HS/"Metrohm", Switzerland; Metrosep A Supp 3/"Metrohm", Switzerland; Metrosep A Supp 10/"Metrohm", Switzerland; Metrosep A Supp 15/"Metrohm", Switzerland; Metrosep A Supp 16/"Metrohm", Switzerland; IonPac AS14; IonPac AS14A; IonPac AS15; IonPac AS4A-SC; IonPac AS9-SC; IonPac AS9-HC; IonPac AS12A; IonPac AS10; IonPac ASH, IonPac AS11-HC; IonPac AS16; IonPac AS17; IonPac AS18; IonPac AS22; IonPac AS23; IonPac AS19; IonPac AS20; IonPac AS21; IonPac AS24; IonPac AS25; IonPac AS26

m. The said anion exchange chromatographic material within each of chromatographic columns may be

equilibrated (conditioned) with an aqueous basic solution .

Another aspect of the present patent application, separation processes disclosed herein can also include a selective membrane separation (e.g., nano-filtration membranes) in combination with the chromatographic separation processes described herein. The selective membrane separation can be performed upstream and/or downstream of a chromatographic separation. For example, selective membrane separation techniques such as nano-filtration (NF) membrane separation can be used to reduce the amount of impurities contained in a mixture (e.g., a mixture obtained from an oxidation process for preparing the glycerol derivative from glycerol) prior feeding the mixture to a chromatographic separation.

Glycerol derivatives

The feed solution may be from a chemical conversion of glycerol by a range of process such as selective oxidation, selective hydrogenolysis , catalyst dehydration, pyrolysis, gasification, selective glycerol transesterification and esterification, selective etherification and carboxylation .

In one embodiment the feed solution is pretreated by any process suitable to obtain a solution of two or more glycerol derivatives with or without unreacted glycerol without impurities from the process of chemical conversion of glycerol including, but not limited to, ion exchange, distillation, centrifugation and filtration.

The glycerol derivatives may be dihydroxyacetone (DHA) , hydroxypyruvic acid (HPA) , glycolic acid (GCO) , oxalic acid

(OXA), mesoxalic acid (MEO), tartronic acid (TTA), glyceric acid (GCA), glyceraldehyde (GLA) or glyoxalic acid (GOX).

The method disclosed herein may be practiced with any simulated moving bed chromatographic apparatus, including but not limited to moving port and moving column systems.

The method of the present patent application is described in further detail in the following nonlimiting example:

Example 1

This example describes the purification of a binary mixture containing Glyceric Acid and Tartronic Acid produced from the catalytic oxidation of glycerol. A solution of Sulfuric Acid 4mM was used as eluent and a Polystyrene Divinylbenzene (PS/DVB) resin (Dowex® 50WX-2), in hydrogen form (2%), mesh of 200-400, from The Dow Chemical Company (United States) was used as separation media.

The SMB experiment was performed in a SMB unit containing 6 stainless steel columns of 100mm of height and 20mm of diameter packed with the acid resin Dowex® 50WX-2.

Internal concentrations profiles samples were collected at 25%, 50%, 75%, of a switch time, through a 6-port valve installed between two columns. As the valve was fixed and as in the SMB technology there is a continuous cyclic switch of the position of all columns relatively to the inlet and outlet streams, this samples provided the required information to determine the internal concentration profile.

A mixture of Glyceric Acid (lOg/L) and Tartronic Acid (5g/L) was separated using a sulfuric acid solution (4mM) as eluent.

The flow rates were: 6.93mL/min for the eluent stream, 1.16mL/min for the feed stream, 4.81mL/min for the raffinate stream, 3.5mL/min for the extract stream and 8.4mL/min for the recycling stream. The switching time was set at 2 min. Additionally, one column per section was used in sections 1 and 4 (of fig. 1) (located between the desorbent and extract streams and between the raffinate and recycling streams, respectively) and two columns per section were used in sections 2 and 3 (located between the extract and feed streams and between the feed and raffinate streams, respectively) (see FIG 1). The internal concentration profile at the middle of the switching time after the cyclic steady state being achieved is shown in the FIG 2.

This is the first industrial production method for Glyceric Acid and Tartronic Acid.

The main performance parameters are presented on the table 1A.

TABLE 1A

Main Performance Parameters	
Productivity of Extract (kg m^{-3}_{ads} day^{-1})	115
Productivity of Raffinate (kg m^{-3}_{ads} day^{-1})	79
DC (m^3desorbent kg^{-}product)	0.5
Purity of Extract (%)	100
Purity of Raffinate (%)	80
Recovery of Extract (%)	96.68
Recovery of Raffinate (%)	97.33

Example 2

This example describes the purification of a pseudo-binary mixture, through which two fractions of glycerol derivatives

(A and B plus C) can be purified. In this case, the separation of fraction A (Oxalic Acid) from fraction B (Glyceric Acid and Unreacted glycerol) plus C (Tartronic Acid). A solution of Sulfuric Acid 4mM was used as eluent and a Polystyrene Divinylbenzene (PS/DVB) resin (Dowex® 50WX-2), in hydrogen form (2%), mesh of 200-400, from The Dow Chemical Company (United States) was used as separation media.

The SMB separation was carried out in a SMB unit containing 6 stainless steel columns of 100mm of height and 20mm of diameter packed with the acid resin Dowex® 50WX-2.

Internal concentrations profiles samples were collected at 25%, 50%, 75%, of a switch time, through a 6-port valve installed between two columns. As the valve was fixed and as in the SMB technology there is a continuous cyclic switch of the position of all columns relatively to the inlet and outlet streams, this samples provided the required information to determine the internal concentration profile.

A mixture of Oxalic Acid (16.5g/L), Tartronic Acid (7.2g/L), Glyceric Acid (0.6g/L), and unreacted Glycerol (0.6g/L) was separated. The flow rates were: 8.37mL/min for the eluent stream, 1.24mL/min for the feed stream, 2.78mL/min for the raffinate stream, 6.83mL/min for the extract stream and 9.07mL/min for the recycling stream. The switching time was set at 2.02 min. Additionally, one column per section was used in sections 1 and 4 (of fig. 1) (located between the desorbent and extract streams and between the raffinate and recycling streams, respectively) and two columns per section were used in sections 2 and 3 (of fig. 1) (located between the extract and feed streams and between the feed and raffinate streams, respectively). The internal concentration

profile at the middle of the switching time after the cyclic steady state being achieved is shown in the FIG 3. The main performance parameters are presented on the table 2A.

TABLE 2A

Main Performance Parameters	
Productivity of Extract (kg m^{-3}_{ads} day^{-1})	110.25
Productivity of Raffinate (kg m^{-3}_{ads} day^{-1})	215.36
DC (m^3desorbent kg^{-}product)	0.31
Purity of Extract (%)	97.94
Purity of Raffinate (%)	99.94
Recovery of Extract (%)	99.39
Recovery of Raffinate (%)	99.83

Example 3

This example describes the purification of a pseudo-ternary mixture, through which three fractions of glycerol derivatives (A, B and C) can be purified. In this case, the separation of fraction A (Oxalic Acid) from fraction B (Glyeric Acid and Unreacted glycerol) and fraction C (Tartronic acid) was first performed following the procedure described in example 2. Then, another SMB unit interconnected in series with the latter proceeded with the final purification between fraction B (Glyeric Acid and Unreacted glycerol) and fraction C (Tartronic acid).

A solution of Sulfuric Acid 4Mm was used as eluent and a Polystyrene Divinylbenzene (PS/DVB)resin (Dowex® 50WX-2), in hydrogen form (2%), mesh of 200-400, from The Dow Chemical Company (United States) was used as separation media.

The SMB separation was carried out in a SMB unit containing 6 stainless steel columns of 100mm of height and 20mm of diameter packed with the acid resin Dowex® 50WX-2.

Internal concentrations profiles samples were collected at 25%, 50%, 75%, of a switch time, through a 6-port valve installed between two columns. As the valve was fixed and as in the SMB technology there is a continuous cyclic switch of the position of all columns relatively to the inlet and outlet streams, this samples provided the required information to determine the internal concentration profile.

A mixture of Tartronic Acid (7.83g/L), Glyceric Acid (0.65g/L) and unreacted Glycerol (0.65g/L) was separated in the second SMB unit. The flow rates were: 5.02mL/min for the eluent stream, 1.21mL/min for the feed stream, 2.69mL/min for the raffinate, 3.55mL/min for the extract stream and 9.07mL/min for the recycling stream. The switching time was set at 2.00 min. Additionally, one column per section was used in sections 1 and 4 (of fig.l) (located between the desorbent and extract streams and between the raffinate and recycling streams, respectively) and two columns per section were used in sections 2 and 3 (of fig. 1) (located between the extract and feed streams and between the feed and raffinate streams, respectively). The internal concentration profile at the middle of the switching time after the cyclic steady state be achieved is shown in the FIG 4. The main performance parameters are presented on the table 3A.

TABLE 3A

Main Performance Parameters	
Productivity of Extract (kg m^{-3}_{ads} day^{-1})	17.17

Productivity of Raffinate (kg m^{-3}_{ads} day^{-3})	105.72
DC (nddesorbent kg⁻^product)	0.68
Purity of Extract (%)	97.27
Purity of Raffinate (%)	99.61
Recovery of Extract (%)	97.22
Recovery of Raffinate (%)	99.37

Brief description of drawings

For easier understanding of this application, figures are attached in the annex that represent the preferred forms of implementation which nevertheless are not intended to limit the technique disclosed herein.

FIG. 1 is a schematic diagram of the process of simulated moving bed chromatography as used for the separation of two water-soluble components, A and B. Section 1 is the zone of potential water recovery, component B conceptually moves with the resin. Section 2 is a zone in which component B moves with the water in an aqueous fluid, and component A conceptually moves with the resin. Section 3 is a zone in which component B moves with the water in an aqueous fluid, and component A conceptually moves with the resin. Section 4 is a section in which purified component A moves with the water in an aqueous fluid.

FIG. 2 show the internal concentration profile at the middle of the switching time after the cyclic steady state be achieved. Dashed lines for GCA and solid lines for TTA. The horizontal coordinate shows the axial position of the columns within the SMB equipment and the vertical coordinate shows the concentration (g/L).

FIG. 3 show the internal concentration profile at the middle of the switching time after the cyclic steady state be achieved. Dashed lines for fraction A and solid lines for fraction B plus fraction C. The horizontal coordinate shows the axial position of the columns within the SMB equipment and the vertical coordinate shows the concentration (g/L).

FIG. 4 show the internal concentration profile at the middle of the switching time after the cyclic steady state be achieved. Dashed lines for fraction C and solid lines for Fraction B. The horizontal coordinate shows the axial position of the columns within the SMB equipment and the vertical coordinate shows the concentration (g/L).

Best mode for carrying out the invention

Now, preferred embodiments of the present application will be described in detail. However, the embodiments described herein are not intended to limit the scope of this application.

In one embodiment the simulated moving bed chromatography method for separating a glycerol derivative from a feed solution comprising said glycerol derivative and one or more other glycerol derivatives, or impurities, comprises:

(a) selecting a simulated moving bed chromatographic apparatus comprising at least two chromatographic columns interconnected in series; wherein Said columns contain a separation media or a mixture of a variety of separation media, comprising ion exchange materials; sequentially comprising first a desorbent port, an extract port, a feed port and a raffinate port; and simultaneously,

(b) contacting, through said feed port, said feed solution with the separation media equilibrated with an acid or basic solution or water-organics mixture or water;
(c) contacting, through said desorbent port, an acid or basic eluent with said separation material, wherein the eluent may also be a water-organics mixture or water; and
(d) withdrawing, through said raffinate or extract port, a raffinate or extract stream, respectively, comprising the fluid mobile phase and mainly one of said glycerol derivatives, and a lower percentage of said other glycerol derivatives, and/or unreacted glycerol, and/or impurity present in said feed solution.

In one embodiment, the simulated moving bed chromatographic apparatus may further comprise additional raffinate or extract streams allowing to perform ternary, pseudo-ternary or higher order separations; withdrawing, through said outlet ports, a raffinate or extract stream comprising the fluid mobile phase, an acid solution or basic solution or water-organics mixture or water itself and mainly one of said glycerol derivative, and a lower percentage of said other glycerol derivative or any impurity present in said feed solution.

In another embodiment, the simulated moving bed chromatographic apparatus may also comprise a second desorbent port to perform solvent gradients inside the unit; contacting, through said second desorbent port, an acid solution or basic solution or water-organics mixture or water itself with said separation material.
In one embodiment, said glycerol derivative is selected from dihydroxyacetone (DHA), hydroxypyruvic acid (HPA), glycolic acid (GCO), oxalic acid (OXA), mesoxalic acid (MEO),

tartronic acid (TTA), glyceric acid (GCA), glyceraldehyde (GLA), glyoxalic acid (GOX), unreacted glycerol or any glycerol derivatives.

In another embodiment, the feed solution is product of a chemical conversion of glycerol by a range of process such as selective oxidation, selective hydrogenolysis , catalyst dehydration, pyrolysis, gasification, selective glycerol transesterification and esterification, selective etherification and carboxylation .

In one embodiment the pH of said feed solution is between 1 and 13 by the addition of an acid or a basic species. In a preferred embodiment the pH of said feed solution is between 1 and 7 by the addition of an acid or a basic species. In a more preferential embodiment the pH of said feed solution is between 1 and 5 by the addition of an acid or a basic species.

In one embodiment the feed solution is pretreated by any process suitable to obtain a solution of two or more glycerol derivatives without impurities; wherein the pretreatment process is a process selected from ion exchange, distillation, centrifugation and filtration.

In another embodiment prior to step (b), the feed solution is pretreated by any process suitable to obtaining a solution of two or more glycerol derivatives without impurities from the process of chemical conversion of glycerol including, but not limited to, centrifugation and filtration including ultrafiltration.

In one embodiment the chromatographic material is a cation or anion exchange chromatographic material, wherein said

cation exchange chromatographic material is selected from alumina, magnesium silicates, silica, glass, controlled pore glass, carbon, porous graphitic carbon, zirconium phosphate, hydroxyapatite, calcium phosphate, magnesium carbonate, and polymers or resins. In a particular embodiment said polymers or resins for the cation exchange chromatography are selected from hydroxyalkylmethacrolate, polyacrylamine, polymacrolate, poly (hydroxyethylmacrolate), polystyrene, styrene-divinylbenzine polymers, poly (ethyleneglycoldimethacrolate), poly (vinylalcohol), Poly (vinylacetate) , and poly (vinylpyridine)

In another embodiment the cation exchange chromatographic material within each of chromatographic columns is equilibrated with an aqueous acid solution.

In one embodiment the anion exchange chromatographic material is selected from polymers, resins, silica, zirconia, carbon and alumina, wherein said polymers or resins for the anion exchange chromatography are selected from sulfonic acid, alkylsulfonic acid, phenylsulfonic acid, alkylphenylsulfonic acid, and salts thereof, poly (vinylalcohol), poly (methacrylates), hypercross-linked polystyrene and poly (ethylene oxide) and styrene or ethylvinylbenzene polymers or copolymers cross-linked with divinylbenzene (e.g., ethylvinylbenzene-divinylbenzene (EVB-DVB) and styrene or polystyrene-divinylbenzene (DVB or PS-DVB) copolymer) of acrylonitrile, acrylic acid, or methacrylic acid, trimethylamine (TMA), trihexylamine (THA) , diethylenetriamine, diethylenetriamine, unsymmetrical dimethylhydrazine (UDMH) , dimethylethanolamine (DMEA) , methylamine (MA) , dimethylamine (DMA) , methyldiethanolamine (MDEA) or triethanolamine (TEA) .

In one embodiment the said anion exchange chromatographic material within each of chromatographic columns is equilibrated with an aqueous basic solution.

In one embodiment the eluent is an acid or basic solution or water .

The simulated moving bed chromatography may be practiced with any simulated moving bed chromatographic apparatus, including but not limited to moving port and moving column systems .

This description is of course not in any way restricted to the forms of implementation presented herein and any person with an average knowledge of the area can provide many possibilities for modification thereof without departing from the general idea as defined by the claims. The preferred forms of implementation described above can obviously be combined with each other. The following claims further define the preferred forms of implementation.

Lisbon, January 9, 2019

CLAIMS

1. A simulated moving bed chromatography method for separating a glycerol derivative from a feed solution comprising said glycerol derivative and/or one or more different glycerol derivatives, and/or unreacted glycerol, and/or impurities, comprising:

(a) selecting a simulated moving bed chromatographic apparatus comprising at least two chromatographic columns interconnected in series; wherein Said columns contain a separation media or a mixture of a variety of separation media, comprising ion exchange materials; sequentially comprising first a desorbent port, an extract port, a feed port and a raffinate port; and simultaneously,

(b) contacting, through said feed port, said feed solution with the separation media equilibrated with an acid or basic solution or water-organics mixture or water;

(c) contacting, through said desorbent port, an acid or basic eluent with said separation material, wherein the eluent may also be a water-organics mixture or water; and

(d) withdrawing, through said raffinate or extract port, a raffinate or extract stream, respectively, comprising the fluid mobile phase and mainly one of said glycerol derivatives, and a lower percentage of said other glycerol derivatives, and/or unreacted glycerol, and/or impurity present in said feed solution.

2. The method according to claim 1, wherein the simulated moving bed chromatographic apparatus further comprises additional raffinate or extract streams; withdrawing, through said outlet ports, a raffinate or extract stream comprising the fluid mobile phase, an acid solution or basic solution or water-organics mixture or water itself and mainly

one of said glycerol derivative, and a lower percentage of said other glycerol derivative or any impurity present in said feed solution.

3. The method according to any of the previous claims, wherein the simulated moving bed chromatographic apparatus further comprises a second desorbent port to perform solvent gradients inside the unit; contacting, through said second desorbent port, an acid solution or basic solution or water-organics mixture or water itself with said separation material .

4. The method according to any of the previous claims, wherein said glycerol derivative is selected from dihydroxyacetone (DHA), hydroxypyruvic acid (HPA), glycolic acid (GCO), oxalic acid (OXA), mesoxalic acid (MEO), tartronic acid (TTA), glyceric acid (GCA), glyceraldehyde (GLA), glyoxalic acid (GOX), unreacted glycerol or any glycerol derivatives.

5. The method according to any of the previous claims, wherein the feed solution is product of a chemical conversion of glycerol by a range of process such as selective oxidation, selective hydrogenolysis , catalyst dehydration, pyrolysis, gasification, selective glycerol transesterification and esterification, selective etherification and carboxylation .

6. The method according to claim 5, wherein the pH of said feed solution is between 1 and 13 by the addition of an acid or a basic species.

7. The method according to claim 6, wherein the pH of said feed solution is between 1 and 7 by the addition of an acid or a basic species.

8. The method according to claim 7, wherein the pH of said feed solution is between 1 and 5 by the addition of an acid or a basic species.

9. The method according to any of the previous claims, wherein the feed solution is pretreated by any process suitable to obtain a solution of two or more glycerol derivatives without impurities.

10. The method according to claim 9, wherein the pretreatment process is a process selected from ion exchange, distillation, centrifugation and filtration.

11. The method according to any of the previous claims, wherein said chromatographic material is a cation or anion exchange chromatographic material.

12. The method according to any of the previous claims, wherein said cation exchange chromatographic material is selected from alumina, magnesium silicates, silica, glass, controlled pore glass, carbon, porous graphitic carbon, zirconium phosphate, hydroxyapatite, calcium phosphate, magnesium carbonate, and polymers or resins.

13. The method according to claim 12, wherein said polymers or resins for the cation exchange chromatography are selected from hydroxyalkylmethacrolate, polyacrylamine, polymacrolate, poly (hydroxyethylmacrolate), polystyrene, styrene-divinylbenzine polymers, poly

(ethyleneglycoldimethacrolate), poly (vinylalcohol), Poly (vinylacetate) , and poly (vinylpyridine).

14. The method according to any of claims 12 and 13, wherein the said cation exchange chromatographic material within each of chromatographic columns is equilibrated with an acid solution or water-organics mixture or water.

15. The method according to claim 11, wherein said anion exchange chromatographic material is selected from polymers, resins, silica, zirconia, carbon and alumina.

16. The method according to claim 11 , wherein said polymers or resins for the anion exchange chromatography are selected from sulfonic acid, alkylsulfonic acid, phenylsulfonic acid, alkylphenylsulfonic acid, and salts thereof, poly (vinylalcohol), poly (methacrylates), hypercross-linked polystyrene and poly (ethylene oxide) and styrene or ethylvinylbenzene polymers or copolymers cross-linked with divinylbenzene (e.g., ethylvinylbenzene-divinylbenzene (EVB-DVB) and styrene or polystyrene-divinylbenzene (DVB or PS-DVB) copolymer) of acrylonitrile, acrylic acid, or methacrylic acid, trimethylamine (TMA), trihexylamine (THA) , diethylenetriamine, diethylenetriamine, unsymmetrical dimethylhydrazine (UDMH) , dimethylethanolamine (DMEA) , methylamine (MA) , dimethylamine (DMA) , methyldiethanolamine (MDEA) or triethanolamine (TEA) .

17. The method according to any of claims 15 and 16, wherein the said anion exchange chromatographic material within each of chromatographic columns is equilibrated with a basic solution or water-organics mixture or water.

18. The method according to any of the previous claims, wherein said eluent is an acid solution or basic solution or water-organics mixture or water.

19. The method according to claim 18, wherein the pH of said eluent solution is between 1 and 13 by the addition of an acid or a basic species.

20. The method according to claim 19, wherein the pH of said eluent solution is between 1 and 7 by the addition of an acid or a basic species

21. The method according to claim 20, wherein the pH of said eluent solution is between 1 and 5 by the addition of an acid or a basic species

22. The method according to any of the previous claims, wherein simulated moving bed chromatography may be practiced with any simulated moving bed chromatographic apparatus, including but not limited to moving port and moving column systems .

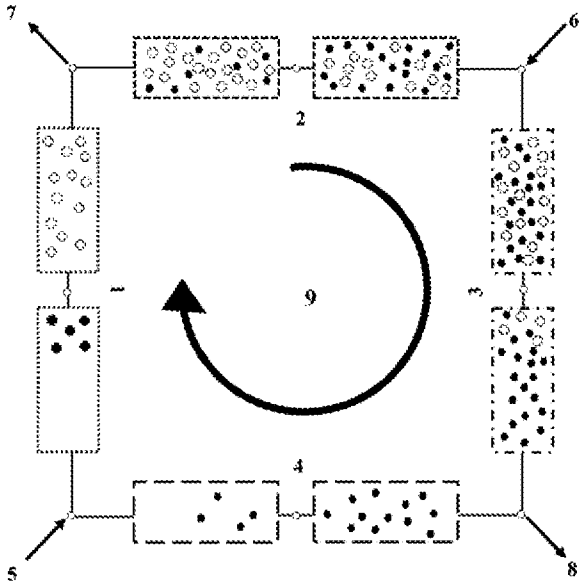

Figure 1

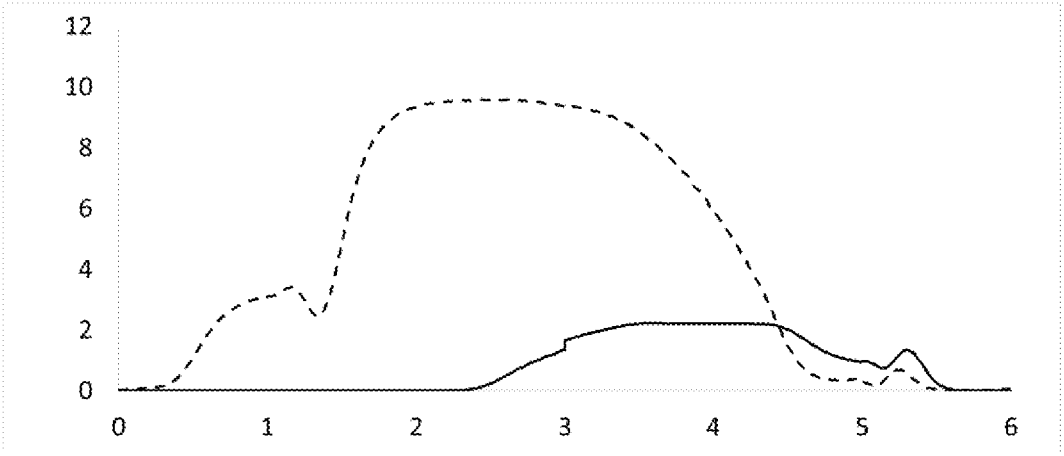

Figure 2

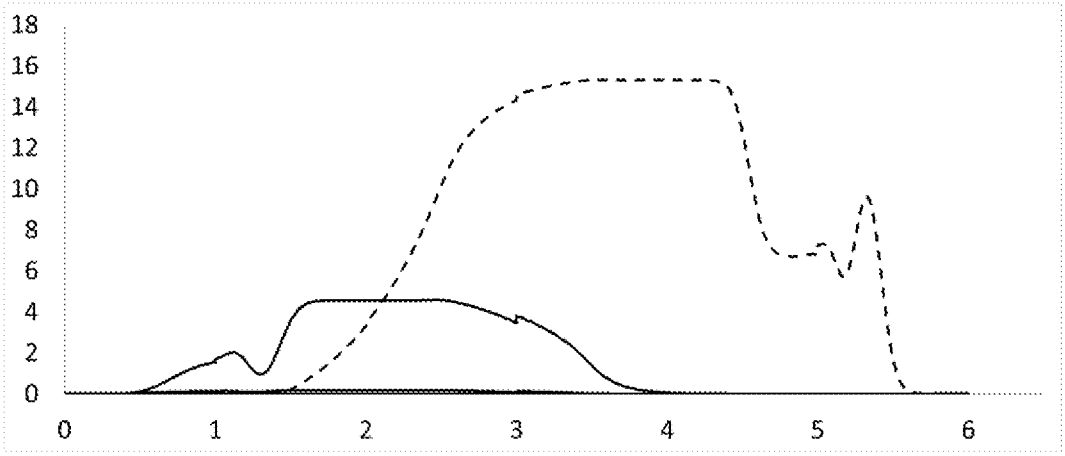

Figure 3

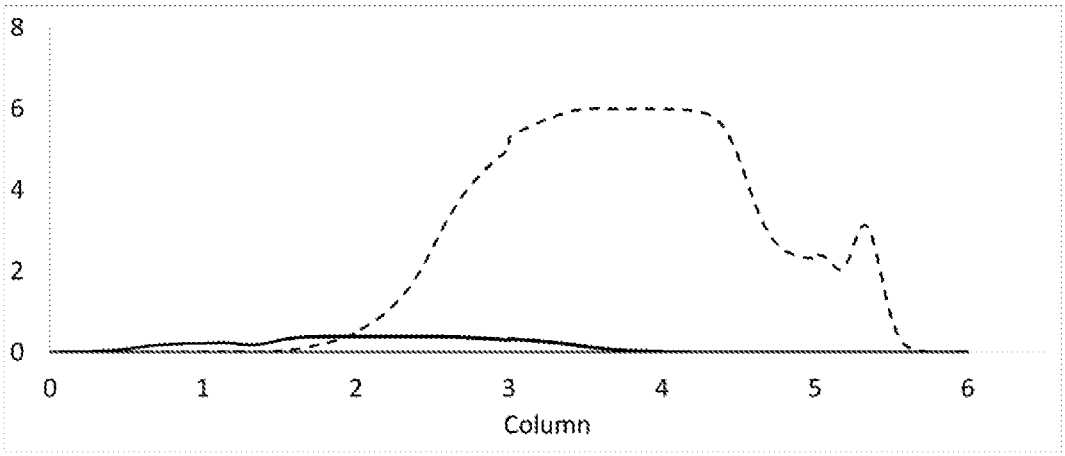

Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/050161

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D15/18 B01D15/36 C07C31/22 C07C7/12 C07C59/06
C07C59/19
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/090346 A1 (DIAMOND GARY M [US] ET AL) 31 March 2016 (2016-03-31) paragraph [0006] - paragraph [0009] paragraph [0030] - paragraph [0033] paragraph [0036] - paragraph [0040] -----	1,2,4,5, 9-22
X	US 2013/345473 A1 (ARCHER RAYMOND [US] ET AL) 26 December 2013 (2013-12-26) paragraph [0007] paragraph [0025]; claims -----	1,3,14, 17,22
X	US 6 224 776 B1 (HEIKKILA HEIKKI [FI] ET AL) 1 May 2001 (2001-05-01) column 4, line 65 - column 5, line 47; claims; table 6B -----	1,4,6-8, 22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
12 April 2019	29/04/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fourgeaud, Damien

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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