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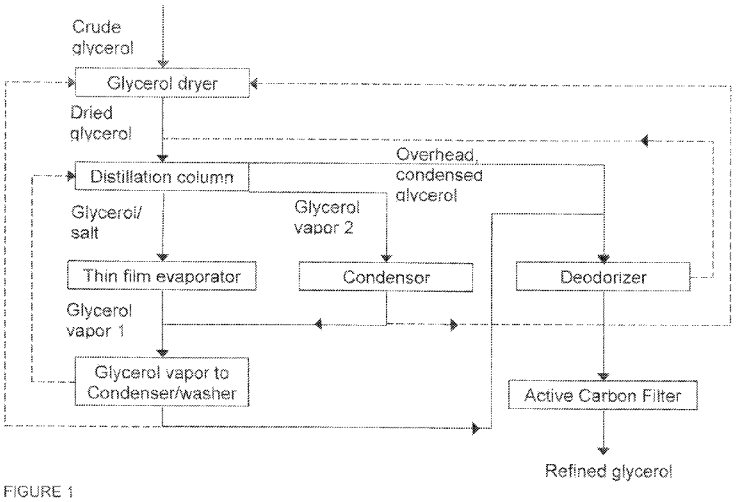

FIGURE 1

(57) Abstract: Processes for removing monochloropropanediols and/or glycidol from glycerol are disclosed. Starting glycerol is subjected to treatment with alkali, heat under vacuum, steam, ion exchange resins, or solids to reduce the level of monochloropropanediol. Glycerol compositions low in monochloropropanediol and glycidol are obtained thereby. These compositions may be suitable for food grade glycerol or for modification into food and chemicals.

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TITLE

PROCESSES FOR REMOVING MONOCHLOROPROPANEDIOLS AND/OR GLYCIDOL FROM GLYCEROL

INVENTORS:

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FIELD OF INVENTION

[0001] The present invention relates to processes for producing glycerol. Specifically, the present approach pertains to processes for producing compositions comprising glycerol having low levels of monochloropropanediol and glycidol contaminants and methods for making the compositions.

BACKGROUND

[0002] Glycerol is obtained from fats and oils by soapmaking, fat splitting for free fatty acid manufacture, and biodiesel manufacture. The glycerol obtained from these processes is usually crude glycerol. Crude glycerol is refined for food use. Contaminants causing potential health hazards have recently been found in glycerol. Monochloropropanediols (MCPD) and glycidol are among the contaminants.

[0003] Glycerol is sold in several categories with a typical purity range of 95-99%. The major refined grades are: USP (U.S. Pharmacopoeia), PH. EUR. (European Pharmacopoeia), Kosher, Vegetable, and Technical. USP glycerol contains not less than 95% glycerin. In the European Union, the European equivalent of USP is PH. EUR. (European Pharmacopoeia). This grade is produced from natural fats or vegetable oil (triglycerides) and generally used in pharmaceuticals, cosmetics and food applications. Kosher grade glycerin meets all USP requirements and is produced either naturally from 100% vegetable oil or synthetically in facilities designated as kosher. Vegetable grade glycerol also meets all USP requirements and is produced naturally from 100% vegetable oil. Technical grade glycerol has no industry standard, although is generally 97-99.5% glycerol.

[0004] Crude glycerol often originates from fats or oils and may be obtained from fat splitting, soapmaking, or biodiesel manufacture. Fat splitting is often carried out with alkali, such as sodium hydroxide, or by applying heat and pressure in the presence of water. Crude glycerol from biodiesel manufacture often contains

significant amounts of alkali, such as sodium hydroxide. The alkali is often neutralized with acid, especially hydrochloric acid, which may also lead to formation of MCPD in the glycerol. It is expected that the use of alternate acids, such as sulfuric or phosphoric rather than hydrochloric, for neutralization and splitting soaps in glycerol would reduce or eliminate potential sources of chloride/chlorine which may contribute to formation of MCPD and glycidol. Crude glycerol from biodiesel manufacture is dried to form dried glycerol (Fig. 1). Dried glycerol is distilled in a distillation column to form an overhead phase comprising glycerol and a bottom phase comprising a mixture of salt and glycerol. Overhead glycerol is sent to a deodorizer, where it is contacted with steam under vacuum to remove impurities which are more volatile than the glycerol, and passed through activated carbon to produce refined glycerol of greater than 99.5% purity. The bottom salt and glycerol phase from the distillation column is processed in a thin film evaporator. The overhead from the thin film evaporator comprising glycerol vapor is condensed and/or washed in a condenser/washer and the condensed glycerol is sent to the deodorizer.

[0005] An alternative source of MCPD and glycidol in glycerol is from oils which have undergone physical refining, such as palm oil. Glycerol obtained from physically refined oils often contains more MCPD than glycerol from chemically refined oils.

[0006] When crude glycerol is processed, monochloropropanediols (3-monochloropropanediol and 2-monochloropropanediol) and/or glycidol may be produced. According to EU Commission Regulation No. 231/2012 (March 9, 2012) regulations laying down a limit of 100 ppb 3-MCPD in food additive glycerol entered into force December 1, 2012.

[0007] Due to improvements in analytical methodology and increases in understanding of toxicology, government regulation and intervention are expected to continue to impose tighter limits on the levels of monochloropropanediols and glycidol in food ingredients and foodstuffs. The removal of glycidol esters and MCPD from vegetable oils has been demonstrated. However, the removal of polar compounds like glycidol and MCPD from a polar matrix such as glycerol is a different and more difficult problem than removing the glycidol esters and MCPD esters from a non-polar matrix, such as vegetable oil. There is a significant commercial demand for glycerol compositions having a low level of monochloropropanediols and glycidol. In spite of this no methods for reducing these contaminants in glycerol have been available.

SUMMARY OF THE INVENTION

[0008] New processes for removing monochloropropanediols, glycidol, or a combination thereof from glycerol are disclosed. In an aspect, glycerol is contacted with a member selected from the group consisting of alkali, heat under vacuum, steam, an ion exchange resin, a solid, and combinations of any thereof, thus producing a purified glycerol.

[0009] In an aspect, a solution comprising contacting glycerol having an initial level of a monochloropropanediols or glycidol with at least one of alkali, heat under vacuum, steam, a solid, or an ion exchange resin to obtain glycerol has been created, wherein the content of at least one monochloropropanediol or glycidol in the glycerol is reduced after contacting.

[0010] In an aspect, glycerol can be produced with low levels MCPD and glycidol. In an additional aspect, a product produced by the processes of the present invention is disclosed.

BRIEF DESCRIPTION OF DRAWINGS

[0011] Figure 1 shows a process block diagram for producing refined glycerol from crude glycerol obtained from biodiesel manufacture. Crude glycerol from biodiesel manufacture is dried to form dried glycerol. Dried glycerol is distilled in a distillation column to form an overhead phase comprising glycerol and a bottom phase comprising a salt/glycerol mixture. Overhead glycerol is sent to a deodorizer, where it is contacted with steam to remove contaminants that are more volatile than glycerol, and passed through activated carbon to produce refined glycerol of greater than 99.5% purity. The bottom salt and glycerol phase from the distillation column is processed in a thin film evaporator. The overhead from the thin film evaporator comprising glycerol vapor is condensed and/or washed in a condenser/washer and the condensed glycerol is sent to the deodorizer.

DETAILED DESCRIPTION

[0012] As used herein, "monochloropropanediol" includes 3-mono-chloropropane-1,2-diol (3-MCPD) and 2- mono-chloropropane-1,2-diol (2-MCPD). Monochloropropanediol is a contaminant that occurs in food in its non-esterified (diol) form.

[0013] As used herein, "contacting glycerol with alkali" refers to contacting glycerol with alkali substances that render starting glycerol streams more alkaline, resulting in the decrease in the content of MCPD or glycidol impurities in subsequent

process compositions. For example, contacting crude glycerol having a given initial pH and an initial level of MCPD or glycidol with alkali will result in an increase in pH and a decrease in the content of MCPD or glycidol in subsequent process streams, such as dried glycerol, overhead phase from a distillation column, a bottom phase mixture of salt and glycerol, overhead from a thin film evaporator, condensed glycerol, or refined glycerol of greater than 99.5% purity.

[0014] As used herein, "contacting glycerol with heat under vacuum" refers to heating a starting glycerol under a vacuum at a defined temperature range, whereby the glycerol is evaporated from the impurities and condensed. The content of at least one monochloropropanediol or glycidol in the condensed glycerol is lower than the level of at least one monochloropropanediol or glycidol in the starting glycerol. The heating may be carried out under conditions of temperature and pressure such that the glycerol is near the evaporation point, for example under 5-30 mbar vacuum and at 150-165 °C. The temperature of the evaporation point of glycerol is related to the vacuum applied.

[0015] As used herein, "contacting glycerol with supplemental steam" refers to contacting glycerol with steam in the deodorizing process, where steam is added to glycerol heated under vacuum. The supplemental steam refers to using a greater amount of steam than is normally used in deodorization of glycerol. For example, glycerol that is normally deodorized with 0.9% steam may be supplemented with steam to supply 1 % or more steam. The content of at least one monochloropropanediol or glycidol in the deodorized glycerol is lower than the level of at least one monochloropropanediol or glycidol in the starting glycerol.

[0016] As used herein, "contacting glycerol with a solid" refers to solids such as silica, cellulose, wood pulp, activated carbon, ion exchange resins, diatomaceous earth, or combinations of any thereof. Suitable solids include silica, such as Trysil™, available from W. R. Grace, Chicago, IL, USA; cellulose, such as wood pulp, including Filtracell EFC 950 C-plus, available from Filtrcell, Johannesburg, South Africa; activated carbon, such as Epibon YM12x40 Donau™, available from Donau Carbon, Springfield, NJ, USA and CAL12x40 Chemviron™, available from Calgon Carbon, Feluy, Belgium; and diatomaceous earth, such as LehVoss Celite 209™, Hamburg, Germany. The content of at least one monochloropropanediol or glycidol in the solid-contacted glycerol is lower than the level of at least one monochloropropanediol or glycidol in the starting glycerol.

[0017] As used herein, "contacting glycerol with ion exchange resins" includes contacting with strong base ion exchange resins, weak base ion exchange resins, strong acid ion exchange resins, weak acid ion exchange resins, nonfunctional resins, mixed bed resins, or combination of any thereof. Exemplary resins include Merck Ion Exchangers, such as type II, type III and type IV, available from Merck, Whitehouse Station, New Jersey; Amberlite™ type IT120, type IRN150, type IR120, type MB6113, Amberjet™ 4200Cl, and Amberlyst™ A2 60H, from Rohm & Haas, Philadelphia, Pennsylvania; Purolite™ type C150S, type Copolymer, type C100, type A100, type A103S, and type A500OH, from Purolite, Ratingen, Germany; Lewatit™ K2629 from Lanxess, Leverkusen, Germany; Dowex™ DRG8 and Dowex™ 22 from Dow Chemical Company, Midland, MI, USA; Diaion™ PA308, Diaion™ HPA 25, and Diaion™ PA412, from Mitsubishi Chemical Co., Tokyo, Japan; Tulsion™ A-30MP, Tulsion™ A-36, Tulsion™ A-74MP, Tulsion™ A72-MP from Thermax USA, Northville, MI, USA; Lewatit™ MP607, Lewatit™ 7468, Lewatit™ VPOC, Lewatit™S4268, and Lewatit™ MP300, from Lanxess, Chardon Ohio, USA;. The content of at least one monochloropropanediol in the glycerol contacted with ion exchange resin is lower than the level of at least one monochloropropanediol or glycidol in the starting glycerol.

[0018] Monochloropropanediols are measured by the DGF Standard Method C-IV 18 (10) at Institut Kirchhoff Berlin GmbH, Berlin, Germany. An alteration of that method using sodium bromide is used to determine glycidol levels. The detection limits of the method are 50 ppb (parts per billion) for 3-MCPD, 2-MCPD, and glycidol. Alternatively, 3-MCPD can be measured according to "Determination of residual free epoxide in polyether polyols by derivatization with diethylammonium N,N-diethyldithiocarbamate and liquid chromatography,"Journal of Chromatography A, vol. 696 (1995) 41-47, with a limit of detection of 10 ppb. Glycidol can also be quantified according to the BfR Method 9 MCPD-FA-Esters "Method-82-FC-009-02" updated 15.02.2010, with a limit of detection of 10 ppb.

[0019] One non-limiting aspect of the present disclosure is directed to a process for removing monochloropropanediols, glycidol, or a combination thereof from glycerol, the process comprising contacting glycerol with a member selected from the group consisting of alkali, heat under vacuum, steam, an ion exchange resin, a solid, and combinations of any thereof, thus producing a purified glycerol.

[0020] One non-limiting aspect of the present disclosure is directed to a glycerol composition in which the level of MCPD or glycidol in the composition is less than 1000 part per billion, less than 500 parts per billion, less than 100 parts per billion, less than 50 parts per billion, or less than 10 parts per billion.

[0021] In another non-limiting aspect of the present disclosure, glycerol may be obtained from fat splitting, soapmaking, or biodiesel manufacture.

[0022] Another non-limiting aspect of the present disclosure is directed to reducing the level of at least one of 3-MCPD, 2-MCPD or glycidol in crude glycerol by contacting the crude glycerol with alkali to raise the pH of the glycerol; the glycerol may then be dried. In a non-limiting aspect of the disclosure, the pH of the glycerol may be raised to at least a pH of 9.

[0023] Another non-limiting aspect of the present disclosure is directed to reducing the level of at least one of 3-MCPD, 2-MCPD or glycidol in glycerol by contacting the glycerol with heat under vacuum. In another non-limiting aspect of the present disclosure the heating under vacuum is carried out under conditions of temperature and pressure such that the glycerol is below an evaporation point of the glycerol.

[0024] Another non-limiting aspect of the present disclosure is directed to reducing the level of at least one of 3-MCPD, 2-MCPD or glycidol in glycerol by contacting the glycerol with heat and steam under vacuum in the presence of steam at a level of greater than 0.9 weight percent steam based on the weight of glycerol. In a non-limiting aspect, the heating under vacuum in the presence of steam takes place in a deodorizer.

[0025] Another non-limiting aspect of the present disclosure is directed to reducing the level of at least one of 3-MCPD, 2-MCPD or glycidol in glycerol by contacting the glycerol with heat under vacuum, wherein the glycerol is evaporated. In another non-limiting aspect of the present disclosure, the evaporated glycerol is condensed and at least one of monochloropropanediols and glycidol are carried away in the vapor phase.

[0026] Another non-limiting aspect of the present disclosure is directed to reducing the level of at least one of 3-MCPD, 2-MCPD or glycidol in glycerol by contacting the glycerol with a solid selected from the group consisting of silica, cellulose, wood pulp, activated carbon, ion exchange resins, diatomaceous earth, and combinations of any thereof.

[0027] Another non-limiting aspect of the present disclosure is directed to reducing the level of at least one of 3-MCPD, 2-MCPD or glycidol in glycerol by contacting the glycerol with an ion exchange resin selected from the group consisting of strong base ion exchange resins, weak base ion exchange resins, strong acid ion exchange resins, weak acid ion exchange resins, mixed bed resins, nonfunctional resins, and combinations of any thereof. In another non-limiting aspect of the present disclosure, glycerol is contacted with a base ion exchange resin and with an acid ion exchange resin. In another non-limiting aspect of the present disclosure, the glycerol that is contacted with a base ion exchange resin and an acid ion exchange resin is contacted with the base ion exchange resin first followed by contacting with the acid ion exchange resin. In another non-limiting aspect of the present disclosure, the glycerol that is contacted with an ion exchange resin is contacted with carbon.

[0028] Another non-limiting aspect of the present disclosure is directed to glycerol obtained by the methods outlined herein. Another non-limiting aspect of the present disclosure is directed to glycerol wherein the content of a monochloropropanediol, the glycidol, or a combination of any thereof is less in the purified glycerol than in the glycerol which has not been contacted. In a further embodiment, products obtained by the methods outlined herein may be used, for example in food and beverages, personal care products, oral care products, tobacco, pharmaceuticals, polyether polyols, propylene glycol, recreational vehicle fluids, per foods, alkyd resins, deicers, completion and fracture fluids, drilling muds, polyglycerols, concrete and asphalt lubrication, and epichlorohydrin production.

EXAMPLES

[0029] The following examples illustrate methods for removing monochloropropanediols and/or glycidol from glycerol, and compositions of glycerol containing low levels of monochloropropanediols and glycidol, according to the present invention. The following examples are illustrative only and are not intended to limit the scope of the invention as defined by the appended claims.

EXAMPLE 1

[0030] Adjustment of pH of glycerol A sample of crude glycerol from biodiesel having a pH value of 7 was obtained (ADM, Hamburg, Germany). The glycerol was subjected to glycerol drying to obtain glycerol dryer bottoms. The glycerol dryer bottoms were analyzed by DGF Standard Method C-IV 18 (10) at Institut Kirchhoff Berlin GmbH, Berlin, Germany (Table 1).

[0031] A second aliquot of the crude glycerol was treated to adjust the pH to a pH value of 12 before being subjected to glycerol drying to obtain glycerol dryer bottoms (from alkali treated glycerol, pH 12). The levels of MCPD were determined (Table 1).

Table 1. Glycerol dryer bottoms from glycerol dryer producing dried glycerol from crude glycerol. Glycidol content was calculated.

	MCPD (ppb)	Glycidol (ppb)
Glycerol bottoms from pH 7 glycerol	5990	150
Glycerol bottoms from pH 12 glycerol	2040	<50

[0032] Glycerol dryer bottoms having an MCPD content of less than 5 ppm were obtained when the pH of the glycerol before glycerol drying and glycerol distillation was adjusted to 12, indicating the ability of contacting the glycerol with alkali to remove MCPD and glycidol.

EXAMPLE 2

[0033] Heating glycerol under vacuum A sample of contaminated overhead glycerol containing 2060ppb 3-MCPD, 8000 ppb 2-MCPD, and 65 ppb glycidol was subjected to heating for one hour to 165 °C (just under the evaporation point of glycerol) under 15 mbar vacuum. Significant reduction in MCPD and glycidol was obtained by heating the glycerol to just under the evaporation point of the glycerol (Table 2), indicating the ability of heating the glycerol to just under the evaporation point of the glycerol to remove MCPD and glycidol.

[0034] Increasing strip steam in deodorizing glycerol Contaminated overhead glycerol (containing 2060ppb 3-MCPD, 8000 ppb 2-MCPD, and 65 ppb glycidol) was subjected to heat and steam under vacuum to carry out glycerol deodorization as normal, with 19 kg/hour (1.2 weight percent steam based on the weight of glycerol) stripping steam (11 bar). Deodorized glycerol containing 310 ppb 3-MCPD, 1110 ppb 2-MCPD and <50 ppb glycidol was obtained. When the same contaminated overhead glycerol was deodorized with supplemental stripping steam (30 kg/hour), contaminant levels in the deodorized glycerol were reduced further to 110 ppb 3-MCPD, 610 ppb 2-MCPD and <50 ppb glycidol (Table 2) indicating the ability of deodorizing the glycerol with supplemental steam to remove MCPD and glycidol.

[0035] Evaporation of glycerol Contaminated overhead glycerol was distilled at various temperatures under vacuum. MCPD and glycidol were carried away in the

vapor phase. Glycerol was condensed to yield refined glycerol having a monochloropropanediol content of less than five parts per million (Table 2).

Table 2. Heating glycerol under vacuum.

	3-MCPD (ppb)	2-MCPD	Glycidol (ppb)
Contaminated overhead glycerol	2060	8000	150
Glycerol heated under vacuum	440	1790	<50
Normal deodorization	310	1110	<50
Deodorization with supplemented steam	110	610	<50
Distilled for 1 h at 150°C under 25 mbar vacuum	820	2950	<50
Distilled for 1 h at 160°C under 15 mbar vacuum	660	2160	<50
Distilled for 1 h at 165°C under 14 mbar vacuum	440	1790	77

[0036] After heating under vacuum, deodorizing with supplemented steam, and condensing evaporated glycerol, glycerol compositions having reduced levels of monochloropropanediols and glycidol were obtained, indicating the ability of evaporating and condensing glycerol to remove MCPD and glycidol.

EXAMPLE 3

[0037] Contacting glycerol with a solid Contaminated refined glycerol containing 470 ppb 3-MCPD, 3200 ppb 2-MCPD, and <50 ppb glycidol (ADM, Hamburg, Germany) was contacted with solids. Solids (5 wt %) were added to contaminated glycerol and stirred for 4 hours at 60 °C, and the resulting solid-contacted glycerol was analyzed.

Table 3. Levels of 3-MCPD and 2-MCPD in contaminated refined glycerol after contacting with solids. Glycerol treated with Trysil was analyzed using the Weisshaar method. Glycidol content was calculated.

	3-MCPD (ppb)	2-MCPD (ppb)	Glycidol (ppb)
Contaminated refined glycerol	470	3500	<50
Trysil™	421	Not determined	Not determined
Wood pulp (cellulose) Filtracell EFC 950 C-plus™	420	1220	50
Epibon YM12x40 Donau™ Activated Carbon	450	3230	52
Epibon YM12x40 Donau™ Activated Carbon	440	3120	65
CAL12x40 Chemviron™	430	3110	<50

Activated Carbon			
CAL12x40 Chemviron™ Activated Carbon	420	3170	<50
LehVoss Celite 209	400	1210	<50

[0038] Slight reduction in the MCPD content of glycerol took place after treatment with activated carbon or Trysil™ silica. After treatment with wood pulp or diatomaceous earth (celite), significant reduction in the MCPD content of glycerol was obtained, indicating the ability of contacting glycerol with a solid to remove MCPD.

EXAMPLE 4

[0039] Contacting glycerol with an ion exchange resin Contaminated refined glycerol from Example 3 was contacted with ion exchange resins (5 vol. percent of the glycerol) for 2 hours at 60 °C with agitation at 150 RPM substantially as outlined in Example 3. (Table 4A).

Table 4A. Levels of 3-MCPD and 2-MCPD in contaminated refined glycerol after contacting with ion exchange resins. Glycidol content was calculated.

	3-MCPD (ppb)	2-MCPD (ppb)	Glycidol (ppb)
Contaminated glycerol	470	3500	<50
Merck Ion Exchanger II™	450	2020	<50
Merck Ion Exchanger III™	190	320	125
Amberlite™ IT120	430	3320	<50
Amberlite™ IRN150	<50	280	120
Amberlite™ IR120	430	3240	<50
Amberlite™ MB6113	<50	420	80
Merck Ion Exchanger IV™	420	3120	<50
Purolite™ C150S	420	3150	<50
Purolite™ Copolymer	430	3160	<50
Purolite™ C100	440	3250	<50
Lewatit™ K2629	460	1300	<50
Dowex™ DRG8	480	1360	<50
Diaion™ PA308	450	1270	<50
Adako™ ACC142200 plus	440	1240	<50
Purolite™ A100	470	3200	<50
Purolite™ A103S	336	2450	<50
Purolite™ A500 OH	<50	<50	274

[0040] Significant reduction in MCPD was obtained with several ion exchange resins. When contaminated glycerol containing 470 ppb 3-MCPD and 3500 ppb 2-MCPD was treated with Purolite™ A500 OH, the levels on 3-MCPD and 2-MCPD were both reduced to below the detection limits of the DGF Standard Method C-IV 18 (10) at Institut Kirchhoff Berlin GmbH, Berlin, Germany, indicating the ability of contacting glycerol with a ion exchange resin to remove MCPD.

[0041] A 3 Normal solution of crude glycerol was spiked with 3-MCPD to contain the 3-MCPD levels indicated in Table 4B and contacted with conditioned ion exchange resins. Resins were conditioned to hydroxide form in a column by passing 5 bed volumes of 5% sodium hydroxide solution through the resin at 5 bed volumes/hour. The resins were rinsed with 10 bed volumes of water, then removed from the column and interparticle water was removed on a Buchner funnel. Glycerol (100 mL) was added to a 250 ml shake flask and 10 mL of conditioned resin was added. The resin and glycerol were shaken together for 4 hours at 60 °C, then the resin was removed by filtration (Table 4B).

Table 4B. Levels of 3-MCPD contaminated refined glycerol after contacting with ion exchange resins. 3-MCPD was determined according to BfR Method 9 MCPD-FA-Esters "Method-82-FC-009-02" updated 15.02.2010.

	3-MCPD (ppb)		
Contaminated glycerol	76347	987	912
Purolite™ A500	659		
Dowex™ 22	133		
Mitsubishi Diaion™ PA412	190	<25	
Mitsubishi Diaion™ PA308	159		
Mitsubishi Diaion™ HPA 25	<25		
Mitsubishi Diaion™ PA312		<10	
Mitsubishi Diaion™ PA418		<25	
Mitsubishi Diaion™ PA408		<25	
Thermax Tulsion™ A-30MP			697
Thermax Tulsion™ A36			71
Thermax Tulsion™ A-74MP			568
Thermax Tulsion™ A-72MP			506
Lewatit™ MP607			90
Lewatit™ 7468			95
Lewatit™ VPOC			279
Lewatit™ S4268			691
Lewatit™ MP300			655
Amberjet™ 4200Cl			720
Amberlyst™ A2 60H			542
Dow Marathon™ A			666
Dowex™ IRA			541

[0042] Some resins were able to reduce the levels of 3-MCPD by more than 100-fold, indicating the ability of contacting glycerol with ion exchange resin to remove MCPD.

[0043] Selected resins from Table 4B were contacted with glycerol spiked with 3-MCPD to contain 1694 ppb 3-MCPD for three hours (Table 4C).

Table 4C. Levels of 3-MCPD contaminated refined glycerol after contacting with ion exchange resins. 3-MCPD was determined according to BfR Method 9 MCPD-FA-Esters "Method-82-FC-009-02" updated 15.02.2010.

	3-MCPD (ppb, 1.5 hours)	3-MCPD (ppb, 3 hours)
Contaminated glycerol	1654	1654
Purolite™ A500	133	<10
Dowex™ 22	1258	<10
Mitsubishi Diaion™ PA412	515	<10
Mitsubishi Diaion™ PA308	344	<10
Mitsubishi Diaion™ HPA 25	86	<10

[0044] Each resin was able to remove 3-MCPD to below detection limits in three hours, indicating the ability of contacting glycerol with ion exchange resin to remove MCPD.

EXAMPLE 5

[0045] Effects of heating on removal of MCPD with ion exchange resin A sample of contaminated overhead glycerol containing 2060 ppb 3-MCPD, 8000 ppb 2-MCPD, and 65 ppb glycidol was obtained from the first glycerol distillation column (ADM, Hamburg, Germany). Aliquots (200 grams) were contacted for 2 hours with 5 wt % Purolite™ A500 strong base ion exchange resin in the hydroxyl form substantially as outlined in Example 3 except that the temperature of contact was varied (Table 5).

Table 5. MCPD and glycidol content of glycerol after treatment with strong base resin at various temperatures. Glycidol content was calculated.

	3-MCPD (ppb)	2-MCPD (ppb)	Glycidol (ppb)
Contaminated glycerol	2060	8000	65
20 °C	1950	6150	220
40 °C	1320	5250	435
60 °C	470	3850	783
80 °C	<50	560	555

[0046] When glycerol was contacted with A500 solid base ion exchange resin for 2 hours, increasing the temperature above 20 °C caused a greater reduction in MCPD. Treatment at 80 °C resulted in a 94% reduction in MCPD, indicating the ability of contacting glycerol with ion exchange resin at a temperature greater than 20 °C to remove MCPD.

EXAMPLE 6

[0047] Contacting glycerol with varying amounts of ion exchange resin Contaminated glycerol from Example 4 was contacted with varying amounts of ion exchange resins for one or two hours at 60 °C substantially as outlined in Example 3

(Table 6). Amberlite™ IRN150 comprises a mixture of cation and anion exchange resins.

Table 6. MCPD and glycidol content of glycerol after treatment with strong base resin at various amounts (volume % resin). Glycidol content was calculated.

Resin/hours	Volume %	3-MCPD (ppb)	2-MCPD	Glycidol (ppb)
Starting glycerol	--	2060	8000	65
Purolite™ A500/ 1 hour	0.5	2380	8910	420
	1	1990	7570	530
	2	1760	7160	770
	3	1460	6440	1110
	4	1320	6040	1410
	5	1000	5250	1560
Purolite™ A500/ 2 hours	0.5	2080	8100	168
	1	1800	7490	306
	2	1180	5880	568
	3	1060	5590	641
	4	730	4520	788
	5	450	3410	882
	7	130	2140	723
	10	<50	940	590
Amberlite™ MB6113 (mixed bed resin)/ 2 hours	0.5	2060	6170	112
	1	2040	5870	155
	2	1780	5650	241
	3	1420	4840	271
	4	1180	4300	297
	5	870	3460	288
	7	680	3670	232
	10	340	2710	159
Merck ion exchanger III™/ 2 hours	0.5	1830	6030	276
	1	1510	5510	396
	2	920	4190	607
	3	820	3940	646
	4	830	4050	659
	5	400	2760	814
	7	140	1540	779
	10	<50	1020	719
Amberlite™ IRN150 (mixed bed)/ 2 hours	0.5	2130	6900	133
	1	1940	6740	194
	2	140	5450	263
	3	1240	5240	301
	4	930	4540	288
	5	820	4240	280
	7	530	3350	288
	10	240	2310	168

[0048] Incubation with 10% Purolite™ A500 strong base resin caused a reduction in MCPD of 38% after one hour and 94% after two hours. Incubation with Amberlite™ MB6113, Merck ion exchanger III™, and Amberlite™ IRN150 (mixed bed) for two hours caused a reduction in MCPD of 70, 90, and 75%, respectively, indicating the ability of contacting glycerol with ion exchange resin to remove MCPD.

EXAMPLE 7

[0049] Continuous contacting glycerol with an ion exchange resin in a column

Purolite™ A500 strong base resin was packed into a column (1 cm diameter, ~6 cm height) and contaminated refined glycerol containing 860 ppb 3-MCPD, 4590 ppb 2-MCPD, and <50 ppb glycidol was contacted with the ion exchange resin at 25 mL/hour and at 24-70 °C in a first cycle to yield a glycerol composition having reduced levels of monochloropropanediols. When the 2-MCPD content of the treated glycerol effluent reached 370 ppb, the base ion exchange resin was regenerated by treating with a 4% solution of sodium hydroxide and a second cycle of contacting with the same feed was carried out. The regeneration cycle after loss of activity was repeated three times without significant loss of performance (Table 7).

Table 7.

	3-MCPD (ppb)	2-MCPD (ppb)	Glycidol (ppb)
Feed glycerol	860	4590	<50
Cycle 1, after 73 bed volumes	<50	<50	288
Cycle 1, after 116 bed volumes	<50	<50	331
Cycle 1, after 133 bed volumes	<50	60	249
Cycle 1, after 296 bed volumes	<50	260	305
Cycle 1, after 306 bed volumes	<50	370	318
Regeneration			
Cycle 2, after 13 bed volumes	<50	70	600
Cycle 2, after 57 bed volumes	<50	110	770
Cycle 2, after 76 bed volumes	<50	180	331
Cycle 2, after 116 bed volumes	<50	100	245
Cycle 2, after 133 bed volumes	<50	180	301
Cycle 2, after 296 bed volumes	<50	530	301
Cycle 2, after 313 bed volumes	<50	590	319
Regeneration			
Cycle 3, after 13 bed volumes	<50	50	288
Cycle 3, after 57 bed volumes	<50	80	293
Cycle 3, after 73 bed volumes	<50	90	323
Cycle 3, after 116 bed volumes	<50	120	314
Cycle 3, after 132 bed volumes	<50	80	349
Cycle 3, after 176 bed volumes	<50	120	331
Cycle 3, after 192 bed volumes	<50	117	331

Cycle 3, after 356 bed volumes	<50	190	310

[0050] The resin was able to remove 3-MCPD throughout but slowly lost the ability to remove 2-MCPD. Regeneration of the ion exchange resin restored the ability of the resin to remove MCPD.

EXAMPLE 8

[0051] Continuous contacting glycerol with an ion exchange resin in a column Three jacketed columns (15 mm inner diameter) were packed with 100 mL strong base ion exchange resin. The first column was packed with Purolite™ A500OH resin; the second was packed with Mitsubishi Diaion™ PA412 resin; the third column was packed with Dowex™ 22 resin. Resins were conditioned by passing 5 bed volumes (BV) of a 5% solution of sodium hydroxide at 8.3 mL/minutes, then 10 BV of deionized water. The column temperatures were set to 60 °C. A starting glycerol comprising U.S.P. glycerol containing 2103 ppb 3-MCPD and 99% glycerol was contacted with the ion exchange resin by heating to 90 °C before passing it from the top through the resin beds at 0.7 mL/minute. The 3-MCPD levels were quantified according to "Determination of residual free epoxide in polyether polyols by derivatization with diethylammonium N,N-diethyldithiocarbamate and liquid chromatography,"Journal of Chromatography A, vol. 696 (1995) 41-47. The limit of detection was 10 ppb. Glycidol was quantified according to the BfR Method 9 MCPD-FA-Esters "Method-82-FC-009-02" updated 15.02.2010; the limit of detection was 10 ppb.

[0052] Four bed volumes of glycerol were passed through each of the columns and the levels of MCPD and glycidol were measured (Table 8).

Table 8. Reduction of 3-MCPD and glycidol after contacting with base ion exchange resins at 60 °C.

Resin/Bed Volumes	3-MCPD (ppb)	Glycidol (ppb)
Feed Glycerol	2103	990.3
Purolite™ A500, after 1.5 bed volumes	<10	638.2
Purolite™ A500, after 3.0 bed volumes	<10	982.3
Purolite™ A500, after 4.0 bed volumes	<10	984.3
Diaion™ PA 412, after 1.5 bed volumes	<10	937.1
Diaion™ PA 412, after 3.0 bed volumes	<10	990.2
Diaion™ PA 412, after 4.0 bed volumes	<10	987.4
Dowex™ 22, after 1.5 bed volumes	<10	902.8
Dowex™ 22, after 3.0 bed volumes	<10	988.5

Dowex™ 22, after 4.0 bed volumes	<10	986.0

[0053] The column packed with Mitsubishi Diaion™ PA412 resin was tested for 19 bed volumes. Glycerol containing 1493 ppb 3-MCPD and 992 ppb glycidol was passed through the resin at 0.7 mL/minute. The level of MCPD was quantified after 7, 13, and 19 bed volumes; in each case, the level of 3-MCPD in the column effluent was <10 ppb, , indicating the ability of contacting glycerol with ion exchange resin to remove MCPD.

[0054] The columns containing Purolite™ A500OH resin and Mitsubishi Diaion™ PA412 resin were regenerated by passing 5 bed volumes (BV) of a 5% solution of sodium hydroxide at 8.3 mL/minutes, then 10 BV of deionized water, then tested again with higher flow rates. Two bed volumes of glycerol were passed through the resins at 1.4 mL/minute, 2.8 mL/minute, 5.6 mL/minute, and 11.2 mL/minute. In each case, the level of 3-MCPD in the column effluent after 2 bed volumes was <10 ppb, indicating the ability of contacting glycerol with regenerated ion exchange resin to remove MCPD.

EXAMPLE 9

[0055] Continuous contacting glycerol with a base ion exchange resin, an acid ion exchange resin, and activated carbon in a column Contaminated refined glycerol containing 500 ppb 3-MCPD, 2625 ppb 2-MCPD, and <50 ppb glycidol was contacted with base ion exchange resin (Purolite™ A500OH) packed in a column (1 cm diameter, ~6 cm height), then contacted with 20 mL of an acid resin (Purolite™ C150S) packed in a second column (1 cm diameter, 12 cm height), then contacted with active carbon at a flow rate of 25 mL/hour. The temperature was varied between 24° to 70 °C. The levels of impurities in the contacted (purified) glycerol were below detection limits (<50 ppb 3MPCD, <50 ppb 2-MCPD, and <50 ppb glycidol) after 328 bed volumes. After 614 bed volumes the levels of 3-MCPD and glycidol in the contacted (purified) glycerol were below detection limits (<50 ppb), and the level of 2-MCPD was 200 ppb , indicating the ability of contacting glycerol with ion exchange resins and carbon to remove MCPD.

EXAMPLE 10

Combination of base ion exchange and acid ion exchange resin columns Crude glycerol (260 ppb 3-MCPD, 1660 ppb 2-MCPD, <50 ppb Glycidol) was passed

through a base ion exchange resin followed by an acidic ion exchange resin. The base ion exchange resin comprised regenerated 10 mL Purolite™ A500 (regenerated as described in Example 7 to 92.9% alkalinity); the acid ion exchange resin comprised 20 mL Purolite™ C150SH. Basic ion exchange resin converted MCPD to glycidol but imparted an odor to the glycerol stream. Treatment with acid resin reduced the glycidol content of the glycerol stream and removed most of the odor that leached from the base resin. Glycerol was passed at 25 mL/h through the columns (1 cm diameter) held at 70 °C. The contact time with the base ion exchange resin was 0.4 hours, and the contact time with the acid resin was 0.8 hours. The level of 3-MCPD in glycerol eluted from the columns was less than 100 µg/kg for the first 368 bed volumes. The level of 3-MCPD in glycerol eluted from the columns was 134 and 263 micrograms/kg through 480 – 857 bed volumes. A total of 939 bed volumes were treated in these columns before regeneration. The 10 mL Purolite™ A500 was regenerated as described in Example 7 to 97.29% of the original alkalinity. Spiked glycerol was prepared by adding 3-MCPD to pure glycerol to obtain spiked glycerol feed containing 655 µg/kg 3-MCPD. No 2-MCPD or glycidol were added. The spiked glycerol feed (899 bed volumes) was passed through the basic and acidic resin to yield 17.9 liters of glycerol containing less than 100 micrograms/kg 3-MCPD, , indicating the ability of contacting glycerol with ion exchange resin to remove MCPD.

EXAMPLE 11

[0056] Capacity of acid resin after treatment with acid Acids were tested as agents for regeneration of acid resins. The capacity of acid resins that had been shown to be effective (Amberlite IRN120 & Purolite C150) was exhausted by contacting the acid resin with sodium chloride solution. The acid resin titrated with 0.1 molar hydrochloric acid using phenolphthalein indicator to confirm that the acid resin was exhausted (capacity of 0.00 mmol/g resin). This point was determined by withdrawing 1 gram of resin from the column, which was stirred in 50 mL 0.1 molar potassium hydroxide for 60 minutes at room temperature. Exhausted resin loaded into a column (1 cm diameter, 25 cm bed height). Exhausted acid resins were treated with citric acid (0.6 mmol/gram of resin), phosphoric acid (1.06 mmol/gram of resin, or hydrochloric acid (1.51 mmol.gram of resin). The acid resin was removed from the column and two bed volumes of the respective acid solution (20% vol/vol solutions of phosphoric and citric acids, and 5% vol/vol solution of hydrochloric acid) at 70 °C was stirred with the resin at 70 °C for 30 minutes. The acid resins treated with phosphoric

and citric acids were washed with 3 bed volumes of deionized water, and the acid resin treated with hydrochloric acid was washed with 3 bed volumes of deionized water. The wash water was free of chloride. The regenerated acid ion exchange resin was contacted with glycerol eluted from a base ion exchange resin to generate glycerol having reduced levels of MCPD and glycidol.

EXAMPLE 12

[0057] Plant scale processing of glycerol Crude glycerol recovered from palm oil biodiesel was continuously dried in a glycerol dryer, then continuously fed to a glycerol distillation column. The bottoms from the glycerol distillation were continuously fed to a thin film evaporator. Glycerol vapor from the thin film evaporator was combined with the glycerol vapor from the glycerol distillation column and condensed continuously. The condensed glycerol was deodorized and passed continuously through two columns (each holding 2 cubic meters). The first column contained base ion exchange resin (Purolite™ A500OH), the second column contained an acid resin (Purolite™ C150S). The effluent from the second column passed continuously through an active carbon filter to yield 611 bed volumes (1539 metric tons) of purified glycerol containing greater than 99.5% pure glycerol and containing less than 100 ppb 3-MCPD.

EXAMPLE 13

[0058] Breakthrough tests of SBA resins Jacketed glass columns (100ml, 15mm diameter) were loaded with the desired SBA resins. These resins were then rinsed with deionized water, followed by a conditioning step in which 500 ml (5 bed volumes (BV)) of 5% NaOH was pumped through the resin at a flow rate of 10ml/min. The column was then rinsed with 5BV of deionized water. The column was then connected to a fraction collector. The column temperature was kept constant at 60°C; glycerol feed spiked with 3-MCPD to contain 1055-1656 ppb 3-MCPD was then applied to the resin column at a rate of 10 ml/min and samples were collected in 500 ml fractions. This test was run until the effluent of any column reached 100ppb 3-MCPD for several samples in a row.

Table 11. Breakthrough tests of SBA resins

Resin Type	BV Treated before breakthrough	Average 3-MCPD Reduction, %
Mitsubishi Diaion™ PA 412	*	99.0
Mitsubishi Diaion™ PA 308	179	92.3
Lewatit™ S6368	109	91.6

Purolite™ A500	86	95.9
Lewatit™ S7468	144	93.8
Dowex™ 22	44	95.4

*The PA 412 column blinded off ; after160 BV it was not possible to pump any more feed through.

[0059] Although the PA412 resin showed the highest average 3-MCPD reduction, the breakthough was never reached due to blinding off of the resin. In addition, 3-MCPD was undetectable in the column effluent for the first 100 bed volumes. The PA308 resin was able to run the longest before the 3-MCPD content of the effluent was as high as the breakthrough level (100 ppb).

[0060] While the foregoing invention has been described in some detail for purposes of clarity and understanding, it will be appreciated by one skilled in the art from a reading of this disclosure that various changes in form and detail can be made without departing from the true scope of the invention and appended claims.

CLAIMS

What is claimed is:

1. A process for removing monochloropropanediols, glycidol, or a combination thereof from glycerol, the process comprising:

contacting glycerol with a member selected from the group consisting of alkali, heat under vacuum, steam, an ion exchange resin, a solid, and combinations of any thereof, thus producing a purified glycerol.

2. The process of claim 1, wherein the monochloropropanediol content of the purified glycerol is less than one thousand parts per billion.

3. The process of claim 1, wherein the monochloropropanediol content of the purified glycerol is less than one hundred parts per billion.

4. The process of claim 1, wherein the monochloropropanediol content of the purified glycerol is less than fifty parts per billion.

5. The process of claim 1, wherein the monochloropropanediol content of the purified glycerol is less ten parts per billion.

6. The process of claim 1, wherein the glycerol is obtained from at least one of fat splitting, soapmaking, and biodiesel manufacture.

7. The process of claim 1, wherein the glycerol comprises crude glycerol, the process further comprising:

raising the pH of the crude glycerol; and

drying the crude glycerol.

8. The process of claim 7, wherein the pH of the crude glycerol is raised to at least a pH of 9.

9. The process of claim 1, wherein the contacting glycerol with heat under vacuum below an evaporation point of the glycerol.

10. The process of claim 1, wherein the contacting glycerol with heat under vacuum is carried out in the presence of steam at a level of greater than 0.9 weight percent steam based on the weight of glycerol.

11. The process of claim 1, the contacting glycerol with heat under vacuum comprises evaporating the glycerol.

12. The process of claim 11, further comprising condensing the evaporated glycerol and wherein at least one of the glycidol and monochloropropandiol contaminants is removed as a vapor phase.

13. The process of claim 1, wherein the contacting glycerol with a solid comprises contacting glycerol with a solid selected from the group consisting of silica, cellulose, wood pulp, activated carbon, ion exchange resins, diatomaceous earth, and combinations of any thereof.

14. The process of claim 1, wherein the ion exchange resin is selected from the group consisting of strong base ion exchange resins, weak base ion exchange resins, strong acid ion exchange resins, weak acid ion exchange resins, mixed bed resins, nonfunctional resins, and combinations of any thereof.

15. The process of claim 14, wherein the contacting glycerol with an ion exchange resin further comprises heating the contacting the glycerol and ion exchange resin at a temperature greater than 20 °C.

16. The process of claim 14, further comprising regenerating the ion exchange resin.

17. The process of claim 14, further comprising contacting the glycerol with carbon.

18. The process of claim 14, wherein the glycerol is contacted with a base ion exchange resin followed by contacting the glycerol with an acid ion exchange resin.

19. The process of any one of claims 1-18, wherein a content of a monochloropropanediol, the glycidol, or a combination of any thereof is less in the contacted glycerol than in the glycerol.

20. A product produced by the process of any one of claims 1-19 for use in a product selected from the group consisting of food, beverages, personal care products, oral care products, tobacco, pharmaceuticals, polyether polyols, propylene glycol, recreational vehicle fluids, per foods, alkyd resins, deicers, completion and fracture fluids, drilling muds, polyglycerols, concrete and asphalt lubrication, epichlorohydrin production and combinations of any thereof.

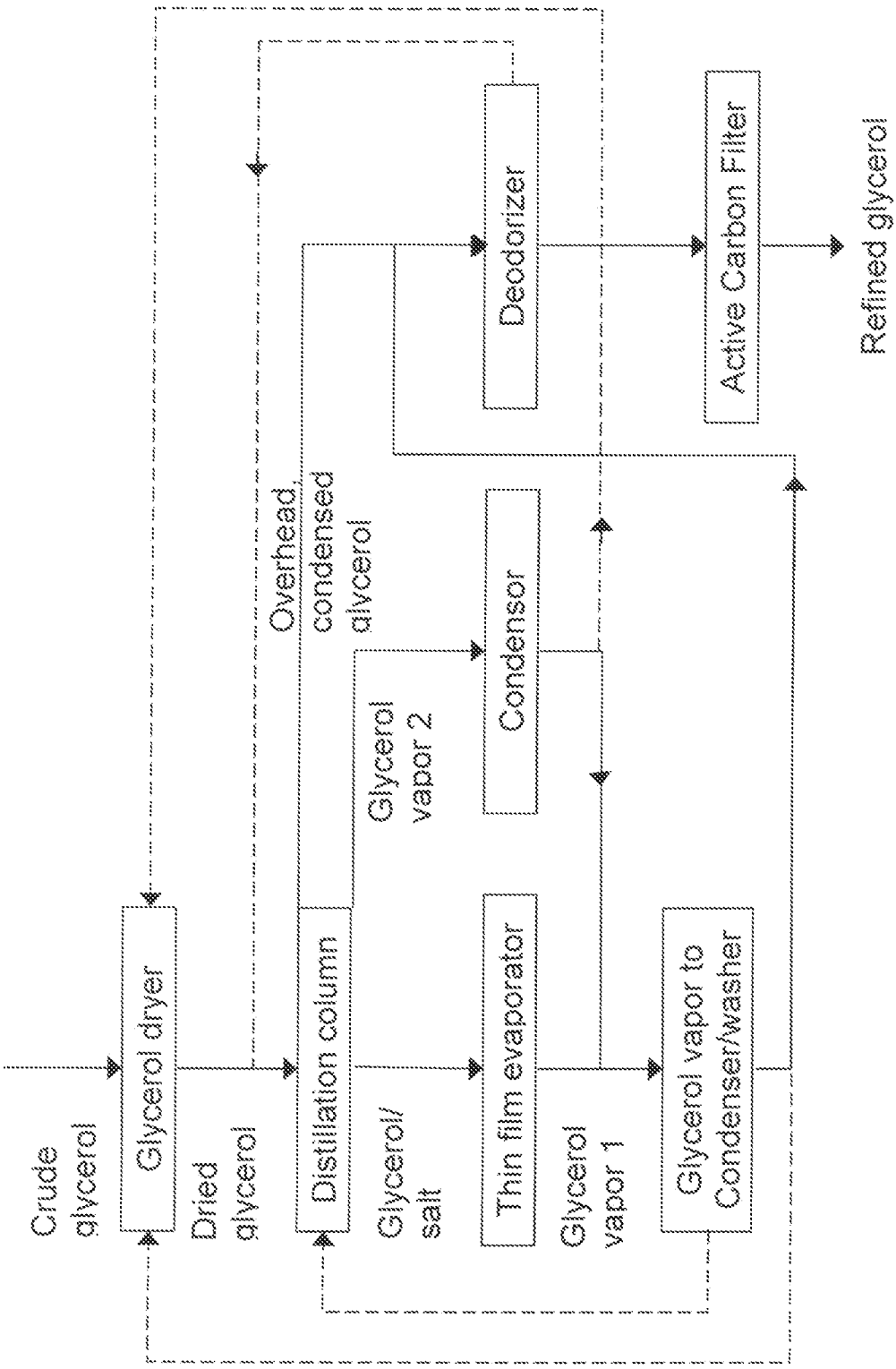
Crude glycerol
Glycerol dryer
Dried glycerol
Distillation column
Overhead condensed glycerol
Glycerol/ salt
Glycerol vapor 2
Thin film evaporator
Condensor
Glycerol vapor 1
Glycerol vapor to Condenser/washer
Deodorizer
Active Carbon Filter
Refined glycerol

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/58121

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08G 65/04 (2013.01)
USPC - 528/518;549/518;568/844; 568/868; 568/861
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)
IPC(8) -C08G 65/04 (2013.01)
USPC ? 528/518;549/518;568/844; 568/868; 568/861

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents, non-patent literature, search term limited

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Patbase (pgpb, uspt, usoc, epab, jpab, dwpi, tdbd), Dialog Proquest (npl), Google Patents (pl, npl), Google scholar (pl, npl); Search Terms: purify, recover, glycerin, glycerine, glycerol, polyol, sulphonic, sulfonic, ion, exchange, acidic, acid, basic, base, alkaline, drying, dried, monochloropropanediol, mcpd, chloropropane, chlorohydrin, ppm, pp

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Duque, J. "Design and analysis of technological schemes for glycerol conversion to added value products" Thesis submitted in partial fulfillment of the requirements for the degree of: Doctor of Philosophy in Engineering. Department of Electricity, Electronic and Computational Engineering. National University of Colombia, 2011.	1-19
Y	US 3,092,669 A (DENTON, et al.) 04 June 1963 (04.06.1963) entire document, especially col 2, ln 43-47, 56-61, 66-70; col 3, ln 62-66; col 4, ln 66-69, 74-col 5, ln 2	1-19
Y	Liu, Wan-yun. "Development and validation of an improved method for determination of chloropropanols in paperboard food packaging by GC-MS." PhD diss., Rutgers University-Graduate School-New Brunswick, May 2012.	2-5, 19/(2-5)
Y	US 4,655,879 A (BROCKMANN, et al) 07 April 1987 (07.04.1987) entire document, especially col 2, ln 18-22, 25-27, 46-49; col 3, ln 31-36; col 4, ln 16-23	7-8, 10, 19/(7-8,10)
Y	WO 2011/030204 A1 (LOURENCO, et al.) 17 March 2011 (17.03.2011) entire document, especially pg 1, ln 6-7; pg 3, ln 7-9, 33-35; pg 4, ln 11-17, 25-28; pg 5, ln 20-23; pg 6, ln 30-31	14-18, 19/(14-18)
Y	US 2011/0004031 A1 (CRUZ, et al.) 06 January 2011 (06.01.2011) entire document, especially para [0014], [0040], [0052]-[0053]	18, 19/18

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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
23 December 2013 (23.12.2013)	30 JAN 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/58121

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.