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(54) Benævnelse: **FREMSTILLING OG SEPARERING AF EN DICARBOXYLSYRE-INDEHOLDENDE BLANDING UNDER ANVENDELSE AF EN DICARBOXYLATFORM AF ET ANIONBYTTERKROMATOGRAFIRESIN**

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DESCRIPTION

FIELD OF THE INVENTION

[0001] The present invention generally relates to processes for separating a di-carboxylic acid or salt thereof from a mixture containing the di-carboxylic acid or salt thereof and one or more other components. Further, the present invention generally relates to processes for preparing an aldaric acid, such as glucaric acid from glucose, which includes separating the aldaric acid from the reaction product.

BACKGROUND OF THE INVENTION

[0002] Processes for the preparation of di-carboxylic acids are known to produce crude mixtures containing various on-path and off-path carboxylic acids. Various waste streams from other processes may also contain di-carboxylic acids. Thus, separation of these mixtures and streams is necessary in order to obtain a sufficiently pure product or recover useful fractions of waste streams containing di-carboxylic acids. Methods for the separation and purification of carboxylic acids have been disclosed (See, for example, U.S. Patent No. 6,284,904, U.S. Patent Application Publication No. 2013/0345473; J. Chromatogr. A. 850, 1999, p187; J. Chromatogr. 57, 1971, p353; J. Chromatogr. 253, 1982, p87). Several of the methods disclosed in the art describe the use of anion exchange column chromatography with particular eluents such as organic acids (e.g., acetic acid or formic acid), bases (e.g., sodium bicarbonate or sodium tetraborate), and strong acids (e.g., sulfuric acid or hydrochloric acid). For example, U.S. 2,664,441 discloses a process for separating an acid of the group consisting of acetic acid, lactic acid, glycolic acid, succinic acid, pyrrolidone carboxylic acid, malic acid, citric acid and oxalic acid from its mixture with at least one other acid of said group which comprises adsorbing such a mixture of acids on an anion exchange bed which has been conditioned exchanger being about 1 to 1.5 pH units less than the pK of the weakest acid contained in said mixture, then eluting the exchanger with a solution of a strong mineral acid.

[0003] Although industrial chromatographic separation methods are one approach for the separation of mono-carboxylic acids and di-carboxylic acids, the use of strong acids, organic acids, bases or eluent components other than water that may be necessary to produce an effective separation and elution is not desirable. These additional components increase reagent costs and may require disposal if recovery is not possible after use. Further, these additional components may necessitate additional equipment for removal and recovery after use, which increases process costs. Accordingly, there remains a need for an industrially advantageous separation process in which the eluent does not introduce extraneous components into process streams. Further, in processes for the production of di-carboxylic acids in which the reaction solvent is water, there remains a need for an industrially advantageous separation process in which water can be used as the primary eluent to facilitate the separation and elution of di-carboxylic acids from other components present in a crude reaction mixture.

[0004] Moreover, in processes for preparing di-carboxylic acids, such as in the oxidation of glucose to glucaric acid as described in U.S. Patent No. 8,669,397 and oxidation of a pentose to pentaric acid (e.g., xylose to xylaric acid) as described in U.S. Patent No. 8,785,683, there remains a need for efficient and cost effective separation techniques for the desired di-carboxylic acid to facilitate improved process yields and economics.

SUMMARY OF THE INVENTION

[0005] Briefly, the present invention includes processes for producing an extract comprising a di-carboxylic acid or salt thereof as defined in the present claims comprising: contacting a separation media in a separation zone with a feed mixture comprising the di-carboxylic acid or salt thereof and a second component, wherein at least a portion of the di-carboxylic acid or salt thereof is separated from the second component and a raffinate is formed comprising at least a portion of the second component; removing the raffinate from the separation zone; and eluting the di-carboxylic acid or salt thereof from the separation media with an eluent comprising water to form the extract comprising the di-carboxylic acid or salt thereof, wherein the separation media comprises a di-carboxylate form of an anion exchange chromatography resin, wherein the di-carboxylate form of the anion exchange chromatography resin is prepared by conditioning the anion exchange chromatography resin with a di-carboxylic acid, and wherein the extraneous acid concentration of the eluent, prior to contact with the separation media, is less than 0.1 wt.%, less than 0.05 wt.%, or less than 0.01 wt.%.

[0006] The present invention also includes processes for preparing an aldaric acid, such as glucaric acid from glucose. The processes comprise: oxidizing an aldose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising the aldaric acid and on-path intermediates to the aldaric acid; removing the oxidation product from the presence of the oxidation catalyst; and producing an extract comprising the aldaric acid according to any of the separation processes described herein, wherein the feed mixture comprises the aldaric acid as the di-carboxylic acid and on-path intermediates to the

aldaric acid as the second component obtained from the oxidation product.

[0007] Other objects and features will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

FIG. 1 depicts an example of a process flow diagram for an oxidation process including a separation process in accordance with the present invention. Other variations are possible.

FIG. 2 depicts the ion-chromatography chromatogram for the concentrated feed in Example 2.

FIG. 3 depicts the ion-chromatography chromatogram for the concentrated extract stream in Example 2.

FIG. 4 presents a representative concentration profile for a separation resin operated under overloading conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] Various aspects of the present invention relate to processes for separating a di-carboxylic acid from a mixture containing the di-carboxylic acid and one or more other components Further, aspects of the present invention relate to processes for preparing an aldaric acid, such as glucaric acid from glucose, which includes separating the aldaric acid from the reaction product. Also, various aspects of the present invention relate to processes for preparing an aldaric acid from an aldose, in which the processes have enhanced overall process yield.

[0010] As used herein, the terms "aldaric acid," "aldonic acid," and species thereof such as "glucaric acid" or "gluconic acid" or "xylaric acid" or "xylonic acid" each refer collectively to the acid and any corresponding lactones of that species that may be present. For example, in the presence of water, glucaric acid is known to be in equilibrium with glucaro-1,4-lactone, glucaro-6,3-lactone, and glucaro-1,4:6,3-dilactone. Therefore, unless specified otherwise, reference to "glucaric acid" is inclusive of these glucarolactone species as well. Also, although the following description refers to feed mixtures containing various mono-carboxylic acids and di-carboxylic acids, the separation processes of the present invention include those where at least a portion of these acids are in salt form, such as sodium, potassium, calcium, and magnesium salts (e.g., sodium glucarate), and the extract comprises a di-carboxylic acid or salt thereof.

[0011] One aspect of the present invention is directed to a chromatographic separation process for separating a di-carboxylic acid from a mixture containing the di-carboxylic acid and one or more other components wherein the eluent comprises water. A chromatographic separation process that uses water as eluent is advantageous because the introduction of extraneous acids or bases (e.g., sulfuric acid, hydrochloric acid, acetic acid, formic acid, sodium bicarbonate, sodium tetraborate, etc.) as eluents is reduced or avoided. A chromatographic separation process that uses water as eluent is especially beneficial in processes where water is the primary solvent because additional equipment for separation of the di-carboxylic acid from the eluent may not be required.

[0012] Another aspect of the present invention is directed to a chromatographic separation process for separating a di-carboxylic acid from a feed mixture containing the di-carboxylic acid and one or more other components wherein the separation media is highly selective for separating the di-carboxylic acid from other components in the feed. A highly efficient separation media and process for using this media advantageously provides an extract containing a greater portion of the desired di-carboxylic acid from the feed and a raffinate containing a greater portion of components from the feed that may be recycled.

[0013] Yet another aspect of the present invention is directed to an oxidation process for preparing aldaric acid from an aldose with enhanced overall process yield. Surprisingly, it has been found that a high overall aldaric acid process yield may be obtained when the oxidation reaction is controlled within certain endpoint limits and the di-carboxylic acid component of the oxidation product is efficiently separated from unreacted aldose and on-path intermediates, and thereby facilitating the recycle of the on-path intermediates to the oxidation reaction step.

[0014] In another aspect of the invention, separation processes of the present invention 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 product mixture obtained from an oxidation process for preparing aldaric acid from an

aldose) prior feeding the mixture to a chromatographic separation.

[0015] Also, another aspect of the present invention is directed to various integrated processes that include the separation process or separation media of the present invention.

Separation Processes and Media

[0016] The separation processes of the present invention include chromatographic separation processes using a separation media to produce an extract comprising a di-carboxylic acid. Typically, the processes comprise contacting a separation media in a separation zone with a feed mixture comprising the di-carboxylic acid and a second component wherein at least a portion of the di-carboxylic acid and the second component are retained on the separation media. The second component can comprise one constituent or a mixture of different constituents. Following contact of the separation media with the feed mixture, the process comprises eluting at least a portion of the second component from the separation media with an eluent to form a raffinate comprising the second component. In this step, at least a portion of the di-carboxylic acid is separated from the second component, and a raffinate is formed comprising at least a portion of the second component. The processes further include removing the raffinate from the separation zone and eluting at least a portion of the di-carboxylic acid from the separation media with the eluent to form the extract comprising the di-carboxylic acid. The eluent in these processes comprises water. The steps in the separation process may be conducted in any order and/or simultaneously. For example, feed mixture can be contacted with the separation media while raffinate is removed from the separation zone, and eluent can be added while raffinate and then extract are removed from the separation zone.

[0017] The separation processes of the present invention can also include an optional rinse step comprising rinsing the separation media, for example, with liquid such as eluent or other wash liquid to remove remaining feed constituents. After rinsing, the rinse liquid can be discharged from the separation zone.

[0018] Optionally, a closed loop recirculation step may be performed. During recirculation, the mobile phase is re-contacted with the separation media. Typically, feed mixture and eluent are not introduced to the separation zone and raffinate is not removed during recirculation of the extract.

[0019] Surprisingly, in various separation processes of the present invention, water has been found to be an effective eluent to elute the di-carboxylic acid from the separation media. Therefore, in separation processes in accordance with the present invention the eluent comprises water. In various embodiments, the eluent comprising water contains little to no extraneous acid. In these and other embodiments, the eluent comprising water contains little to no extraneous base. "Extraneous acid" refers to acid that is added to the eluent. Similarly, "extraneous base" refers to base that is added to the eluent. Extraneous acid can also include acids that are not present in the separation feed mixture. Extraneous acids can include inorganic acids such as sulfuric acid and hydrochloric acid. Extraneous acids can also include organic acids such as acetic acid, formic acid, and oxalic acid. Oxalic acid may be present in the feed mixture of some processes. Thus, in some processes, the extraneous acid includes sulfuric acid, hydrochloric acid, acetic acid, and formic acid. Bases include, for example sodium hydroxide and potassium hydroxide.

[0020] Accordingly, one process for producing an extract comprising a di-carboxylic acid in accordance with the present invention comprises contacting a separation media in a separation zone with a feed mixture comprising the di-carboxylic acid and a second component, wherein at least a portion of the di-carboxylic acid is separated from the second component and a raffinate is formed comprising at least a portion of the second component; removing the raffinate from the separation zone; and eluting the di-carboxylic acid from the separation media with an eluent comprising water to form the extract comprising the di-carboxylic acid, wherein the extraneous acid concentration of the eluent, prior to contact with the separation media, is less than 0.1 wt.%, less than 0.05 wt.%, or less than 0.01 wt.%. In various embodiments, the eluent does not contain any extraneous acid (e.g., does not contain any measurable amount of extraneous acid). Further, in some embodiments, the eluent consists essentially of water or is water. In these various processes, when the separation media is contacted with the feed mixture, at least a portion of the di-carboxylic acid and the second component are retained on the separation media. Also, the raffinate comprising the second component is formed by eluting at least a portion of the second component from the separation media with the eluent. As a result of these separation processes, the weight ratio of the di-carboxylic acid to the second component in the extract is greater than the weight ratio of the di-carboxylic acid to the second component in the feed mixture and/or the raffinate.

[0021] In various separation processes of the present invention, the eluent is makeup water and/or process water. Makeup water can be, for example, deionized or distilled water. Process water is typically obtained from a process stage that generates water. For example, processes integrating a separation process of the present invention may include one or more stages for the concentration of various streams such as the extract, raffinate, or the feed mixture. In these stages, water may be removed from these process streams, for example, by flashing or evaporating to form process water. The process water removed from these streams may contain minor amounts of non-extraneous feed mixture components, such as mono- and di-carboxylic acids.

[0022] The eluent (e.g., water with little to no extraneous acid content, makeup water, and/or process water) can also be characterized by its pH. Accordingly, the pH of the eluent comprising water can be between 5 and 7.5, between 5.5 and 7.5, between 6 and 7.5, between 6.5 and 7.5, between 5 and 7, between 5.5 and 7, between 6 and 7, between 6.5 and 7, or approximately neutral.

[0023] Generally, the flow rate of the eluent to the separation zone is at least 1, at least 10, at least 50, at least 100, at least 500, or at least 1,000 kg/hr, or at least 10,000 kg/hr.

[0024] The feed mixture may optionally be degassed (or deoxygenated) using standard procedures to prevent or limit oxidative damage to the separation media and thereby extend the operational lifetime of the separation media. Standard procedures can include bubbling an inert gas such as nitrogen through the feed solution and can also include subjecting the feed to solution to a vacuum or low pressure protocol to facilitate degassing.

[0025] A wide variety of separation media can be used in the separation processes of the present invention (e.g., silicas, functionalized silicas, aluminas, carbons, functionalized and unfunctionalized polystyrene, polyacrylamide, cross-linked polystyrenes, polyacrylates and other resins). For example, separation media comprising a basic chromatography media has been found to be particularly useful for the separation processes of the present invention. The basic chromatography media can comprise a basic chromatography resin. More particularly, the basic chromatography resin can comprise an anion exchange chromatography resin.

[0026] In various embodiments, the basic chromatography media comprises a weakly basic anion exchange chromatography resin. Weakly basic anion exchange chromatography resin can be further specified on the percentage of weak base and strong base functionality. Weak base functionality of an anion exchange chromatography resin is typically produced by activating the resin with a secondary amine, resulting in primary, secondary, or tertiary amine functional groups. On the other hand, strong base functionality of an anion exchange chromatography resin is typically produced by activating the resin with a tertiary amine, resulting in quaternary amine functional groups. Basic anion exchange chromatography resins can be bifunctional by including a mixture of weak base and strong base functionalities. U.S. Patent Nos. 4,952,608; 4,988,738; 5,464,875; and 6,699,913, describe various processes for preparing basic anion exchange chromatography resins. Accordingly, in various embodiments, the basic chromatography media comprises from 60% to 100%, from 60% to 90%, from 70% to 90%, from 70% to 85%, from 70% to 80%, or from 75% to 80% weak base functionality. In these and other embodiments, the basic chromatography media comprises from 0% to 40%, from 10% to 25%, from 0% to 10%, from 5% to 40%, from 5% to 25%, from 5% to 10%, from 10% to 40%, from 10% to 35%, from 15% to 35%, from 15% to 30%, from 20% to 30%, or from 20% to 25% strong base functionality.

[0027] Applicants have discovered that a separation media comprising a di-carboxylate form of an anion exchange chromatography resin is especially suited for various separation processes of the present invention. Accordingly, the separation media comprising the di-carboxylate form of the anion exchange chromatography resin is used in various separation processes, including any of the separation processes described herein. Yet another process for producing an extract comprising a di-carboxylic acid in accordance with the present invention comprises contacting a separation media in a separation zone with a feed mixture comprising the di-carboxylic acid and a second component, wherein at least a portion of the di-carboxylic acid is separated from the second component and a raffinate is formed comprising at least a portion of the second component; removing the raffinate from the separation zone; and eluting the di-carboxylic acid from the separation media with an eluent comprising water to form the extract comprising the di-carboxylic acid, wherein the separation media comprises a di-carboxylate form of an anion exchange chromatography resin. As noted, when the separation media is contacted with the feed mixture, at least a portion of the di-carboxylic acid and the second component are retained on the separation media. Also, the raffinate comprising the second component is formed by eluting at least a portion of the second component from the separation media with the eluent. As a result of these separation processes, the weight ratio of the di-carboxylic acid to the second component in the extract is greater than the weight ratio of the di-carboxylic acid to the second component in the feed mixture and/or the raffinate.

[0028] Without being bound by theory, applicants believe that separation media comprising the di-carboxylate form of an anion exchange chromatography resin do not function primarily as conventional ion exchange resins where ions on the resin exchange with one or more components in the feed solution thereby reversibly binding the component to the exchange resin. Instead, the separation media of the present invention is believed to bind or attract the di-carboxylic acid primarily by chemical affinity. As a result of this functionality, water can be used more effectively as an eluent when using the separation media.

[0029] The separation media for use in various separation processes described herein can comprise a C_2-C_6 di-carboxylate form of the anion exchange chromatography resin. In various embodiments, the di-carboxylate form of the anion exchange chromatography resin comprises an aldarate form of the anion exchange chromatography resin. In further embodiments, the di-carboxylate form of the anion exchange chromatography resin is selected from the group consisting of the oxalate, tartronate, malonate, tartrate, succinate, xylarate, arabinarate, ribarate, glutarate, glucarate, adipate, and mixtures thereof. One preferred form of the anion exchange chromatography resin includes the glucarate form. Another preferred form of the anion exchange chromatography resin includes the xylarate form. Yet another preferred form of the anion exchange chromatography resin includes the oxalate form.

[0030] The di-carboxylate form of the anion exchange chromatography resin is prepared by conditioning the anion exchange

chromatography resin with a di-carboxylic acid solution (i.e., flowing a di-carboxylic acid solution through a column containing the resin). For example, to prepare the glucarate form of the anion exchange chromatography resin, the anion exchange chromatography resin can be conditioned by flowing a solution of glucaric acid through the resin.

[0031] The di-carboxylic acid used to condition the anion exchange chromatography resin can comprise a di-carboxylic acid that is the same as an acid that is present in the feed mixture to the separation process. For example, in various separation processes of the present invention, the feed mixture comprises a di-carboxylic acid, which can include glucaric acid, and the separation media can comprise the glucarate form of an anion exchange chromatography resin.

[0032] Also, the di-carboxylic acid used to condition the anion exchange chromatography media can comprise a di-carboxylic acid that is present in the feed mixture to the separation process and is also the highest concentration di-carboxylic acid in the feed mixture. For example, in various separation processes of the present invention, the feed mixture comprises glucaric acid and if glucaric acid is the highest concentration di-carboxylic acid in the feed, then the separation media can comprise the glucarate form of an anion exchange chromatography resin.

[0033] Further, the di-carboxylic acid used to condition the anion exchange chromatography resin can comprise a di-carboxylic acid that is present in the feed mixture to the separation process and is also the di-carboxylic acid with the lowest pKa in the feed mixture. For example, in various separation processes of the present invention, the feed mixture comprises a mixture of di-carboxylic acids such as oxalic acid and glucaric acid and since oxalic acid has a pKa lower than glucaric acid, then the separation media can comprise the oxalate form of an anion exchange chromatography resin.

[0034] In various embodiments, the feed mixture can be used to condition the anion exchange chromatography resin. Using the feed mixture, which comprises the di-carboxylic acid selected as the conditioning acid, advantageously avoids costs associated with using a purified source of the di-carboxylic acid as the conditioning agent.

[0035] Conditioning of the anion exchange chromatography resin is preferably performed in a manner in which a high percentage (e.g., 90-100%) of the functional sites are conditioned to the di-carboxylate form. For example, in some circumstances, the pH of the conditioning solution may be adjusted (e.g., adjusted to a higher pH) to enhance the conditioning process such that a high percentage of the functional sites of the resin are converted to the di-carboxylate form. Conductivity and pH measurements can be used on the resin conditioning agent effluent to monitor the point at which the conditioning is completed.

[0036] The separation media as described herein can comprise a resin (e.g., a cross-linked polymer or copolymer of acrylonitrile, acrylic acid, or methacrylic acid). In various embodiments, the resin comprises a styrene-divinylbenzene (DVB) copolymer. In further embodiments, the resin comprises an acrylate-divinylbenzene (DVB) copolymer, methyl acrylate-divinylbenzene (DVB) copolymer, polyacrylonitrile polymer, polyacrylate polymer, or polymethacrylate polymer. For example, one preferred separation media in accordance with the present invention comprises an anion exchange chromatography resin in the di-carboxylate form wherein the resin comprises a styrene-divinylbenzene (DVB) copolymer.

[0037] The resin can be gel-type or macroporous resins. Gel-type resins are gel polymers that develop interchain porosity on swelling by a miscible liquid and have a pore size distribution having a significant fraction of micropores (i.e., pores having diameters less than 20 Å). In the polymerization process of gel-type resins, a cross-linker is more or less evenly distributed throughout the matrix. The pores are very small and their size is typically only a few Angstroms (Å), but the size is relatively constant. Hence, the gel-type resin matrix has a pseudo-crystalline structure. Macroporous resins are porous polymeric material with a non-collapsible, permanent pore structure in both the dry and solvated states and have a pore size distribution having a significant fraction of macropores (i.e., pores having diameters larger than 500 Å). Macroporous resins can be prepared using porogens or phase extenders to create artificial porosity in the tri-dimensional matrix. Once the polymerization reaction is finished, the porogen is removed from the matrix leaving voids in the polymer structure. In various embodiments, the separation media comprises a macroporous resin.

[0038] The separation processes of the present invention involve fractionating (i.e., separating) a di-carboxylic acid from a feed mixture comprising a di-carboxylic acid and a second component. Typically, the feed mixture comprises the di-carboxylic acid and the second component dissolved in water. Accordingly, the dissolved solids content of the feed mixture is generally at least 20 wt.%, at least 30 wt.%, at least 40 wt.%, or at least 50 wt.%, or at least 60 wt.%. The dissolved solids content of the feed mixture can be from 20 wt.% to 70 wt.%, from 20 wt.% to 60 wt.%, from 30 wt.% to 70 wt.%, from 30 wt.% to 60 wt.%, from 30 wt.% to 50 wt.%, or from 40 wt.% to 60 wt.%. The di-carboxylic acid concentration in the feed mixture can comprise at least 20 wt.%, at least 30 wt.%, at least 40 wt.%, or at least 50 wt.% of the dissolved solids content. In various embodiments, the di-carboxylic acid concentration in the feed mixture is from 20 wt.% to 70 wt.%, from 20 wt.% to 60 wt.%, from 30 wt.% to 70 wt.%, from 30 wt.% to 60 wt.%, from 40 wt.% to 70 wt.%, or from 40 wt.% to 60 wt.% of the dissolved solids content. Further, the second component concentration in the feed mixture is from 10 wt.% to 80 wt.%, from 20 wt.% to 80 wt.%, from 30 wt.% to 80 wt.%, from 20 wt.% to 50 wt.%, from 30 wt.% to 50 wt.%, from 30 wt.% to 40 wt.%, from 35 wt.% to 50 wt.%, or from 35 wt.% to 45 wt.% of the dissolved solids content.

[0039] Generally, the separation processes of the present invention form an extract comprising at least a portion of the di-carboxylic

acid. In these processes, the extract can comprise at least 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, or at least 90 wt.% of the di-carboxylic acid content of the feed mixture. In various embodiments, the extract comprises from 55 wt.% to 100 wt.%, from 55 wt.% to 99 wt.%, from 55 wt.% to 95 wt.%, from 55 wt.% to 90 wt.%, from 55 wt.% to 85 wt.%, from 55 wt.% to 80 wt.%, from 60 wt.% to 90 wt.%, from 60 wt.% to 85 wt.%, from 60 wt.% to 80 wt.%, from 70 wt.% to 90 wt.%, from 70 wt.% to 85 wt.%, or from 70 wt.% to 80 wt.% of the di-carboxylic acid content of the feed mixture.

[0040] Generally, the separation processes also forms a raffinate comprising at least a portion of the second component. The raffinate can comprise at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, or at least 95 wt.% of the second component content of the feed mixture. In various embodiments, the raffinate comprises from 60 wt.% to 100 wt.%, from 60 wt.% to 95 wt.%, from 60 wt.% to 90 wt.%, from 70 wt.% to 100 wt.%, from 70 wt.% to 95 wt.%, from 70 wt.% to 90 wt.%, from 80 wt.% to 100 wt.%, from 80 wt.% to 95 wt.%, or from 80 wt.% to 90 wt.% of the second component content of the feed mixture.

[0041] The separation processes in accordance with the present invention are useful for separating a di-carboxylic acid (i.e., at least one di-carboxylic acid or a mixture of two or more di-carboxylic acids), and/or its corresponding salt from a feed mixture. The di-carboxylic acid comprises a C_2 to C_6 di-carboxylic acid. Further, the di-carboxylic acid can comprise an aldaric acid, such as a C_3 to C_6 aldaric acid. In various embodiments, the di-carboxylic acid comprises one or more acids selected from the group consisting of oxalic acid, tartronic acid, malonic acid, tartaric acid, succinic acid, xylaric acid, arabinaric acid, ribaric acid, glutaric acid, glucaric acid, adipic acid and mixtures thereof.

[0042] In various embodiments, the di-carboxylic acid comprises a C_6 di-carboxylic acid. One preferred C_6 di-carboxylic acid comprises glucaric acid. In other embodiments, the di-carboxylic acid comprises a C_5 di-carboxylic acid. Preferred C_5 di-carboxylic acids include C_5 aldaric acids. In various embodiments, the C_5 aldaric acids acid comprises at least one acid selected from the group consisting of xylaric acid, ribaric acid, arabinaric acid, and mixtures thereof.

[0043] The second component of the feed mixture generally includes one or more constituents other than the di-carboxylic acid. For example, the second component comprises a C_1 to C_6 mono-carboxylic acid (i.e., at least one mono-carboxylic acid or a mixture of two or more mono-carboxylic acids). Further, the second component can comprise an aldonic acid, such as a C_3 to C_6 aldonic acid. In various embodiments, the second component comprises a mono-carboxylic acid selected from the group consisting of a C_2 mono-carboxylic acid, a C_3 mono-carboxylic acid, a C_4 mono-carboxylic acid, a C_5 mono-carboxylic acid, a C_6 mono-carboxylic acid, and mixtures thereof.

[0044] In various embodiments, the second component comprises a C_6 mono-carboxylic acid selected from the group consisting of gluconic acid, guluronic acid, glucuronic acid, and mixtures thereof. In further embodiments, the second component comprises a mixture comprising gluconic acid, guluronic acid, glucuronic acid, one or more ketogluconic acids. In other embodiments, the second component comprises at least one C_5 aldonic acid. In various embodiments, the C_5 aldonic acid comprises at least one acid selected from the group consisting of xylonic acid, ribonic acid, arabinonic acid, and mixtures thereof.

[0045] The second component can also comprise a sugar (in combination with one or more C_1 to C_6 mono-carboxylic acids). Typically, the sugar is selected from the group consisting of a pentose, hexose, and mixtures thereof. In various embodiments, the second component comprises glucose. In other embodiments, the second component comprises a pentose. In various embodiments, the pentose comprises at least one sugar selected from the group consisting of xylose, ribose, arabinose, and mixtures thereof.

[0046] Accordingly, the second component can comprise a mixture of the mono-carboxylic acids and sugars mentioned above.

[0047] Also, although the description herein refers to various mono-carboxylic acids and di-carboxylic acids, it should be noted that the processes of the present invention are also suitable for use in connection with the separation of such acids in circumstances where at least a portion of these acids are in salt form, such as sodium (e.g., sodium glucarate), potassium, calcium, magnesium, or other salt.

[0048] Further, the feed mixture, extract and/or raffinate can be essentially free of nitric acid and salts thereof. For example, the feed mixture, extract and/or raffinate can contain less that than 0.1 wt.% or less than 0.01 wt.% of nitric acid and salts thereof. The feed mixture, extract and/or raffinate can be free of nitric acid and salts thereof.

[0049] The separation processes of the present invention can be batch, semi-batch, or continuous. Advantageously, the separation processes of the present invention can be continuous separation processes. As a result, these separation processes can be integrated into existing continuous processes without significantly impacting production rates. In any of the separation processes disclosed herein the contacting the separation media with the feed mixture; eluting the second component from the separation media; removing the raffinate from the separation zone; and eluting the di-carboxylic acid from the separation media can be performed continuously.

[0050] In various separation processes of the present invention the separation zone can be a simulated moving bed (SMB) chromatography stage. Also, the separation zone can comprise a plurality of chromatography beds. The SMB stage can comprise sequential SMB (SSMB). Furthermore, the SMB chromatography stage comprises continuous SMB.

[0051] SMB is generally considered a continuous separation process that has many important industrial applications. In comparison to batch chromatography, SMB processes often have higher productivities, higher product purities and lower solvent consumption. See chapter 1 in Encyclopedia of Industrial Biotechnology: Bioprocesses, Bioseparation and Cell Technology: Wiley and Sons, 2009. SMB has been used in recovery and purification of several large-scale chemical products, including *p*-xylene, ethylbenzene, *p*-cresol, and *p*-cymene. SMB is employed at very large scale for separating glucose and fructose in the production of high fructose corn syrups using water alone as an eluent. See for example, Chem. Eng. Sci. 1989, 44, p 1011. SMB has also been used for the separation of carboxylic acids. See for example, Biotechnol. Prog. 2004, 20, p179 and J. Chromatogr. A. 2009, 1216, p8793.

[0052] In an SMB process, the use of multiple columns in a closed loop, coupled with coordinated valve switching between columns, enables the simulated movement of the stationary phase (separation media) in a counter-current direction to the movement of the mobile phase. A feed mixture containing two or more components to be separated is fed to the middle of the column configuration. The component that has the higher affinity for the solid phase travels in the direction of the simulated movement of the stationary phase while the component with the lower affinity for the stationary phase travels in the direction of the liquid-phase flow. This enables the separation and withdrawal of enriched fractions of the components as extract and raffinate streams.

[0053] The SMB can be continuous or sequential or comprise a combination of a continuous method and a sequential method. Sequential SMB can be considered a "continuous process" from an overall process stand point if operated under certain conditions. In a continuous SMB process, feed, eluent, raffinate, and extract streams typically flow continuously. In the sequential SMB process, some of the streams do not necessarily flow continuously. The sequential SMB process commonly comprises three basic phases: a feeding phase, an elution phase and a circulation phase. During the feeding phase, a feed solution and possibly also an eluent during a simultaneous eluting phase, is introduced into a predetermined column containing one or more packed beds, and simultaneously a product fraction or fractions are withdrawn. During the eluting phase, the eluent is introduced into a predetermined packed bed or predetermined packed beds, and during these phases two, three or even four product fractions are withdrawn. During the circulation phase the columns are connected into a loop, whereby no feed solution or eluent is supplied to the partial packed beds and no product fractions are withdrawn. However, circulation as such takes place during the three phases.

[0054] The continuous SMB process has been described, for example, in U.S. Patent No. 2,985,589 (Universal Oil Prod. Co (UOP)). In this process the mixture to be fractionated is introduced into one partial packed bed and an eluent is introduced into another partial packed bed, and two product fractions are withdrawn substantially simultaneously. U.S. Patent No. 5,198,120 (Japan Organo Co., Ltd.) describes a continuous SMB process in which the feed point is fixed. The feed is introduced sequentially once a cycle and simultaneously with the introduction of the feed a first extract fraction and raffinate are taken out from the system. The examples of this patent use a SMB consisting of eight packed columns linked with each other in series.

[0055] Sequential SMB (SSMB) processes are described in U.S. Patent Nos. 4,332,623 (Mitsubishi Chemical Industries, Ltd.), 4,379,751 (Sanmatsu Kogyo Co., Ltd.) and 4,970,002 (Mitsubishi Kasei Technoengineers Ltd.), for instance. A sequential SMB process for the recovery of betaine and sucrose from beet molasses is described in U.S. Patent No. 5,127,957 (Heikkilä, H. et al.). SSMB is an enhanced version of the original SMB chromatography process, proposed early the 1980s by Yoritomi et al (US patent 4,379,751). These SSMB processes are today the most efficient chromatographic processes for separation a feed stream into two product streams, the "extract" and the "raffinate" streams, and are used in a wide range of applications and industries (food, chemistry, antibiotics, and pharmaceuticals). While conventional SMB has only one step per column (six steps for a six column design), SSMB processes have at least two or three steps per column, which allows a better separation by increasing the injection and recovery accuracies.

[0056] To increase the separation capacity, yields and fraction purities and fraction dry substance concentrations, SMB modes including two or more loops or two or more separation profiles have been developed. In U.S. Patents Nos. 6,093,326 (Danisco Finland Oy) and 5,637,225 (Xyrofin Oy), SMB processes including multiple loops are described. U.S. patent 6,224,776 (Cultor Corp.) discloses a method for fractionating a solution into two or more fractions in a SMB process where the separation system comprises at least two separation profiles in the same loop. Further, WO 2001/054790 A1 (also US 7,390,408) (Amalgamated Res. Inc.) describes a column apparatus for a fluid processing system containing a shallow bed of material between fluid distribution plates of fractal design (Shallow Bed SMB and Fractal Fluid Distribution).

[0057] Important performance metrics for commercial scale SMB are 1) the productivity of the separation expressed in units of g (processed feed) per liter of stationary phase (resin) per day, and 2) the eluent (or water) to feed ratio which is defined as the ratio of the volume of eluent (or water) necessary to process one volume of feed material through the SMB unit for the desired separation. The productivity of the separation in g (processed feed) per liter of stationary phase material (resin) per day is directly related to a) the amount of the resin needed for the desired separation and b) the size and number of the SMB systems required at commercial scale. The productivity therefore has an inverse relationship with the cost of the SMB unit at scale and a high productivity is desirable

for a lower cost separation. The water (or eluent) to feed ratio also impacts the cost of the separation and product purification as a higher water/eluent to feed ratio will increase the dilution of the product during the separation and necessitate a greater expense to evaporate the water for the isolation (or other further processing) of the product. It is therefore desirable to run the separation with a low water/eluent to feed ratio.

[0058] The present invention is directed to various separation processes which combine any one of the features described herein. For example, various processes for producing an extract comprising a di-carboxylic acid including a combination of features can comprise:

- contacting a separation media in a separation zone with a feed mixture comprising the di-carboxylic acid and second component, wherein at least a portion of the di-carboxylic acid is separated from the second component and a raffinate is formed comprising at least a portion of the second component;
- removing the raffinate from the separation zone; and
- eluting the di-carboxylic acid from the separation media with an eluent comprising water to form the extract comprising the di-carboxylic acid. The extraneous acid concentration of the eluent, prior to contact with the separation media, is less than 0.1 wt.%, less than 0.05 wt.%, or less than 0.01 wt.%.The eluent can be (i) makeup water and/or (ii) process water comprising water and optionally feed mixture constituents. Also, the separation media comprises a di-carboxylate form of an anion exchange chromatography resin.

[0059] More particularly, various processes for producing an extract comprising a di-carboxylic acid including a combination of features can comprise:

- contacting a separation media in a separation zone with a feed mixture comprising the di-carboxylic acid and a second component wherein at least a portion of the di-carboxylic acid and the second component are retained on the separation media;
- eluting at least a portion of the second component from the separation media with an eluent to form a raffinate comprising the second component;
- removing the raffinate from the separation zone; and
- eluting the di-carboxylic acid from the separation media with the eluent to form the extract comprising the di-carboxylic acid, wherein the weight ratio of the di-carboxylic acid to the second component in the extract is greater than the weight ratio of the di-carboxylic acid to the second component in the feed mixture and/or the raffinate. The eluent comprises water and the extraneous acid concentration of the eluent, prior to contact with the separation media, is less than 0.1 wt.%, less than 0.05 wt.%, or less than about 0.01 wt.% and/or the eluent is (i) makeup water and/or (ii) process water comprising water and optionally feed mixture constituents. Also, the separation media comprises a di-carboxylate form of an anion exchange chromatography resin.

[0060] Any of the features or modifications described above can be incorporated into this process. For example, contacting the separation media with the feed mixture; removing the raffinate from the separation zone; and eluting the di-carboxylic acid (e.g., glucaric acid) from the separation media can be performed continuously. Also, the separation zone can be a SMB chromatography stage. The separation zone can comprise a plurality of chromatography beds. Further, the SMB stage can comprise sequential SMB and/or continuous SMB chromatography.

[0061] The separation processes of the present invention can also include additional separation techniques. For example, it may be beneficial to remove certain impurity components from the feed mixture prior to the separation step. Certain impurity components that may preferentially bind to the separation media can impair the separation efficiency and potentially reduce the lifetime of the separation media. Components that can preferentially bind may include oligomers or polymers or other impurities such as color bodies. Such impurity components may be present at low concentrations in the feed mixture. Removal of such impurities can be accomplished by passing the feed mixture through a column containing an absorbent material such as polystyrene resin, ion exchange resin, and/or activated carbon. For example, exemplary ion exchange resins include anion exchange resins.

[0062] The separation processes of the present invention 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 prior feeding to the chromatographic separation. In various embodiments, a NF membrane with a suitable Molecular Weight Cut Off (MWCO) can be used to separate lower molecular weight di-carboxylic acid such as one or more of C_2-C_5 di-carboxylic acids (including oxalic acid, tartronic acid, tartaric acid and/or trihydroxyglutaric acid) when present from higher molecular weight di-carboxylic acids such as C_6 di-carboxylic acids (e.g., glucaric acid). Specific examples of suitable NF membranes include, for example and without limitation, spiral wound NF membranes having a MWCO of 150-300 available from GE Water & Process

Technologies, Inc. (DURACID KH-type, DL-type, HL-type, DK-type), Dow Water and Process Solutions (FilmTec Series), Koch Membrane Systems (SELRO series), Evonik Membrane Extraction Technologies (DURAMEM Series), and Borsig Membrane Technology GmbH (GMT-oNF Series). The NF membrane separation produces a permeate comprising one or more of the C_2-C_5 di-carboxylic acids and a retentate comprising a higher concentration of the higher molecular weight acids such as glucaric acid, gluconic acid, guluronic acid, glucuronic acid and ketogluconic acids.

[0063] Furthermore, the extract comprising the di-carboxylic acid obtained from a chromatographic separation process described herein can also contain C_2-C_5-diacids produced in the oxidation process. Accordingly, in various embodiments of the present invention include use of NF separation membranes to further purify the extract by separating lower in molecular weight di-carboxylic acids such as C_2-C_5 di-carboxylic acids higher molecular weight acids including di-carboxylic acids (e.g., glucaric acid). In these embodiments, the NF membrane separation produces a permeate comprising one or more of the C_2-C_5 di-carboxylic acids and a retentate comprising a higher concentration (and higher purity) of higher molecular weight acids including di-carboxylic acids. Additionally, since water can pass through to the permeate, the membrane separation will also concentrate the acids contained in the retentate. NF membrane separation techniques can be used to purify and concentrate the extract solution from a chromatographic separation process described herein.

[0064] Generally, a NF separation zone may comprise one or more NF membranes or modules and can be configured as either a single-pass or a multi-pass system. The membrane modules may be of various geometries and include flat (plate), tubular, capillary, or spiral wound membrane elements and the membranes may be of mono- or multilayer construction. The separation membranes and other components (e.g. support structure) of the membrane modules are preferably constructed to adequately withstand the conditions presented by the products to be purified. For example, the separation membranes are typically constructed of organic polymers such as cross-linked aromatic polyamides in the form of one or more thin film composites.

[0065] Membrane separation methods such as NF membrane separations are pressure-driven separation processes driven by the difference between the operating pressure and the osmotic pressure of the solution on the feed (or retentate) side of a membrane. The operating pressure within a membrane separation unit will vary depending upon the type of membrane employed, as osmotic pressure is dependent upon the level of transmission of solutes through the membrane. Operating pressures in the membrane separation unit are suitably achieved by passing the feed stream (e.g., incoming reaction constituents in the combination removed from the reaction zone or chromatographic separation system) through one or more pumps upstream of the membrane unit, for example, a combination booster pump and high-pressure pump arrangement. Generally, ultra-filtration operations exhibit lower osmotic pressures than NF operations, given the same feed solution. The driving force for transmission through the membrane (i.e., permeate flux) increases with the operating pressure. However, the benefits of increased operating pressure must be weighed against the increased energy (i.e., pumping) requirements and the detrimental effects (i.e., compaction) on membrane life.

[0066] Typically, the operating pressure utilized in the ultra-filtration operation is less than 800 kPa absolute and preferably from 200 to 500 kPa absolute. Typically, the operating pressure utilized in the NF operation is less than 1200 kPa absolute and preferably from 600 to 900 kPa absolute. High temperatures tend to decrease the useful life of selective membranes. Accordingly, the temperature of the aqueous combination introduced into the NF membrane separation unit is generally from 20°C to 100°C, and from 30°C to 60 °C, or from 30°C to 50 °C. If necessary, the mixture fed to the membrane separation zone can be cooled prior to being introduced, for example, by indirect heat exchange with other process streams or with cooling water (e.g., as part of the quench step).

[0067] In order to maintain or enhance membrane separation efficiency and permeate flux, the membranes are periodically cleaned so as to remove contaminants from the surface of the membrane. Suitable cleaning includes cleaning-in-place (CIP) operations wherein the surface of the membrane is exposed to a cleaning solution while installed.

Oxidation Processes

[0068] Further aspects of the present invention are directed to various processes for preparing an aldaric acid by the selective oxidation of an aldose. Aldoses include, for example, pentoses and hexoses (i.e., C-5 and C-6 monosaccharides). Pentoses include ribose, arabinose, xylose, and lyxose, and hexoses include glucose, allose, altrose, mannose, gulose, idose, galactose, and talose. Generally, processes for the selective oxidation of an aldose to an aldaric acid comprise reacting the aldose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising the aldaric acid. Processes for the selective oxidation of glucose to glucaric acid and pentose to pentaric acid (e.g., xylose to xylaric acid) are described in U.S. Patent No. 8,669,397 and U.S. Patent No. 8,785,683, respectively.

[0069] The selective oxidation of an aldose typically produces not only aldaric acid but various on-path intermediates to the aldaric acid. On-path intermediates include, for example, various aldonic acids, uronic acids and/or unreacted aldose, which upon further oxidation yield the aldaric acid. Recovery and recycle of these on-path intermediates increases the overall aldaric acid process yield and improves process economics. Accordingly, an oxidation process in accordance with the present invention comprises reacting an aldose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising the

aldaric acid and on-path intermediates to the aldaric acid; removing the oxidation product from the presence of the oxidation catalyst; and producing an extract comprising the aldaric acid according to any of the separation processes of the present invention described herein, wherein the feed mixture comprises the aldaric acid as the di-carboxylic acid and on-path intermediates to the aldaric acid as the second component obtained from the oxidation product.

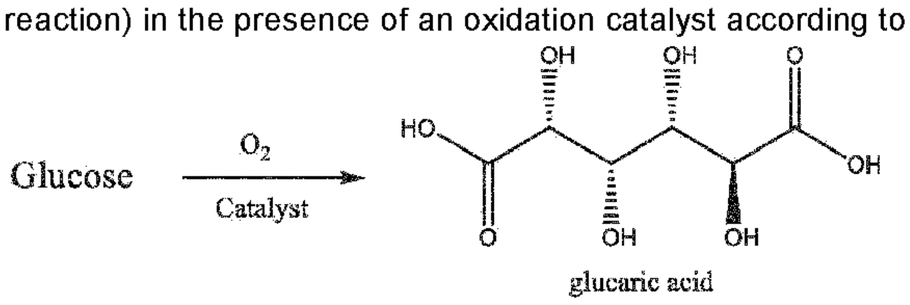
[0070] For instance, one oxidation process in accordance with the present invention comprises reacting an aldose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising the aldaric acid and on-path intermediates to the aldaric acid; removing the oxidation product from the presence of the oxidation catalyst; contacting a separation media in a separation zone with a feed mixture comprising the aldaric acid and on-path intermediates, wherein at least a portion of the aldaric acid is separated from the on-path intermediates and a raffinate is formed comprising at least a portion of the on-path intermediates; removing the raffinate from the separation zone; and eluting the aldaric acid from the separation media with an eluent comprising water to form the extract comprising the aldaric acid. When the separation media is contacted with the feed mixture, at least a portion of the aldaric acid and the on-path intermediates are retained on the separation media. Also, the raffinate comprising the on-path intermediates is formed by eluting at least a portion of the on-path intermediates from the separation media with the eluent. As a result, the weight ratio of the aldaric acid to the on-path intermediates in the extract is greater than the weight ratio of the aldaric acid to the on-path intermediates in the feed mixture and/or the raffinate.

[0071] FIG. 1 presents a process flow diagram for an oxidation process in accordance with the present invention. Oxidation reactor feed 1 comprising an aldose such as glucose is introduced into oxidation reaction zone 2. Oxidation product 3 exits the oxidation reaction zone 2 and can be collected as product, recycled and/or fed to optional concentration zone 4 where water 5 can be removed to concentrate the oxidation product. In various embodiments, the oxidation reactor zone can be operated with recycle loop 16 to enhance temperature control and mass transport. In this scenario the recycle flow and the flow of oxidation product 3 from zone 2 to optional zone 4 are both operated continuously. Product collection from the recycle loop enables the collection of useful glucaric acid products further described herein. Optional concentration zone 4 can include, for example, one or more evaporators and/or flash separators. The oxidation product 3 or concentrate thereof 6 (separation zone feed mixture) can then be fed to separation zone 7 (a chromatographic separation zone). In this zone, di-carboxylic acid (i.e., aldaric acid such as glucaric acid) is separated from a second component (e.g., comprising aldonic acid such as gluconic acid) of the separation zone feed mixture. The separation media in the separation zone is contacted with the feed mixture. Components of the feed mixture are retained on the separation media. Eluent is then introduced into the separation zone. Raffinate 9 comprising at least a portion of the second component is eluted and removed from the separation zone and optionally recycled to the oxidation reactor either directly or in combination with the aldose in feed 1. Eluent is also introduced to the separation zone to produce extract 10 comprising at least a portion of the di-carboxylic acid. A portion of raffinate 9 may optionally be purged (14) as needed to avoid accumulation of off-path intermediates. Fresh makeup water 15 may be added to raffinate 9 that is recycled. Alternatively, the raffinate can be introduced to a concentration zone (not shown) to remove water before recycling to the oxidation reactor.

[0072] Extract 10 is removed from separation zone 7 and can be introduced into optional concentration zone 11 to further concentrate the extract. Extract 10 or concentrated extract 13 can be removed from the process as products or sent to downstream processes for further conversion. Process water 5, process water 12 or fractions thereof that are removed from optional concentration zones 4 and 11 (and optionally from the raffinate stream 9) can be recycled for use as eluent 8. Multiple variations of the process scheme shown in Fig. 1 are possible.

[0073] Any features described herein with respect to the separation process can be used either singularly or in combination in conjunction with the separation of a di-carboxylic acid from the oxidation product produced as described herein. For example, the extraneous acid concentration of the eluent, prior to contact with the separation media, less than 0.1 wt.%, less than 0.05 wt.%, or less than 0.01 wt.%. Further, the eluent can be (i) makeup water and/or (ii) process water comprising water and optionally feed mixture constituents. Also, the separation media can comprise a di-carboxylate form of an anion exchange chromatography resin.

[0074] As noted above, in various embodiments, the aldose is glucose. Glucose may be converted to glucaric acid by reacting glucose with oxygen (e.g., air, oxygen-enriched air, oxygen alone, or oxygen with other constituents substantially inert to the reaction) in the presence of an oxidation catalyst according to the following reaction:



glucaric acid

The oxidation can be conducted in the absence of added base (e.g., KOH) or where the initial pH of the reaction medium and/or the pH of reaction medium at any point in the reaction is no greater than about 7, no greater than 7.0, no greater than 6.5, or no greater than 6. The initial pH of the reaction mixture is the pH of the reaction mixture prior to contact with oxygen in the presence of an oxidation catalyst. In fact, catalytic selectivity can be maintained to attain glucaric acid yield in excess of 30%, 40%, 50%, 60% and, in some instances, attain yields in excess of 65% or higher. The absence of added base advantageously facilitates separation and isolation of the glucaric acid, thereby providing a process that is more amenable to industrial application, and improves overall

process economics by eliminating a reaction constituent. The "absence of added base" as used herein means that base, if present (for example, as a constituent of a feedstock), is present in a concentration which has essentially no effect on the efficacy of the reaction; i.e., the oxidation reaction is being conducted essentially free of added base.

[0075] The oxidation reaction may be conducted under increased oxygen partial pressures and/or higher oxidation reaction mixture temperatures, which tends to increase the yield of glucaric acid when the reaction is conducted in the absence of added base or at a pH below 7. Typically, the partial pressure of oxygen is at least 15 pounds per square inch absolute (psia) (104 kPa), at least 25 psia (172 kPa), at least 40 psia (276 kPa), or at least 60 psia (414 kPa). The partial pressure of oxygen can be up to 1,000 psia (6895 kPa), more typically in the range of from 15 psia (104 kPa) to 500 psia (3447 kPa), from 40 psia (276 kPa) to 250 psia (1724 kPa), from 75 psia (517 kPa) to 500 psia (3447 kPa), from 100 psia (689 kPa) to 500 psia (3447 kPa), from 150 psia (1034 kPa) to 500 psia (3447 kPa). Generally, the temperature of the oxidation reaction mixture is at least 40°C, at least 60°C, at least 70°C, at least 80°C, at least 90°C, at least 100°C, at least 110°C, at least about 120°C, or higher. The temperature of the oxidation reaction mixture can be from 40°C to 200°C, from 60°C to 200°C, from 70°C to 200°C, from 80°C to 200°C, from 80°C to 180°C, from 80°C to 150°C, from 90°C to 180°C, or from 90°C to 150°C.

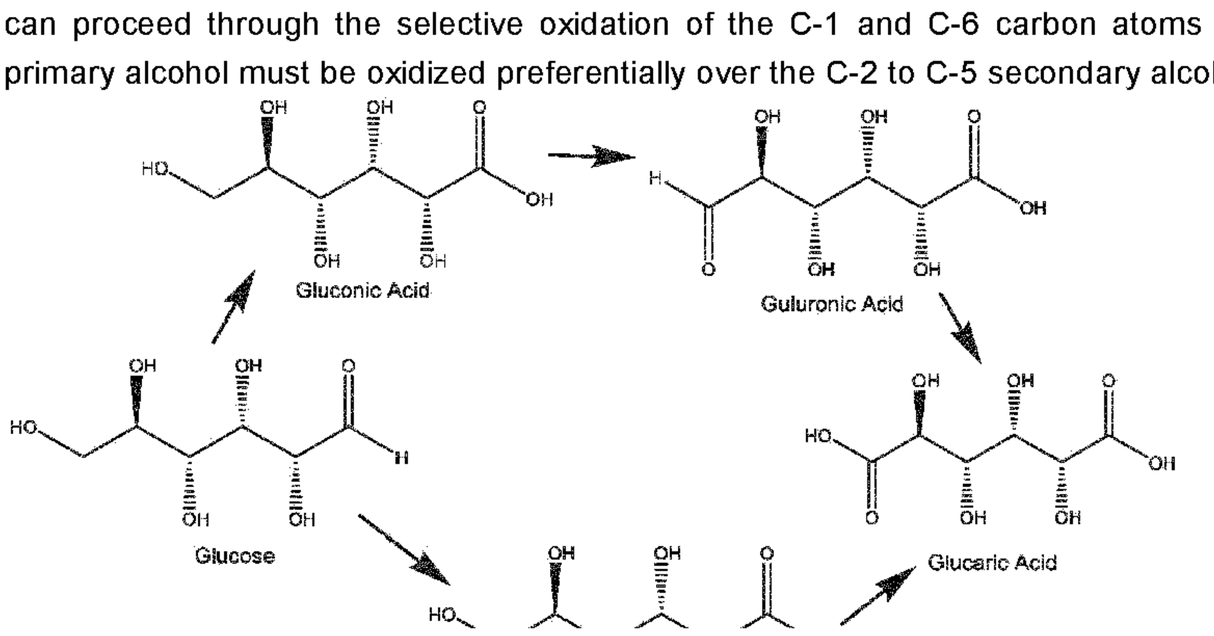
[0076] Oxidation of glucose to glucaric acid can also be conducted in the absence of nitrogen as an active reaction constituent. Some processes employ nitrogen compounds such as nitric acid as an oxidant. The use of nitrogen in a form in which it is an active reaction constituent, such as nitrate or nitric acid, results in the need for NO_x abatement technology and acid regeneration technology, both of which add significant cost to the production of glucaric acid from these known processes, as well as providing a corrosive environment which may deleteriously affect the equipment used to carry out the process. By contrast, for example, in the event air or oxygen-enriched air is used in the oxidation reaction of the present invention as the source of oxygen, the nitrogen is essentially an inactive or inert constituent. An oxidation reaction employing air or oxygen-enriched air is a reaction conducted essentially free of nitrogen in a form in which it would be an active reaction constituent. Thus, in various embodiments, the oxidation reaction mixture (i.e., glucaric acid product and process streams obtained therefrom, including the feed mixture to the chromatographic separation process as described herein, the resulting extract and/or raffinate can be free or essentially free of nitric acid and salts thereof. For example, these process streams can contain less that than 0.1 wt.% or less than 0.01 wt.% of nitric acid and salts thereof.

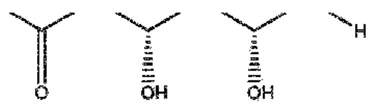
[0077] Generally, the oxidation catalyst comprises at least one d-block metal as the catalytically active component. More typically, the oxidation comprises at least one metal selected from the group consisting of platinum, palladium, and a combination thereof. Preferred oxidation catalysts comprise at least platinum as a catalytically active component. The oxidation catalyst can comprise a second metal. One preferred second metal includes gold. Oxidation catalysts are described in U.S. Patent Application Publication 2011/0306790. This publication describes various oxidation catalysts comprising platinum and gold, which are useful for the selective oxidation of compositions comprised of a primary alcohol group and at least one secondary alcohol group (e.g., glucose). Thus, one preferred oxidation catalyst comprises at least platinum and gold as the catalytically active component.

[0078] The oxidation catalyst is preferably a heterogeneous catalyst. Catalyst supports for the heterogeneous catalyst include zirconias, titania, or carbon (especially porous carbon black supports) as described in PCT/US2015/028358. The supports can be shaped supports such as extrudates, spheres, beads, cylinders, pellets, multi-lobed shapes, rings, stars, wheels, etc. Preferred shaped supports include extruded cylinders or extruded multi-lobed shapes such as trilobes. Accordingly, one oxidation catalyst comprises platinum and gold on a porous carbon black support. The platinum and gold can optionally be in a shell layer at or near external surfaces of the shaped porous carbon black support. For example, one oxidation catalyst contains platinum and gold in a shell wherein the shell thickness is from 10 μm to 400 μm.

[0079] The oxidation of glucose to glucaric acid may be conducted in various known industrial reactor formats such as batch slurry, continuous slurry based stirred tanks or loop reactors, fixed bed, ebulated bed, bubble column, etc. A preferred reactor is a continuous flow fixed bed reactor. The oxidation reaction zone can comprise one or more reactors.

[0080] The oxidation of glucose to glucaric acid proceeds according to a multi-step reaction pathway as shown below. The reaction can proceed through the selective oxidation of the C-1 and C-6 carbon atoms in either order. For a selective reaction, the C-6 primary alcohol must be oxidized preferentially over the C-2 to C-5 secondary alcohol groups.





Glucuronic Acid

Thus, as shown in the scheme above, the principal on-path intermediates present in the selective oxidation of glucose are mono-carboxylic acids: gluconic acid, guluronic acid, and glucuronic acid.

[0081] In many processes for the direct catalytic oxidation of glucose to glucaric acid, molar glucaric acid yields are limited to 65% and below. One of the reasons for the yield limitation is associated with the fact that glucaric acid can be further oxidized under the reaction conditions, and consequently as the concentration of glucaric acid increases in the reaction mixture, the oxidation of glucaric acid takes place which typically yields shorter chain, lower carbon number di-carboxylic acids (for example, di-carboxylic acid with 5 carbon atoms (e.g. xylaric acid), 4 carbon atoms (e.g. tartaric acid), 3 carbon atoms (e.g. tartronic acid), and 2 carbon atoms (e.g. oxalic acid)). Additionally, the production of other side-products is also known to lower the yield of glucaric acid. Ketogluconic acids can be produced from the oxidation of the secondary alcohol groups of the intermediate gluconic acid. Ketogluconic acids can also be oxidized to shorter chain di-acids and thereby reduce the yield of glucaric acid. Consequently, multiple competing reactions can reduce the selectivity for the oxidation of glucose to glucaric acid resulting in lower yields than desirable

[0082] A direct consequence of the presence of high quantities of on-path intermediates such as gluconic acid and guluronic acid and off-path intermediates such as ketogluconic acids and numerous other di-carboxylic acids, is a difficult and costly purification of glucaric acid from a complex reaction product mixture. However, applicants have discovered that the separation processes of the present invention are especially suited for separating glucaric acid from a complex oxidation reaction mixture. Accordingly, another oxidation process in accordance with the present invention comprises reacting glucose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising glucaric acid and on-path intermediates to glucaric acid; removing the oxidation product from the presence of the oxidation catalyst; and producing an extract comprising glucaric acid according to any of the separation processes of the present invention described herein, wherein the feed mixture to the separation process comprises glucaric acid as the di-carboxylic acid and on-path intermediates to glucaric acid as the second component obtained from the oxidation product. Unreacted glucose can also be separated from glucaric acid with the on-path intermediates.

[0083] Another oxidation process in accordance with the present invention comprises reacting glucose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising glucaric acid and on-path intermediates to glucaric acid; removing the oxidation product from the presence of the oxidation catalyst; contacting a separation media in a separation zone with a feed mixture comprising glucaric and on-path intermediates, wherein at least a portion of glucaric acid is separated from the on-path intermediates and a raffinate is formed comprising at least a portion of the on-path intermediates; removing the raffinate from the separation zone; and eluting glucaric acid from the separation media with an eluent comprising water to form the extract comprising glucaric acid. When the separation media is contacted with the feed mixture, at least a portion of the glucaric acid and the on-path intermediates are retained on the separation media. Also, the raffinate comprising the on-path intermediates is formed by eluting at least a portion of the on-path intermediates from the separation media with the eluent. As a result of these separation processes, the weight ratio of the glucaric acid to the on-path intermediates in the extract is greater than the weight ratio of the glucaric acid to the on-path intermediates in the feed mixture and/or the raffinate.

[0084] It has been found that a high overall glucaric acid process yield may be obtained when the oxidation reaction is controlled within certain endpoint limits, the di-carboxylic acid component of the oxidation product is separated from on-path intermediates, and the on-path intermediates are recycled back to the oxidation reaction. The process discovered by applicants reduces the concentration of off-path intermediates such as C_2-C_5 di-acids while providing relatively high yields of glucaric acid under the oxidation reaction conditions. This process for preparing glucaric acid in accordance with the present invention generally comprises reacting glucose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising glucaric acid and on-path intermediates to glucaric acid; removing the oxidation product from the presence of the oxidation catalyst at a reaction endpoint; separating a glucaric acid product from on-path intermediates to glucaric acid obtained in the oxidation product; and; and recycling the on-path intermediates to the oxidation reaction zone. In this process, the glucaric acid product is an extract prepared according to any of the separation processes of the present invention described herein, wherein the feed mixture to the separation process comprises glucaric acid as the di-carboxylic acid and the second component comprises the on-path intermediates to glucaric acid obtained from the oxidation product.

[0085] In oxidation processes, the reaction endpoint can be established according to a certain maximum molar yield of glucaric acid and lactones thereof (collectively referred to as glucaric acid yield). As noted, lactones of glucaric acid generally include glucaro-1,4-lactone, glucaro-1,4:3,6-dilactone, and glucaro-3,6-lactone. Applicants have found that if the molar glucaric acid yield is controlled within a certain range, then the concentration of less desirable shorter chain, lower carbon number di-carboxylic acid byproducts is reduced and the majority of the constituents of the reaction mixture are glucaric acid plus on-path intermediates to glucaric acid (i.e., gluconic acid, guluronic acid, and glucuronic acid). More particularly, the oxidation product can be removed from the presence of the oxidation catalyst at a reaction endpoint wherein the molar yield of glucaric acid and lactones thereof at the reaction endpoint does not exceed 30%, 40%, 45%, 50%, or 60%. In various embodiments, the oxidation product can be removed from the presence of the oxidation catalyst at a reaction endpoint wherein the molar yield of glucaric acid and lactones thereof at the reaction endpoint is from 30% to 65%, from 30% to 60%, from 30% to 50%, from 40% to 65%, from 40% to 60%, from 50% to 65%, or from 50% to 60%

[0086] Another important metric for a high overall process yield for glucaric acid is the "on-path percentage" for glucaric acid which includes unconverted glucose in the reactor exit, on-path intermediates to glucaric acid, and glucaric acid. For the purposes of establishing a reaction endpoint (based on on-path percentage), the on-path percentage is calculated according to equation (A):

$$\text{On path percentage} = \sum \text{(molar yield of glucaric acid + \% of unconverted glucose + molar yield of on path intermediates)} \quad \text{(A)}$$

where the on-path intermediates are (i) gluconic acid, (ii) guluronic acid, and (iii) glucuronic acid. Unless otherwise stated, "yields" of the reaction constituents referred to herein are calculated according to equation (B):

$$\frac{\text{moles of reaction constituent}}{\text{moles of glucose in oxidation reactor feed}} \text{ x } 100\% \quad \text{(B)}$$

[0087] Accordingly, the oxidation product can be removed from the presence of the oxidation catalyst at a reaction endpoint wherein the on-path percentage (according to equation (A)) at the reaction endpoint is at least 60%, at least 70%, at least 75%, or at least 80%, at least 85%, or at least 90%. In various embodiments, the oxidation product can be removed from the presence of the oxidation catalyst at a reaction endpoint wherein the on-path percentage at the reaction endpoint is from 60% to 100%, from 65% to 100%, from 70% to 100%, from 60% to 99%, from 65% to 99%, from 70% to 99%, from 60% to 95%, from 65% to 95%, or from 70% to 95%.

[0088] In various processes, a combination of the molar yield of glucaric acid and lactones thereof and the on-path percentage can be used as an important metric to help maximize overall process yield of glucaric acid. Accordingly, another process for preparing glucaric acid comprises reacting glucose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising glucaric acid and on-path intermediates to glucaric acid; removing the oxidation product from the presence of the oxidation catalyst at a reaction endpoint wherein the molar yield of glucaric acid and lactones thereof at the reaction endpoint does not exceed 30%, 40%, 45%, 50%, or 60% and the on-path percentage at the reaction endpoint is at least 60%, at least 70%, at least 75%, or at least 80%, or at least 85%, or at least 90%, producing an extract comprising glucaric acid, wherein the feed mixture comprises glucaric acid as the di-carboxylic acid and on-path intermediates to glucaric acid as the second component obtained from the oxidation product; and recycling the on-path intermediates to the oxidation reaction zone.

[0089] In certain instances, applicants have found that if the molar glucaric acid yield is limited, then the on-path percentage is high. In particular, when the molar glucaric acid yield is limited to less than 60%, then the on-path percentage is at least 75%. In some instances, when the molar glucaric acid yield is limited to less than 60%, then the on-path percentage is at least 80%. In other instances, when the molar glucaric acid yield is limited to less than 50%, then the on-path percentage is at least 85%, or in some embodiments at least 90%.

[0090] Applicants have found that a process to convert glucose to glucaric acid in which the oxidation reaction is run to lower molar yields with high on-path percentage coupled with an efficient separation of glucaric acid and recycle of glucose and the reaction intermediates enables a glucaric acid process yield at least 75%, at least 80%, at least 85%, or at least 90%, where yield is calculated according to equation B.

[0091] The manner in which the molar yield of glucaric acid is limited (i.e., to prevent further oxidation at the reaction endpoint) can be carried out in various known industrial reactors. For example, a continuous flow fixed bed reactor containing the oxidation catalyst composition can be run in a manner to limit the molar yield of glucaric acid by choosing an appropriate temperature, oxygen partial pressure, oxygen to glucose molar ratio and residence time in the fixed bed reactor.

[0092] The present invention is directed to various oxidation processes which combine any one of the features described herein. For example, one process featuring a combination of features is a process for preparing glucaric acid. This process comprises

- reacting glucose with oxygen in the presence of an oxidation catalyst in an oxidation reaction zone to form an oxidation product comprising glucaric acid and on-path intermediates to glucaric acid;
- removing the oxidation product from the presence of the oxidation catalyst at a reaction endpoint wherein the molar yield of glucaric acid and lactones thereof at the reaction endpoint does not exceed 30%, 40%, 45%, 50%, or 60% and the on-path percentage at the reaction endpoint is at least 60%, at least 70%, at least 75%, or at least 80%; or at least 85% or at least 90%.
- contacting a separation media in a separation zone with a feed mixture comprising the glucaric acid and on-path intermediates, wherein at least a portion of the glucaric acid is separated from the on-path intermediates and a raffinate is formed comprising at least a portion of the on-path intermediates;
- removing the raffinate from the separation zone; and
- eluting the glucaric acid from the separation media with an eluent comprising water to form the extract comprising the glucaric acid; and
- recycling the on-path intermediates to the oxidation reaction zone.

When the separation media is contacted with the feed mixture, at least a portion of the glucaric acid and the on-path intermediates are retained on the separation media. Also, the raffinate comprising the on-path intermediates is formed by eluting at least a portion of the on-path intermediates from the separation media with the eluent. As a result of these separation processes, the weight ratio of the glucaric acid to the on-path intermediates in the extract is greater than the weight ratio of the glucaric acid to the on-path intermediates in the feed mixture and/or the raffinate. In accordance with the present invention, the extraneous acid concentration of the eluent, prior to contact with the separation media, is less than 0.1 wt.%, less than 0.05 wt.%, or less than 0.01 wt.%.The eluent can be (i) makeup water and/or (ii) process water comprising water and optionally feed mixture constituents. Also, the separation media can comprise a di-carboxylate form of an anion exchange chromatography resin, more particularly the glucarate form of an anion exchange chromatography resin.

[0093] Any of the features or modifications described above can be incorporated into this process. For example, contacting the separation media with the feed mixture; removing the raffinate from the separation zone; and eluting the glucaric acid from the separation media can be performed continuously. Also, the separation zone can be a SMB chromatography stage. The separation zone can comprise a plurality of chromatography beds. Further, the SMB stage can comprise sequential SMB and/or continuous SMB chromatography.

Glucaric Acid Products

[0094] A glucaric acid product can be obtained from the oxidation reaction zone or subsequent concentration zone(s). Not only is this product useful as an intermediate in the production of compounds such as adipic acid, but also in commercial applications such as de-icing fluids, acidulants, detergent builders, pH regulators, chelants, de-scalers, corrosion inhibitors, metal cleaning and finishing agents, a component of cement formulations (concrete admixtures including water reducing and set retarding formulations). Generally, the dissolved solids of this glucaric acid product are a mixture comprising large portions of glucaric acid or salt thereof and gluconic acid or salt thereof and can optionally include lesser portions of ketogluconic acids (i.e., 2-ketogluconic acid, 3-ketogluconic acid, 4-ketogluconic acid, and 5-ketogluconic acid), C_2-C_5 di-acids (e.g., xylaric acids, tartaric acid, tartronic acid, and oxalic acid), salts of any one of the aforementioned acids, and glucose. In particular, this glucaric acid product comprises from 30 wt.% to 65 wt.% glucaric acid, from 25 wt.% to 70 wt.% gluconic acid, less than 10 wt.% of one or more ketogluconic acids, less than 5 wt.% of one or more C_2-C_5 di-acids, and less than 5 wt.% glucose, wherein each weight percent is based on the dissolved solids content of the glucaric acid product. In other embodiments, products include those in which at least a portion of the various component mon-carboxylic and di-carboxylic acids described herein are in salt form, such as in the form of a sodium, potassium, calcium, magnesium, or other salt (e.g., sodium glucarate).

[0095] The glucaric acid concentration of the glucaric acid product can be from 20 wt.% to 65 wt.% glucaric acid, from 25 wt.% to 65 wt.% glucaric acid, from 30 wt.% to 65 wt.% glucaric acid, from 40 wt.% to 65 wt.%, from 40 wt.% to 60 wt.%, from 45 wt.% to 65 wt.%, from 45 wt.% to 60 wt.%, from 50 wt.% to 65 wt.%, or from 50 wt.% to 60 wt.% of the dissolved solids contents. Further, the gluconic acid concentration can be from 25 wt.% to 65 wt.%, from 25 wt.% to 60 wt.%, from 25 wt.% to 55 wt.%, from 25 wt.% to 50 wt.%, from 25 wt.% to 45 wt.%, from 30 wt.% to 70 wt.%, from 30 wt.% to 65 wt.%, from 30 wt.% to 60 wt.%, from 30 wt.% to 55 wt.%, from 30 wt.% to 50 wt.%, from 30 wt.% to 45 wt.%, from 30 wt.% to 40 wt.%, or from 50 wt.% to 70 wt.% of the dissolved solids contents. The concentration of the ketogluconic acids can be less than 5 wt.%, from 1 wt.% to 10 wt.%, or from of 1 wt.% to 5 wt.% of the dissolved solids contents. The concentration of the C_2-C_5 di-acids can be from 1 wt.% to 5 wt.% of the dissolved solids contents. Also, the glucose concentration can be less than 2.5 wt.%, from 0.01 wt.% to 5 wt.%, or from 0.1 wt.% to 2.5 wt.%, or from 0.001 wt.% to 2.5 wt.% of the dissolved solids contents.

[0096] The glucaric acid product can further comprise from 1 wt.% to 20 wt.%, from 1 wt.% to 15 wt.%, from 1 wt.% to 10 wt.%, from 1 wt.% to 5 wt.%, from 5 wt.% to 20 wt.%, from 5 wt.% to 15 wt.%, or from 5 wt.% to 10 wt.% guluronic acid based on the dissolved solids content. The glucaric acid product can further comprise from 0.01 wt.% to 1 wt.% or from 0.01 wt.% to 0.5 wt.% glucuronic acid based on the dissolved solids content.

[0097] In various embodiments, the glucaric acid product comprises from 30 wt.% to 50 wt.% glucaric acid, from 20 wt.% to 45 wt.% gluconic acid, from 5 wt.% to 15 wt.% guluronic acid, less than 2 wt.% of glucuronic acid, less than 6 wt.% of one or more ketogluconic acids, less than 5 wt.% of one or more C_2-C_5 di-acids, and less than 2 wt.% glucose, wherein each weight percent is based on the dissolved solids content of the glucaric acid product.

[0098] In some embodiments, the glucaric acid product comprises from about 35 wt.% to 45 wt.% glucaric acid, from 25 wt.% to 40 wt.% gluconic acid, from 5 wt.% to 15 wt.% guluronic acid, less than 2 wt.% of glucuronic acid, less than 6 wt.% of one or more ketogluconic acids, less than 5 wt.% of one or more C_2-C_5 di-acids, and less than 2 wt.% glucose, wherein each weight percent is based on the dissolved solids content of the glucaric acid product.

[0099] Moreover, the glucaric acid product typically does not contain a significant fraction of undissolved solids, such as heterogeneous catalyst particles. Therefore, the glucaric acid product can have an undissolved solids content of less than 5 wt.%,

less than 1 wt.%, or less than 0.1 wt.% based on the total weight of the glucaric acid product.

[0100] Also, the glucaric acid product typically does not contain a significant portion of metal contaminants. Accordingly, the glucaric acid product can have a metal content of less than 1 wt.%, less than 0.1 wt.%, less than 0.01 wt.%, less than 0.001 wt.%, less than 1 ppm, or less than 0.1 ppm based on the total weight of the glucaric acid product. Further, the glucaric acid product can have a transition metal content of less than 1 wt.%, less than 0.1 wt.%, less than 0.01 wt.%, less than 0.001 wt.%, less than 1 ppm, or less than 0.1 ppm based on the total weight of the glucaric acid product. More particularly, the glucaric acid product can have a noble metal content of less than 1 wt.%, less than 0.1 wt.%, less than 0.01 wt.%, less than 0.001 wt.%, less than 1 ppm, or less than 0.1 ppm based on the total weight of the glucaric acid product.

[0101] Further, a concentrated glucaric acid product can be obtained from the separation zone or concentration zone(s) subsequent thereto. Not only is this product useful as an intermediate in the production of compounds such as adipic acid, but can also be used in pharmaceutical, food, and other commercial applications such as detergent builders, corrosion inhibitors, metal cleaning and finishing agents, a component of cement formulations, and metal sequestration. Generally, the dissolved solids of this concentrated glucaric acid product comprise a large portion of glucaric acid and optionally includes lesser portions of gluconic acid, ketogluconic acids (i.e., 2-ketogluconic acid, 3-ketogluconic acid, 4-ketogluconic acid, and 5-ketogluconic acid), C_2-C_5 di-acids (e.g., pentaric acids, tartaric acid, tartronic acid, and oxalic acid), and glucose. In particular, this concentrated glucaric acid product comprises from 85 wt.% to 99 wt.% glucaric acid, less than 5 wt.% gluconic acid, less than 2.5 wt.% of one or more ketogluconic acids, and less than 10 wt.% of one or more C_2-C_5 di-acids, less than 1 wt.% glucose, wherein each weight percent is based on the dissolved solids content of the concentrated glucaric acid product.

[0102] The glucaric acid concentration of the concentrated glucaric acid product can be from 90 wt.% to 99 wt.% or from 90 wt.% to 95 wt.% of the dissolved solids contents. The gluconic acid concentration can be from 1 wt.% to 5 wt.% or from 1 wt.% to 2.5 wt.% of the dissolved solids contents. The concentration of the ketogluconic acids can be less than 1 wt.%, less than 0.5 wt.%, less than 0.1, less than 0.01 wt.%, or from 0.01 wt.% to 1 wt.% of the dissolved solids contents. The concentration of the C_2-C_5 di-acids can be less than 7.5 wt.%, less than 5 wt.%, from 1 wt.% to 10 wt.%, from 1 wt.% to 7.5 wt.%, or from 2.5 wt.% to 7.5 wt.% of the dissolved solids contents. The glucose concentration can be less than 0.5 wt.%, less than 0.1, or less than 0.01 wt.% of the dissolved solids contents.

[0103] The concentrated glucaric acid product can further comprise from 0.1 wt.% to 5 wt.% or from 0.1 wt.% to 2.5 wt.% guluronic acid based on the dissolved solids content.

[0104] The glucaric acid product and concentrated glucaric acid can be essentially free of nitric acid and salts thereof. For example, the glucaric acid product and concentrated glucaric acid can contain less that than 0.1 wt.% or less than 0.01 wt.% of nitric acid and salts thereof. The glucaric acid product and concentrated glucaric acid can be free of nitric acid and salts thereof.

[0105] As mentioned else herein, the terms "glucaric acid" "gluconic acid," and "guluronic acid" each refer collectively to the acid and any corresponding lactones that may be present. For example, the term "glucaric acid" is inclusive of glucaric acid, glucaro-1,4-lactone, glucaro-6,3-lactone, and glucaro-1,4:6,3-dilactone.

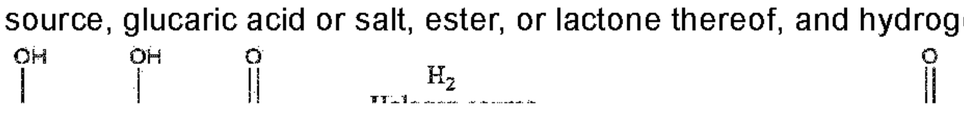
Integrated Processes

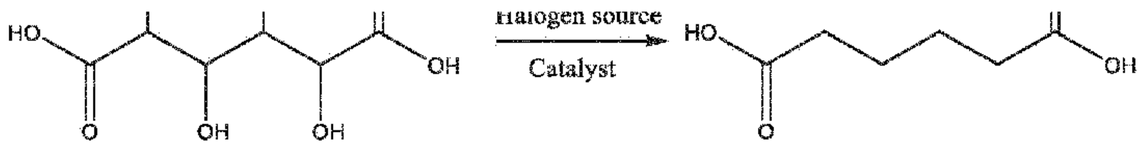
[0106] A further aspect is directed to various integrated processes that include the separation process, separation media, and/or oxidation processes in accordance with various other aspects. For example, one process includes the selective halide-promoted hydrodeoxygenation of an aldaric acid or salt, ester, or lactone thereof to a di-carboxylic acid. As such, a process for the selective halide promoted hydrodeoxygenation of an aldaric acid comprises reacting the aldaric acid or salt, ester, or lactone thereof that is obtained from any one of the oxidation process of the present invention with hydrogen in the presence of a halogen-containing compound and a catalyst composition as described herein to form a di-carboxylic acid. Preferred aldaric acids include glucaric acid (and lactones thereof) and xylaric acid.

[0107] Typically, the catalyst composition comprises at least one noble metal as a catalytically active component. U.S. Patent Nos. 8,669,397 and 8,669,397 referenced above describe chemocatalytic processes for the hydrodeoxygenation of glucaric acid to adipic acid and xylaric acid to glutaric acid.

[0108] Adipic acid is an especially useful industrial di-carboxylic acid. The process for preparing adipic acid comprises reacting at least a portion of the glucaric acid and lactones thereof obtained from any one of the oxidation process of the present invention with hydrogen in the presence of a halogen-containing compound and a catalyst in hydrodeoxygenation reaction zone to form adipic acid.

[0109] Adipic acid or salts and esters thereof may be prepared by reacting, in the presence of a hydrodeoxygenation catalyst and a halogen source, glucaric acid or salt, ester, or lactone thereof, and hydrogen, according to the following reaction:





In the above reaction, glucaric acid or salt, ester, or lactone thereof is converted to an adipic acid product by catalytic hydrodeoxygenation in which carbon-hydroxyl groups are converted to carbon-hydrogen groups. In various embodiments, the catalytic hydrodeoxygenation is hydroxyl-selective wherein the reaction is completed without substantial conversion of the one or more other non-hydroxyl functional group of the substrate.

[0110] The halogen source may be in a form selected from the group consisting of ionic, molecular, and mixtures thereof. Halogen sources include hydrohalic acids (e.g., HCl, HBr, HI and mixtures thereof; preferably HBr and/or HI), halide salts, (substituted or unsubstituted) alkyl halides, or molecular (diatomic) halogens (e.g. chlorine, bromine, iodine or mixtures thereof; preferably bromine and/or iodine). The halogen source can be diatomic, hydrohalic acid, or halide salt and, more preferably, diatomic form or hydrohalic acid. In certain embodiments, the halogen source is a hydrohalic acid, in particular hydrogen bromide.

[0111] Generally, the molar ratio of halogen to the glucaric acid or salt, ester, or lactone thereof is about equal to or less than 1. The mole ratio of halogen to the glucaric acid or salt, ester, or lactone thereof can be typically from 1:1 to 0.1:1, more typically from 0.7:1 to 0.3:1, and still more typically 0.5:1. Typically, the reaction allows for recovery of the halogen source and catalytic quantities (where molar ratio of halogen to the glucaric acid or salt, ester, or lactone thereof is less than 1) of halogen can be used, recovered and recycled for continued use as a halogen source.

[0112] Generally, the temperature of the hydrodeoxygenation reaction mixture is at least 20°C, typically at least 80°C, and more typically at least 100°C. The temperature of the hydrodeoxygenation reaction can be conducted in the range of from about 20°C to 250°C, from 80°C to 200°C, from 120°C to 180°C, or from 140°C to 180°C. Typically, the partial pressure of hydrogen is at least 25 psia (172 kPa), more typically at least 200 psia (1379 kPa) or at least 400 psia (2758 kPa). The partial pressure of hydrogen can be from 25 psia (172 kPa) to 2500 psia (17237 kPa), from 200 psia (1379 kPa) to 2000 psia (13790 kPa), or from 400 psia (2758 kPa) to 1500 psia (10343 kPa).

[0113] The hydrodeoxygenation reaction may be conducted in the presence of a solvent. Solvents suitable for the selective hydrodeoxygenation reaction include water and carboxylic acids, amides, esters, lactones, sulfoxides, sulfones and mixtures thereof. Preferred solvents include water, mixtures of water and weak carboxylic acid, and weak carboxylic acid. A preferred weak carboxylic acid is acetic acid.

[0114] The catalytically active component may include noble metals selected from the group consisting of ruthenium, rhodium, palladium, platinum, and combinations thereof. The hydrodeoxygenation catalyst can comprise two or more metals. For example, the first metal can be selected from the group consisting of cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum (more particularly, ruthenium, rhodium, palladium, and platinum) and the second metal is selected from the group consisting of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, ruthenium, rhodium, palladium, silver, tungsten, iridium, platinum, and gold (more particularly, molybdenum, ruthenium, rhodium, palladium, iridium, platinum, and gold). Preferably, the first metal can be selected from the group of platinum, rhodium and palladium, and the second metal is selected from the group consisting of ruthenium, rhodium, palladium, platinum, and gold. More preferably, the first metal is platinum and the second metal is rhodium. The platinum to rhodium molar ratio of the catalyst composition is typically in the range of from 3:1 to 1:2 or from 3:1 to 1:1.

EXAMPLES

[0115] The following non-limiting examples are provided to further illustrate the present invention.

Example 1. Oxidation of Glucose to Glucaric Acid with Moderate Single-Pass Glucaric Acid Yield and High On-Path Percentage

[0116] 137.8 g of carbon black powder (Monarch 700 supplied by Cabot) was added in multiple portions to an aqueous solution (603.5 g) containing 30.7 wt.% ADM Dextrose (DE 99) and 3.3 wt.% hydroxyethylcellulose (Sigma-Aldrich, SKU 54290, 2% in H_2O). The mixture was stirred well to produce a paste. This paste was loaded into a syringe and the material was extruded into spaghetti-like strings with approximately 1.5 mm diameter. After drying in an 80°C oven for 16 hours under a dry air purge, these strings were cut into small pieces about 6.0 mm long. Then they were treated at 800°C for 2 hours after heating to 800°C at a 5°C/min temperature ramp rate under continuous N_2 flow to produce carbon black extrudates.

[0117] To 91.5 g of these extrudates, an aqueous solution (32.0 ml) containing 0.73 g Au in the form of Me_4NAuO_2 and 1.10 g Pt in the form of $PtO(NO_3)$ was added. The mixture was agitated to impregnate the carbon black support and was dried at 70°C under a

dry air purge. The sample was then reduced at 350°C under forming gas (5% H_2 and 95% N_2) atmosphere for 4 hours after heating to 350°C with a 2°C/min temperature ramp rate. The final catalyst was composed of ca. 0.80 wt.% Au and 1.2 wt.% Pt. The recipes were repeated in batches to generate the quantity of material necessary for testing in the fixed bed reactor.

Testing of Au/Pt on carbon black extrudate catalyst in a fixed-bed reactor for glucose oxidation

[0118] Reactions were conducted in a 1-inch OD by 5.5 feet (66 inches) long 316 stainless steel tube with co-current down-flow feed of gas and liquid. The tube was packed with 1.0 mm glass beads at the bottom of the tube (30 cm depth), followed by catalyst (344 g, 0.80 wt.% Au + 1.2 wt.% Pt on carbon black pellets) then 1.0 mm glass beads at the top to approximately 18 cm depth.

[0119] The temperature of the packed reactor tube was control through the use of an oil jacket with a continuous flow of oil connected to a reservoir equipped with temperature control. Gas (compressed dry air) and liquid flows were regulated by mass flow controller, pumps, and Coriolis flow meters, respectively. A pressure control valve is used to regulate the reactor pressure. A 30 wt.% solution of glucose was fed into the reactor under 2 different flow conditions: First flow condition = 1.3 kg/hour glucose solution flow along with a stream of air at a pressure of 775 psi and a flow rate of 700 standard liters per hour. Second flow condition = 0.65 kg/hr glucose solution flow along with a stream of air at a pressure of 775 psi and a flow rate of 350 standard liters per hour. Under both conditions, the catalyst bed was kept at a temperature of 140°C. Product collected from the exit of the reactor was analyzed by ion chromatography. A Dionex ICS-3000 Chromatography system equipped with Corona CAD detector (Thermo Scientific) was used. Samples were first diluted with deionized water to suitable concentrations, then separated on an Ionpac® AS11-HC column and quantified by conductivity and Corona CAD detection through comparison with calibration standards. Product analyses for representative samples collected are shown in Table 1 (molar yields). A representative sample from flow condition 1 was taken at around 1200 hours of continuous on-stream operation. For flow condition 2, a representative sample was taken after a further 50 hours on stream.

Example 2. Separation of Glucaric Acid from Gluconic Acid and other On-Path Intermediates

[0120] The sequential simulated moving bed (SSMB-6) system used for this example was built by Novasep and comprised six columns in which two different streams can be fed by two pumps, and two different outlets are connected to each column. Each column is equipped with five automatic valves. Each inlet stream is flow controlled and monitored, while the outlets are pressure controlled to ensure a steady flow rate in the columns, plus one loop control with pump and flow meter. The columns are jacketed to provide accurate temperature control. For each column, two inlet valves select the feed stream (feed or eluent), one valve allows the connection to the next column, and two outlets valves select the outlet stream (extract or raffinate). The six columns are connected in series.

[0121] The resin used for the sequential SMB (SSMB) separation was Lanxess Lewatit MDS 4368, a styrene/divinylbenzene cross-linked macroporous anion exchange resin (75-80% weak-base + 25-20% strong-base functionality) with 1.4 eq./L exchange capacity and 0.3 mm bead size. Before loading in the SSMB unit, the free-base and OH^- forms of the resin were converted to the glucarate form through treatment with a 1 M glucaric acid solution (prepared through the hydrolysis of a solution of D-glucaro-1,4:6,3-dilactone in water at room temperature for 24 hours). After treatment, the resin was thoroughly washed with DI water (monitored by conductivity) to remove excess glucaric acid.

[0122] The resin in the glucarate form was loaded into a six column SSMB unit. Each column was 2.5 cm in diameter and 2 m in length, containing ca. 1 L of resin each. The column temperatures were regulated at 60°C. The eluent was composed of degassed and demineralized water pre-heated to 60°C. The feed solution was prepared by concentrating product from the oxidation reactor of Example 1 to 48 wt.% dissolved solids (DS) in a tubular up-flow continuous evaporator operating at 40°C and 100 mbar vacuum. The feed was pre-heated to 60°C.

[0123] Component analysis of feed, extract and raffinate streams was conducted using ion-chromatography (IC) with conductivity and Corona CAD detection as previously described of Example 1.

[0124] The separation was performed on 284 L of concentrated feed, collecting 920 L of extract and 330 L of raffinate, respectively. Extract and raffinate solutions from the SSMB separation were concentrated (using the same evaporation equipment and conditions as for the feed solution) to 120 L and 175 L, respectively. Tables 2, 3, and 4 show a) the mM concentrations, b) the mol% of the dissolved solids, and c) the mass balance of the components of the concentrated feed, extract, and raffinate streams. Table 5 shows the % recovery of on-path intermediates in the raffinate stream. Table 6 shows operating parameters from the SSMB, including separation productivity and eluent (water)/feed ratio. FIGS. 2 and 3 depict the ion-chromatography chromatograms for the concentrated feed and extract streams.

[0125] Table 3 shows that SSMB enabled enrichment of the glucaric acid content from 47.9 mol% in the feed solution to 90.1 mol%

in the extract. In addition, Table 5 shows that the majority (97% by mass) of the unconverted glucose and on-path intermediates are concentrated in the raffinate stream, thus available for recycle back to the oxidation reactor. Table 6 shows that the SSMB separation can be accomplished with very high productivity with respect to volume of resin required per mass of product separated, conducted with a low water to feed ratio below 3.5.

Table 1. Product Analysis (molar yield % unless indicated)

Flow Rate (kg/hr)	Glucose	Gluconic Acid	Glucaric Acid	Guluronic Acid	Glucuronic Acid	2- and 3-Ketogluconic Acids	4- and 5-Ketogluconic Acids	Sum of C_5-C_2 Di-acids	On Path Percentage (%)
1.3	0.4	43.6	37.8	7.4	0.6	2.7	4.1	3.7	90
0.65	0	20.7	58.3	4.4	0.5	1.3	3.8	5.3	84

Table 2. Composition of Concentrated Feed, Extract and Raffinate Streams from SSMB Separation (mM)

Sample	Glucose	Gluconic Acid	Glucaric Acid	Guluronic Acid	Glucuronic Acid	2- and 3-Ketogluconic Acids	4- and 5-Ketogluconic Acids	C5-Di-acid + Tartaric Acid	Tartronic Acid + Oxalic Acid
Feed	20.7	1030.7	1285.0	80.8	12.2	37.2	50.4	79.6	19.1
Extract	0.0	46.1	2074.6	25.7	0.0	14.3	11.2	124.5	6.1
Raffinate	37.6	1649.7	567.7	116.3	7.9	45.6	73.1	61.3	0.8

Table 3. Components of Feed, Extract and Raffinate Streams from SSMB Separation (mol% of dissolved solids)

Sample	Glucose	Gluconic Acid	Glucaric Acid	Guluronic Acid	Glucuronic Acid	2- and 3-Ketogluconic Acids	4- and 5-Ketogluconic Acids	C5-Di-acid + Tartaric Acid	Tartronic Acid + Oxalic Acid
Feed	0.8	39.4	49.1	3.1	0.5	1.4	1.9	3.0	0.7
Extract	0.0	2.0	90.1	1.1	0.0	0.6	0.5	5.4	0.3
Raffinate	1.5	64.4	22.2	4.5	0.3	1.8	2.9	2.4	0.0

Table 4. Analytical Mass Balance of Feed, Extract and Raffinate Streams from SSMB Separation (kg of dissolved solids)

Sample	Glucose	Gluconic Acid	Glucaric Acid	Guluronic Acid	Glucuronic Acid	2- and 3-Ketogluconic Acids	4- and 5-Ketogluconic Acids	C5-Diacid + Tartaric Acid	Tartronic Acid + Oxalic Acid
Feed	1.1	57.4	76.7	4.5	0.7	2.1	2.8	3.7	0.6
Extract	0.0	1.1	52.3	0.6	0.0	0.3	0.3	2.5	0.1
Raffinate	1.2	56.6	20.9	4.0	0.3	1.5	2.5	1.8	0.0

Table 5. % Recovery of On-Path Intermediates

Sample	Glucose (kg)	Gluconic Acid (kg)	Guluronic Acid (kg)	Glucuronic Acid (kg)	Total
Feed	1.1	57.7	4.5	0.7	64.0
Raffinate	1.2	56.6	4.0	0.3	62.1
% Recovery	100%	98%	89%	43%	97%

Table 6. SSMB Performance Metrics

Productivity (gDS/L resin•day)	Water:Feed Ratio
1500	3.4:1

Example 3. Overloading Test with Gluconic and Glucaric Acids Using Finex AA 543 Anion Exchange Resin in Oxalate, Glucarate, and Sulfate Forms

[0126] The overloading test provides information about the competitive absorption of glucaric acid and gluconic acid on a separation resin under overloading conditions and indicates the feasibility for the resin to be deployed in an industrial simulated moving bed chromatography system.

[0127] The overloading test was conducted using the equipment listed below:

- A chromatography column (1 m bed length and 2.5 cm diameter fitted with a double jacket).
- A water bath connected to the chromatography column double jacket for temperature control.

- A pump with a regulated flow rate control.
- A feed tank.
- An elution tank containing demineralized water.
- A fraction collector.

[0128] The chromatography column was packed with Finex AA 543, a 400-500 µm diameter acrylic divinyl benzene weak base anion exchange resin from Finex Oy, Kotka, Finland. The oxalate, glucarate, and sulfate forms of the resin were tested. The resin was converted to the oxalate and glucarate forms by flowing a solution containing the corresponding acid (i.e., oxalic acid, glucaric acid, and sulfuric acid, respectively) through the column in an upward direction. The water bath temperature was set to 30°C for the overloading tests.

[0129] The overloading test was conducted in two stages: (1) product loading and adsorption and (2) desorption and elution with eluent, using the protocol described as follows. Two bed volumes of a product solution containing 345 g/L glucaric acid and 181 g/L gluconic acid were pumped in down-flow mode through the column at a flow velocity of 2.5 m/hour after which the column was rinsed with 6.5 bed volumes of water also at a flow velocity of 2.5 m/hour. Fractions were collected regularly from the outlet of the column and analyzed for gluconic acid and glucaric acid concentrations using a Dionex HPLC fitted with an Ionpac AS 15 ion exchange column and a conductivity detection system calibrated with gluconic acid and glucaric acid calibration standards.

[0130] The resin performance in the overloading test was by the determination of parameters 1-4:

1. 1) Sweet-on retention time: The bed volume (of liquid flow) corresponding to gluconic acid or glucaric acid reaching 50% of the feed concentration during the adsorption phase.
2. 2) Sweet-off retention time: The bed volume (of liquid flow) corresponding to gluconic acid or glucaric acid reaching 50% of the feed concentration during the desorption phase.
3. 3) The resolution: The bed volume difference between the sweet-on and sweet-off retention times of gluconic acid and glucaric acid.
4. 4) Rinsing volume: The volume of eluent required to rinse the glucaric acid to a concentration below 10 g/L during the desorption phase

   Parameters 1-4 are illustrated for a representative separation in FIG. 4.

[0131] FIG. 4 shows that compound B is adsorbed more strongly than compound A leading to a partial separation. The sweet-on and sweet-off differences (the resolution) in FIG. 4 indicate that the resin can perform an effective separation of compound A from compound B when used in an industrial simulated moving bed chromatography system. A rinsing volume below three bed volumes will minimize the dilution of the separated compounds which is important to keep product isolation costs low.

[0132] Table 7 shows the data from the overloading test using Finex AA 543 anion exchange resin in oxalate, glucarate, and sulfate forms using water as the eluent. Table 7 demonstrates that an effective separation of gluconic acid from glucaric acid can be performed using Finex AA 543 anion exchange resin in oxalate and glucarate forms using water as the eluent.

Table 7. Overloading Test Results Using Finex AA 543 with Water as the Eluent

Compound	Time period	AA 543 Oxalate Form Resin	AA 543 Glucarate Form Resin	AA 543 Sulfate Form Resin
Gluconic Acid	Sweet-On (BV)	0.74	0.62	0.62
	Sweet-Off (BV)	2.58	2.58	2.65
Glucaric Acid	Sweet-On (BV)	0.98	0.85	0.82
	Sweet-Off (BV)	2.90	2.85	2.85
Glucaric-Gluconic Sweet-On Difference (BV)		0.24	0.23	0.20
Glucaric-Gluconic Sweet-Off Difference (BV)		0.32	0.27	0.20
Rinsing to Glucaric Acid Concentration at <10 g/L		2.57	2.85	1.88
*BV: bed volumes				

[0133] Additional overloading tests were conducted with the oxalate and glucarate forms of the following resins and using water as the eluent: Finex AA532 (a strong base anion Type 2, PS/DVB resin), Finex Ethylamine (a weak base anion, PS-DVB resin), Finex Dimethylamine (a 64% weak base anion/36% strong base anion, PS-DVB resin), Finex Butylamine (a weak base anion, PS-DVB

resin), Mitsubishi UMA150 (strong base anion Type 1, PS-DVB resin), Mitsubishi WAG-M1 (weak base anion, polyacrylic DVB resin), Lanxess MDS 4368 (75-80% weak base anion/20-25% strong base anion, PS-DVB resin), Lanxess MDS 4468 (92% weak base anion/8% strong base anion, PS-DVB resin), Lanxess MDS 4568 (weak base anion, PS-DVB resin), Lanxess MDS FO36ZII(weak base anion, PS-DVB resin), and Lanxess KPN 19494(79.5 weak base anion/20.5 weak acid cation, PS-DVB resin). The results for these resins were similar to those for Finex AA543 and demonstrate that an effective separation of gluconic acid from glucaric acid can be performed using these resins and water as the eluent.

[0134] Table 8 shows the data from the overloading test using Finex AA 543 anion exchange resin in oxalate, glucarate, and sulfate forms, but using various acid-containing solutions as the eluents (i.e., oxalic acid, glucaric acid (as a solution of glucarodilactone), and sulfuric acid).

Table 8. Overloading Test Results Using Finex AA 543 with Acid-Containing Solutions as the Eluents

Compound	Time period	AA 543 Oxalate Form Resin (1 g/L oxalic acid eluent)	AA 543 Glucarate Form Resin (1 g/L glucaro dilactone eluent)	AA 543 Sulfate Form Resin (2 g/L sulfuric acid eluent)
Gluconic Acid	Sweet-On (BV)	0.62	0.65	0.60
	Sweet-Off (BV)	2.60	2.58	2.60
Glucaric Acid	Sweet-On (BV)	0.80	0.85	0.78
	Sweet-Off (BV)	2.85	2.88	2.80
Glucaric-Gluconic Sweet-On Difference (BV)		0.18	0.20	0.18
Glucaric-Gluconic Sweet-Off Difference (BV)		0.25	0.30	0.20
Rinsing to Glucaric Acid Concentration at <10 g/L		2.05	2.85	1.63
*BV: bed volume				

[0135] When introducing elements of the present invention or the preferred embodiments(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive or open-ended and mean that there may be additional elements other than the listed elements and do not exclude unrecited elements or steps.

REFERENCES CITED IN THE DESCRIPTION

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Patentkrav

1. Fremgangsmåde til fremstilling af et ekstrakt omfattende et C_2- til C_6-di-carboxylsyre eller salt deraf, hvilken fremgangsmåde omfatter:

at bringe et separationsmedie i en separationszone i kontakt med en udgangsblanding omfattende C_2 til C_6-di-carboxylsyren eller salt deraf og en anden komponent omfattende en C_1- til C_6-mono-carboxylsyre, hvor mindst en del af C_2- til C_6-di-carboxylsyren eller salt deraf og den anden komponent fastholdes på separationsmediet;

at eluere mindst en del af den anden komponent fra separationsmediet med et elueringsmiddel omfattende vand for at danne et raffinat omfattende den anden komponent;

at fjerne raffinatet fra separationszonen; og

at eluere C_2- til C_6-di-carboxylsyren eller salt deraf fra separationsmediet med elueringsmidlet omfattende vand for at danne ekstraktet omfattende C_2- til C_6-di-carboxylsyren eller salt deraf, hvor ekstraktet omfatter mindst 50 vægtprocent af C_2- til C_6-di-carboxylsyreindholdet af udgangsblandingen,

hvor separationsmediet omfatter en di-carboxylatform af et anionbytterkromatografiresin,

hvor di-carboxylatformen af anionbytterkromatografiresinet fremstilles ved konditionering af anionbytterkromatografiresinet med en di-carboxylsyre, og

hvor den fremmede syrekoncentration af elueringsmidlet, forud for kontakt med separationsmediet, er mindre end 0,1 vægtprocent.

2. Fremgangsmåden ifølge krav 1, hvor den fremmede syrekoncentration af elueringsmidlet, forud for kontakt med separationsmediet, er mindre end 0,01 vægtprocent.

3. Fremgangsmåden ifølge krav 1 eller 2, hvor di-carboxylatformen af anionbytterkromatografiresinet omfatter en form valgt fra gruppen bestående af

oxalat, tartronat, malonat, tartrat, succinat, xylarat, arabinarat, ribarat, glutarat, glucarat, adipat, og blandinger deraf.

4. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 3, hvor di-carboxylatsyren anvendt til at konditionere anionbytterkromatografiresinet omfatter en di-carboxylsyre der er til stede i udgangsblandingen.

5. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 4, hvor anionbytterkromatografiresinet omfatter et lavbasisk anionbytterkromatografiresin.

6. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 5, hvor ekstraktet omfatter fra 55 vægtprocent til 99 vægtprocent af C_2- til C_6-di-carboxylsyreindholdet af udgangsblandingen og raffinatet omfatter fra 60 vægtprocent til 95 vægtprocent af den anden komponent indhold af udgangsblandingen.

7. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 6, hvor det opløste faststofindhold af udgangsblandingen er fra 20 vægtprocent til 70 vægtprocent og C_2- til C_6-di-carboxylsyrekoncentrationen i udgangsblandingen er fra 20 vægtprocent til 70 vægtprocent af det opløste faststofindhold.

8. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 7, hvor den anden komponent omfatter en C_6-mono-carboxylsyre valgt fra gruppen bestående af glukonsyre, guluronsyre, glukuronsyre, og blandinger deraf.

9. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 8, hvor den anden komponent yderligere omfatter et sukker valgt fra gruppen bestående af et pentose, hexose, og blandinger deraf.

10. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 9, hvor den anden komponent yderligere omfatter glukose.

11. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 10, hvor C_2- til C_6-di-carboxylsyren omfatter en eller flere syrer valgt fra gruppen bestående af oxalsyre, tartronsyre, malonsyre, vinsyre, ravsyre, xylarsyre, arabinarsyre, ribarsyre, glutarsyre, glucarsyre, adipinsyre og blandinger deraf.

12. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 11, hvor di-carboxylsyren omfatter glucarsyre.

13. Fremgangsmåden ifølge et hvilket som helst af kravene 1 til 12, hvor separationszonen er et simulated-moving-bed-kromatografitrin.

14. Fremgangsmåde til fremstilling af et aldarsyre, hvilken fremgangsmåde omfatter:

at oxidere et aldose med oxygen i tilstedeværelsen af en oxideringskatalysator i en oxideringsreaktionszone for at danne et oxideringsprodukt omfattende aldarsyren og on-path-intermediater til aldarsyren;

at fjerne oxideringsproduktet fra tilstedeværelsen af oxideringskatalysatoren; og

at fremstille et ekstrakt omfattende aldarsyren i henhold til fremgangsmåden ifølge et hvilket som helst af kravene 1 til 13, hvor udgangsblandingen omfatter aldarsyren som di-carboxylsyren og on-path-intermediater til aldarsyren som den anden komponent opnået fra oxideringsproduktet.

15. Fremgangsmåden ifølge krav 14, hvor aldosen omfatter glucose og aldarsyren omfatter glucarsyre.

DRAWINGS

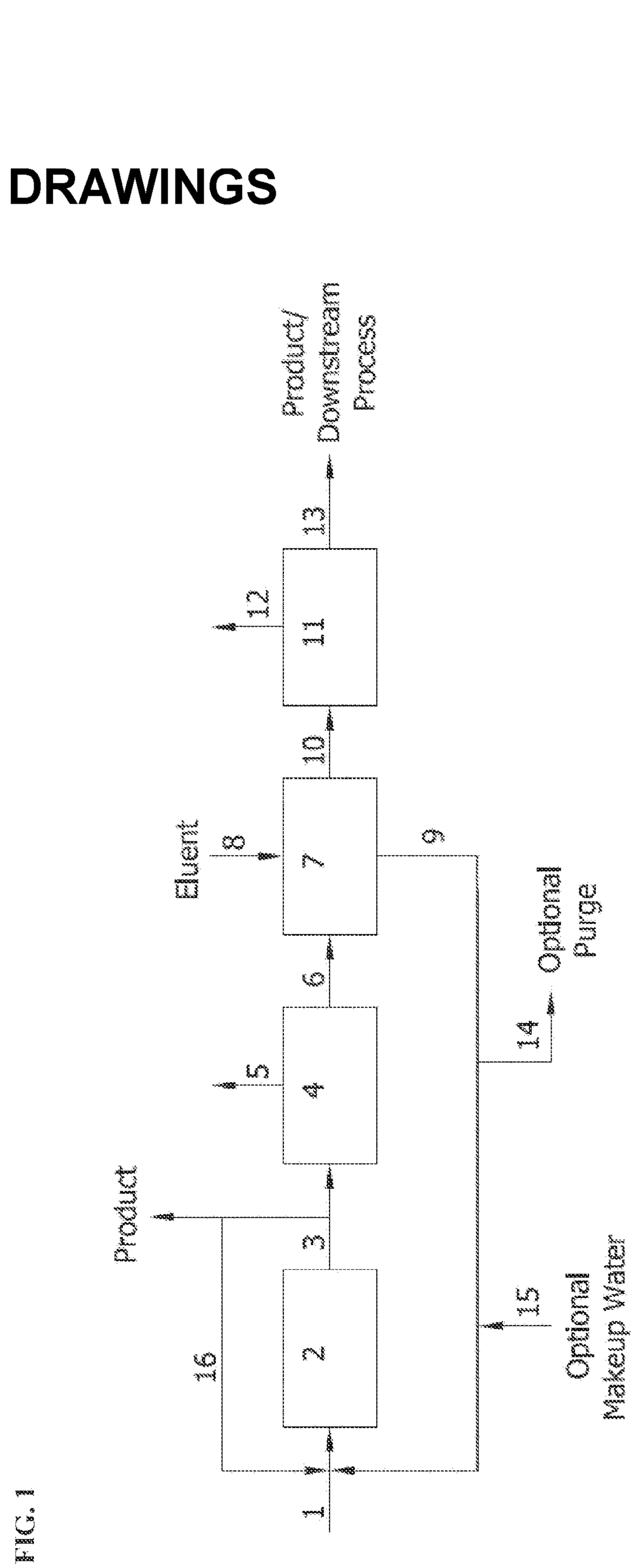
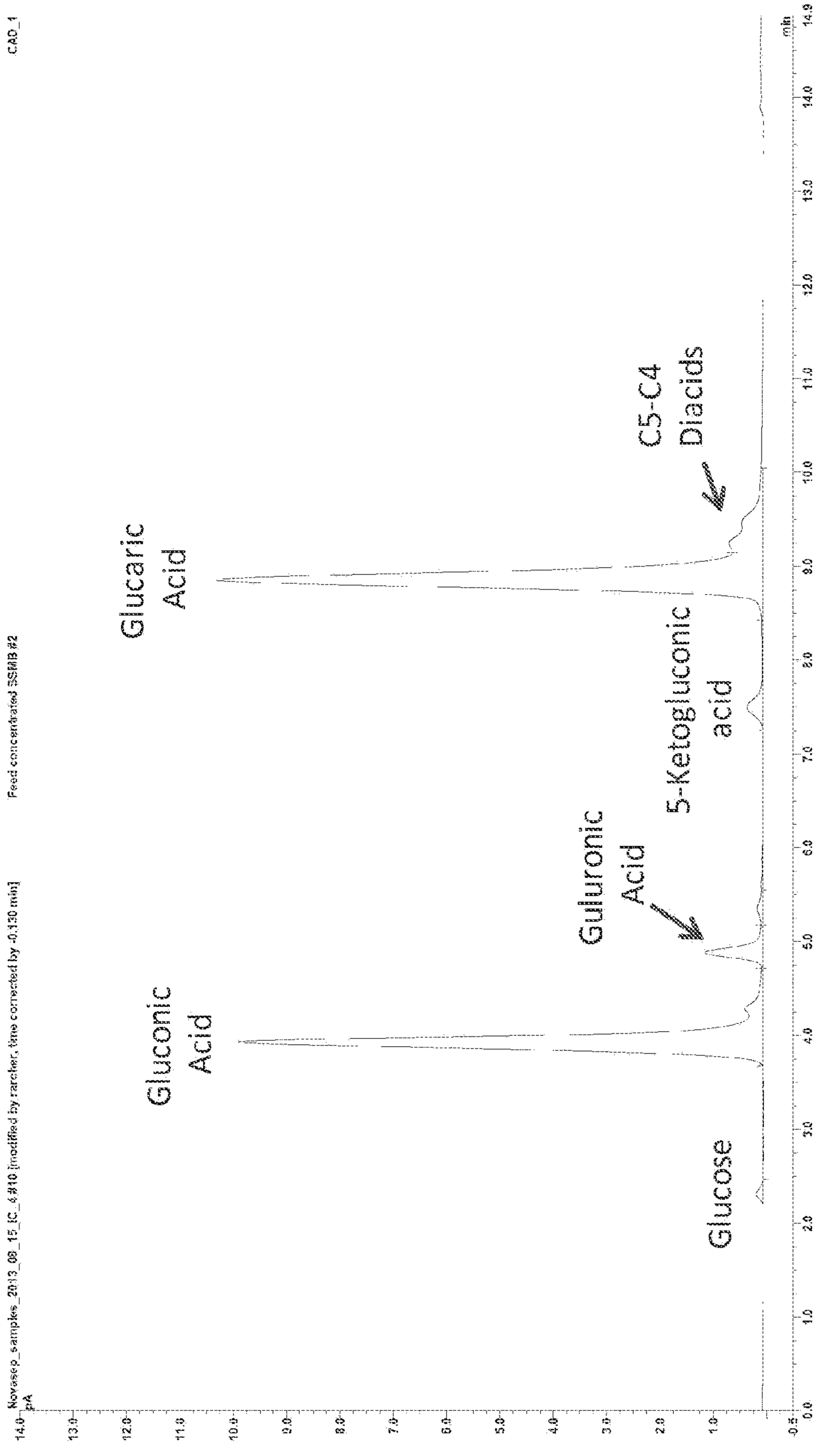


FIG. 1

FIG. 2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Glucaric Acid
5-Ketogluconic acid
C5-C4 Diacid
Glucose
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13.0
12.0
11.0
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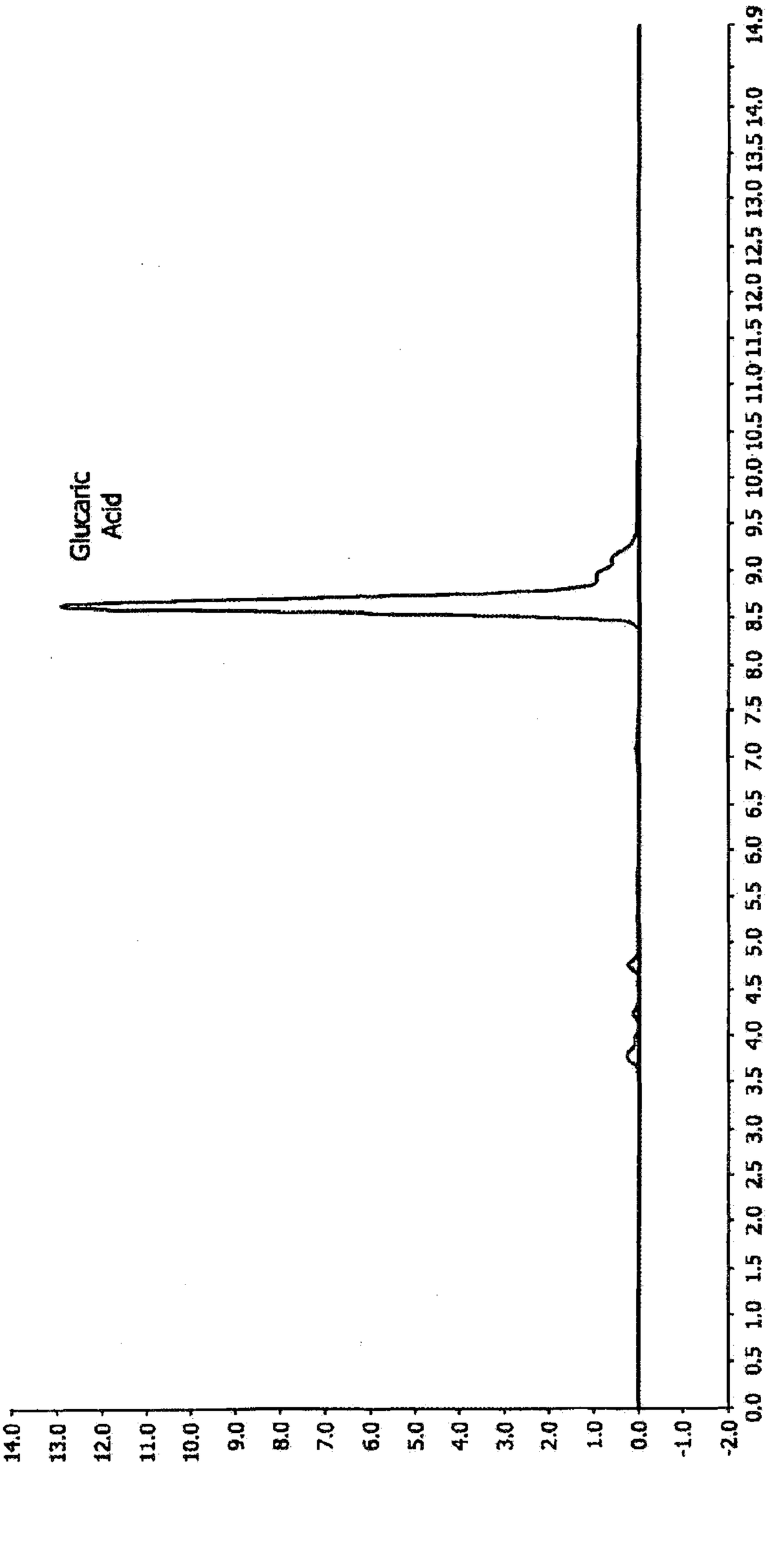
Glucaric Acid
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3.0
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-2.0
14.0
13.0
12.0
11.0
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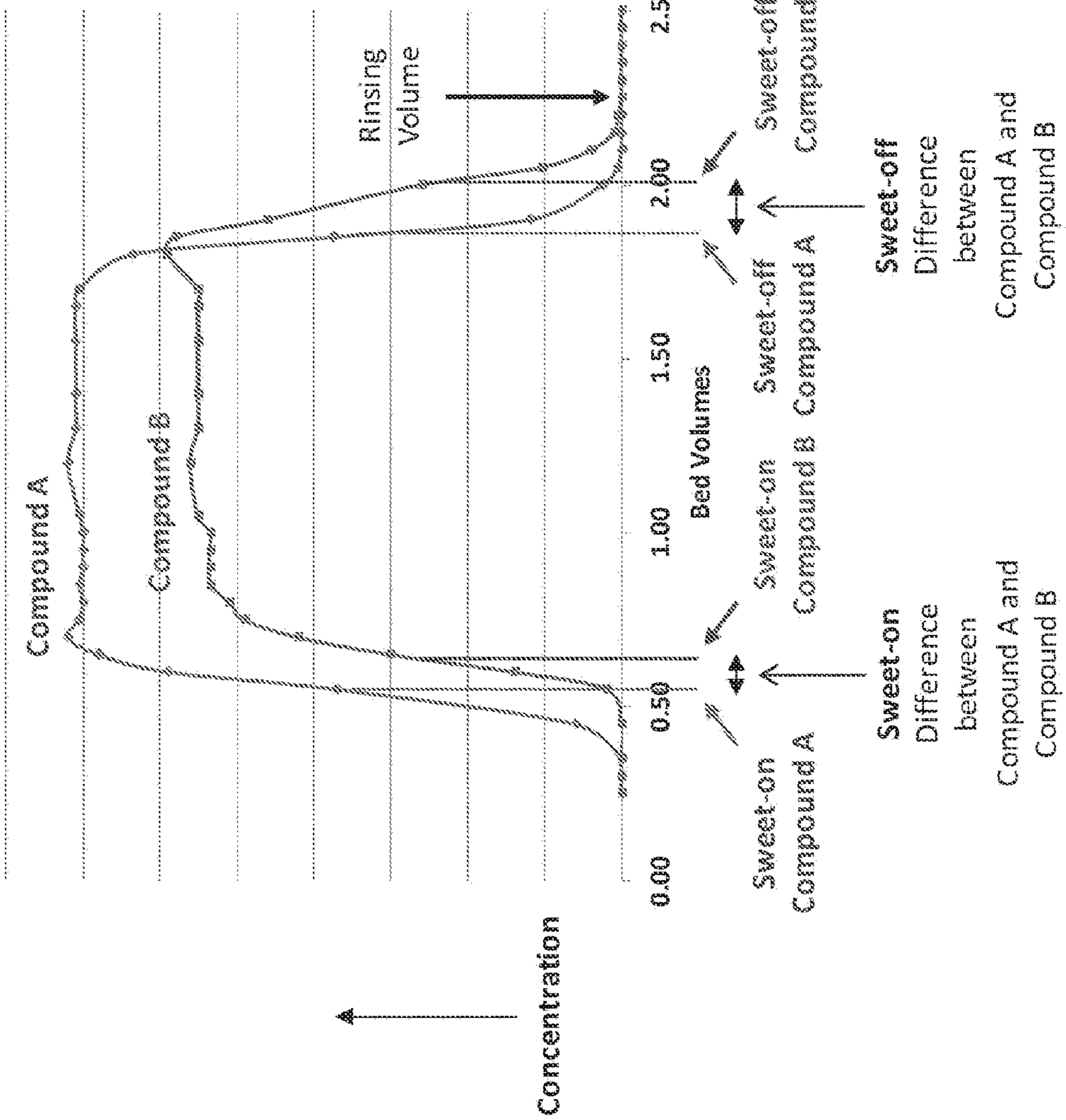
-2.0

FIG. 3


Concentration
Bed Volumes
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1.00
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2.00
2.50
Rinsing Volume
Compound A
Compound B
Sweet-on Compound A
Sweet-on Compound B
Sweet-on Difference between Compound A and Compound B
Sweet-off Compound A
Sweet-off Compound B
Sweet-off Difference between Compound A and Compound B

FIG. 4