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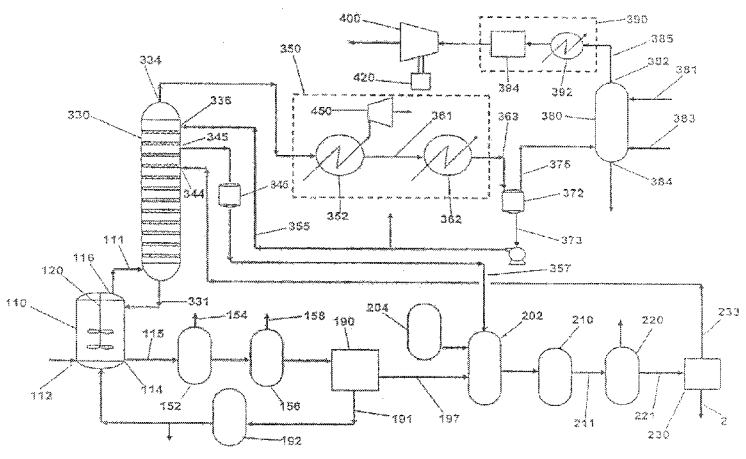
Figure 1



(57) Abstract: An improved process for preparing aromatic carboxylic acids by fee exothermic liquid-phase oxidation reaction of an aromatic feedstock compound wherein water is efficiently recovered from the exothermic liquid-phase oxidation reaction and treated to reduce corrosive agents residing therein.

WO 2015/094911 A1

IMPROVED PROCESS AND APPARATUS FOR MANUFACTURING AROMATIC CARBOXYLIC ACIDS

Cross-Reference to Related Applications

[0001] This application claims benefit of U.S. provisional patent application Serial No. 61/917,465 filed December 18, 2013, and entitled "Improved Process and Apparatus for Manufacturing Aromatic Carboxylic Acids" which is hereby incorporated herein by reference in its entirety for all purposes.

Field of the Invention

[0002] This invention relates to an improved process for preparing aromatic carboxylic acids by the exothermic liquid-phase oxidation reaction of an aromatic feedstock compound wherein water is efficiently recovered from the exothermic liquid-phase oxidation reaction and treated to reduce corrosive agents residing therein.

Background of the Invention

[0003] Terephthalic acid and other aromatic carboxylic acids are widely used in manufacture of polyesters, commonly by reaction with ethylene glycol, higher alkylene glycols or combinations thereof, for conversion to fiber, film, containers, bottles and other packaging materials, and molded articles.

[0004] In commercial practice, aromatic carboxylic acids are commonly made by liquid phase oxidation in an aqueous acetic acid solvent of methyl-substituted benzene and naphthalene feedstocks, in which the positions of the methyl substituents correspond to the positions of carboxyl groups in the desired aromatic carboxylic acid product, with air or another source of oxygen, which is normally gaseous, in the presence of a bromine-promoted catalyst comprising cobalt and manganese. The oxidation is exothermic and yields aromatic carboxylic acid together with by-products, including partial or intermediate oxidation products of the aromatic feedstock, and acetic acid reaction products, such as methanol, methyl acetate, and methyl bromide. Water is also generated as a by-product. Aromatic carboxylic acid, typically accompanied by oxidation by-products of the feedstock are commonly formed dissolved or as suspended solids in the liquid phase reaction mixture and are commonly recovered by crystallization and solid-liquid separation techniques. The exothermic oxidation reaction is commonly conducted in a suitable reaction vessel at elevated temperature and pressure. A liquid phase reaction mixture is maintained in the vessel and a vapor phase formed as a result of the exothermic oxidation is evaporated from the liquid

phase and removed from the reactor to control reaction temperature. The vapor phase comprises water vapor, vaporized acetic acid reaction solvent and small amounts of by-products of the oxidation, including both solvent and feedstock by-products. It usually also contains oxygen gas not consumed in oxidation, gaseous methyl bromide, minor amounts of unreacted feedstock, carbon oxides and, when the oxygen source for the process is air or another oxygen-containing gaseous mixture, nitrogen, carbon oxides and other inert gaseous components of the source gas.

[0005] Pure forms of aromatic carboxylic acids are often favored for manufacture of polyesters for important applications, such as fibers and bottles, because impurities, such as by-products generated from aromatic feedstocks in such oxidation processes and, more generally, various carbonyl-substituted aromatic species are known to cause or correlate with color formation in polyesters made from the acids and, in turn, off-color in polyester converted products. Aromatic carboxylic acids with reduced levels of impurities can be made by further oxidizing crude products from liquid phase oxidation as described above at one or more, progressively lower temperatures and oxygen levels, and during crystallization to recover products of the oxidation, for conversion of feedstock partial oxidation products to the desired acid product, as known from U.S. Pat. Nos. 4,877,900, 4,772,748 and 4,286,101. Preferred pure forms of terephthalic acid and other aromatic carboxylic acids with lower impurities contents, such as purified terephthalic acid or "PTA", are made by catalytically hydrogenating less pure forms of the acids, such as crude product comprising aromatic carboxylic acid and by-products generated by liquid phase oxidation of aromatic feedstock or so-called medium purity products, in solution at elevated temperature and pressure using a noble metal catalyst. In commercial practice, liquid phase oxidation of alkyl aromatic feed materials to crude aromatic carboxylic acid and purification of the crude product are often conducted in continuous integrated processes in which crude product from liquid phase oxidation is used as starting material for purification.

[0006] The high temperature and pressure vapor phase generated by liquid phase oxidation in such processes is a potentially valuable source of recoverable acetic acid reaction solvent, unreacted feed material and reaction by-products, as well as energy. Its substantial water content, high temperature and pressure and corrosive nature due to components such as gaseous methyl bromide, acetic acid solvent and water, however, pose technical and economic challenges to separating or recovering components for recycle and recovering its energy content. Further, impurities that remain unseparated in recovered process streams can prevent re-use of streams if impurities adversely affect other process aspects, equipment or

product quality. As described in U.S. Pat. No. 5,200,557, for example, monocarboxylic acids adversely affect hydrogenation catalysts used in purification processes, with even low levels of acetic acid residues such as present in crude aromatic carboxylic acid products recovered from oxidation reaction liquids being considered detrimental.

[0007] British Patent Specification 1,373,230, U.S. Pat. Nos. 5,304,676; 5,723,656; 6,143,925; 6,504,051, European Patent Specification 0 498 591 B1 and International Application WO 97/27168 describe processes for manufacture of aromatic carboxylic acids by liquid phase oxidation of aromatic feed materials in which a high pressure off-gas is removed from oxidation and treated for recovery and recycle of portions or components thereof and, in some cases, recovery of energy. Condensation of off-gas, as in U.S. Pat. No. 5,304,676, is effective for recovery of water, acetic acid and other condensable components of the off-gas but separating water, acetic acid and other components in the resulting condensate is technically complex and economically impractical. High pressure off-gas separations, as in processes of U.S. Pat. Nos. 5,723,656, 6,143,925, 6,504,051 and WO 97/27168, can be effective for separating off-gases to recover acetic acid-rich liquids and gases comprising water vapor suitable for further processing. However, certain by-products of the oxidation tend to apportion into both liquid and gas phases in such separations, complicating their recovery and potentially adversely impacting other process streams and steps. These difficulties are compounded by build-up of such by-products in processes in which by-product-containing streams, such as mother liquor remaining after recovery of pure forms of aromatic carboxylic acid from a purification liquid reaction mixture or liquids condensed effluent gases from high pressure separations are used in separations. None of the processes according to the cited patents uses liquid condensed from a high pressure off-gas from a liquid phase oxidation as solvent or other liquid comprising water in the purification of impure aromatic carboxylic acids and recoveries of materials and energy in such processes often are accomplished at the expense of each other, for example due to loss of energy content on cooling or depressurizing to recover materials, burning of materials to control atmospheric emissions and other losses of oxidation solvent, feedstock and by-products that result if a high temperature and pressure vapor phase from oxidation is not cooled or depressurized for removal of such materials.

[0008] Impurities remaining in recycle streams can upset process operation, corrode equipment, and impair product quality. Added equipment and process steps for recovering materials, energy or both can add further process complexities and limit or preclude their practical utility if they add costs that outweigh materials and energy savings. Impact of such

factors, lost energy and lost materials are magnified by scale of process operations. In world-scale commercial manufacturing plants with annual capacities of 500,000 to 1,000,000 or more tons of product, even fractional percentages or hundreds of parts per million of feedstock and solvent lost or converted to undesired or unusable by-products, minor inefficiencies in energy recovery and incremental additions to effluent water treatment translate to significant practical losses of materials, increases in consumption of fuel or electricity and added processing, as well as unpredictable process efficiencies and economics due to differences and variations in costs for energy, materials and requirements for treatment of gaseous and liquid emissions and effluents.

Summary of the Invention

[0009] The present invention provide a continuous process for preparing aromatic carboxylic acids by the exothermic liquid-phase oxidation reaction of an aromatic feedstock compound wherein water is efficiently recovered from the exothermic liquid-phase oxidation reaction, which process comprises:

[00010] (a) oxidizing an aromatic feedstock compound to an aromatic carboxylic acid in a liquid-phase reaction mixture comprising water, a low-molecular weight monocarboxylic acid solvent, a heavy metal oxidation catalyst and a source of molecular oxygen, under reaction conditions which produce a gaseous high pressure overhead stream comprising water, gaseous by-products, and gaseous low-molecular weight monocarboxylic acid solvent;

[00011] (b) separating in a high efficiency separation apparatus a solvent monocarboxylic acid-rich first liquid phase and a water-rich second liquid phase comprising dissolved oxygen and methyl bromide; and

[00012] (c) reducing the amount of at least one of dissolved oxygen and methyl bromide present in the second liquid phase providing a treated second liquid phase.

[00013] In one embodiment the step of treating the second liquid phase comprises flashing the second liquid phase.

[00014] In one embodiment flashing the second liquid phase results in a drop in pressure from about 5 kg/cm^2 to about 40 kg/cm^2 to about atmospheric or ambient pressure.

[00015] In one embodiment flashing the second liquid phase results in a drop in pressure from about 10 kg/cm^2 to about 20 kg/cm^2 to about atmospheric or ambient pressure.

[00016] In one embodiment the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 1.0 ppmw after flashing.

[00017] In one embodiment the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 0.5 ppmw after flashing.

[00018] In one embodiment the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 0.05 ppmw after flashing.

[00019] In one embodiment the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 0.006 ppmw after flashing.

[00020] In one embodiment the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.02 ppmw after flashing.

[00021] In one embodiment the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.01 ppmw after flashing.

[00022] In one embodiment the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.009 ppmw after flashing.

[00023] In one embodiment the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.006 ppmw after flashing.

[00024] In one embodiment the step of treating the second liquid phase further comprises a step of steam stripping the second liquid phase after flashing.

[00025] In one embodiment the step of treating the second liquid phase further comprises a step of stripping the second liquid phase with nitrogen after flashing.

[00026] In one embodiment, the treated second liquid phase is suitable for use as liquid comprising water in one or more steps of a process for purifying impure forms of aromatic carboxylic acid.

[00027] In another embodiment, the treated second liquid phase is suitable for use as a seal flush.

Brief Description of the Drawings

[00028] The invention is described with reference to the drawings, in which:

[00029] FIG. 1 is a flow diagram illustrating an apparatus and process according to preferred embodiments of the invention, including integration of the apparatus

with other equipment used for manufacture and purification of aromatic carboxylic acids according to embodiments of the invention; and

[00030] FIG. 2 is an expanded view of a preferred form of apparatus according to preferred embodiments of the invention and useful for carrying out the process according to embodiments thereof.

Detailed Description of the Invention

Aromatic carboxylic acids

[00031] Aromatic carboxylic acids for which the invention is suited include mono- and polycarboxylated species having one or more aromatic rings and which can be manufactured by reaction of gaseous and liquid reactants in a liquid phase system. Examples of such aromatic carboxylic acids include terephthalic acid, trimesic acid, trimellitic acid, phthalic acid, isophthalic acid, benzoic acid and naphthalene dicarboxylic acids. The invention is particularly suited for manufacture of pure forms of terephthalic acid including purified terephthalic acid and so-called medium purity terephthalic acids.

Oxidation Step

[00032] An oxidation step of the invented process is a liquid phase oxidation that comprises contacting oxygen gas and a feed material comprising an aromatic hydrocarbon having substituents oxidizable to carboxylic acid groups in a liquid phase reaction mixture comprising a monocarboxylic acid solvent and water in the presence of a catalyst composition comprising at least one heavy metal component. The oxidation step is conducted at elevated temperature and pressure effective to maintain a liquid phase reaction mixture and form a high temperature, high pressure vapor phase. Oxidation of the aromatic feed material in the liquid phase oxidation step produces aromatic carboxylic acid as well as reaction by-products such as partial or intermediate oxidation products of the aromatic feed material and solvent by-products. The liquid-phase oxidation step and associated process steps can be conducted as a batch process, a continuous process, or a semi-continuous process. The oxidation step can be conducted in one or more reactors.

Feed Materials

[00033] Suitable aromatic feed materials for the oxidation generally comprise an aromatic hydrocarbon substituted at one or more positions, normally corresponding to the positions of the carboxylic acid groups of the aromatic carboxylic acid being prepared, with at least one group that is oxidizable to a carboxylic acid group. The oxidizable substituent or substituents can be alkyl groups, such as a methyl, ethyl or isopropyl groups, or groups already containing oxygen, such as a hydroxyalkyl, formyl or keto group. The substituents

can be the same or different. The aromatic portion of feedstock compounds can be a benzene nucleus or it can be bi- or polycyclic, such as a naphthalene nucleus. The number of oxidizable substituents on the aromatic portion of the feedstock compound can be equal to the number of sites available on the aromatic portion, but is generally fewer than all such sites, preferably 1 to about 4 and most preferably 2. Examples of useful feed compounds, which can be used alone or in combinations, include toluene, ethylbenzene and other alkyl-substituted benzenes, o-xylene, p-xylene, m-xylene, tolualdehydes, toluic acids, alkyl benzyl alcohols, 1-formyl-4-methylbenzene, 1-hydroxymethyl-4-methylben-zene, methylacetophenone, 1,2,4-trimethylbenzene, 1-formyl-2,4-dimethyl-benzene, 1,2,4,5-tetramethyl-benzene, alkyl-, formyl-, acyl-, and hydroxylmethyl-substituted naphthalenes, such as 2,6-dimethylnaphthalene, 2,6-diethylnaphthalene, 2,7-dimethylnaphthalene, 2,7-diethylnaphthalene, 2-formyl-6-methylnaphthalene, 2-acyl-6-methylnaphthalene, 2-methyl-6-ethylnaphthalene and partially oxidized derivatives of the foregoing.

[00034] For manufacture of aromatic carboxylic acids by oxidation of their correspondingly substituted aromatic hydrocarbon pre-cursors, e.g., manufacture of benzoic acid from mono-substituted benzenes, terephthalic acid from para-disubstituted benzenes, phthalic acid from ortho-disubstituted benzenes, and 2,6 or 2,7 naphthalene dicarboxylic acids from, respectively, 2,6- and 2,7-disubstituted naphthalenes, it is preferred to use relatively pure feed materials, and more preferably, feed materials in which content of the pre-cursor corresponding to the desired acid is at least about 95 wt. %, and more preferably at least 98 wt. % or even higher. A preferred aromatic hydrocarbon feed for use to manufacture terephthalic acid comprises para-xylene. A preferred feed material for making benzoic acid comprises toluene.

Solvent

[00035] Solvent for the liquid phase reaction of aromatic feed material to aromatic carboxylic acid product in the liquid phase oxidation step comprises a low molecular weight monocarboxylic acid, which is preferably a C.sub.1-C.sub.8 monocarboxylic acid, for example acetic acid, propionic acid, butyric acid, valeric acid and benzoic acid. Lower aliphatic monocarboxylic acids and benzoic acid are preferred because they are less reactive to undesirable reaction products than higher molecular weight monocarboxylic acids under reaction conditions used in for liquid phase oxidations to aromatic carboxylic acids and can enhance catalytic effects in the oxidation. Acetic acid is most preferred. Solvents in the form of aqueous solutions thereof, for example about 80 to about 95 wt. % solutions of the acid are most commonly used in commercial operations.

Ethanol and other co-solvent materials that oxidize to monocarboxylic acids under the liquid phase oxidation reaction conditions also can be used as is or in combination with monocarboxylic acids with good results. When using a solvent comprising a mixture of a monocarboxylic acid and such a co-solvent, co-solvents oxidizable to the same monocarboxylic are preferably used so that solvent separation steps are not further complicated.

[00036] In regard to solvents for the liquid phase oxidation according to the invention, the expression "solvent monocarboxylic acid" as used herein in reference to a component of various gaseous or liquid streams refers to a monocarboxylic acid having the same chemical composition as the monocarboxylic acid used as solvent for the liquid phase oxidation. Such usage also distinguishes those chemical compositions from other monocarboxylic acids that may be present as oxidation by-products. By way of example, when the liquid phase reaction mixture for oxidation includes acetic acid solvent, the expression "solvent monocarboxylic acid" refers to acetic acid but not other monocarboxylic acid species such as benzoic and toluic acids which are common partial or intermediate oxidation by-products of aromatic feed materials used according to the invention. Also, as will be clear from context, the word "solvent" as used in the expression "solvent monocarboxylic acid" may, but does not necessarily, refer to the function of the monocarboxylic acid to which it refers. Thus, again by way of example, "solvent monocarboxylic acid" described as a component of a liquid phase oxidation reaction mixture is present as solvent for the mixture; however, "solvent monocarboxylic acid" described as a component present in a high pressure vapor phase generated in the oxidation or as a component of a liquid phase separated from such a vapor phase is not intended to denote that the monocarboxylic acid is functioning as a solvent.

Catalysts

[00037] Catalysts used for the liquid oxidation comprise materials that are effective to catalyze oxidation of the aromatic feed material to aromatic carboxylic acid. Preferred catalysts are soluble in the liquid phase reaction mixture used for oxidation because soluble catalysts promote contact among catalyst, oxygen gas and liquid feed materials; however, heterogeneous catalyst or catalyst components may also be used. Typically, the catalyst comprises at least one heavy metal component such as a metal with atomic weight in the range of about 23 to about 178. Examples of suitable heavy metals include cobalt, manganese, vanadium, molybdenum, chromium, iron, nickel, zirconium, cerium or a lanthanide metal such as hafnium. Suitable forms of these metals include, for example,

acetates, hydroxides, and carbonates. Preferred catalysts comprise cobalt, manganese, combinations thereof and combinations with one or more other metals and particularly hafnium, cerium and zirconium.

Promoters

[00038] In preferred embodiments, catalyst compositions for liquid phase oxidation also comprise a promoter, which promotes oxidation activity of the catalyst metal, preferably without generation of undesirable types or levels of by-products. Promoters that are soluble in the liquid reaction mixture used in oxidation are preferred for promoting contact among catalyst, promoter and reactants. Halogen compounds are commonly used as a promoter, for example hydrogen halides, sodium halides, potassium halides, ammonium halides, halogen-substituted hydrocarbons, halogen-substituted carboxylic acids and other halogenated compounds. Preferred promoters comprise at least one bromine source. Suitable bromine sources include bromo-anthracenes, Br_2, HBr, NaBr, KBr, NH_4Br, benzyl-bromide, bromo acetic acid, dibromo acetic acid, tetrabromoethane, ethylene dibromide, bromoacetyl bromide and combinations thereof. Other suitable promoters include aldehydes and ketones such as acetaldehyde and methyl ethyl ketone.

Oxygen source

[00039] Reactants for the liquid phase reaction of the oxidation step also include a gas comprising molecular oxygen. Air is conveniently used as a source of oxygen gas. Oxygen-enriched air, pure oxygen and other gaseous mixtures comprising molecular oxygen, typically at levels of at least about 10 vol. %, also are useful. As will be appreciated, as molecular oxygen content of the source increases, compressor requirements and handling of inert gases in reactor off-gases are reduced. When air or other oxygen-containing gaseous mixtures are used as an oxygen source for the process, the high pressure vapor phase generated by the liquid phase reaction in the oxidation step comprises nitrogen or other inert gas components of the oxygen source.

Oxidation

[00040] Proportions of aromatic feed material, catalyst, oxygen and solvent are not critical to the invention and vary with factors that include choice of reactants, solvent and catalyst compositions and intended aromatic carboxylic acid product, details of process design and operating factors. Solvent to aromatic feedstock weight ratios ranging from about 1:1 to about 30:1 are preferred, with about 2:1 to about 5:1 being more preferred although higher and lower ratios, even in the range of hundreds to one also can be used. Oxygen gas typically is used in at least a stoichiometric amount based on aromatic feed material but not

so great, taking into account reaction conditions, rates and organic components of the high pressure vapor phase resulting from the liquid phase reaction that a flammable mixture exists in the vapor phase. In commercial operations using preferred aromatic feed materials, solvent monocarboxylic acid, catalyst compositions and operating conditions, oxygen gas, most commonly supplied in the form of air, is preferably supplied to the liquid phase oxidation at a rate effective to provide at least about 3 to about 5.6 moles molecular oxygen per mole of aromatic hydrocarbon feed material. A high pressure vapor phase resulting from liquid phase oxidation is preferably removed from the reaction at a rate such that oxygen content of the vapor phase in a reaction zone contains from about 0.5 to about 8 vol. % oxygen measured on a solvent-free basis. Other things being equal, variations in vapor phase oxygen contents, such as by increasing or decreasing reaction rates by use of greater or lesser amounts of catalyst in the liquid phase oxidation, can influence by-product generation in the oxidation, with lower vapor phase oxygen contents, for example up to about 3 vol. %, or from about 0.5 to about 2.5 vol. %, tending to favor more complete conversion of aromatic hydrocarbon feed to the aromatic carboxylic acid and, in turn, reduced oxidation by-products of the aromatic feedstock but with increased generation of solvent by-products. By way of example, in liquid phase oxidations using para-xylene feed materials and acetic acid as solvent for oxidation, vapor phase oxygen contents of about 0.5 to about 3 vol. % are preferred for making aromatic carboxylic acid products in which levels of para-xylene by-products are reduced but acetic acid by-products are increased as compared to operation at higher vapor phase oxygen contents. Catalyst suitably is used in concentrations of catalyst metal, based on weight of aromatic hydrocarbon feed and solvent, greater than about 100 ppmw, preferably greater than about 500 ppmw, and less than about 10,000 ppmw, preferably less than about 6,000 ppmw, more preferably less than about 3,000 ppmw. Preferably a halogen promoter and more preferably a promoter comprising bromine, is present. Such a promoter is present in an amount such that the atom ratio of halogen to catalyst metal suitably is greater than about 0.1:1, preferably greater than about 0.2:1 and suitably is less than about 4:1, preferably less than about 3:1. The atom ratio of halogen to catalyst metal most preferably ranges from about 0.25:1 to about 2:1. Other things being equal, reaction rates and consumption of oxygen gas in liquid phase oxidation increase and levels of unreacted oxygen in the vapor phase from oxidation decrease, with increased catalyst concentrations in the oxidation reaction mixture.

[00041] The liquid phase reaction for oxidation of aromatic feed material to product comprising aromatic carboxylic acid is conducted in a suitable oxidation reaction zone, which normally comprises one or more oxidation reaction vessels. Suitable oxidation

reaction vessels are configured and constructed to withstand the high temperature and pressure conditions and corrosive liquid and vapor phase contents used and present in the reaction zone and to provide for addition and mixing of catalyst, liquid and gaseous reactants and solvent, removal of aromatic carboxylic acid product or a liquid comprising such product for recovery thereof, and removal of a high pressure vapor phase generated by the liquid phase reaction for controlling heat of reaction. Reactor types which can be used include continuous stirred tank reactors and plug-flow reactors. Commonly, oxidation reactors comprise a columnar vessel, normally with a central axis which extends vertically when the vessel is positioned for process use, having one or more mixing features for mixing liquid reactants and distributing oxygen gas within the liquid phase boiling reaction mixture. Typically, the mixing feature comprises one or more impellers mounted on a rotatable or otherwise movable shaft. For example, impellers may extend from a rotatable central vertical shaft Reactors may be constructed of materials designed to withstand the particular temperatures, pressures and reaction compounds used. Generally, suitable oxidation reactors are constructed using inert, corrosion-resistant materials such as titanium or with at least their surfaces that define interior space or volume in which liquid reaction mixture and reaction off-gas are contained lined with materials such as titanium or glass.

[00042] A reaction mixture for the liquid phase oxidation is formed by combining components comprising aromatic feed material, solvent and catalyst and adding gaseous oxygen to the mixture. In continuous or semi-continuous processes, components preferably are combined in one or more mixing vessels before being introduced to the oxidation zone; however, the reaction mixture can also be formed in the oxidation zone. The source of oxygen gas can be introduced into the reactor in one or more locations and is typically introduced in such a manner as to promote contact between the molecular oxygen and the other reaction compounds, for example, by introduction of compressed air or other gaseous oxygen source into the liquid body within a lower or intermediate portion of the interior volume of the reaction vessel.

[00043] Oxidation of aromatic feed material to product comprising aromatic carboxylic acid is conducted under oxidation reaction conditions effective to maintain a liquid phase reaction mixture and form aromatic carboxylic acid and impurities comprising by-products of the aromatic hydrocarbon precursor dissolved or suspended in the liquid phase reaction mixture and generate a high temperature and pressure vapor phase, gaseous components of which are primarily solvent monocarboxylic acid (for example, acetic acid when the oxidation reaction solvent includes acetic acid) and water and, in minor amounts,

oxidation by-products of the solvent monocarboxylic acid, such as lower alcohols and solvent monocarboxylic acid esters thereof (for example, methanol and methyl acetate when the solvent includes acetic acid) and oxidation by-products of the aromatic hydrocarbon feed material such as partial and intermediate oxidation products (for example, benzoic acid and p-toluic acid when the aromatic feed material includes para-xylene). Solvent by-product contents of the vapor phase typically range from about 0.5 to about 2 wt. %. Aromatic hydrocarbon precursor by-product levels are typically about 0.01 to about 0.05 wt. %. The high pressure vapor phase commonly also comprises unreacted aromatic feed material and oxygen gas that enter the vapor phase. When using air, as commonly practiced in commercial scale operations, or other oxygen gas sources comprising nitrogen or other inert gas components, the vapor phase will also comprise those inert components. Heat generated by oxidation is dissipated by boiling the liquid phase reaction mixture and removing an overhead vapor phase from the reaction zone.

[00044] Generally temperatures of the liquid phase reaction are maintained at about 120°C or greater, and preferably at about 140°C or greater, but less than about 250°C and preferably less than about 230°C. Reaction temperatures in the range of about 145°C to about 230°C are preferred in the manufacture of aromatic carboxylic acid products such as terephthalic acid, benzoic acid and naphthalene dicarboxylic acid. At temperatures lower than about 120°C, the liquid phase oxidation can proceed at rates or with conversions that are economically unattractive or may adversely affect product quality. For example, manufacture of terephthalic acid from para-xylene feedstock at a temperature less than about 120°C can take more than 24 hours to proceed to substantial completion and the resulting terephthalic acid product can require additional processing due to its impurities content. Temperatures above 250°C are not preferred due to potential for undesirable burning and loss of solvent. Pressure of the liquid phase reaction mixture can be used to control the temperature at which the liquid phase reaction mixture boils and is selected to maintain a substantial liquid phase reaction mixture. Pressures of about 5 to about 40 kg/cm^2 gauge are preferred, with preferred pressures for particular processes varying with feed and solvent compositions, temperatures and other factors and more preferably ranging between about 10 to about 30 kg/cm^2. At a reaction pressure of about 7 to about 21 kg/cm^2, temperature of a reaction mixture comprising acetic acid as solvent, and of the vapor phase resulting from the liquid phase reaction, is about 170 to about 210°C. Residence times in the reaction vessel can be varied as appropriate for given throughputs and conditions, with about 20 to about 150 minutes being generally suited to a range of processes. For manufacture of some aromatic carboxylic acids, such as

manufacture of terephthalic acid from para-xylene feed materials using acetic acid solvent for the reaction mixture, solids contents in the boiling liquid phase reaction mixture can be as high as about 50 wt. % of the liquid reaction mixture, with levels of about 10 to about 35 wt. % being more common. In processes in which the aromatic acid product is substantially soluble in the reaction solvent, solid concentrations in the liquid body are negligible. As will be appreciated by persons skilled in the manufacture of aromatic carboxylic acids, preferred conditions and operating parameters vary with different products and processes and can vary within or even beyond the ranges specified above.

[00045] Products of the liquid phase oxidation reaction include aromatic carboxylic acid oxidized from the aromatic feed material, impurities comprising by-products generated as a result of the liquid phase reaction and, as noted above, a high pressure vapor phase that results from the liquid phase reaction, including boiling of the liquid phase reaction mixture to allow removal of the vapor phase for control of reaction temperature. Specific examples of by-products of the aromatic feed material include partial or intermediate oxidation products such as toluic acids, tolualdehydes, carboxybenzaldehydes and hydroxymethyl benzoic acids. By-products of the liquid phase reaction also include solvent reaction products such as methanol and other lower aliphatic alcohols oxidized from the reaction solvent and esters generated by reaction of such alcohols with the solvent, examples of which include methyl acetate, methyl propionate, methyl butyrate and the like. By-products commonly are present in one or both the liquid phase oxidation reaction mixture and the vapor phase resulting therefrom. Carbon oxide by-products can result from oxidation of solvent, feed materials or their by-products. In embodiments of the invention in which the liquid phase reaction is conducted using a source of bromine as promoter, by-products also typically include lower alkyl bromides, e.g., methyl bromide when using acetic acid as the reaction solvent, which commonly forms by reaction of bromide ions with acetic acid. As above, these bromine-containing by-products and impurities may be present in one or both of the liquid phase reaction mixture and the high pressure vapor phase generated therefrom. In some embodiments of the invented process, for example those in which solid product from liquid phase oxidation is purified and a mother liquor or other recycle streams comprising purification step liquids or components thereof are transferred directly or indirectly to a liquid phase oxidation or to off-gas separation as reflux liquid, additional by-products such as benzoic acid and toluic acids carried over into purification liquids as well as hydrogenated derivatives of various by-product compounds resulting from purification steps and unreacted

aromatic hydrocarbon feed to oxidation carried into purification also may be introduced to the liquid phase oxidation reaction mixture and off-gases.

[00046] Water also is produced as a by-product of the liquid phase reaction in the oxidation step. However, because water may also be present in the liquid phase reaction mixture as a result of addition thereto, for example when using aqueous monocarboxylic acid solvents or in recycle streams from other process steps, and also due to the significant amounts of water present in the oxidation step, whether as by-product or deliberate addition, and inability or lack of need to distinguish between water of reaction and water added deliberately, the expression "by-products of the liquid phase reaction" and like expressions used herein do not refer to water unless stated otherwise. Similarly, when water or water vapor is described herein as a component of various process liquids, gases or streams, it is without regard to whether the water is by-product water from liquid phase oxidation, deliberately added in the process or both unless otherwise stated or clear from context.

[00047] Aromatic carboxylic acid reaction product slurried or dissolved in a portion of the liquid reaction mixture from the liquid phase oxidation can be treated using any suitable techniques for recovering aromatic carboxylic acid reaction product contained therein. Typically, aromatic carboxylic acid product and by-products of the aromatic feed material to oxidation slurried, dissolved or slurried and dissolved in liquid reaction mixture are removed from the reaction zone used for the liquid phase reaction and recovered by suitable techniques. Thus, liquid phase oxidation according to invented process can comprise, in addition to the oxidation reaction, a step comprising recovering from a liquid phase oxidation reaction mixture a product comprising aromatic carboxylic acid and impurities comprising reaction by-products. The product preferably is recovered as a solid product.

[00048] Soluble product dissolved in the liquid can be recovered by crystallization, which usually is accomplished by cooling and releasing pressure on a liquid slurry or solution removed from the oxidation reaction zone. Solid product slurried in the liquid and solids crystallized from reaction liquid or from crystallization solvents are conveniently separated from the liquids by centrifuging, filtration or combinations thereof. Solid products recovered from the reaction liquid by such techniques comprise aromatic carboxylic acid and impurities comprising by-products of the aromatic feed material. Liquid remaining after recovery of solid product from the liquid reaction mixture, also referred to as oxidation mother liquor, comprises solvent monocarboxylic acid, water, catalyst and promoter, soluble by-products of the liquid phase oxidation and impurities that may be present such as from recycle streams. The mother liquor normally also contains minor

amounts of aromatic carboxylic acid and partial or intermediate oxidation products of the aromatic feed material remaining unrecovered from the liquid. The mother liquor is preferably returned at least in part to the reaction zone of at least one liquid phase oxidation so that components thereof that are useful in the liquid phase reaction, such as catalyst, promoter, solvent and by-products convertible to the desired aromatic carboxylic acid, can be re-used.

[00049] In preferred embodiments of the invention, a liquid phase reaction mixture from oxidation comprising aromatic carboxylic acid and by-products of a liquid phase oxidation reaction is recovered from the liquid by crystallization in one or more stages, such as in a single crystallization vessel or a series of crystallization vessels, with sequential reductions in temperature and pressure from earlier to later stages to increase product recovery. Crystallization in two to four stages, for example from an oxidation reaction temperature in the range of about 140 to about 250°C and pressure in the range of about 5 to about 40 kg/cm^2 gauge to a final crystallization temperature in the range of about 110 to about 150°C and pressure of ambient to about 3 kg/cm^2, provides substantial crystallization of solid aromatic acid product. Mother liquor separated from the solid product by crystallization can be returned to the liquid phase reaction as described above. Heat is removed from the vessels used for crystallization by removal of a gas phase formed as a result of flashing or other pressure letdown of the reaction liquid, with a vapor phase removed from one or more stages preferably condensed and, directly or indirectly through one or more additional recovery stages, as discussed below, returned at least in part to the reaction zone for use in liquid phase oxidation.

[00050] Solid product recovered from the liquid phase oxidation, typically comprising aromatic carboxylic acid and impurities comprising oxidation by-products such as intermediate oxidation products of the aromatic feed material, can be separated from liquid oxidation mother liquor resulting from recovery of the solid product by any suitable technique. Examples include centrifuging, vacuum filtration, pressure filtration and filtration using belt filters. The resulting solid product is preferably washed after separation with liquid comprising water such as pure water or a wash liquid comprising minor amounts of solvent monocarboxylic acid, catalyst, aromatic feedstock, oxidation by-products or combinations thereof that can be beneficially recycled to oxidation, either directly or combined with other liquids such as oxidation mother liquor recycle or other liquids returned to the reaction zone. Separation of solid impure aromatic carboxylic acid recovered from an oxidation mother liquor and washing of solid product can be conveniently accomplished by solvent exchange

filtration under pressure using pressure filters such as are disclosed in U.S. Pat. Nos. 5,679,846, and 5,200,557. A preferred filtration device for such separations is a BHS Fest filter as described more fully in U.S. Pat. No. 5,200,557. Mother liquor and wash liquids removed from the filtered cake can be transferred directly or indirectly to liquid phase oxidation. Filtration and washing of the solid product in multiple stages and with increasingly pure wash liquids, for example liquids removed from filter cake in downstream stages as wash liquid in prior stages, can provide additional benefit by concentrating solvent monocarboxylic acid displaced from filtered solids for return to oxidation. In a more specific embodiment, the filtered cake wet with wash liquid resulting from such positive displacement filtration is directed from a final wash stage to a drying stage wherein it is optionally contacted with inert gas, typically under light to moderate pressure, for substantial removal of residual liquid from the cake. After washing and substantial removal of wash liquid from solid product comprising aromatic acid and by-products, the resulting solid can be dried and directed to storage or other steps, which may include preparation of a reaction solution for purification of the solid product. Preferably, levels of residual solvent monocarboxylic acid in solid product directed to purification are about 5,000 parts per million by weight ("ppmw") or less. Solid product can be dried with a flowing stream of nitrogen or other inert gas to reduce residual solvent levels.

[00051] In addition to the aromatic carboxylic acid reaction product formed in the liquid phase reaction of an oxidation step according to the invented process, a high pressure vapor phase is generated, comprising solvent monocarboxylic acid, water and by-products of the liquid phase oxidation, as described above. The vapor phase commonly also contains minor amounts of unreacted aromatic feed material, unconsumed oxygen gas and, if present, inert components of the oxygen source. Temperature and pressure of the vapor phase present in the reaction zone corresponds to conditions of the liquid phase reaction. An off-gas separation according to the invention provides for recoveries of materials and in some embodiments, energy and combinations thereof from the high temperature and pressure off-gas removed from a liquid phase oxidation reaction.

Separation of monocarboxylic acid-rich first liquid phase and water-rich second liquid phase

[00052] An off-gas separation according to the invented process comprises transferring the vapor phase removed from the reaction zone of a liquid phase oxidation to a separation zone capable of substantially separating solvent monocarboxylic acid, water and oxidation by-products into at least one solvent monocarboxylic acid-rich first liquid phase

and at least one water-rich second liquid phase that is substantially free of solvent monocarboxylic acid and at least one solvent monocarboxylic acid-depleted second high pressure vapor phase comprising water vapor such that oxidation by-products of the aromatic hydrocarbon precursor are preferentially apportioned to the first liquid phase and oxidation by-products of the solvent monocarboxylic acid are preferentially apportioned to the second high pressure vapor phase. A solvent monocarboxylic acid-rich first liquid phase and a water-rich second liquid phase that is substantially free of solvent monocarboxylic acid and oxidation by-products thereof and a second high pressure vapor phase that is substantially free of oxidation by-products of the aromatic hydrocarbon precursor are removed from the separation zone. Separation is conducted with the high pressure vapor phase at a temperature and under pressure not substantially less than temperature and pressure of the vapor phase in the liquid phase oxidation step from which the vapor phase is removed.

[00053] In greater detail, separation comprises directing a high pressure and temperature vapor phase removed from the reaction vessel used for liquid phase oxidation to a separation zone that is capable of operating with the vapor phase at high temperature and pressure to substantially separate water and solvent monocarboxylic acid in the vapor phase and apportion by-products from the oxidation among liquid and gas phases resulting from the separation such that solvent by-product content of the liquid phases and aromatic hydrocarbon oxidation by-product content of a gas phase removed from separation are minimized. The high pressure vapor phase can be transferred from the reaction zone of a liquid phase oxidation to the separation zone directly, as where a separation device is mounted directly or in close association with an oxidation reaction vessel or other reaction zone, or indirectly, for example by means suitable conduits, valves, pumps and the like for effecting transfer. A minor portion of the high pressure and high temperature vapor phase from the liquid phase oxidation may be directed to other uses, such as generation of high pressure steam or heat exchange fluid. Preferably, the vapor phase transferred to separation remains at high enough temperature and pressure so that energy content of the vapor phase entering the separation zone is at least substantially retained and the vapor phase provides sufficient heat for separation in contact with reflux liquid supplied to the separation zone. Most preferably, transfer of the vapor phase to the separation zone is achieved by passage directly from the reaction zone or through suitable pressure rated piping such that temperature of the vapor phase entering the separation zone is no more than about 10°C cooler than the reaction temperature in the liquid phase oxidation and pressure of the vapor phase entering the separation zone is no more than about 3 kg/cm^2 less than the pressure in

the liquid phase oxidation. The separation zone also is designed for operation at high temperature and pressure, and preferably at temperatures and pressures not substantially less than the temperature and pressure of the high pressure vapor phase present in the reaction zone to avoid loss of energy content of the vapor phase from the reaction zone. More preferably, the separation zone is designed for treating a vapor phase under pressure of at least about 80%, more preferably at least about 90%, and still more preferably at least about 95%, of the pressure of the vapor phase in the oxidation step. Pressure rating of equipment of the separation zone preferably is at least about 80%, more preferably about 90 to about 110%, of the rating of the oxidation reaction vessel or zone of the oxidation step of the invented process from which the vapor phase is directed to separation. Temperatures of the vapor phase in the separation zone preferably range from about 140 to about 200°C and more preferably from about 160 to about 185°C. Pressures from about 5 to about 40 kg/cm^2 are preferred, with about 10 to about 20 kg/cm^2 being more preferred.

[00054] The separation zone is capable of substantially separating solvent monocarboxylic acid and water vapors in the high pressure vapor phase introduced to separation. Preferably the separation zone is capable of separating water and solvent in the high pressure vapor phase such that a high pressure gas resulting from the separation contains no more than about 10%, and more preferably no more than about 5% of the solvent monocarboxylic acid content of the vapor phase introduced to the separation zone. More preferably, solvent monocarboxylic acid content of a second high pressure gaseous effluent from separation is no more than about 2%, and still more preferably no more than about 1%, of the solvent monocarboxylic acid content of the vapor phase introduced to the separation zone. The separation zone is also adapted for preferentially apportioning to at least one liquid phase by-products of the aromatic feed material to oxidation and to the second high pressure vapor phase by-products of the solvent monocarboxylic acid that otherwise apportion normally to both vapor and liquid phases at the temperatures and pressures at which the separation is conducted. For example, in the case of liquid phase oxidation of para-xylene feed materials in a liquid phase reaction mixture comprising acetic acid solvent, benzoic acid and p-toluic acid by-products of the para-xylene and methanol and methyl acetate by-products of the acetic acid can apportion at practically significant levels between vapor and liquid phases. The separation zone is capable of apportioning by-products such that the second high pressure vapor phase is substantially free of by-products of the aromatic hydrocarbon precursor and preferably contains no more than about 10 wt. %, and more preferably about 1 to about 5 wt. % thereof. By-products of the aromatic hydrocarbon

precursor removed to the first, solvent monocarboxylic acid-enriched liquid phase and the second, water-enriched liquid phase are preferably apportioned preferentially to the first phase, and more preferably such that about 75 wt %, still more preferably at least about 85 wt. %, to about 100 wt. % thereof, are present in the first liquid phase and no more than about 25 wt. %, still more preferably no more than about 2 to about 10 wt. %, thereof are present in the second liquid phase. By-products of the solvent monocarboxylic acid comprising alcohols and solvent acid esters thereof are preferably apportioned to the second high pressure vapor phase resulting from separation of water and solvent monocarboxylic acid in the inlet high pressure vapor phase, preferably such that such that the second, water enriched, liquid phase contains no more than about 10 wt. %, and more preferably no more than about 1 to about 4 wt. % of such by-products.

[00055] The separation zone for off-gas separation according to the invention can comprise any device or means suitable for substantially separating solvent monocarboxylic acid and water in the high temperature and pressure vapor phase removed from the liquid phase oxidation and apportioning oxidation by-products present in the device at high temperature and pressure to obtain a liquid phase rich in solvent monocarboxylic acid, a second liquid phase enriched in water and a second high pressure vapor phase comprising water, as described above.

[00056] In one embodiment, a preferred separation zone is adapted for contact between vapor and refluxing liquid phases flowing countercurrently therethrough such that solvent monocarboxylic acid in the high pressure vapor phase introduced to the separation zone from a liquid phase reaction zone is substantially removed from the vapor phase to the liquid phase to form a first liquid phase which is enriched in the solvent monocarboxylic acid, and such that water from a resulting solvent monocarboxylic acid-depleted high pressure vapor phase is removed into the refluxing liquid phase for withdrawal from the separation zone of a second liquid phase which is enriched in water. Oxidation by-products of the aromatic feed to liquid phase oxidation that tend to apportion between both the vapor and liquid phases under conditions in the separation are present in the high pressure vapor phase introduced to the separation zone from a liquid phase oxidation and may also be introduced into the separation zone in reflux liquids supplied thereto. Such by-products apportioned to the liquid phase to which solvent monocarboxylic acid from the high pressure vapor phase from oxidation is removed can be removed in the first liquid phase. Such by-products present in the solvent monocarboxylic acid-depleted vapor phase are further apportioned to that liquid phase and also enter the liquid phase to which water from the solvent-depleted vapor

phase is removed due to contact with the refluxing liquid phase. By-products of the solvent monocarboxylic acid that tend to apportion between vapor and liquid phases can be present in the high pressure vapor phase from oxidation introduced to the separation zone. They also can be present in reflux liquids supplied to the separation zone. Such by-products present in the refluxing liquid phase in the separation device are stripped from the vapor phase by the refluxing liquid.

[00057] The flow of refluxing liquid in such a separation device comprises liquid components removed or apportioned from the vapor phase to the liquid phase as well as components of reflux liquids supplied to the separation zone that are or remain in the liquid phase.

[00058] A preferred separation zone according to a more specific embodiment of the invention is configured for stagewise contact between liquid and vapor phases in countercurrent flow through portions or regions of the separation zone. The vapor phase flow is preferably an ascending flow through the portions of the separation zone and the liquid phase flow preferably is a descending flow therethrough. Separation of water, solvent monocarboxylic acid and by-products is accomplished by directing the high pressure vapor phase removed from the reaction zone to a first portion of the separation zone and a reflux liquid to a third portion of the separation zone such that a vapor phase flow through the first portion to a second portion to a third portion of the separation zone is in contact with a countercurrent flow of refluxing liquid phase through the third to the second to the first portion of the separation zone. Reflux liquid supplied to the third portion comprises water and preferably is substantially free of oxidation by-products of the aromatic feed materials for liquid phase oxidation. Water and solvent monocarboxylic acid in the countercurrently flowing vapor phase and refluxing liquid phase are substantially separated in the first portion such that a solvent monocarboxylic acid-rich first liquid phase and a high pressure, solvent monocarboxylic acid-depleted intermediate vapor phase are formed. The solvent-rich first liquid phase from the first portion is collected for removal from the separation zone. The vapor phase flow from the first to the second portion of the separation device includes the intermediate vapor phase from the first portion. Water and by-products in the countercurrently flowing vapor phase and refluxing liquid phase in the second portion are separated such that by-products of the aromatic hydrocarbon precursor are removed to the refluxing liquid phase and a high pressure second intermediate vapor phase comprising water vapor substantially free of solvent monocarboxylic acid and by-products of the aromatic hydrocarbon precursor is formed. The flow of vapor phase from the second to the third

portions of the separation zone includes the second intermediate vapor phase. Water and by-products of the solvent monocarboxylic acid in the countercurrently flowing vapor phase and refluxing liquid phase in the third portion are separated such that a water-enriched second liquid phase substantially free of solvent monocarboxylic acid and by-products thereof and a second high pressure vapor phase comprising water vapor and by-products of the solvent monocarboxylic acid and substantially free of by-products of the aromatic hydrocarbon precursor are formed. The water-enriched second liquid phase from the third portion is collected for withdrawal from the separation device in a liquid stream separate from that in which the first liquid phase is withdrawn. The second high pressure vapor phase is removed from the separation device as an exit gas. The flow of refluxing liquid phase through the separation zone can be supplemented by supplying additional reflux liquid comprising water to one or more portions of the separation zone. In preferred embodiments, liquid comprising water is supplied as additional reflux between the second and third portions of such a separation zone.

[00059] In such a staged separation, the first portion of the separation zone preferably is capable of separating solvent monocarboxylic acid and water such that at least 95 wt. %, and more preferably at least about 98 wt. %, of the solvent is removed to the first liquid phase. The second portion is preferably capable of apportioning by-products of the aromatic precursor for the liquid phase oxidation to the first and second liquid phases such that the second high pressure vapor phase contains no more than about 10%, and more preferably about 1 to about 5%, of the amount of such by-products present in the first and second liquid phases and the second high pressure vapor phase. The third portion of the separation zone preferably is capable of apportioning liquid phase oxidation by-products of the solvent monocarboxylic acid to the second high pressure vapor phase such that the second liquid phase contains no more than about 10%, and more preferably about 1 to about 4%, of the amount of such by-products present in the first and second liquid phases and the second high pressure vapor phase.

[00060] In preferred embodiments, a first portion of the separation zone is defined as a region of the separation zone located between an inlet for receiving high pressure vapor phase removed from a liquid phase oxidation into the separation zone and an inlet for introducing a liquid comprising water to the separation zone as reflux. A second portion of the separation zone is defined by a region of the zone positioned between an inlet for introducing liquid comprising water as reflux to the first portion and an outlet for removing the water-rich second liquid phase collected from the third portion. The third portion is

defined as a region between an outlet for removing water-enriched second liquid phase collected from the third portion and an inlet for introducing liquid comprising water substantially free of oxidation by-products of the aromatic feed material for liquid phase oxidation to the separation device.

[00061] According to embodiments of the invention, a separation zone for the separation and preferential apportionment of water, solvent monocarboxylic acid and by-products comprises a fractionating zone having at least about 20 theoretical equilibrium stages for substantially separating water and solvent monocarboxylic acid in the high pressure vapor from liquid phase oxidation. More preferably, such a fractionating zone has about 20 to about 60 theoretical equilibrium stages. A fractionating zone with at least about 2 theoretical equilibrium stages is preferred for separating water and oxidation by-products of the aromatic feed material. More preferably, such a fractionating zone provides about 2 to about 10 theoretical equilibrium stages. A fractionating zone for separating water and oxidation by-products of the solvent monocarboxylic acid preferably has at least one, and more preferably about 1 to about 10 theoretical equilibrium stages.

[00062] Preferred separation devices are various columns or towers, often referred to as distillation columns and towers, dehydration towers, rectifying columns, water removal columns and high efficiency separation devices, that are designed for contact between gas and liquid phases flowing therethrough for mass transfer between the phases in a plurality of theoretical equilibrium stages, also sometimes referred to as "theoretical plates," configured for separating and preferentially apportioning components of the flowing gas and liquid phases. Contact between flowing gas and liquid phases is promoted by internal structure, such as trays or packing providing surfaces for gas-liquid contact and theoretical equilibrium stages for separations. Temperature of the high pressure vapor phase removed from oxidation normally is high enough that there is no need for reboiling capability beyond that provided by the liquid phase oxidation reaction. Countercurrent flow of gas and liquid phases, such as by introducing the high pressure vapor phase from oxidation at a lower portion of the device and reflux liquid at least one, and preferably two or more upper portions, is preferred for promoting contact between gas and liquid phases in the separation device.

[00063] The separation zone according to the invention can comprise a single device or multiple devices, such as towers, columns or other structure, in series. When using two or more devices in series, they are configured, and their respective inlets and outlets communicate such that high pressure vapor phase removed from an oxidation reaction vessel

flows into the series with separation and apportionment of solvent monocarboxylic acid, water and by-products in flowing vapor and reverse flows of refluxing liquid in and through the series.

[00064] Reflux liquid supplied to the separation zone comprises water. Any suitable source of liquid comprising water and substantially free of impurities detrimental to separation can be utilized. Demineralized water or other purified sources can be used but preferred sources of reflux liquid include liquids condensed from high pressure gases removed from separation and/or condensing zones according to the invented process. In another preferred embodiment, purification mother liquor obtained in recovery of a purified aromatic carboxylic acid product from at least one purification liquid reaction mixture is directed to separation such that reflux to the separation comprises the purification mother liquor. Most preferably, reflux liquid for separation comprises such a purification mother liquor and liquid comprising water condensed from high pressure gases removed from a separation zone, which may be supplied to separation individually or combined in one or more individual streams.

[00065] In a staged separation according to preferred embodiments of the invention as described above, reflux liquid comprising purification mother liquor is introduced to the separation zone for flow of liquid phase components thereof through the second portion of the zone and condensate liquid recovered from a second high pressure vapor phase removed from the separation zone is introduced for flow through the third portion. The purification mother liquor typically contains by-products of the aromatic hydrocarbon feed material to liquid phase oxidation, including hydrogenated derivatives thereof resulting from purification, but such by-products are preferentially apportioned to the liquid phases recovered in separation, and predominantly to a solvent monocarboxylic acid-rich first liquid phase, which is suitable for return to oxidation to provide make-up solvent. Liquid comprising water condensed from the second high pressure vapor phase removed from the separation zone is substantially free of by-products of the aromatic feed material but can contain by-products of the solvent monocarboxylic acid stripped into the second high pressure vapor phase in separation which, in turn, may be present in liquid comprising water condensed from the second high pressure gas. Such by-products returned to separation in reflux liquid supplied to a third portion of the separation zone are stripped back into the second high pressure vapor phase in separation. Undesirable accumulation of such by-products is prevented in preferred embodiments of the invention in which a portion of the

condensate liquid recovered from the second high pressure vapor phase from separation is purged or directed to treatment for recovery of such by-products.

[00066] Reflux liquid preferably is supplied at a rate and temperature effective to quench heat of the liquid phase oxidation reaction transferred to the separation zone in the vapor phase from the oxidation. When the separation zone is coupled to a reaction vessel from liquid phase oxidation for substantially direct transfer of vapor phase from oxidation to separation, the reaction vessel functions as a reboiler. In such embodiments, the rate at which liquid reflux is supplied to the separation zone is conveniently expressed as weight of liquid provided to the zone relative to weight of aromatic feed material introduced to the liquid phase oxidation. Preferably, reflux liquid provided to the separation zone according to the invented process is at a temperature in the range of about 120 to about 170°C and more preferably at about 130 to about 160°C. At such temperatures, liquid preferably is supplied to separation at a rate of about 4 to about 5 weights of the liquid per weight of aromatic precursor introduced to the liquid phase oxidation. When reflux liquid is supplied separately to different stages of a separation zone it preferably is apportioned between the different stages such that reflux supplied to a first stage of the separation zone makes up at least 40%, and more preferably about 60 to about 90%, of the volumetric flow of reflux liquid.

[00067] Water and solvent monocarboxylic acid vapors contained in the high pressure vapor stream removed from a liquid phase oxidation step and introduced into the separation zone are separated such that a solvent monocarboxylic acid-rich first liquid phase which is lean in water is recovered. The separated first liquid phase preferably comprises at least about 60 wt. % solvent monocarboxylic acid and no more than about 35 wt % water. More preferably, water content of the separated liquid phase is about 15 to about 30 wt %. The liquid stream from separation also contains minor amounts of heavier impurities, such as partial or intermediate oxidation by-products of the aromatic feed material and hydrogenated derivatives thereof, such as benzoic acid and, depending on aromatic precursor used in the oxidation, m-toluic acid and/or p-toluic acid, washed or transferred into the first liquid phase in the separation zone. The first liquid phase may also include other components, such as aromatic carboxylic acid product and catalyst metals. Content of such heavier components can be as high as about 2 wt. % but preferably is no more than about 0.5 wt. %.

[00068] The solvent monocarboxylic acid-rich liquid phase condensed from the vapor phase in the separation zone is a valuable source of solvent for liquid phase oxidation. As described above, it also may include oxidation by-products of the aromatic feed material and other components suitable for being returned to oxidation and converted to the desired

aromatic carboxylic acid. Other suitable uses for the liquid condensate include wash liquids for rotary vacuum filters or other devices used for solid-liquid separations of recovered solid products of a liquid phase oxidation from oxidation mother liquors or crystallization solvents and make up to scrubbers, such as oxidation dryer scrubbers if used in the process. In a preferred embodiment of the invented process, at least a portion, and, more preferably, all or substantially all of the separated first liquid phase removed from the separation zone is returned to liquid phase oxidation, either directly to a reaction vessel or to holding vessels used for supply of makeup solvent to a reaction zone. In such embodiments, water and solvent monocarboxylic acid in the high pressure vapor phase introduced to the separation zone are preferably separated such that a liquid phase resulting from the separation contains about 15 to about 30 wt. % water and, more preferably, such that water content of the separated liquid together with water returned to oxidation in other liquid streams from the process are substantially balanced with water vapor removed from oxidation in the high pressure overhead vapor phase and liquid water removed from oxidation for recovery and separation of aromatic carboxylic acid product of the oxidation.

The Second Liquid Phase

[00069] The second liquid phase recovered from separation is enriched in water and substantially free of solvent monocarboxylic acid by-products thereof from liquid phase oxidation. It may contain minor amounts of by-products of the aromatic feed material to the liquid phase oxidation as a result of preferential apportionment of such by-products to liquid phases in separations according to the invention. Solvent monocarboxylic acid content of the second liquid phase typically is less than about 5 wt. % and preferably about 1/2 to about 3 wt. %. Solvent by-product levels typically are no greater than about 1 wt. % and preferably about 0.05 to about 0.2 wt. %. By-products of aromatic feed materials present in the second liquid phase typically range from about 0.003 to about 0.1 wt. % and preferably about 0.005 to about 0.05 wt. %. The second liquid phase further comprises dissolved O_2 and gaseous methyl bromide wherein O_2 is present in an amount of about 2.2 ppmw and methyl bromide is present in an amount of about 0.03 ppmw.

[00070] It has been discovered however that use of the recovered second liquid phase in other parts of the process prior to further treatment to remove the dissolved O_2 and methyl bromide can cause corrosion. Therefore the second liquid phase must undergo further treatment to reduce the amount of corrosive compounds residing or dissolved therein to reduce its corrosive effects. Surprisingly, it has been found that flashing the second liquid phase as it exits the separation zone significantly reduces the amount of dissolved O_2 and

methyl bromide dissolved in the treated second liquid phase to wherein the amount of O_2 is less than about 1.0 ppmw, and more preferably the amount of O_2 is less than about 0.5 ppmw, and even more preferably the amount of O_2 is less than about 0.05 ppmw, and most preferably the amount of O_2 is less than about 0.006 ppmw, and the amount of methyl bromide is less than about 0.02ppmw, and more preferably the amount of methyl bromide is less than about 0.01, and even more preferably the amount of methyl bromide is less than about 0.009, and most preferably the amount of methyl bromide is less than about 0.006 ppmw after flashing. As used herein the term "flashing" or "flashed" refers to the immediate drop in pressure ranging from about 5 kg/cm^2 to about 40 kg/cm^2 in the separation zone to atmospheric or ambient pressure in the flash tank, or more preferably from about 10 kg/cm^2 to about 20 kg/cm^2 in the separation zone to atmospheric or ambient pressure in the flash tank that the second liquid phase experiences as it exits the separation zone into a flash tank.

[00071] Another method of treating the second liquid phase to reduce or eliminate the dissolved O2 and methyl bromide is steam stripping the second liquid phase after it has exited the separation zone and is in a flash tank at atmospheric or ambient pressure. Yet another method of treating the second liquid phase to reduce or eliminate the dissolved O2 and methyl bromide is to use gaseous nitrogen to strip the second liquid phase after it has exited the separation zone and is in a flash tank at atmospheric or ambient pressure. In yet another embodiment, the second liquid phase is stripped with steam or nitrogen while under a pressure of from about 5 to about 40 kg/cm^2 and more preferably under a pressure of from about 10 to about 20 kg/cm^2.

[00072] The treated second liquid phase is suitable for use as liquid comprising water in one or more steps of a process for purifying impure forms of aromatic carboxylic acid as described more fully herein. Other uses for the treated second liquid phase include seal flush liquids to solid-liquid separation devices used for separating oxidation mother liquor and wash liquids from impure solid aromatic carboxylic acid product recovered from a liquid phase oxidation reaction mixture.

The second high pressure gas

[00073] The second high pressure gas resulting from separation comprises a substantial volume of water and is relatively free of solvent monocarboxylic acid. Preferably the gas comprises at least about 55 vol. %, and more preferably at least about 65 vol. %, water. Solvent monocarboxylic acid content of the gas is generally less than about 5 and preferably less than about 3 wt %. The gas also may contain unreacted aromatic feed material and by-products of the liquid phase oxidation although they typically are present in minor or

trace amounts no greater than about 2 wt %. Oxygen gas content of the pressurized gas from separation typically ranges up to about 4 vol. %, preferably from about 1 to about 4 vol. %. Inert gas components of the oxygen source, which typically include nitrogen and carbon oxides, can constitute up to about 45 vol. % of the pressurized gas; when using air as a gaseous oxygen source, nitrogen content of the pressurized gas typically ranges from about 30 to about 40 vol. %.

[00074] Preferably, pressure of the second high pressure vapor phase from the separation is up to about 1 kg/cm^2 gauge less than the pressure in the liquid phase oxidation reaction. Temperature of the high pressure gas from separation is preferably up to about 20°C less than the temperature of the liquid phase oxidation reaction, and more preferably about 5°C to about 15°C less than the oxidation reaction temperature. Preferably, the high pressure gas from the separation is at a temperature greater than about 100°C, more preferably greater than about 120°C, and less than about 250°C, more preferably less than about 230°C. Pressure of the pressurized gas remaining after the separation is about 4 to about 40 kg/cm^2 gauge.

[00075] The second high pressure vapor phase removed from separation can be directed to a condensing zone for condensing from the vapor phase a liquid condensate comprising water substantially free of organic impurities such as solvent monocarboxylic acid and by-products of the aromatic feed material and solvent from oxidation. The condensing zone can comprise any means effective for condensing water substantially free of organic impurities from the high pressure gas introduced to the condensing zone. Preferably, it includes one or more condenser or heat exchange means effective for providing indirect heat transfer between a high pressure gas phase and a heat sink material, and preferably a heat exchange fluid. A single device or a plurality of devices in series can be employed. Shell and tube heat exchangers and kettle type condensers are examples of preferred devices. Preferably, all or substantially all of the high pressure vapor from separation is directed to the condensing zone to enable substantial recovery of both heat energy and materials therefrom. Cooling preferably is conducted under conditions such that a condensing zone exhaust gas under pressure not substantially reduced from that of the gas introduced to the condensing zone remains after condensing the liquid condensate and is withdrawn from the condensing means. That pressurized condensing zone exhaust gas comprises incondensable components of the high pressurize gas from the separation zone, gaseous reaction by-products and may also contain minor amounts of aromatic feed material from the liquid phase oxidation off-gas or reflux liquids directed to separation and remaining unseparated in the second high pressure

vapor phase. The exhaust gas from the condensing zone most preferably is at a temperature of about 50 to about 150°C and under pressure that is no more than about 3 kg/cm^2 less than the pressure of the inlet gas to the condensing zone. More preferably, the pressure differential between a gas removed from the separation device and the condensing zone exhaust gas after condensation of liquid condensate is about 2 kg/cm^2 or less and most preferably about 0.5 to about 1 kg/cm^2.

[00076] Cooling of high pressure gas by heat exchange with a heat sink material in the condensing zone also serves to heat the heat sink material. The heat sink material preferably is a heat sink fluid, and most preferably water. When using water as the heat exchange fluid, heat exchange with the high pressure gas from separation converts the water to steam which can be directed to other parts of the invented process for heating or to uses outside the process. Similarly, heat exchange between the pressurized gas and liquids from other process steps can be used for heating such liquids. Thus the invention includes embodiments in which heat exchange between the high pressure gas from the separation zone introduced to the condensing zone and heat exchange fluid comprising water is conducted in a series of heat exchangers operated at successively cooler temperatures such that steam at different pressures is generated from the heat exchange water. Steam at different pressures is preferably directed to one or more process steps in which steam under corresponding pressure or pressures is useful for heating, while liquid condensate comprising water at successively lower temperatures is generated from the pressurized gas.

[00077] Energy can be recovered from exhaust gas from the condensing zone in the form of heat, in the form of work or as both. Recovering energy as heat for the process can reduce consumption of fuel that would otherwise be needed to generate heat for the process. Energy recovered as work can be converted to electricity for use in the process, thereby reducing consumption of electricity from external sources if used in the process.

[00078] While preferred embodiments of the invention comprise condensing all or substantially all of the high pressure gas transferred to the condensing zone, in some embodiments of the invention, condensation of high pressure gas removed from the separation zone is conducted by extracting heat energy from the gas such that only a portion of the water content of the gas is condensed or by directing a portion of the second high pressure vapor phase from separation to condensing means and directing another portion to means for recovery of energy by conversion to mechanical energy. Partial condensation of the second high pressure vapor phase removed from separation or splitting the stream for condensation of only a portion thereof allows recovery of a liquid condensate comprising

substantially pure water with low organic impurities content and useful as reflux liquid for separation as described above and recovery of heat energy transferred to a heat exchange fluid on cooling of the high pressure gas to condense the liquid condensate, while also leaving uncondensed water in a high pressure condensing zone exhaust gas for further energy recovery in the form of work.

[00079] According to other embodiments of the invention, all or substantially all of the second high pressure vapor phase from separation of monocarboxylic acid and water in the high pressure vapor phase from oxidation and oxidation by-products is condensed by heat exchange with a heat sink fluid. Condensation of all or substantially all of the condensable components of the high pressure gas from separation reduces the volumetric flow of gas remaining after condensation to subsequent processing steps and permits use of metals with only low or moderate corrosion resistance, such as stainless steels, mild steels or duplex steels, as alternatives to more expensive, highly corrosion resistant metals or alloys in equipment for subsequent off-gas treatment steps that may be included in the process. Substantially complete condensation of condensable components of a high pressure gas removed from separation also increases the volume of liquid condensate comprising water substantially free of organic impurities generated according to the invented process and can facilitate enhanced recovery of aromatic feed material and solvent monocarboxylic acid or liquid phase oxidation by-products thereof remaining in uncondensed gases remaining after condensation.

[00080] Condensation can be conducted in a single step. It also can be conducted in multiple steps in which a gas stream comprising high pressure gas removed from a separation zone is cooled to a first temperature in a first stage to yield a first stage condensate liquid and an uncondensed portion of the gas which is subsequently condensed at a lower temperature in a second stage to provide a second stage condensate liquid and an uncondensed portion of the gas introduced to the second stage, and optionally one or more additional stages in which an uncondensed portion of gas from a prior stage is condensed at a lower temperature than in the previous stage to form a liquid condensate and a remaining uncondensed gaseous portion. Heat exchange between the pressurized gas and uncondensed portions thereof in the staged condensers provides heat exchange fluid at different temperatures or pressures, for example moderate and low pressure steam, which can be used for heating in other process steps or outside the process. In preferred embodiments of the invention, two or more levels of steam are produced for energy recovery, which is conveniently accomplished using a condensing or other low pressure steam turbine. In such

embodiments, condensate liquid removed at different temperatures can be directed to other process uses with corresponding temperatures, thereby avoiding additional heating or cooling of the condensate portions and, in some cases, limiting buildup of impurities such as solvent monocarboxylic acid oxidation by-products in steps to which condensate liquids are recycled. For example, condensate liquids recovered at higher temperatures, for example in the range of about 130 to about 160°C, are well suited, with little or no additional heat input, as reflux to separation as such or in combination with aqueous liquids from other process steps such as mother liquor remaining after recovery and/or separation of purified aromatic carboxylic acid in a purification step. Such high temperature condensate liquids can provide additional benefit when used as reflux to separation due to their lower content of light components, such as lower alcohols and solvent monocarboxylic acid esters thereof that are generated as solvent by-products in liquid phase oxidation and tend to condense in greater concentrations in lower temperature condensate liquids. Lower temperature condensates, for example those in the range of about 60 to about 90°C, are also well suited for hot condensate uses such as wash liquids for product separations and seal flush liquids in liquid phase oxidation, purification or both, and still cooler condensate, for example in the range of about 40 to about 50°C, for cold condensate uses such as scrubber washes. While condensation at different temperatures such that condensate liquid can be directed to other process uses with compatible temperatures provides options for favorable energy management in the invented process, it will be appreciated that liquid condensate portions or streams condensed at higher or lower temperatures than may be needed or preferred for use in other steps can be cooled or heated as may be desired, for example by heat exchange, for use in such other steps.

[00081] Exhaust gas from the condensing zone preferably is under pressure and, while substantially free of water vapor according to preferred embodiments of the invention, can retain a portion of the water from the second high pressure vapor phase from separation depending on the extent of condensation in the condensation step. In addition to such water vapor as may be present in the exhaust gas, the gas can comprise incondensable components from the liquid phase oxidation off-gas, such as unreacted oxygen from oxidation, nitrogen, carbon oxides and other inert gas components if present in the oxygen source for oxidation, and carbon oxides, and may contain minor amounts of solvent monocarboxylic acid by-products from oxidation and traces of solvent monocarboxylic acid, other oxidation by-products and unreacted aromatic hydrocarbon feed material not removed in other steps. Even when water in the exhaust gas is substantially completely condensed into the liquid condensate, such that the uncondensed exhaust gas remaining after condensation is

substantially free of water, pressure of the exhaust gas is also sufficiently high and, especially when the gaseous oxygen source for liquid phase oxidation is air or another gaseous mixture with significant inert gas content such that the vapor phase removed from oxidation and, in turn, pressurized gases from the separation and condensing zones contain substantial inert gas content, volume of the condensing zone exhaust gas is such that it can be a useful source for recovery of energy.

[00082] According to embodiments of the invention, energy can be recovered from the pressurized exhaust gas from condensation. Preferably, energy is recovered in the form of work. In these embodiments, a pressurized gas stream comprising exhaust gas from the condensing zone is transferred, directly or indirectly, to a device for recovering energy as work. A preferred energy recovery device is an expander or similar apparatus adapted to receive a flow of gas under pressure and equipped with blades capable of being rotated by the flowing gas, thereby generating work useful in other process steps or outside the process and a cooled gas under reduced pressure. Work extracted from the pressurized gas can be used, for example, to generate electricity using a generator or for operating a compressor used to compress air or sources of gaseous oxygen used in liquid phase oxidation or other equipment requiring mechanical work. Such extracted energy can be used elsewhere in the process or in other processes. Alternatively, it can be stored or delivered to an electrical grid for transmission to other locations. Exhaust gas remaining after recovery of energy as work can be vented, preferably after being subjected to additional treatments, for example condensation to remove water if present in appreciable amounts in the condensing zone exhaust gas, and caustic scrubbing to remove bromine or other compounds which may be undesirable for atmospheric release. If desired, energy recovery can be conducted after scrubbing or otherwise treating the gas for removal of corrosive components. Removal of corrosive components before recovery of energy can be beneficial in allowing internal components of an expander or other power recovery device to be constructed of less corrosion-resistant materials than might otherwise be preferred; however, treatment for removal of such components also can reduce power recoverable from the gas.

[00083] As an alternative to recovering energy from a condensing zone high pressure exhaust gas or, more preferably, as an additional step preceding recovery of energy as in the form of work as described above, exhaust gas from condensation can be treated for removal of organic and other combustible compounds and corrosive components. Such treatments, in some embodiments, are particularly useful for recovering minor amounts of reaction products of solvent monocarboxylic acid from oxidation as well as traces of

unreacted aromatic hydrocarbon feed material that may remain in the exhaust gas. In embodiments of the invention in which condensation of high pressure gas from separation includes one or more condensations at a temperature low enough that water in the gas is substantially, and preferably at least about 80%, condensed and volatile impurities such as lower alcohol and ester reaction products of the solvent monocarboxylic acid are substantially retained in an uncondensed exhaust gas phase that is cooled sufficiently, preferably to a temperature in the range of about 40 to about 90°C, treatment for recovery of such impurities is facilitated because the uncondensed exhaust gas from condensation is cool enough for use of liquid scrubbing agents for recovery. In other embodiments, treatment is beneficial to reduce or eliminate organic species such as such unreacted feed material and solvent by-products if not removed otherwise, as well as corrosive alkyl bromide reaction by-products from liquid phase oxidations in which a source of bromine is used as promoter for the liquid phase oxidation catalyst and carried over into the high pressure vapor phase generated in the liquid phase oxidation and, in turn, into the high pressure gas removed from separation and exhaust gas removed from condensation. It will be appreciated that such treatments can affect the amount of energy recoverable from the exhaust gas after condensation. Accordingly, in embodiments of the invention in which condensing zone exhaust gas is treated before recovery of energy in the form of work, preferred treatments are conducted without substantial loss of pressure or volume of the gas. When condensing zone exhaust gas has appreciable water content it also is preferred that any such treatment be conducted without appreciable condensation of water from the gas or cooling to such an extent that recovery of energy in the form of work results in significant condensation of water. In such embodiments, pre-heating of the treated gas before recovery of energy may be beneficial.

[00084] In embodiments of the invention comprising treating a pressurized exhaust gas from condensation for removal of unreacted feed material and solvent by-products generated in the liquid phase oxidation, such as lower alkyl esters of the solvent monocarboxylic acid, treatment is beneficial in allowing for return of such components to oxidation. Treatment also can reduce presence of such impurities in process recycle streams and steady state equilibrium levels thereof in overall process operation. Uncondensed gas under pressure removed from condensation can be contacted, preferably at a temperature of about 35 to about 60°C, with liquid scrubbing agent to provide a scrubbed gaseous phase with reduced levels of aromatic feed material and/or solvent by-products and a liquid product comprising the scrubbing agent and enriched in at least one of unreacted aromatic feed material and solvent monocarboxylic acid reaction products from liquid phase oxidation. The

liquid product is preferably returned to the reaction zone in a liquid phase oxidation step. Scrubbing can be accomplished using any suitable scrubbing device and scrubbing agents for contacting a gas stream comprising the high pressure condensation exhaust gas to remove volatile components such as unreacted feed material and solvent monocarboxylic acid by-products from oxidation from the gas into a liquid phase. High pressure absorption columns with internal structure, such as trays or packed beds, for promoting contact between gases to be scrubbed and liquid scrubbing agent are commonly utilized. Suitable scrubbing agents are materials that are liquid at the temperature of the gas to be scrubbed and in which the materials to be recovered have substantial solubility. Examples include lower alcohols and C.sub.1-8 carboxylic acids such as acetic acid, propionic acid, butyric acid and the like. A preferred liquid scrubbing agent is the monocarboxylic acid used as solvent for liquid phase oxidation and mixtures thereof with water. Suitable scrubbing agents, equipment and use thereof for recovery of off-gas components from liquid phase oxidation of aromatic feed materials to aromatic carboxylic acids are described in further detail in U.S. Pat. No. 6,143,925, which is incorporated herein by reference.

[00085] Pressurized condenser exhaust gas, with or without prior treatment as for scrubbing of unreacted feed material or solvent by-products as described above, can also be treated to remove corrosive or other combustible materials. While any means for such removal without substantial loss of pressure and volume of the gas can be employed, the gas preferably is subjected to an oxidation process, and most preferably a catalytic oxidation process for removal of organic, combustible and corrosive components. Such treatments generally comprise heating an uncondensed gas under pressure, and comprising exhaust gas under pressure removed from condensation or after scrubbing or other treatment, and gaseous oxygen in a combustion zone under pressure not substantially less than that of the pressurized gas and at elevated temperature effective to oxidize organic, combustible and corrosive components to a less corrosive or more environmentally compatible gas comprising carbon dioxide and water. Heating under pressure with oxygen gas preferably is conducted in the presence of a suitable oxidation catalyst disposed within the combustion zone so as not to interrupt flow of the pressurized gas therethrough. The pressurized gas can optionally be subjected to preheating before oxidation. Preheating can be accomplished by any suitable means such as by heat exchange, direct steam injection or other suitable means. Optionally, combustion treatment can also include scrubbing a pressurized gas removed from combustion to remove acidic, inorganic materials such as bromine and hydrogen bromide which are

generated by oxidation of alkyl bromides present in the condenser exhaust gas when a bromine source is used for liquid phase oxidation as noted above.

[00086] Catalysts for catalytic oxidation generally comprise at least one transition group element of the Periodic Table (IUPAC). Group VIII metals are preferred, with platinum, palladium and combinations thereof and with one or more additional or adjuvant metals being especially preferred. Such catalyst metals may be used in composite forms such as oxides. Typically, the catalyst metals are disposed on a support or carrier material of lower or no catalytic activity but with sufficient strength and stability to withstand the high temperature and pressure oxidizing environment of the combustion zone. Suitable catalyst support materials include metal oxides comprising one or more metals, examples of which include mullite, spinels, sand, silica, alumina silica alumina, titania and zirconia. Various crystalline forms of such materials can be utilized, such as alpha, gamma, delta and eta aluminas, and rutile and anatase titanias. Catalyst metal loadings on support compositions are suitably fractions to several percents by weight, with higher loadings being preferred for use when treating gases with significant water vapor content, such as about 20 vol. % or more. Catalysts can be used in any convenient configuration, shape or size. For example, the catalyst can be in the form of pellets, granules, rings, spheres, and the like and preferably may be formed into or disposed on a rigid cellular, honeycomb, perforated or porous structural configuration to promote contact with gases present in the combustion zone without impeding gas flow through the zone. Specific examples of catalytic oxidation catalysts for combustion treatment of exhaust gas removed from condensation in off-gas treatment according to the invention comprise about one-half to about one wt % palladium supported on an alumina monolith support.

[00087] In embodiments of the invention in which energy in the form of work is recovered from gas comprising exhaust gas removed from a condensing zone, and especially when such a gas comprises appreciable water, e.g., at least about 5 vol. %, the gas can optionally be heated to guard against presence of liquid water in the gas directed to energy recovery. Such heating can take place before, after or in combination with other treatments or treatment steps such as thermal or catalytic oxidations. In such embodiments, heating can be accomplished by any suitable technique, such as by heat exchange or direct injection of steam or other heated gas. Heating to about 200°C. or greater is effective for avoiding condensation of water, with temperatures of about 250 to about 350°C preferred.

[00088] In addition to the condensing zone exhaust gas remaining after condensation of high pressure gas removed from the separation zone, condensation according

to an off-gas treatment step of the invented process results in condensation of a liquid from the pressurized gas. The condensate liquid comprises water of substantial purity as described above and, according to preferred embodiments of the invention, is directed at least in part to the separation zone such that reflux liquid supplied to the separation zone comprises such condensate liquid. The condensate liquid also is suitable for other uses such as wash liquid for solid-liquid separations of impure aromatic carboxylic acid products from liquid phase oxidation. As between the condensate liquid and the water-enriched second liquid phase removed from off-gas separation according to the invented process, the second liquid phase is preferred for use in integrated process that include purification of impure aromatic carboxylic acids, such as are recovered from liquid phase oxidation, due to lower solvent monocarboxylic acid oxidation by-product content than in the condensate liquid recovered from the second high pressure vapor phase from separation.

Purification

[00089] In embodiments of the invention comprising purification or manufacture of purified aromatic carboxylic acids, purification comprises at least one step that comprises contacting with hydrogen at elevated temperature and pressure in the presence of a catalyst comprising a hydrogenation catalyst metal a purification reaction solution comprising a liquid that comprises water and has dissolved therein aromatic carboxylic acid and impurities to form a purification liquid reaction mixture comprising the aromatic carboxylic acid and hydrogenated impurities dissolved in a liquid comprising water. In preferred embodiments, a purification reaction solution is formed by dissolving in a liquid comprising water a crude solid product recovered from liquid phase oxidation comprising aromatic carboxylic acid and impurities comprising oxidation by-products of the aromatic feed material for the oxidation. Pure forms of aromatic carboxylic acid product containing reduced levels of impurities can be recovered from the purification liquid reaction mixture, preferably by crystallization, and the resulting pure form of product can be separated from a liquid purification mother liquor remaining after recovery of the pure form of product and/or from one or more liquids comprising water, such as crystallization solvents and wash liquids. The invention includes embodiments in which at least one liquid comprising water that is used in the purification comprises a water-enriched second liquid phase removed from the separation zone of an off-gas separation according to the invention. As indicated above, in other embodiments purification mother liquor from at least one purification is directed to off-gas separation for introduction to the separation zone as reflux liquid comprising water.

As described above, aromatic carboxylic acid products obtained by liquid phase oxidation of feed materials comprising aromatic compounds with oxidizable substituents, also sometimes referred to as a crude aromatic carboxylic acid product or crude product from liquid phase oxidation, comprise aromatic carboxylic acid and one or more oxidation intermediates or by-products. Although specific chemical compositions of intermediates and by-products vary depending composition of the oxidation feed material, oxidation reaction conditions and other factors, and even for given feed materials may not be fully known, they are known to comprise one or more aromatic carbonyl compounds, such as benzaldehydes, carboxybenzaldehydes, fluorenones and anthraquinones, that cause or correlate with undesirable color of desired aromatic carboxylic acid products or of polyesters made therefrom and can be hydrogenated to species more soluble in aqueous solution than the aromatic carbonyl compounds and aromatic carboxylic acid or to species with less color or color-forming tendencies. Preferred impure aromatic carboxylic acid products to be purified according to embodiments of the invention are crude product comprising aromatic carboxylic acid and by-products produced by liquid phase oxidation of aromatic feed material in a liquid phase oxidation, and most preferably continuous processes in which liquid phase oxidation and purification steps are integrated such that a crude solid product of liquid phase oxidation is a starting material for the purification. However, it also will be appreciated that the starting material for purification can be or include an impure product comprising an aromatic carboxylic acid and aromatic carbonyl impurities as described above, whether present or generated as by-products from an integrated or non-integrated liquid phase oxidation of aromatic feed material or from other processes or sources. Thus, the invention includes embodiments in which an impure aromatic carboxylic acid product starting material for purification comprises aromatic carboxylic acid and at least one aromatic carbonyl impurity that forms a hydrogenated, carbonyl-substituted aromatic product with greater solubility in aqueous solution or less color or color-forming tendencies than the unhydrogenated aromatic carbonyl impurity. Impure forms of aromatic carboxylic acid product suitable as starting materials for purification, including crude products recovered from a liquid phase oxidation according to embodiments of the invention, also may contain minor amounts of solvent monocarboxylic acid residues that remain in the impure product. Amounts ranging from several hundred to thousands ppmw as commonly present in products from commercial scale liquid phase oxidations do not adversely affect purification according to the invented process. Most preferably, solvent monocarboxylic acid content of an aromatic carboxylic acid product to be purified does not exceed about 10 wt %.

[00090] In greater detail, a preferred purification step according to the invention comprises dissolving in a liquid comprising water, at least a portion of which most preferably comprises a second liquid phase comprising water removed from off-gas separation according to the invention, a solid product comprising aromatic carboxylic acid and impurities to form a purification reaction solution, contacting the purification solution at elevated temperature and pressure with hydrogen in the presence of a hydrogenation catalyst to form a purification liquid reaction mixture, recovering from the purification liquid reaction mixture a solid purified product comprising aromatic carboxylic acid with reduced levels of impurities and separating an aqueous liquid purification mother liquor comprising oxidation by-products, hydrogenation products thereof and combinations thereof from the recovered solid purified product.

[00091] Hydrogenation of impure aromatic carboxylic acids to reduce impurities levels is conducted with the impure acid in aqueous solution. A preferred solvent for the purification solution in some embodiments of the invention comprises a second liquid phase removed from the separation zone of an off-gas separation according to the invention. Supply of second liquid phase directly from separation and without added or intermediate treatments for removal of by-products or impurities is preferred in continuous and integrated process operations to avoid costs, complexities and additional equipment for added handling, storage or treatment of the condensate liquid, although it will be appreciated that such added treatments, while unnecessary to render the second liquid phase suitable as a solvent for purification, are not precluded. Similarly, while unnecessary for obtaining a liquid of sufficient purity for use as purification solvent according the invention, it will be appreciated that the invention contemplates use of other suitable water sources such as fresh demineralized water or other purified sources of water in addition to or as alternatives to the second liquid phase from off-gas separation. Preferably the water-enriched second liquid phase from separation according to the invention makes up at least about 50% of the solvent for the purification reaction solution and more preferably about 80 to about 100%.

[00092] Concentrations in the purification solvent of impure aromatic carboxylic acid to be treated in a purification step generally are low enough that the impure acid is substantially dissolved and high enough for practical process operations and efficient use and handling of liquid used as solvent and remaining as purification mother liquor after recovery of a pure form of aromatic carboxylic acid with reduced impurities from purification reaction mixtures. Suitably, solutions comprising about 5 to about 50 parts by weight impure aromatic carboxylic acid per hundred parts by weight solution at process temperatures

provide adequate solubility for practical operations. Preferred purification reaction solutions contain about 10 to about 40 wt %, and more preferably about 20 to about 35 wt %, impure aromatic carboxylic acid at the temperatures used for purification by catalytic hydrogenation.

Catalysts suitable for use in purification hydrogenation reactions comprise one or more metals having catalytic activity for hydrogenation of impurities in impure aromatic carboxylic acid products, such as oxidation intermediates and by-products and/or aromatic carbonyl species. The catalyst metal preferably is supported or carried on a support material that is insoluble in water and unreactive with aromatic carboxylic acids under purification process conditions. Suitable catalyst metals are the Group VIII metals of the Periodic Table of Elements (IUPAC version), including palladium, platinum, rhodium, osmium, ruthenium, iridium, and combinations thereof. Palladium or combinations of such metals that include palladium are most preferred. Carbons and charcoals with surface areas of several hundreds or thousands $m.^2/g$ surface area and sufficient strength and attrition resistance for prolonged use under operating conditions are preferred supports. Metal loadings are not critical but practically preferred loadings are about 0.1 wt % to about 5 wt % based on total weight of the support and catalyst metal or metals. Preferred catalysts for conversion of impurities present in impure aromatic carboxylic acid products comprising crude terephthalic acid obtained by liquid phase oxidation of a feed material comprising para-xylene contain about 0.1 to about 3 wt % and more preferably about 0.2 to about 1 wt % hydrogenation metal. For such uses, the metal most preferably comprises palladium.

[00093] For practical applications, catalyst is most preferably used in particulate form, for example as pellets, extrudate, spheres or granules, although other solid forms also are suitable. Particle size of the catalyst is selected such that a bed of catalyst particles is easily maintained in a suitable purification reactor but permits flow of the purification reaction mixture through the bed without undesirable pressure drop. Preferred average particle sizes are such that catalyst particles pass through a 2-mesh screen but are retained on a 24-mesh screen (U.S. Sieve Series) and, more preferably, through a 4-mesh screen but with retention on a 12-mesh and, most preferably 8-mesh, screen.

[00094] Contacting aqueous purification reaction solution with hydrogen in the presence of catalyst for purification is conducted at elevated temperatures and pressures. Temperatures range from about 200 to about 370°C, with about 225 to about 325°C. being preferred and about 240 to about 300°C. being most preferred. Pressure is at a level sufficient to maintain a liquid phase comprising the aqueous reaction solution. Total pressure is at least

equal to, and preferably exceeds, the sum of the partial pressures of the hydrogen gas introduced to the process and water vapor that boils off from the aqueous reaction solution at the temperature of operation. Preferred pressures are about 35, and more preferably about 70, to about 105 kg/cm.^{2}.

[00095] The aqueous purification reaction solution is contacted with hydrogen gas under hydrogenation conditions as described above in a suitable reaction vessel capable of withstanding reaction temperatures and pressures and also the acidic nature of its liquid contents. A preferred reactor configuration is a cylindrical reactor with a substantially central axis which, when the reactor is positioned for process use, is vertically disposed. Both upflow and downflow reactors can be used. Catalyst typically is present in the reactor in one or more fixed beds of particles maintained with a mechanical support for holding the catalyst particles in the bed while allowing relatively free passage of reaction solution therethrough. A single catalyst bed is often preferred although multiple beds of the same or different catalyst or a single bed layered with different catalysts, for example, with respect to particle size, hydrogenation catalyst metals or metal loadings, or with catalyst and other materials such as abrasives to protect the catalyst, also can be used and may provide benefits. Mechanical supports in the form of flat mesh screens or a grid formed from appropriately spaced parallel wires are commonly employed. Other suitable catalyst retaining means include, for example, a tubular Johnson screen or a perforated plate. Internal components and surfaces of the reactor and the mechanical support for the catalyst bed are constructed of materials that are suitably resistant to corrosion from contact with the acidic reaction solution and reaction product mixture. Most suitably, supports for catalyst beds have openings of about 1 mm or less and are constructed of metals such as stainless steel, titanium or Hastelloy C.

[00096] In preferred embodiments of the invention, aqueous solution of impure aromatic carboxylic acid to be purified is added to the reactor vessel at elevated temperature and pressure at a position at or near the top portion of the reactor vessel and the solution flows downwardly through the catalyst bed contained in the reactor vessel in the presence of hydrogen gas, wherein impurities are reduced with hydrogen, in many cases to hydrogenated products with greater solubility in the reaction mixture than the desired aromatic carboxylic acid or with less color or color-forming tendencies. In such a preferred mode, a liquid purification reaction mixture comprising aromatic carboxylic acid and hydrogenated impurities is removed from the reactor vessel at a position at or near a lower portion or bottom of the reactor.

[00097] Reactors used for purification may be operated in several modes. In one mode, a predetermined liquid level is maintained in the reactor and, for a given reactor pressure, hydrogen is fed at a rate sufficient to maintain the predetermined liquid level. The difference between the actual reactor pressure and the vapor pressure of the vaporized purification solution present in the reactor head space is the hydrogen partial pressure in the head space. Alternatively, hydrogen can be fed mixed with inert gas such as nitrogen or water vapor, in which case the difference between the actual reactor pressure and the vapor pressure of the vaporized reaction solution present is the combined partial pressure of hydrogen and the inert gas mixed therewith. In such cases hydrogen partial pressure may be calculated from the known relative amounts of hydrogen and inert gas present in the mixture.

[00098] In another operating mode, the reactor can be filled with the aqueous liquid reaction solution so that there is essentially no reactor vapor space but a hydrogen bubble at the top or in the head of the reactor that expands or contracts in size to provide volume in the reactor head so that hydrogen added to the reactor is dissolved into the incoming purification reaction solution. In such an embodiment, the reactor is operated as a hydraulically full system with dissolved hydrogen being fed to the reactor by flow control. The concentration of hydrogen in solution may be modulated by adjusting the hydrogen flow rate to the reactor. If desired, a pseudo-hydrogen partial pressure value may be calculated from the solution hydrogen concentration which, in turn, may be correlated with the hydrogen flow rate to the reactor.

[00099] When operating such that process control is effected by adjusting the hydrogen partial pressure, the hydrogen partial pressure in the reactor is preferably in the range of about one-half to about 15 kg/cm.^{2} gauge or higher, depending on pressure rating of the reactor, impurities levels of the impure aromatic carboxylic acid, activity and age of the catalyst and other considerations known to persons skilled in the art. In operating modes involving directly adjusting hydrogen concentration in the feed solution, the solution usually is less than saturated with respect to hydrogen and the reactor itself is hydraulically full. Thus, an adjustment of the hydrogen flow rate to the reactor will result in the desired control of hydrogen concentration in the solution.

[000100] Space velocity, expressed as weight of the impure aromatic acid in the purification reaction solution per weight of catalyst per hour, during hydrogenation is typically about 1 hour^{-1} to about 25 hour^{-1}, and preferably about 2 hours^{-1} to about 15 hours^{-1}. Residence time of the purification liquid stream in the catalyst bed varies depending on the space velocity.

[000101] Pure forms of aromatic carboxylic acid product with reduced levels of impurities relative to the crude or other impure aromatic carboxylic acid product used for preparing the purification solution is recovered from the liquid purification reaction mixture. The purification reaction mixture, comprising aqueous reaction solvent having dissolved therein aromatic carboxylic acid and hydrogenated aromatic impurities having greater solubility in the aqueous reaction liquid than their unhydrogenated precursors, is cooled to separate a pure form of solid aromatic carboxylic acid with reduced impurities from the reaction mixture, leaving a liquid purification mother liquor having hydrogenated impurities dissolved therein. Separation is commonly achieved by cooling to a crystallization temperature, which is sufficiently low for crystallization of the aromatic carboxylic acid to occur, thereby producing crystals within the liquid phase. The crystallization temperature is sufficiently high so that dissolved impurities and their reduction products resulting from hydrogenation remain dissolved in the liquid phase. Crystallization temperatures generally range up to 160°C. and preferably up to about 150°C. In continuous operations, separation normally comprises removing liquid purification reaction mixture from the purification reactor and crystallization of aromatic carboxylic acid in one or more crystallization vessels. When conducted in a series of stages or separate crystallization vessels, temperatures in the different stages or vessels can be the same or different and preferably decrease from each stage or vessel to the next. Crystallization typically also results in flashing of liquid from the purification liquid reaction mixture, which can be recovered by condensation and recycled to one or more of purification, one or more upstream crystallization stages or, in preferred embodiments of the invention, to separation of solvent monocarboxylic acid and water vapor in a high pressure vapor phase from liquid phase oxidation. Liquid comprising water, which preferably comprises the water-enriched liquid recovered as a second liquid phase in an off-gas separation according to the invented process, is preferably added to the crystallized product recovered from purification liquid reaction mixture recovered in stagewise crystallizations either directly or, more preferably, indirectly in one or more wash liquids for the crystallized product.

[000102] Thereafter, crystallized, purified aromatic carboxylic acid product is separated from the purification mother liquor, including hydrogenated impurities dissolved therein. Separation of the crystallized product is commonly conducted by centrifuging or by filtration. A preferred separation comprises pressure filtration of an aqueous slurry of pure forms of aromatic carboxylic acid and washing of filter cake resulting from filtration with a liquid comprising water as described in U.S. Pat. No. 5,175,355, which is incorporated herein

by reference. The water-enriched second liquid phase from an off-gas separation as described herein is a preferred liquid comprising water for use as wash liquid for the pure form of aromatic carboxylic acid.

[000103] Purification mother liquor remaining after recovery of solid purified aromatic carboxylic acid from the purification reaction mixture comprises water and hydrogenated derivatives of by-products or impurities present in the impure aromatic carboxylic acid starting material. The mother liquor commonly also includes minor amounts of aromatic carboxylic acid that remain in solution. Such hydrogenated derivatives include compounds suitable for conversion to aromatic carboxylic acid by liquid phase oxidation and, accordingly, in preferred embodiments of the invention, at least a portion of such hydrogenated derivatives are transferred directly or indirectly to a liquid phase oxidation. Residual aromatic carboxylic acid present in the mother liquor also can be transferred directly or indirectly to liquid phase oxidation after separation from, or more preferably, together with, such hydrogenated derivatives. Transfer of such derivatives and aromatic carboxylic acid to oxidation is conveniently accomplished by directing at least a portion of a purification mother liquor remaining after separation of a solid pure form of aromatic carboxylic acid to a liquid phase oxidation step. Water content of purification mother liquor can upset water balance in oxidation unless water from purification mother liquor directed to oxidation is accounted for in other streams that may be returned to oxidation. Transfer of hydrogenated impurities in a purification mother liquor, alone or preferably in combination with aromatic carboxylic acid present in the mother liquor, to liquid phase oxidation is preferably accomplished without upsetting water balance in the oxidation. More preferably, at least a portion, and most preferably substantially all, of a liquid mother liquor remaining after separation of the solid purified aromatic carboxylic acid from the liquid purification reaction mixture is transferred directly or indirectly to a separation zone of off-gas separation according to the invention where it is used as reflux liquid as previously described. Purification reactor and catalyst bed configurations and operating details and crystallization and product recovery techniques and equipment useful in the process according to this invention are described in further detail in U.S. Pat. Nos. 3,584,039, 4,626,598, 4,629,715, 4,782,181, 4,892,972, 5,175,355, 5,354,898, 5,362,908 and 5,616,792 which are incorporated herein by reference.

[000104] FIG. 1 illustrates in further detail embodiments of a process for manufacture of aromatic carboxylic acids and apparatus for off-gas separation according to the invention. While the figure illustrates, and is described with specific reference to,

manufacture of a selected aromatic carboxylic acid, terephthalic acid, by liquid phase oxidation of para-xylene as a preferred feedstock in a liquid phase reaction mixture comprising water and acetic acid as solvent monocarboxylic acid for the oxidation and off-gas separation of acetic acid, water and by-products of the oxidation, and additional preferred embodiments and features of the invention according to which oxidation and off-gas separation are integrated with additional steps including recovery and separation of a crude product from the liquid phase oxidation, purification of liquid phase oxidation product and various additional by-product and energy recoveries, it will be understood that specific embodiments, features, details and preferences are described to aid in understanding the invention but not to limit the invention or its features in any aspect or embodiment.

[000105] The process illustrated in FIG. 1 also reflects preferred embodiments of the invented process in which liquid phase oxidation, off-gas separation and purification are integrated such that crude aromatic carboxylic acid product from the liquid phase oxidation is directed to purification for use to form a purification solution, a high pressure off-gas from the oxidation is directed to the off-gas separation, liquid phase from the off-gas separation is used as a purification liquid, and reflux liquid to the separation comprises mother liquor from the purification; however, it will be understood that the invention is not to be considered limited to the particular integration scheme represented in the figure and that various multiple train, shared train and other integrated and non-integrated configurations are contemplated according to the invention. By way of illustrative examples, product comprising aromatic carboxylic acid and reaction by-products from multiple liquid phase oxidations can be directed to a single purification step in which a liquid phase recovered in off-gas separation of a high pressure vapor phase from one or more of those or other liquid phase oxidations is directed for use as a process liquid. As additional such examples, crude product from a single liquid phase oxidation can be purified in separate purification trains operated in parallel, with high pressure vapor phase from the liquid oxidation subjected to off-gas separation for recovery of a water-enriched liquid phase substantially free of solvent by-products and transfer thereof to either or both such purification trains, or as an alternative or in addition, to a process in which impure aromatic carboxylic acid from a separate oxidation or process is purified in a purification process or process steps as described herein.

[000106] The figure also represents a separation apparatus according to the invention and also according to further embodiments of the invention in which the apparatus is integrated with other equipment such as a reaction vessel for liquid phase oxidation.

[000107] Liquid and gaseous streams and materials used and present in the process represented in FIG. 1 are typically directed and transferred through suitable transfer lines, conduits and piping constructed of appropriate materials for process use and safety. It will be understood that particular elements may be physically juxtaposed and can, where appropriate, have flexible regions, rigid regions or both. In directing streams or compounds, intervening apparatus or optional treatments can be included. For example, appropriate pumps, valves, manifolds, gas and liquid flow meters and distributors, sampling and sensing devices and other equipment for monitoring, controlling, adjusting and diverting pressures, flows and other operating parameters may be present.

[000108] Referring to the figure, separation apparatus 330 is a columnar structure that defines an enclosed interior space and is adapted for receipt of a high pressure vapor phase removed from oxidation reactor 110 in stream 111 and for removal of a second high pressure vapor phase through gas outlet 334. It also includes inlets as at 336 and 344 for introduction of reflux liquids supplied from external sources such as in streams from other process steps or from holding vessels. An outlet as at 345 is positioned intermediately relative to reflux inlets 336 and 344 for removal of a second liquid phase collected in the column. Structure in the interior space of the column and positioned intermediately between an inlet for receipt of the high pressure vapor phase from oxidation reactor 110 and reflux inlet 336 provides a fractionating zone in the interior.

[000109] The separation device is designed so that in operation it is capable of substantially separating C_{1-8} monocarboxylic acid and water in the high pressure and temperature oxidation reactor overhead gas introduced to the device and preferentially apportioning by-products of the liquid phase oxidation such that a first liquid phase rich in the monocarboxylic acid, a second liquid phase rich in water but substantially free of the solvent and by-products thereof generated in the liquid phase oxidation and a second high pressure vapor phase comprising water and substantially free of solvent and by-products of the aromatic feed to liquid phase oxidation are formed. In preferred embodiments, direct association or close coupling of the oxidation reactor and separation device are effectuated by connection directly or by suitable pressure rated piping or other conduits between one or more vents in the oxidation reaction vessel and one or more gas inlets to a separation device, such that a vapor phase under liquid phase reaction conditions is removed from the reaction vessel and introduced into the separation device at the same or substantially the same temperature and pressure as in the reaction zone.

[000110] A fractionating zone of the separation apparatus is configured with a plurality of theoretical equilibrium stages such as can be provided by internal trays, structured packing, combinations of trays and packing, or other structure or combinations thereof providing surfaces within the interior of the device for mass transfer between gaseous and liquid phases present in the device. At least about 20 theoretical equilibrium stages are provided. Separation efficiency increases with increasing theoretical equilibrium stages, other things being equal, so there is no theoretical upper limit to the number of equilibrium stages that may be included in the separation apparatus used according to the invention. However, for practical purposes, separation such that solvent monocarboxylic acid in the high pressure vapor phase introduced to the separation device is substantially removed into a liquid phase can be accomplished with at least about 20, and preferably at least about 25 theoretical equilibrium stages, while separation beyond that provided by about 100 such stages make additional stages impractical or economically inefficient.

[000111] A preferred separation device with structured packing has at least about 3 beds or zones of packing, and more preferably about 4 to about 8 such beds, to provide adequate surface and theoretical equilibrium stages for separation. An example of a suitable packing material is Flexipac structured packing, which is available from KGGP LLC in the form of thin sheets of corrugated metal arranged in a crisscrossing relationship to create flow channels and such that their intersections create mixing points for liquid and vapor phases. A preferred separation device with trays includes 30 to about 90 trays, at least about 70% of which are positioned between an inlet for the high pressure gas introduced to the separation device from the reaction vessel, as best seen in FIG. 2 at 338, and at least one reflux liquid inlet. Trays in the form or sieve or bubble cap trays are preferred and preferably have separation efficiencies of about 30 to about 60%. The number of trays for a given number of theoretical equilibrium stages can be calculated by dividing the number of stages by efficiency of the trays.

[000112] In process use, gas and liquid phases introduced into the separation device and present therein are at elevated temperatures and include water, solvent monocarboxylic acid and other corrosive components, for example, bromine compounds and their disassociation products such as hydrogen bromide that are present in an oxidation reaction overhead gas when the catalyst used for the oxidation includes a source of bromine. Therefore, in preferred embodiments of the invention, internal structure and other features of the separation apparatus that contact gases and liquids during process operation are constructed of suitable metals to resist corrosion and other damage due to such contact.

Titanium metal is a preferred material of construction for such surfaces, including trays, packings or other structure of the fractionating zone. Titanium surfaces of such structure may be subject to undesirable accumulation of solid deposits comprising iron oxides from impurities present in liquids circulated through the equipment. Processes for controlling accumulations of iron oxide deposits or content of soluble iron impurities in process liquids are described in commonly assigned U.S. Pat. No. 6,852,879 and US 2002/374719 which are incorporated herein by reference.

[000113] In the embodiment of the invention represented in the drawing, separation device 330 is a high pressure distillation column having a plurality of trays, individual examples of which are best seen at 333 and 337 in FIG. 2. Also as seen in FIG. 2, the column comprises at least one lower outlet, as at 332, for removal of liquid from the column, for example to oxidation. Gas inlet 338 is positioned at a lower portion of the column for receipt of oxidation reactor off-gas and vent 334 is located at an upper portion for removal of the second high pressure vapor phase as an exit gas. For stagewise separations according to the invention, the region between gas inlet 338 and reflux liquid inlet 344 includes trays providing theoretical equilibrium stages for substantial separation of solvent monocarboxylic acid and water in the high pressure vapor phase removed from liquid phase oxidation in a first stage or portion of column 330. Trays positioned between reflux inlet 344 and second liquid outlet 345 and providing theoretical equilibrium stages for separation of by-products of an aromatic feed material to oxidation and water to apportion such by-products to a refluxing liquid phase provide a second portion of a separation zone in the column. Trays positioned between liquid outlet 345 and reflux inlet 336, such as are illustrated at 333 and 337, provide theoretical stages for separation of solvent monocarboxylic acid oxidation by-products and water in a third portion of separation zone. Liquid outlet 332 is positioned for removal as a bottoms liquid of a first liquid phase that is enriched in solvent moncarboxylic acid separated from the oxidation off-gas in a first portion of the separation zone. A tray configured with a boot, trough, accumulation channel or other collection means at a circumferential boundary thereof as at 339 is in flow communication with liquid outlet 345 and adapted for collection of a second liquid phase of refluxing liquid flowing through separation for removal through outlet 345. Outlet 345 in combination with associated internal structure of the separation apparatus for collecting a refluxing liquid phase at or from between trays or packing beds or other structure of a fractionating zone, such as collection means 339, provide a side draw from the column for collecting and removing a water-enriched, second liquid phase recovered in the apparatus.

[000114] Referring again to FIG. 1, the separation apparatus is adapted to receive a high pressure vapor phase from liquid phase oxidation reaction zone 110. In some embodiments, apparatus according to the invention comprises a separation apparatus in combination with at least one liquid phase oxidation reactor in flow communication with the separation apparatus such that a high pressure overhead gas removed from the vessel through at least one overhead gas vent, as at 116, is received into the separation device. In such embodiments, reaction vessel 110 preferably comprises a substantially cylindrical shell that defines a substantially enclosed interior volume. In use, a lower portion of the interior volume contains a liquid reaction body while an overhead reaction off-gas is contained in a portion of the interior volume above the liquid level. The interior volume is in communication with the exterior of the reaction vessel through a plurality of inlets, an example of which is seen as 112 in FIG. 1, through which liquid aromatic feed material, solvent and soluble forms of catalyst are introduced from liquid charge vessels (not shown) and compressed air or another source of oxygen gas is introduced from a compressor or other suitable device (not shown) via suitable transfer lines (not shown). The inlets preferably are disposed such that liquid and gaseous components are introduced below the liquid level in the interior of the vessel. The reaction vessel also includes at least one outlet, as at 114, for removing from the interior a liquid phase reaction mixture which includes a crude product comprising aromatic carboxylic acid and oxidation by-products. Reaction vessel 110 also comprises at least one vent or outlet as at 116 for removal from the vessel interior of a high pressure vapor phase evaporated from the liquid reaction body. Vent 116 preferably is positioned to correspond to an upper portion of the vessel when it is in position for process use.

[000115] A preferred reaction vessel design is a substantially cylindrical vessel having a central axis extending substantially vertically when the vessel is positioned for process use. The vessel is adapted for use with a stirring mechanism 120 comprising a shaft having one or more impellers mounted thereon and capable of being rotated within the interior of the reaction vessel to stir the liquid reaction mixture present in the vessel during process use. In preferred embodiments of the invention, at least two impellers or mixing features are mounted on the shaft for mixing of gaseous and liquid components within the liquid reaction body without adverse settling of solids in lower portions of the vessel. Axial flow impellers, generally configured as propellers, radial flow mixers, such as flat blade disc turbines and disperser discs, helical ribbon mixing elements, pitched blade turbines with blades pitches for upward or downward flow, anchor-type mixers providing predominantly tangential flow and other configurations are suited for mixing the liquid phase oxidation

reaction system and preferably are used in various combinations to account for greater solids content in lower regions of the liquid reaction mixture, greater gas content in upper regions and other characteristics of the liquid phase reaction mixture that can vary throughout the liquid body. Other designs are disclosed in U.S. Pat. No. 5,198,156, describing mixing elements with radially extending, rotating blades mounted on a flat rotor and having a hollow blade configuration with a discontinuous leading edge, continuous trailing edge, absence of external concave surfaces and an open outer end and preferably used in conjunction with a vertical pipe or perforated gas sparger for gas distribution, and U.S. Pat. No. 5,904,423, which describes a mixer in which stirring elements are mounted at a downward angle on a central, rotating shaft and are wedge-shaped in the direction of movement through the liquid, with radial inner ends of the trailing edges of the blades angled outwardly in the direction of motion of the blades, and used with features for introducing a gas from below the stirring elements into a central cavity formed by a conical disk at an end of the shaft.

[000116] At least those portions of the reaction vessel, agitator shaft and mixing elements that contact the liquid reaction mixture and overhead gas in process use are constructed of substantially corrosion resistant materials. Examples include titanium metal, which is preferred, alloys and duplex stainless steels.

[000117] According to the preferred process embodiment represented in FIG. 1 liquid para-xylene feed material comprising at least about 99 wt % para-xylene, aqueous acetic acid solution, preferably containing about 70 to about 95 wt % acetic acid, soluble compounds of cobalt and manganese, such as their respective acetates, as sources oxidation catalyst metals and of bromine, such as hydrogen bromide as promoter for the catalyst and air are continuously charged to oxidation reaction vessel 110, which is a pressure rated, continuous stirred tank reactor, through inlets, one of which is depicted for purposes of illustration as at 112. Solvent and para-xylene feed are charged at rates providing a solvent to feed weight ratio of about 2:1 to about 5:1. Cobalt and manganese sources preferably are used in amounts providing about 100 to about 800 ppmw each based on weight of para-xylene feed material. Bromine preferably is used in an amount such that the atom ratio of bromine to catalyst metals is about 0.1:1 to about 1.5:1.

[000118] Stirring is provided by rotation of agitator 120, the shaft of which is driven by an external power source (not shown) causing impellers mounted on the shaft and located within the liquid body in the reactor to provide forces for mixing of liquids and dispersion of gases within the liquid body and avoiding settling of solids in its lower regions. Catalyst and promoter, each preferably as a solution in acetic acid solvent, are introduced into

the liquid body in the reaction vessel. Air is supplied from below and within the sweep path of a lower impeller at a rate effective to provide at least about 3 moles molecular oxygen per mole of aromatic feed material.

[000119] Para-xylene oxidizes in the stirred liquid reaction mixture in reactor 110, predominantly to terephthalic acid, but also reacts to form by-products including partial and intermediate oxidation products, such as 4-carboxybenzaldehyde, 1,4-hydroxymethyl benzoic acid and p-toluic acid, and others such as benzoic acid. Solid reaction products comprising terephthalic acid and para-xylene oxidation by-products precipitate from the liquid reaction mixture, with lesser amounts thereof remaining dissolved in the liquid. Solids content of the liquid slurry typically ranges up to about 50 wt. % and preferably from about 20 to about 40 wt. %. Water is also generated as a product of the oxidation. The oxidation reaction is exothermic and heat generated by the reaction causes boiling of the liquid phase reaction mixture and formation of an overhead vapor phase comprising vaporized acetic acid, water vapor and gaseous by-products from the oxidation reaction, carbon oxides, nitrogen from the air charged to the reaction and unreacted oxygen. The vapor phase may also include minor amounts of unreacted para-xylene feed. The interior volume of reactor 110 is maintained under pressure sufficient to maintain the liquid phase nature of the reaction mixture, preferably at about 5 to about 21 kg/cm.^{2} gauge. Overhead vapor is removed from the reactor through vent 116. The reactor contents are maintained at an operating temperature in the range of about 160 to about 225°C. based on the rate of removal of the vapor phase also taking into account temperatures and flow rates of streams removed from and returned to the reactor as described below.

[000120] A liquid effluent comprising solid para-xylene oxidation products, including terephthalic acid, slurried in the liquid phase reaction mixture, which also contains dissolved para-xylene, oxidation by-products and catalyst metals, is removed from reaction vessel 110 through slurry outlet 114 and directed in stream 115 to a crystallization zone for recovery of a solid product of the oxidation comprising terephthalic acid and oxidation by-products of the para-xylene feedstock.

[000121] In the embodiment of the invention illustrated in FIG. 1, crystallization is conducted in multiple stirred crystallization vessels, 152 and 156 in series and in flow communication for transfer of product slurry from vessel 152 to vessel 156. Cooling in the crystallization vessels is accomplished by pressure release, with the slurry cooled in vessel 152 to a temperature in the range of about 150-190°C. and then further to about 110-150°C in vessel 156. One or more of the crystallization vessels is vented, as at 154 and 158,

respectively, for removal to heat exchange means (not shown) of vapor resulting from pressure let down and generation of steam from the flashed vapor. Vapor removed from one or more upstream crystallization vessels, such as vessel 152, to heat exchange means is preferably condensed and liquid condensate comprising water, acetic acid solvent and soluble products and by-products of the oxidation can directed to one or more downstream crystallization vessels, as at 156, to allow for recovery of crystallizable components such as terephthalic acid and oxidation by-products entering and condensed from the flashed vapors from one or more upstream vessel.

[000122] Crystallization vessel 156 is in fluid communication with a solid-liquid separation device 190, which is adapted to receive from the crystallization vessel a slurry of solid product comprising terephthalic acid and oxidation by-products in a mother liquor from the oxidation comprising acetic acid and water, and to separate a crude solid product comprising terephthalic acid and by-products from the liquid. Separation device 190 is a centrifuge, rotary vacuum filter or pressure filter. In preferred embodiments of the invention, the separation device is a pressure filter adapted for solvent exchange by positive displacement under pressure of mother liquor in a filter cake with wash liquid comprising water. The oxidation mother liquor that results from the separation exits separation device 190 in stream 191 for transfer to mother liquor drum 192. A major portion of the mother liquor is transferred from drum 192 to oxidation reactor 110 for return to the liquid phase oxidation reaction of acetic acid, water, catalyst and oxidation reaction by-products dissolved or present as fine solid particles in the mother liquor. Crude solid product comprising terephthalic acid and impurities comprising oxidation by-products of the para-xylene feedstock is conveyed, with or without intermediate drying and storage, from separation device 190 to purification solution make up vessel 202 in stream 197. The crude solid product is slurried in make up vessel 202 in purification reaction solvent, all or at least a portion, and preferably about 60 to about 100 wt. %, of which, comprises a second liquid phase from an off-gas separation of water and acetic acid in a vapor phase removed from reactor 110 to column 330 and by-products of the oxidation. If used, make up solvent, such as fresh demineralized water or suitable recycle streams such as liquid condensed from vapors resulting from pressure letdown in crystallization of purified terephthalic acid product as discussed below, can be directed to make up tank 202 from vessel 204. Slurry temperature in the make up tank preferably is about 80 to about 100°C.

[000123] Crude product is dissolved to form a purification reaction solution by heating, for example to about 260 to about 290°C in makeup tank 202 or by passage through

heat exchangers (not shown) as it is transferred to purification reactor 210. In reactor 210, the purification reaction solution is contacted with hydrogen under pressure preferably ranging from about 85 to about 95 kg/cm.^{2}.

[000124] A portion of the purification liquid reaction mixture is continuously removed from hydrogenation reactor 210 in stream 211 to crystallization vessel 220 where terephthalic acid and reduced levels of impurities are crystallized from the reaction mixture by reducing pressure on the liquid. The resulting slurry of purified terephthalic acid and liquid formed in vessel 220 is directed to solid-liquid separation apparatus 230 in stream line 221. Vapors resulting from pressure letdown in the crystallization reactor can be condensed by passage to heat exchangers (not shown) for cooling and the resulting condensate liquid redirected to the process, for example as recycle to purification feed makeup tank 202, through suitable transfer lines (not shown). Purified terephthalic acid exits solid-liquid separation device 230 in stream 231. The solid-liquid separation device can be a centrifuge, rotary vacuum filter, a pressure filter or combinations of one or more thereof. A second liquid phase removed from column 330 can be directed to the separation device as wash liquid for separation to replace or reduce demineralized water requirements for final washing of the purified product.

[000125] Purification mother liquor from which the solid purified terephthalic acid product is separated in solid-liquid separator 230 comprises water, minor amounts of dissolved and suspended terephthalic acid and impurities including hydrogenated oxidation by-products dissolved or suspended in the mother liquor. According to the preferred process embodiment illustrated in FIG. 1, at least a portion, and preferably all or substantially all, of the purification mother liquor is directed in stream 233 to oxidation reaction off-gas separation in high pressure distillation column 330 and introduced thereto. The purification mother liquor directed to column 330 is introduced to the column at a lower portion thereof, as at 344, to provide liquid reflux for separation. Transfer of purification mother liquor from solid-liquid separation device 230 to the high pressure distillation column also allows for recycle of terephthalic acid and impurities in the mother liquor, such as benzoic acid and p-toluic acid by-products to oxidation reactor 110 where they are oxidized or converted to terephthalic acid, while water content of the purification mother liquor vaporizes and refluxes in the distillation column, exiting in a pressurized gas and/or a second liquid phase removed from column, without significantly impacting water balance in oxidation. Transfer of purification mother liquor from solid-liquid separation device 230 to the distillation column also reduces the volume of liquid effluent that needs to be directed to liquid waste treatment

and provides for return of valuable terephthalic acid to oxidation and, in turn, removal thereof for recovery in oxidation crystallizers 152 and 156.

[000126] Reaction off-gas generated by the liquid phase oxidation of para-xylene feedstock in reactor vessel 110 is removed from the reactor through vent 116 and directed in stream 111 to separation in column 330 which, as depicted in FIG. 2, represents a high pressure distillation column having a plurality of trays preferably providing about 28 to about 63 theoretical plates and to which is supplied liquid for reflux through liquid inlets 336 and 344. The vapor stream from oxidation is introduced to column 330 preferably at temperature and under pressure of about 150 to about 225°C. and about 4 to about 21 kg/cm^2 gauge, respectively, and not substantially less than in oxidation reactor 110. As described above, FIG. 1 illustrates a preferred embodiment in which reflux liquid introduced to the column comprises purification mother liquor from which solid purified terephthalic acid is separated in solid-liquid separation device 230. Column 330 includes 80 trays, about 50 to about 70 of which are disposed below reflux inlet 344, with the remainder positioned above reflux inlet 344 but below introduction of a second reflux liquid at 336. Inlets 336 and 344 are positioned so that they are separated by trays corresponding to at least about three theoretical equilibrium stages, and preferably about 3 to about 20 such stages. According to preferred embodiments of the invention as represented in FIG. 1, reflux liquid supplied to the column at 336 is preferably a condensate liquid recovered by condensation of a high pressure and temperature second vapor phase removed from distillation column 330 in condensing zone 350 and directed to the column in stream 355, while reflux liquid supplied at reflux inlet port 344 from stream 233 is preferably a purification mother liquor directed to the column for such use from solid-liquid separation of a purified product from the liquid phase oxidation. Reflux supplied to the column at inlet preferably provides about 70 to about 85% of the volumetric flow of reflux liquid added to the column at inlets 344 and 336.

[000127] A first liquid phase rich in acetic acid solvent for the liquid phase oxidation recovered from the high pressure inlet gas to column 330 together with para-xylene oxidation by-products such as benzoic acid and p-toluic apportioned to the liquid phase in column 330 is collected at a lower portion of the column. A second liquid phase, which is predominantly water but also contains minor amounts of benzoic acid and p-toluic acid by-products apportioned to the liquid phase as well as oxygen and methyl bromide, is collected and removed from the column at side draw outlet 345. A second high pressure vapor comprising water vapor, incondensable components of the oxidation off-gas and acetic acid

by-products such as methanol and methyl acetate preferentially apportioned to the gas phase is removed from the column as an exit gas through overhead vent 334.

[000128] The acetic acid-rich first liquid phase resulting from separation in distillation column 330 exits the column at a lower portion thereof and preferably is returned directly or indirectly to oxidation reactor 110, as in stream 331. Return of the liquid phase to oxidation provides make up solvent acetic acid to the oxidation reaction and reduces feedstock loss by allowing for conversion to desired products of intermediates and by-products condensed from the oxidation vapor phase as well as those recycled from purification mother liquor reflux to the column. The second liquid phase withdrawn from the column at side draw outlet 345 is discharged into flash vessel 346 which is at ambient or atmospheric pressure to remove corrosive components such as dissolved oxygen and methyl bromide prior to being directed to purification solution makeup vessel 202 in stream 357 for use in forming the crude product slurry and purification reaction solution that is directed to purification reactor 210. Other purification vessels and liquid receiving equipment and uses to which the water-enriched second liquid phase can be directed to after flashing include crystallization vessel 220 for use as clean make-up solvent to replace purification reaction liquid vaporized in the crystallizer and solid liquid separation device 230 for use as wash liquid or seal flush. The condensate liquid also is suitable for uses outside a purification step, such as wash liquid for solvent exchange filters.

[000129] Exit gas withdrawn from the column at vent 334 is directed to condensing means 350, which as depicted in FIG. 1, includes condensers 352 and 362, and disengagement drum 372. Preferably, condensation is conducted such that liquid condensate water at a temperature of about 40 to about 60°C. is recovered in at least one stage. In the embodiment illustrated in the figure, condensation is conducted by indirect heat exchange in condensing means 352 with water at a temperature of about 120 to about 170°C and the resulting liquid condensate is directed to column 330 in stream 355 for addition at reflux inlet 336. Liquid and uncondensed gas from condenser 352 is directed to condenser 362 in stream 361 for condensation using cooling water at about 30 to about 40°C. Gas and liquid effluent from condenser 362 is directed in stream 363 to drum 372 in which condensate liquid comprising water is collected and removed in stream 373, which can be directed to other uses such as seal flush liquid or to a purge stream. A condenser exhaust gas under pressure is withdrawn as in stream 375.

[000130] Water used as heat exchange fluid for condensation of the second high pressure gas from distillation column 330 is heated by heat exchange in condensing means

350 to generate pressurized steam which can be directed to an energy recovery device such as steam turbine 450 in the process embodiment depicted in FIG. 1. Condensation using two or more condensers in series using heat exchange fluids at successively lower temperatures allows for generation of steam at different pressures, thereby allowing for efficiencies in use of steam at the different pressures by matching with differing heat or energy inputs to operations in which steam is used.

[000131] Uncondensed exhaust gas from condensation removed in stream 375 comprises incondensable components such as unconsumed oxygen from oxidation, nitrogen from the air used as oxygen source to the oxidation, carbon oxides from such air as well as from reactions in oxidation, and traces of unreacted para-xylene and its oxidation by-products, methyl acetate and methanol, and methyl bromide formed from the bromine promoter used in oxidation. In the embodiment illustrated in the figure, the uncondensed gas is substantially free of water vapor owing to substantially complete condensation into the condensate liquid recovered in the condensing means.

[000132] Uncondensed exhaust gas from condensing means 350 is under pressure of about 10 to about 15 kg/cm^2 and can be transferred directly to a power recovery device or to a pollution control device for removing corrosive and combustible species in advance of power recovery. As depicted in FIG. 1, uncondensed gas is first directed to treatment to remove unreacted feed materials and traces of solvent acetic acid and/or reaction products thereof remaining in the gas. Thus, uncondensed gas is transferred in stream 375 to high pressure absorber 380 for absorbing para-xylene, acetic acid, methanol and methyl acetate without substantial loss of pressure. Absorption tower 380 is adapted for receipt of the substantially water-depleted gas remaining after condensation and for separation of para-xylene, solvent acetic acid and its reaction products from oxidation from the gas by contact with one or more liquid scrubbing agents. A preferred absorber configuration, illustrated in the figure, comprises tower 380 having a plurality of internally disposed trays or beds or structured packing (not shown) to provide surface for mass transfer between gas and liquid phases. Inlets (not shown) for addition of scrubbing agent to the absorber in streams 381 and 383, respectively, are disposed at one or more upper, and one or more lower portions of the tower. The absorber also includes an upper vent 382 from which a scrubbed gas under pressure comprising incondensable components of the inlet gas to the absorber is removed in stream 385 and a lower outlet 384 for removal of a liquid acetic acid stream into which components from the gas phase comprising one or more of para-xylene, acetic acid, methanol

from a lower portion of the tower and directed to reaction vessel 110 for reuse of recovered components.

[000133] Pressurized gas removed from condensing means 350 or, as depicted in FIG. 1, from the vent 382 from the high pressure absorber, can be directed to pollution control means, as at 390, for converting organic components and carbon monoxide in the gas from the condenser or the absorber to carbon dioxides and water. A preferred pollution control means is a catalytic oxidation unit adapted for receiving the gas, optionally heating it to promote combustion and directing the gas into contact with a high temperature-stable catalyst disposed on a cellular or other support such that gas flow through the device is substantially unaffected. Overhead gas from absorber 380 is directed to pollution control system 390 which includes preheater 392 and catalytic oxidation unit 394. The gas is heated to about 250 to 450°C in the preheater and passed under pressure of about 10 to 15 kg/cm.sup.2 to oxidation unit 394 where organic components and by-products are oxidized to compounds more suited for beneficial environmental management.

[000134] An oxidized high pressure gas is directed from catalytic oxidation unit 394 to expander 400 which is connected to generator 420. Energy from the oxidized high pressure gas is converted to work in the expander 400 and such work is converted to electrical energy by generator 420. Expanded gas exits the expander and can be released to the atmosphere, preferably after caustic scrubbing and/or other treatments for appropriately managing such releases.

Claims

1. A continuous process for preparing aromatic carboxylic acids by the exothermic liquid-phase oxidation reaction of an aromatic feedstock compound wherein water is efficiently recovered from the exothermic liquid-phase oxidation reaction, which process comprises:

(a) oxidizing an aromatic feedstock compound to an aromatic carboxylic acid in a liquid-phase reaction mixture comprising water, a low-molecular weight monocarboxylic acid solvent, a heavy metal oxidation catalyst and a source of molecular oxygen, under reaction conditions which produce a gaseous high pressure overhead stream comprising water, gaseous by-products, and gaseous low-molecular weight monocarboxylic acid solvent;

(b) separating in a high efficiency separation apparatus a solvent monocarboxylic acid-rich first liquid phase and a water-rich second liquid phase comprising dissolved oxygen and methyl bromide; and

(c) reducing the amount of at least one of dissolved oxygen and methyl bromide present in the second liquid phase providing a treated second liquid phase.

2. The process of claim 1 wherein step (c) comprises flashing the second liquid phase to reduce the amount of at least one of dissolved oxygen and methyl bromide.

3. The process of claim 2, wherein flashing the second liquid phase results in a drop in pressure from about 5 kg/cm^2 to about 40 kg/cm^2 to about atmospheric or ambient pressure.

4. The process of claim 2, wherein flashing the second liquid phase results in a drop in pressure from about 10 kg/cm^2 to about 20 kg/cm^2 to about atmospheric or ambient pressure.

5. The process of claim 2, wherein the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 1.0 ppmw after flashing.

6. The process of claim 2, wherein the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 0.5 ppmw after flashing.

7. The process of claim 2, wherein the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 0.05 ppmw after flashing.

8. The process of claim 2, wherein the amount of dissolved oxygen in the second liquid phase is reduced from an amount of about 2.2 ppmw to an amount of less than about 0.006 ppmw after flashing.

9. The process of claim 2, wherein the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.02 ppmw after flashing.

10. The process of claim 2, wherein the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.01 ppmw after flashing.

11. The process of claim 2, wherein the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.009 ppmw after flashing.

12. The process of claim 2, wherein the amount of dissolved methyl bromide in the second liquid phase is reduced from an amount of about 0.03 ppmw to an amount of less than about 0.006 ppmw after flashing.

13. The process of claim 2 further comprises a step of steam stripping the second liquid phase after flashing.

14. The process of claim 2 further comprises a step of stripping the second liquid phase with nitrogen after flashing.

15. The process of claim 1, wherein the treated second liquid phase is suitable for use as liquid comprising water in one or more steps of a process for purifying impure forms of aromatic carboxylic acid.

16. The process of claim 1, wherein the treated second liquid phase is suitable for use as a seal flush.

Figure 1

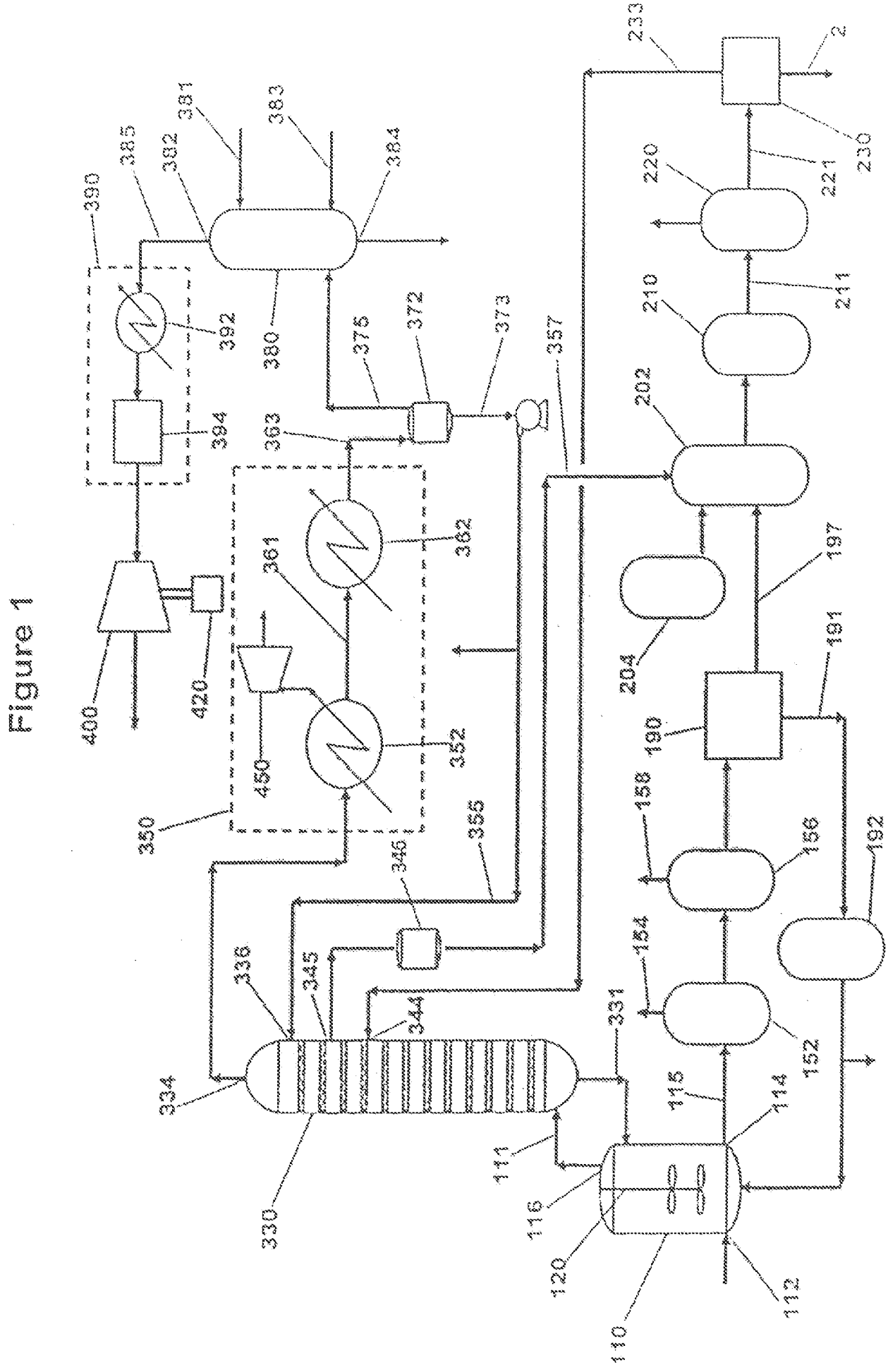

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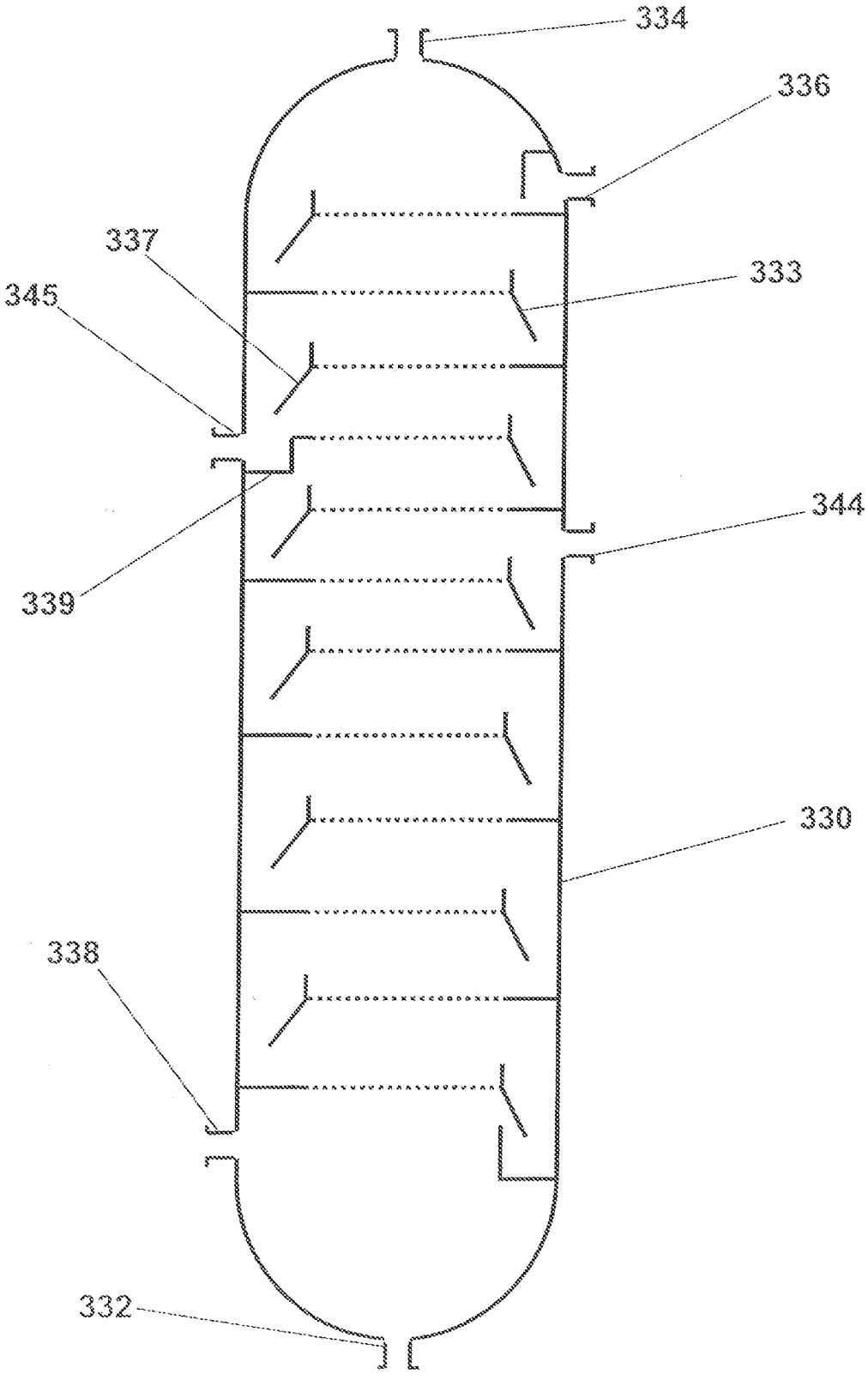
Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/069779

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C51/255 C07C51/265
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/220800 A1 (BARTOS THOMAS M [US]) 30 August 2012 (2012-08-30) paragraphs [0127] - [0131]; claim 1	1-16
A	WO 96/39595 A1 (ICI PLC [GB]; TURNER JOHN ARTHUR [GB]; JEFFERY IAN CHARLES [GB]) 12 December 1996 (1996-12-12) claim 16	1-16
A	US 5 723 656 A (ABRAMS KENNETH J [US]) 3 March 1998 (1998-03-03) cited in the application claim 1	1-16
A	WO 02/098833 A1 (EASTMAN CHEM CO [US]) 12 December 2002 (2002-12-12) example 1	1-16

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

☒ See patent family annex.

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

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 March 2015	13/03/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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