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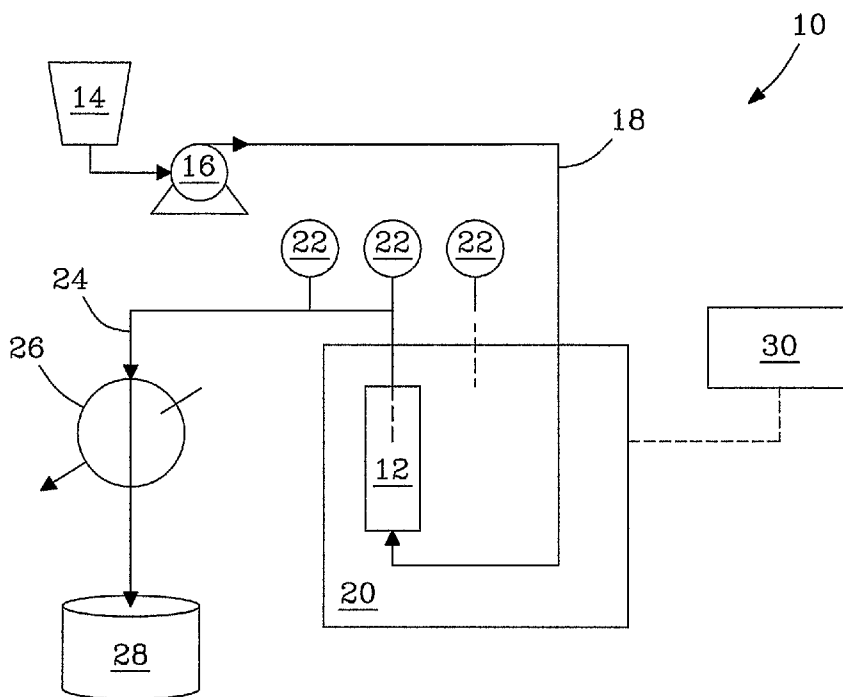
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(54) Title: METHOD FOR THE PREPARATION OF ALPHA-BETA-UNSATURATED CARBONYL COMPOUNDS



(57) Abstract: A process is disclosed for conversion of ammonium salts of β -hydroxy carbonyl compounds forming useful conversion products including, e.g., α , β -unsaturated carbonyl compounds and/or ammonium salts of α , β -unsaturated carbonyl compounds recovered at a high molar yield. Conversion products find use, e.g., as feedstock and/or end-use chemicals.

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METHOD FOR THE PREPARATION OF ALPHA-BETA-UNSATURATED CARBONYL COMPOUNDS

[0001] This invention was made with Government support under Cooperative Research and Development Agreement (CRADA) Number PNNL-217 between Battelle, as operator of Pacific Northwest National Laboratory under U.S. Department of Energy Contract DE-AC0676RLO-1830, and Cargill, Inc. The Government has certain rights in the invention.

FIELD OF THE INVENTION

[0002] The present invention relates generally to a method for conversion of β -hydroxy carbonyl compounds to conversion products including, e.g., acrylic acid [CAS No. 79-10-7], acrylates, and acrylamide [CAS No. 79-06-01]. The conversion products find use as, e.g., feedstock and/or end-use chemicals.

BACKGROUND OF THE INVENTION

[0003] While many chemical intermediates (e.g., lactic acid and succinic acid) can be produced via bio-derived processes such as fermentation, in order to match the scale, flexibility, and efficiency of the petrochemical industry, the bioproducts industry must develop additional chemical building blocks that are versatile and competitive. For example, acrylic acid is a prominent chemical that is polymerized into a broad range of versatile chemicals and resins, including plastics and hydrogels. Acrylic acid is also a co-polymer component in aerosol hair sprays and

finds application as a foam stabilizer in shampoos. In medicine and dentistry, acrylic acid is used in the manufacture of dental plates, artificial teeth, and orthopedic cements. Acrylic acid is also a chemical intermediate used in the formation of acrylates which find application in polymer solutions for coating applications, emulsion polymers, paint formulations, and paper coatings. And, esters of acrylic acid play major roles in coatings, textiles, adhesives, paper, and plastics.

[0004] Accordingly, there remains a need to develop processes for production of such chemical intermediates from which a host of useful products can be made.

SUMMARY OF THE INVENTION

[0005] In one aspect, the invention is a process comprising the steps of providing a material comprising an ammonium salt of a β -hydroxy carbonyl compound to a reactor in a substantially liquid form at a flow rate and a temperature whereby said material reacts substantially inside the reactor in the absence of a flow of inert gas; and wherein the material is converted to one or more reaction products capable of vaporizing from the reactor at the temperature upon conversion, the reaction products comprising an α , β -unsaturated carbonyl compound and/or an ammonium salt of an α , β -unsaturated carbonyl compound recovered at a high molar yield.

[0006] In another aspect, the invention is an apparatus comprising a reactor for converting a material, wherein the material comprising an ammonium salt of a β -hydroxy carbonyl compound is provided to the reactor in a substantially liquid

form at a flow rate and a temperature whereby the material reacts substantially inside the reactor in the absence of a flow of inert gas; and wherein the material is converted to one or more reaction products capable of vaporizing from the reactor at the temperature upon conversion, the reaction products comprising an α,β -unsaturated carbonyl compound and/or an ammonium salt of an α,β -unsaturated carbonyl compound recovered at a high molar yield.

[0007] In one embodiment, the β -hydroxy carbonyl compound is selected from the group of 3-hydroxypropionic acid, 3-hydroxypropionic acid ester dimers, 3-hydroxypropionic acid ether dimers, or combinations thereof.

[0008] In another embodiment, the material is converted in conjunction with a catalyst.

[0009] In another embodiment, the catalyst is a dehydration catalyst.

[0010] In another embodiment, the catalyst is selected from the group of solid oxides, solid acids, acidic catalysts, weakly acidic catalysts, strongly acidic catalysts, basic catalysts, ion-exchange resins, acidic gases, basic gases, or combinations thereof.

[0011] In another embodiment, the solid oxide catalyst is selected from the group consisting of TiO_2 , ZrO_2 , Al_2O_3 , SiO_2 , ZnO_2 , SnO_2 , WO_3 , MnO_2 , Fe_2O_3 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, ZrO_2/WO_3 , $\text{ZrO}_2/\text{Fe}_2\text{O}_3$, $\text{ZrO}_2/\text{MnO}_2$, or combinations thereof.

[0012] In another embodiment, the acidic or weakly acidic catalyst is selected from the group of titanate acids, metal oxide hydrates, metal sulfates, metal oxide sulfates, metal phosphates, metal oxide phosphates, mineral acids, carboxylic

acids, salts thereof, acidic resins, acidic zeolites, clays, carbon dioxide, or combinations thereof.

[0013] In another embodiment, the acidic or weakly acidic catalyst is selected from the group consisting of Ti-0720®, SiO₂/H₃PO₄, fluorinated Al₂O₃, Nb₂O₃/PO₄⁻³, Nb₂O₃/SO₄⁻², Nb₂O₅·H₂O, phosphotungstic acids, phosphomolybdic acids, silicomolybdic acids, silicotungstic acids, carbon dioxide, salts thereof, PVPH⁺Cl⁻®, ECS-3®, or combinations thereof.

[0014] In another embodiment, the basic catalyst is selected from the group of ammonia, polyvinylpyridine, metal hydroxides, Zr(OH)₄, or amines of the form NR₁R₂R₃, wherein R₁, R₂, and R₃ are selected from the group consisting of H, alkyl and aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

[0015] In another embodiment, ammonia is added to the reactor at a partial pressure and/or liquid concentration sufficient to promote amide formation.

[0016] In another embodiment, the amide formation comprises formation of acrylamide.

[0017] In another embodiment, an inhibitor is added to the reactor to minimize formation of polymers.

[0018] In another embodiment, the providing comprises introducing the material to the reactor in a solvent at a concentration in the range from about 5% to about 50%.

[0019] In another embodiment, providing comprises introducing the material to the reactor substantially continuously.

[0020] In another embodiment, the solvent is selected from the group of donor solvents, non-donor solvents, non-protic solvents, acceptor solvents, protic solvents, or combinations thereof.

[0021] In another embodiment, the protic solvent is selected from the group of alcohols, water, or combinations thereof.

[0022] In another embodiment, alcohols are selected from the group of alkanols containing from 1 to 20 carbon atoms.

[0023] In another embodiment, the reactor is a continuous flow reactor or a component of a continuous flow reactor system.

[0024] In another embodiment, the reactor is selected from the group of trickle-bed, fixed-bed, fluidized bed, stirred tank, continuous stirred tank, ebulating bed, membrane, Berty, plug-flow, bubble-column, reactive-distillation column, or combinations thereof.

[0025] In another embodiment, providing comprises introducing a material to a reactor at a rate in the range from about 0.05 WHSV to about 10 WHSV.

[0026] In another embodiment, providing comprises introducing a material to said reactor at a rate in the range from about 0.2 WHSV to about 0.4 WHSV.

[0027] In another embodiment, temperature is selected in the range from about 90 °C to about 250 °C.

[0028] In another embodiment, temperature is selected in the range from about 90 °C to about 220 °C and a partial vacuum in the range from about 0.1 mm Hg to about 200 mm Hg.

[0029] In another embodiment, temperature is selected in the range from about 180 °C to about 220 °C at atmospheric pressure.

[0030] In another embodiment, temperature is selected in the range from about 200 °C to about 500 °C and a pressure in the range from about 0 psig to about 500 psig.

[0031] In another embodiment, conversion is in the range from about 60 percent to about 100 percent.

[0032] In another embodiment, the one or more reaction products are selected from the group of acrylic acid, methacrylic acid, amides thereof, salts thereof, acrolein, water, or combinations thereof.

[0033] In another embodiment, the one or more reaction products have a molar yield of up to about 100 percent, or alternatively in the range from about 80 percent to about 100 percent, or alternatively in the range from about 90 percent to about 100 percent.

[0034] In another embodiment, one or more of the one or more reaction products formed from the conversion are recovered by removing from the reactor.

[0035] In another embodiment, the removing comprises vaporization from the reactor for recovery of the one or more reaction products.

[0036] In another embodiment, the one or more reaction products are recovered in a substantially neat form from the reactor.

[0037] In another embodiment, removing of the one or more reaction products is substantially continuous.

[0038] In another embodiment, the material is partially converted in a first stage of the reactor and finally converted in a second stage of the reactor.

[0039] In another embodiment, the first stage of the reactor comprises a slurry tank or a stirred tank for mixing and the second stage of the reactor comprises a rotary calciner/extruder, auger reactor, or a stirred tank for mixing.

[0040] In another embodiment, the calciner/extruder further comprises a member selected from the group of stirred tank, rotary calciner, Auger reactor, extruder, evaporator, evacuator, or combinations thereof.

[0041] In another embodiment, removing comprises vaporization from the reactor for recovery of the one or more reaction products.

[0042] In another embodiment, vaporization comprises substantially continuous steam-stripping of the one or more reaction products in one or more effluent streams, whereby cooling and/or condensing of the one or more effluent streams recovers the one or more reaction products.

[0043] In another embodiment, condensing comprises isolating and recovering the one or more reaction products in separate product streams from one or more effluent streams.

[0044] In another embodiment, condensing comprises isolating and recovering the one or more reaction products from the reactor in separate product streams.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045] A more complete appreciation of the invention will be readily obtained by reference to the following description of the accompanying drawings in which like numerals in different figures represent the same structures or elements.

[0046] **FIG. 1** illustrates a fixed-bed reactor or reactor system for practicing the process of the invention.

[0047] **FIG. 2** illustrates a generalized reaction process for conversion of a source material comprising β -hydroxy carbonyl compounds yielding acrylic acid as a reaction product, according to an embodiment of the invention.

[0048] **FIG. 3** illustrates a generalized reaction process for conversion a source material comprising salts of β -hydroxy carbonyl compounds including, e.g., alkali metal salts, alkaline earth metal salts, and/or ammonium salts, yielding one or more reaction products selected from acrylate salts (e.g., sodium acrylate, ammonium acrylate), acrylamide, and/or mixtures thereof, according to another embodiment of the invention.

[0049] **FIG. 4** illustrates various reaction pathways for conversion of a source material comprising salts of 3-hydroxypropionic acid, or the respective free acids, to useful conversion and/or reaction products including, e.g., acrylates, or the corresponding free acids, according to an embodiment of the invention.

[0050] **FIG. 5** illustrates a system of a commercial-scale design for conversion of a source material comprising salts of β -hydroxy carbonyl compounds to one or more reaction products, including, e.g., acrylates and acrylamide, according to an embodiment of the invention.

[0051] FIG. 6 illustrates a system of a commercial-scale design for conversion of a source material comprising salts of β -hydroxy carbonyl compounds to one or more reaction products, according to another embodiment of the invention.

[0052] FIG. 7 illustrates a generalized reaction process for conversion of a source material comprising ammonium salts of β -hydroxy carbonyl compounds to one or more reaction products selected from ammonium acrylates, acrylamide, or mixtures thereof, according to an embodiment of the invention.

[0053] FIG. 8 illustrates various and potentially useful pathways for conversion of a source material comprising β -hydroxy carbonyl compounds or their salts to one or more reaction products.

DETAILED DESCRIPTION OF THE INVENTION

[0054] While the present invention is described herein with reference to the preferred embodiments thereof, it should be understood that the invention is not limited thereto, and various alternatives in form and detail may be made therein without departing from the spirit and scope of the invention.

[0055] The present invention relates generally to a method for conversion of salts of β -hydroxy carbonyl compounds as a source material to conversion products including, e.g., α , β -unsaturated carbonyl compounds and/or ammonium salts of α , β -unsaturated carbonyl compounds recovered at high molar yield, including, e.g., acrylic acid, methacrylic acid, amides thereof, ammonium salts thereof, acrolein, or combinations thereof. The term "source material" or "material" as used herein refers

to one or more β -hydroxy carbonyl compounds introduced to a reactor giving rise to the desired conversion products. The term encompasses all associated reagents and/or chemical constituents introduced therewith including, e.g., solvents, inhibitors, stabilizers, or the like. In one embodiment, a source material is composed substantially of an ammonium salt of a β -hydroxy carbonyl compound, wherein the β -hydroxy carbonyl compound is selected from the group of 3-hydroxypropionic acid, 3-hydroxypropionic acid ester dimers, 3-hydroxypropionic acid ether dimers, or combinations thereof. No limitations are intended.

[0056] The term "conversion" as used herein refers to the quantity of a source material consumed in a specified reaction as a function of the quantity of the material introduced to a reactor or a stage thereof, as defined by equation [1]:

$$\text{Conversion} = \left(\frac{\text{Moles Source Material Consumed}}{\text{Moles Source Material Fed to Reactor}} \right) \quad [1]$$

[0057] The term "partial conversion" as used herein refers to conversion of a source material in a reactor or stage thereof wherein quantities of conversion products are determined by reaction equilibria in the selected medium. For example, partial conversion in aqueous media is on the order of about 50%, but is not intended to be limiting, as equilibria may be controlled as described herein providing conversion yields above the equilibrium controlled maximum.

[0058] The term "final conversion" or "finally converted" as used herein refers to conversion of a source material above its "partial conversion" or equilibrium-

controlled maximum. Final conversion may be achieved as described herein, e.g., in a reactor or stage coupled to, or secondary with, a primary equilibrium-controlled reactor or stage.

[0059] The term “conversion products” as used herein refers to one or more reaction products generated in conjunction with the apparatus', processes, and/or systems described herein that find use as feedstock and/or end-use chemicals, and/or that play a reactive and/or chemical role in the apparatus, processes, and/or systems described. The terms “conversion products” and “reaction products” are used synonymously. No limitations are intended.

[0060] The term “molar selectivity” as used herein refers to the quantity (moles) of reaction (or conversion) products formed as a ratio of the moles of source material consumed, determined from equation [2]:

$$\text{Molar Selectivity} = \left(\frac{\text{Moles of Product Formed}}{\text{Moles of Source Material Consumed}} \right) \quad [2]$$

[0061] The term “molar yield” as used herein is defined by equation [3] as the moles of reaction (or conversion) products formed as a ratio of the moles of a source material introduced (fed) to a reactor:

$$\text{Molar Yield} = \left(\frac{\text{Moles of Product Formed}}{\text{Moles of Source Material Fed to Reactor}} \right) \quad [3]$$

[0062] The term “high molar yield” as used herein refers to a molar yield of greater than or equal to about 70 percent.

[0063] The term “flow rate” as used herein is defined as the weight-hourly space velocity (WHSV), given by equation [4]:

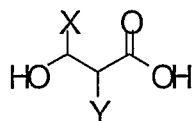
$$\text{Flow Rate} = \left(\frac{\text{g Source Material}}{\text{g Catalyst}} \right) / \text{hour} \quad [4]$$

[0064] Reactions involved in conversion of source materials to products of interest include, but are not limited to, amination, deamination, dehydration, etherification, esterification, hydrolysis, or combinations thereof. The person of skill in the art will appreciate that processes as set forth herein for producing and converting specific moieties, and their chemical derivatives and intermediates, will occur at a variety of conversion rates, selectivities, and/or molar yields. All conversions as will be considered significant by the person of skill in the art are within the scope and spirit of the invention. No limitations are hereby intended.

[0065] In one embodiment, the invention provides for continuous production of, e.g., acrylic acid as a conversion product of a source material comprising a β -hydroxy carbonyl compound. β -Hydroxy carbonyl compounds include, but are not limited to, 3-hydroxypropionic acid, substituted 3-hydroxypropionic acids, 3-hydroxypropionic esters, 3-hydroxypropionic ester dimers, 3-hydroxypropionic acid ethers, 3-hydroxypropionic acid ether dimers, 3-hydroxypropionic acid salts,

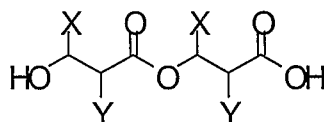
3-hydroxypropionic amides, 3-aminopropionic acids, 3-hydroxypropionaldehydes, or combinations thereof.

[0066] Substituted 3-hydroxypropionic acids comprise the group of compounds having the general form:



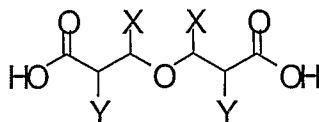
where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

[0067] 3-Hydroxypropionic acid ester dimers, also known as 3-Hydroxypropionic acid acrylate ester dimers, comprise the group of compounds having the general form:



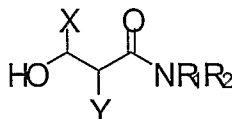
where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

[0068] 3-Hydroxypropionic acid ether dimers, also known as 3-Hydroxypropionic acid acrylate ether dimers, comprise the group of compounds having the general form:



where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

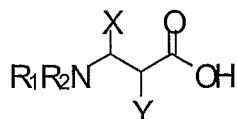
[0069] 3-Hydroxy-propionic amides comprise the group of compounds having the general form:



where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof, and where R₁ and R₂ are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons

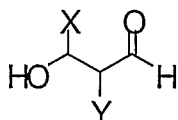
containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

[0070] 3-Amino-propionic acids comprise the group of amino acid compounds having the general form:



where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof, and where R₁ and R₂ are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

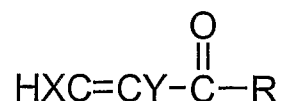
[0071] 3-Hydroxypropionic propionaldehydes comprise the group of compounds having the general form:



where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted

hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

[0072] Reaction or conversion products derived from source materials comprising β -hydroxy carbonyl compounds include the family of α,β -unsaturated carbonyl compounds having the general form:



where X and Y are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof; functional group R includes members independently selected from H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof. Stereochemistry about the double bond is not shown, but is not intended to be limiting. Reaction products comprising α,β -unsaturated carbonyl compounds include, but are not limited to, e.g., acrylic acid, methacrylic acid, salts thereof, esters thereof, acrolein, or combinations thereof. In other processes, reaction products include formation of acrylates, acrylamide, polymers thereof, or combinations thereof. In still yet other processes, reaction products include formation of acrylic acid, methacrylic acid, amides thereof, salts thereof, acrolein, or

combinations thereof. However, reaction products are not limited thereto. For example, water is easily generated from dehydration reactions occurring within the reactor. Thus, no limitations are intended.

Catalysts

[0073] Any catalyst capable of assisting in the conversion of a source material to desired end-use and/or reaction products may be selected without limitation. Catalysts are selected from classes including, e.g., acidic, neutral, or basic depending on desired reaction conditions promoted and respective conversion performance, as will be understood by those of skill in the art. For example, some reaction conditions will involve low pH conditions, e.g., when the source material is a carboxylic acid. In this case acidic catalysts are preferred. When the source material comprises, e.g., a carboxylic ester or a salt, reaction conditions will be of a neutral pH and catalysts may be selected from any appropriate class as long as the catalyst has sufficient activity. In conditions where ammonia is added, or e.g., a compound comprising an ammonium salt is present, basic catalysts are preferred. In short, pH suitable catalysts can be employed depending on reaction conditions.

[0074] Catalysts include, but are not limited to, solid oxides, solid acids, acidic catalysts, weakly acidic catalysts, strongly acidic catalysts, basic catalysts, ion-exchange resins, acidic gases, basic gases, or combinations thereof.

[0075] Solid oxide catalysts include, but are not limited to, e.g., TiO_2 , ZrO_2 , Al_2O_3 , SiO_2 , ZnO_2 , SnO_2 , WO_3 , MnO_2 , Fe_2O_3 , V_2O_5 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, ZrO_2/WO_3 , $\text{ZrO}_2/\text{Fe}_2\text{O}_3$, $\text{ZrO}_2/\text{MnO}_2$, or combinations thereof.

[0076] Acidic or weakly acidic catalysts include, but are not limited to, e.g., titanitic acids, metal oxide hydrates, metal sulfates (MSO_4 where $\text{M} = \text{Zn}, \text{Sn}, \text{Ca}, \text{Ba}, \text{Ni}, \text{Co}$, or other transition metals), metal oxide sulfates, metal phosphates [e.g., $\text{M}_3(\text{PO}_4)_2$ where $\text{M} = \text{Ca}, \text{Ba}$], metal phosphates, metal oxide phosphates, carbon (e.g., transition metals on a carbon support), mineral acids, carboxylic acids, salts thereof, acidic resins, acidic zeolites, clays, or combinations thereof. Acidic or weakly acidic catalysts further include Ti-0720® (titanium oxide-based catalyst, Engelhard, Iselin, NJ), $\text{SiO}_2/\text{H}_3\text{PO}_4$, fluorinated Al_2O_3 (e.g., $\text{Al}_2\text{O}_3 \cdot \text{HF}$), $\text{Nb}_2\text{O}_3/\text{PO}_4^{-3}$, $\text{Nb}_2\text{O}_3/\text{SO}_4^{-2}$, $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$, phosphotungstic acids, phosphomolybdic acids, silicomolybdic acids, silicotungstic acids, carbon dioxide, salts thereof, PVPH^+Cl^- ® (acidic polyvinylpyridine hydrochloride salt catalyst, Reilly, Indianapolis, IN), ECS-3® (hydrated acidic silica catalyst, Engelhard, Iselin, NJ), or combinations thereof. No limitations are intended.

[0077] Basic catalysts include, but are not limited to, e.g., ammonia, polyvinylpyridine, metal hydroxides, $\text{Zr}(\text{OH})_4$, and amines of the form $\text{NR}_1\text{R}_2\text{R}_3$, where R_1 , R_2 , and R_3 are independently selected from the group of side chain or functional groups including, but not limited to, e.g., H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof. No limitations are intended.

Solvents

[0078] Solvents include, but are not limited to, donor solvents, non-donor solvents, non-protic solvents, acceptor solvents, and protic solvents. Protic solvents include, e.g., alcohols, water, and combinations thereof. Alcohols include, but not limited to, alkanols composed of from 1 to 20 carbon atoms (e.g., methanol, ethanol, etc). No limitations are intended.

[0079] A packed, fixed-bed reactor of a continuous flow design will now be described in reference to **FIG. 1**.

[0080] **FIG. 1** illustrates a reactor system **10** for practicing the process of the invention, according to one embodiment of the invention. Appropriate scale-up of system components can be effected within the scope of the present invention suitable for industrial and/or manufacturing applications. All equipment and system configurations as will be implemented by the person of skill in the art are incorporated herein. No limitations are intended. System **10** comprises a reactor **12**, e.g., of a catalyst bed type, coupled to a feed source **14** for introducing a source material (i.e., "the material") to reactor **12**, a pumping system **16** for moving materials and fluids in/out of reactor **12**. Reactor **12** is located within a heating source **20**, e.g., a fluidized heating bed, furnace, or other heating source. Source material comprises any of a variety of β -hydroxy carbonyl compounds, including, but not limited to, e.g., 3-hydroxypropionic acid, which is introduced to reactor **12** from source **14** at a flow rate defined, e.g., as a weight hourly space velocity (WHSV)

optimized for conversion of the material in reactor **12**. In particular, flow rate is selected in the range from about 0.05 WHSV to about 10 WHSV. More particularly, flow rate is in the range from about 0.2 WHSV to about 0.4 WHSV. However, flow rates are not limited thereto. Any flow rate optimizing conversion of the selected source material in reactor **12** or other reactor systems described herein which may be employed is within the scope of the invention. For example, rates will depend in part on reactor design (e.g., whether bench-scale, pilot-scale, commercial-scale, continuous-flow, batch, etc.), quantity of catalyst employed, reactor temperatures, as well as other associated reactor conditions and parameters. Thus, no limitations are hereby intended.

[0081] In the instant embodiment, reactor **12** is mounted within heating source **20** coupling to a pump or other pumping system **16** via ½-inch stainless steel tubing **18**, but is not limited thereto. Pumping system **16** introduces source material to the bottom of reactor **12**, the material flowing up through reactor **12** but is again not limited thereto. Temperature is measured with thermocouples **22** or other suitable temperature indicating devices placed at various locations within system **10**, e.g., of heating source **20** and of reactor **12**. In the instant embodiment, conversion products are collected as an effluent stream from the top of reactor **12** in a collection vessel **28** coupled to reactor **12** via 1/16-inch stainless steel tubing **24**. In an alternate configuration, conversion products are distilled from reactor **12** into individual product streams given vapor pressure and/or boiling points differences between the various reaction products of interest. Reactor **12** is further configured with an optional by-pass loop **26** used as a sampling line for taking process

samples. No limitations are hereby intended. Devices and processes occurring within system **10** may be automated by linking with a computer **30**. All configurations as will be envisioned and/or implemented by those of skill in the art are within the scope of the invention.

[0082] System **10** operates at atmospheric pressure at a temperature above the boiling temperature of water, permitting a feed material in a condensed form to be used. Direction of flow of the source material within and through system **10** and/or reactor **12** is not limited. For example, source material may be introduced to reactor **12** from a point entering anywhere along the vertical length (e.g., center and side) of reactor **12**, e.g., whereby solvents when used will flow downward through reactor **12** for collection and recycle from the bottom of reactor **12** and reaction products will distill individually from the top of reactor **12** for collection. Products are removed as they are formed retarding polymerization within reactor **12**.

[0083] Various catalysts may be employed in reactor **12**, as described herein, or operated in the absence of catalysts, permitting substantial control of reaction conditions and operation parameters. For example, catalysts may be introduced to reactor **12** prior to introduction of a source material or be introduced simultaneously with the source material in continuous mode operation. No limitations are hereby intended. For example, other components and devices may be incorporated within system **10** including, but not limited to, temperature and pressure controllers and devices, transfer systems (e.g., fluids, solvents, conversion products, reagents, and the like), and/or associated equipment including those for collecting and storing data as will be contemplated by the person of skill in the art. Further, as will be

understood by those of skill in the art, components and devices within system 10 may be controlled and/or interfaced in conjunction with computers and/or other associated electronic devices without reservation, e.g., for collecting data, controlling pressure and temperature, and the like. No limitations are hereby intended.

[0084] Conversion involves heating the material in the presence of a catalyst at a temperature and residence time with the catalyst yielding various reaction products.

[0085] Molar yields for reaction products are achieved in the range up to about 100 percent. More particularly, molar yields are in the range from about 80 percent to about 100 percent. Most particularly, yields are in the range from about 90 percent to about 100 percent. High yields for reaction and/or conversion products of interest are obtained at least in part by removing at least one of the conversion products upon formation thereby controlling and/or limiting further reactions and/or chemistries including, but not limited to, e.g., dimerization, oligomerization, re-hydration. In one example, high yield of acrylic acid from conversion of 3-hydroxypropionic acid is obtained by removing acrylic acid (e.g., by vaporization) as it is formed thereby controlling reaction equilibria and limiting potential for dimerization, oligomerization, or re-hydration (i.e., formation of the source material again). Choice of reaction temperature has also proven important to process yields. In particular, reaction temperatures are selected in the range from about 90 °C to about 250 °C. More particularly, reaction temperatures are selected in the range from about 90 °C to about 180 °C in conjunction with a partial vacuum in the range

from 20 mm Hg to about 200 mm Hg. Alternatively, temperatures are selected in the range from about 180 °C to about 200 °C at atmospheric pressure. In an alternate configuration, temperatures are selected in the range from about 200 °C to about 500 °C in conjunction with a pressure in the range from about 20 psig to about 500 psig.

[0086] Various reactors may be employed without departing from the scope of the invention, including, but not limited to, trickle-bed, fixed-bed, fluidized bed, stirred tank, continuous stirred tank, ebulating bed, membrane, Berty, plug-flow, bubble-column, reactive-distillation column, or combinations thereof. In addition, various and multiple reactor configurations may be employed without limitation. In but one example of an industrial scale design, multiple and/or various reactors may be arranged, e.g., side by side, in conjunction with, e.g., a centralized heating source for heating reactors and providing for heat transfer, a centralized material source for supplying source material to the reactor at a suitable flow rate (WHSV), the industrial scale design providing for removal of reaction (or conversion) products as described herein whereby high product yields are obtained.

[0087] **FIG. 2** illustrates a generalized reaction process for conversion of β -hydroxy carbonyl compounds in a source material **50** yielding acrylic acid, according to an embodiment of the invention. Sources for β -hydroxy carbonyl compounds include, but are not limited to, e.g., fermentation, other chemical processes, or the like. Source material **50** can include monomers, dimers, oligomers, or combinations thereof. Further, as described herein, various solvents may be added, but are not mandatory. For example, in the instant embodiment, the

source material **50** comprises water, but the invention is not limited thereto. No limitations are intended.

[0088] In the instant embodiment, source material **50** comprising, e.g., 3-hydroxypropionic acid, is converted via dehydration reaction to acrylic acid **52** plus water **54**. Source material **50** is provided under generally continuous flow to reactor **12**, packed with, e.g., a dehydration catalyst in a fixed-bed configuration. Material **50** is heated in the presence of the catalyst at a temperature and residence time sufficient to dehydrate the material in contact with the catalyst, yielding the desired reaction product at high conversion and high molar yield. Temperature for conversion of the source material **50** is in the range from about 100 °C to about 250 °C. In an alternate operation, temperature is selected in the range from 180 °C to about 220 °C at atmospheric pressure. In an alternate operation, temperature for conversion is in the range from about 100 °C to about 180 °C in a partial vacuum of from about from about 20 mm Hg to about 200 mm Hg. Conversion of source material **50** comprising 3-hydroxypropionic acid of at least up to about 90% has been demonstrated with a selectivity of at least up to about 95%. In the instant embodiment, source material **50** was prepared in a water solvent, but is not limited thereto. Other solvents may be used as described herein. In other processes or configurations, solvents are not required. Thus, no limitations are hereby intended.

[0089] **FIG. 3** illustrates a generalized reaction process for conversion of salts of β -hydroxy carbonyl compounds (e.g., alkali metal salts, alkaline earth metal salts, and/or ammonium salts, yielding acrylate salts (e.g., sodium acrylate, ammonium acrylate), acrylamide, and/or mixtures thereof, according to another embodiment of

the invention. In the figure, source material **60** comprising, e.g., the sodium salt of 3-hydroxypropionic acid optionally in a solvent is converted via dehydration reaction to a sodium salt of acrylic acid **62** plus water **64** as reaction or conversion product. Various factors effect the conversion of β -hydroxy carbonyl compound salts. For example, under aqueous conditions, dehydration is controlled by reaction equilibria. Such equilibria can require long reaction times permitting concomitant production of acrylate polymers via etherification and/or esterification to occur, a potentially undesirable outcome. Control of reaction conditions, therefore, is important to achieve high conversion of the β -hydroxy carbonyl compound salts forming acrylate salts. In particular, source material **60** can be provided under continuous flow packed with a reaction catalyst, e.g., a fixed-bed reactor configuration, or under batch reaction conditions. Material **60** is heated in the presence of the catalyst at a temperature and residence time sufficient to dehydrate material **60** in contact with the catalyst yielding the desired reaction products **62**, e.g., acrylate salts (e.g., sodium acrylate), at high conversion and high molar yield. In one embodiment, temperature for conversion of the source material **60** is in the range from about 100 °C to about 250 °C. In another embodiment, temperature for conversion is selected in the range from 180 °C to about 220 °C at atmospheric pressure. In yet another embodiment, temperature for conversion is in the range from about 100 °C to about 180 °C in a partial vacuum in the range from about 20 mm Hg to about 200 mm Hg. No limitations are hereby intended. Conversion of salts of 3-hydroxypropionic acid of up to about 95% has been demonstrated with selectivities to conversion products of up to about 100%. Reaction products can be used as chemical intermediates, or

feedstock materials for generating further reaction and conversion products. No limitations are intended.

[0090] Conversion of the β -hydroxy carbonyl compound salts provides some potential advantages over conversion of the free acid forms. For example, fermentation processes typically occur under neutral pH conditions yielding 3-hydroxypropionic acid salts, not the free acid. The free acid form of the 3-hydroxypropionic acid and/or of its conversion products can require additional processing steps including, e.g., acidification, separation, and/or removal of the salts, e.g., in a "salt-splitting" step, adding processing costs. To the extent that the salt forms of the conversion product can be used directly in end-use applications, e.g., in formation of super absorbent polymers, conversion of the salts as opposed to the free acid or non-salt forms can minimize separations requirements and/or other associated processing steps. However, no limitations are hereby intended. Reactions that form acrylates or acrylamides can be further optimized in conjunction with use of suitable stabilizing agents or inhibiting agents reducing likelihood of polymer formation. Stabilizing agents and/or inhibiting agents include, but are not limited to, e.g., phenolic compounds (e.g., dimethoxyphenol (DMP) or alkylated phenolic compounds such as di-tert-butyl phenol), quinones (e.g., t-butyl hydroquinone or the monomethyl ether of hydroquinone (MEHQ)), and/or metallic copper or copper salts (e.g., copper sulfate, copper chloride, or copper acetate). Inhibitors and/or stabilizers can be used individually or in combinations as will be known by those of skill in the art. Further, such reagents can be added to the source material, to the catalyst reactor bed, delivered or sprayed onto the walls of

the reactor, or be added as a component of a mixture comprising, e.g., 3-hydroxypropionic acid, a catalyst, an inhibitor, and/or other reagent. No limitations are hereby intended. For example, in other embodiments, stabilizing agents and/or inhibiting agents are not used to stabilize the reaction or conversion products. All uses of selected reagents as will be implemented by those of skill in the art are hereby incorporated.

[0091] **FIG. 4** illustrates various reaction pathways for conversion of a source material comprising salts of 3-hydroxypropionic acid **90** (or the respective free acids) to useful conversion and/or reaction products, e.g., acrylates **92** (or the corresponding free acids), according to an embodiment of the invention. In the source material **50**, salts of 3-hydroxypropionic acid **90** can dimerize in the reactor yielding, e.g., 3-hydroxypropionic acid acrylate ester dimers **94** and/or 3-hydroxypropionic acid acrylate ether dimers **96**, or other oligomeric and/or polymeric species **98** as intermediate and/or end-use conversion products. Experiments detailed in Example 2 below, have demonstrated that despite any potential to form dimers, oligomers, and/or polymeric reaction products, all such moieties convert to desired conversion products, e.g., to useful acrylate salts. For example, results show dimers of 3-hydroxypropionic acid yield reaction products at high conversion and selectivity. Thus, dimeric, oligomeric, and/or polymeric moieties can be used as source materials and can increase the potential applications of the conversion systems described herein. That is, all mixtures and/or combinations of β -hydroxy compounds convert to useful products.

[0092] One illustrative system of a commercial-scale design for conversion of salts of source materials comprising β -hydroxy carbonyl compounds, e.g., 3-hydroxypropionic acid, will now be described with reference to **FIG. 5**.

[0093] **FIG. 5** illustrates a system **100** of a commercial-scale design for conversion of salts of β -hydroxy carbonyl compounds to desirable reaction products, according to an embodiment of the invention. Salts of 3-hydroxypropionic acid, e.g., sodium or other salt, from source **102** are introduced to mixing tank **104** in a substantially continuous or batch mode operation. A catalyst and/or inhibitor are optionally introduced from inhibitor source **106** and catalyst source **108**, respectively. In an alternative mode of operation, source **102** may comprise the source material premixed optionally in water or other solvent for delivery to tank **104**. Alternatively, the source material may be provided as a complete mixture (e.g., including catalyst and/or inhibitor) directly to dryer **112**. Thus, no limitations are intended. Only partial conversion (~50%) of source material occurs in tank **104**, when used, due to reaction equilibria governing conversion in the aqueous medium. However, conversion in the aqueous mixture is rapid and presents a preferred approach when processing time is premium. In addition, greater product selectivity is observed in the aqueous medium, which favors its use, but is not limited thereto. From tank **104**, the mixture is next injected into spray dryer **112** which provides heat necessary for removing process water, including water removed from dehydration reactions, and continued dehydration, driving conversion of the 3-hydroxypropionic acid salts to acrylates. In the instant embodiment, spray dryer **112** acts both as an evaporator and dehydration reactor, but is not limited thereto. Reaction products

can be separated from the catalyst by injection of water or other solvent. For example, solids from spray dryer **112** are delivered to dissolver tank **114** and water or other solvent is added from, e.g., a solvent source **110**, whereby acrylate conversion salts are dissolved in the solvent and catalyst is filtered away in filter tank **116**. Recovered catalyst is recycled in tank **118** and re-introduced to source **108** for reuse. Acrylate conversion salts are recovered in storage tank **120**.

[0094] **FIG. 6** illustrates a system **200** of a commercial-scale design for conversion of salts of β -hydroxy carbonyl compounds to desirable reaction products, according to another embodiment of the invention. In an exemplary mode of operation, salts of 3-hydroxypropionic acid, e.g., a sodium or other salt, are provided from source **202** and introduced to mixing tank **204** in a substantially continuous or batch mode operation. A catalyst and/or inhibitor are optionally introduced from inhibitor source **206** and catalyst source **208**, respectively. In an alternative mode of operation, source **202** may comprise the source material premixed optionally in water for delivery to tank **204**. Alternatively, source material may be provided as a complete mixture (e.g., including catalyst and/or inhibitor) directly to evaporator **212** and delivered to feed hopper **214** where any remaining residual water is removed by introducing solids and/or salt concentrates to a rotary calciner or Auger reactor **216** finalizing conversion of 3-hydroxypropionic acid salts to acrylates. Thus, no limitations are intended. Only partial conversion (~50%) of source material occurs in tank **204**, when used, due to reaction equilibria governing conversion in the aqueous medium. However, conversion in the aqueous mixture is highly selective. Thus, partial conversion may be advantageous. The equilibrium

mixture from tank **204** is moved into, e.g., an evaporator tank **212** (evaporator) providing heat necessary for removing excess process water. Concentrates or solids from evaporator **212** are delivered to feed hopper **214** where any remaining residual water, including removal of water from dehydration reactions, is removed by introducing solids and/or salt concentrates to a rotary calciner or Auger reactor **216** finalizing conversion of 3-hydroxypropionic acid salts to acrylates.

[0095] Acrylate conversion products can be separated from any catalysts when present by injection of water or other solvent. For example, in one approach, solids from rotary calciner or Auger reactor **216** may be delivered to dissolver tank **218** and water or other solvent added from, e.g., a solvent source **210** dissolving the acrylate salts. Catalyst can then be filtered away in filter tank **220**, separating the acrylates from the catalyst. Recovered catalyst may be subsequently recycled in tank **222** and re-introduced to source **208** for reuse. Dissolved acrylate salts may then be stored, e.g., as a solution in storage tank **224**.

[0096] **FIG. 7** illustrates a generalized reaction process for conversion of ammonium salts of β -hydroxy carbonyl compounds including, e.g., the ammonium salt of 3-hydroxypropionic acid **70**, to ammonium acrylates **72**, acrylamide **74**, or mixtures thereof, according to an embodiment of the invention. Dehydration, amidation, and hydrolysis represent three principal reactions illustrated, but are not limited thereto. For example, reaction sequences are immaterial, as dehydration, amidation, and/or hydrolysis reactions can occur simultaneously, consecutively, independently, and/or reversibly, or not at all. In the figure, a single dehydration reaction converts a source material comprising, e.g., the ammonium salt of

3-hydroxypropionic acid **70** to ammonium acrylate **72**. Amidation forms acrylamide **74**. Conversion can be done catalytically (i.e., in the presence of a reaction catalyst), non-catalytically, or with no additional catalyst added. Products formed, whether, e.g., acrylates (by dehydration) or acrylamide (via amidation) are further controlled by presence and quantity of water and/or ammonia. For example, when greater than one equivalent of ammonia is present, an increase in the yield of acrylamide is effected. Reaction processes are thus tunable to a desired product mix by control of various reaction parameters including, but not limited to, e.g., concentration and temperature. In other processes, one can add amines (e.g., alkyl amines or dialkyl amines) to form N-substituted acrylamides. Amines are of the form NHR_1R_2 , where R_1 and R_2 are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

[0097] FIG. 8 illustrates various and potentially useful pathways for conversion of source materials comprising β -hydroxy carbonyl compounds or their salts (e.g., 3-hydroxypropionic acid and 3-hydroxypropionic acid salts) to desirable conversion products. In one reaction pathway **300**, illustrated in the figure, the ammonium salt of 3-hydroxypropionic acid **305** can be converted (i.e., by removing water **310**) to form acrylamide **315**, a useful conversion product.

[0098] In another reaction pathway **400**, acrylamide **430** can be produced from 3-hydroxypropionic acid **405** via formation of poly- and/or oligo-3-hydroxypropionic acid moieties **410**, with subsequent amination using ammonia gas

415 forming an amide **420**, followed by dehydration (e.g., either in the presence or absence of dehydration catalysts as disclosed herein) and subsequent loss of water **425**.

[0099] In another reaction pathway **500**, acrylamide **530** can be produced in a reaction process involving esterification of terminal –OH groups of a source material comprising 3-hydroxypropionic acid **505** using reagents known in the art, including, but not limited to, e.g., alkanols composed of from 1 to 20 carbon atoms (e.g., methanol, dodecanol, etc), yielding various 3-hydroxypropionic acid esters **510**. For example, methanol as a substitution reagent yields a C₁ (i.e., methyl) R-substituted ester; dodecanol as a substitution reagent yields a C₁₂ (i.e., dodecyl) R-substituted ester. Subsequent amidation of the esterified 3-hydroxypropionic acid moieties **510** using NH₃ **515** yields free amide **520** moieties. Dehydration of the amide **520** and loss of water **525** yields the free acrylamide **530**.

[00100] In another reaction pathway **600**, acrylamide **615** can be produced by amidation of acrylic acid **605** using NH₃ **610**.

[00101] All conversion pathways as will be implemented by those of skill in the art are encompassed herein. No limitations are hereby intended.

[00102] The following examples are intended to promote a further understanding of the present invention.

EXAMPLES

[00103] Example 1 details catalytic conversion of 3-hydroxypropionic acid in the presence of a reaction catalyst forming acrylic acid in either a continuous or a batch mode of operation. Example 2 details catalytic conversion of ammonium salts of 3-hydroxypropionic acid forming tunable mixtures of various conversion products. Example 3 details conversion of source material both with and without catalysts in a continuous mode of operation for extended periods with productive yields of conversion products. Example 4 details catalytic conversion of sodium salts of 3-hydroxypropionic acid in a batch mode of operation forming important conversion products.

EXAMPLE 1

[00104] Example 1 describes catalytic conversion of 3-hydroxypropionic acid in the presence of a reaction catalyst forming acrylic acid in a continuous mode of operation. In one exemplary test, system **10** was configured as follows: a 12.2 wt% source material comprising β -hydroxy carbonyl compounds (including, e.g., 9.19 wt% 3-hydroxypropionic acid, 1.22 wt% 3-hydroxypropionic acid ether dimers, and 1.48 wt% 3-hydroxypropionic acid ester dimers) was prepared in water. Catalyst reactor **12** was packed with 5.9 g of a 16-30 mesh titanium catalyst, e.g., Ti-0720® (Engelhard Corp., Iselin, NJ). Source material was fed to reactor **12** from source **14** at a rate of about 0.2 WHSV at a temperature of about 180 °C. Samples were collected in approximately one hour increments for 44 hours. Total source material

delivered to reactor **12** was 69.13 g. Samples were analyzed by HPLC for acrylic acid, 3-hydroxypropionic acid, and other potential byproducts, and results for conversion and selectivity were calculated using equations [1] and [2]. Quantity of product recovered, by weight, were determined to be 1.20 g 3-hydroxypropionic acid (residual source material) and 54.00 g acrylic acid. Results showed a total conversion of 3-hydroxypropionic acid of 98.3%. Acrylic acid selectivity was 99.4%. Total molar recovery (molar balance) of acrylic acid was 99.4%. Results further showed the titania catalyst had no detectable decrease in activity, indicating a long potential lifetime, e.g., up to one year. Results further showed any dimers of 3-hydroxypropionic acid present in the source material or inadvertently formed during processing were converted to acrylic acid, the desired end product. Thus, dimers can also be considered valuable feedstock materials rather than low-value byproducts.

[00105] In another test, a higher flow rate (0.4 WHSV) with an 8.8 wt% source material at a temperature in the range between about 180 °C and 190 °C provided a similar selectivity and conversion. Results showed a conversion for 3-hydroxypropionic acid of about 100 percent, with a molar selectivity for acrylic acid of about 100 percent. Mass balances (~100%) were also achieved while total weight balances were consistently only slightly lower (~95% to 98%) indicating only water was lost from the product receiver. Results further show no byproducts were detected by HPLC.

[00106] As discussed herein, conversion of 3-hydroxypropionic acid source material in an aqueous medium is subject to reaction equilibria, which can be

controlled by removing various reaction products (e.g., acrylic acid and/or water) from the reactive medium in reactor **12**. For example, conversion products are generally volatile and can be removed from the gas stream, further driving the conversion reaction thereby controlling and/or limiting further reactions and/or chemistries including, but not limited to, e.g., dimerization, oligomerization, re-hydration. In addition, flow rates and temperatures can be selected that optimize reactor conditions. No limitations are intended.

EXAMPLE 2

[00107] Example 2 details catalytic conversion of ammonium salts of 3-hydroxypropionic acid in a continuous mode of operation producing ammonium acrylates and/or easily separable mixtures of ammonium acrylates plus acrylamide on a commercial scale.

[00108] In an exemplary test, system **10** was configured as follows. An 8.62 wt% source material comprising ammonium salts of 3-hydroxypropionic acid was prepared in water. Reactor **12** was packed with 5.8 g of titanium catalyst, e.g., Ti-0720® (Engelhard Corp., Iselin, NJ). Source material was introduced to reactor **12** from source **14** at a flow rate of about 0.2 (WHSV) at a temperature of about 180 °C. Samples were collected in approximately one hour increments for a total of about 37 hours. Total source material delivered to the reactor was 41.43 g.

Samples were analyzed by HPLC for acrylic acid, 3-hydroxypropionic acid, acrylamide, and other potential byproducts, and results for conversion and selectivity were calculated. Quantity of products recovered, by weight, was determined to be 21.49 g acrylic acid (as acrylates), 0.49 g acrylamide, and 2.45 g 3-hydroxypropionic acid (unreacted source material). Total conversion of the source material was 94%. Molar recovery was 72%. Molar yield of acrylic acid was 65%. Molar yield of acrylamide was 1.5%. Test results indicate a continuous reactor can be operated for extended periods without a decrease in productive yields. Addition of acrylamide and/or acrylic acid stabilizers can be expected to enhance the product yields.

[00109] In another test, a 10.1% source material comprising ammonium salts of 3-hydroxypropionic acid was reacted at a temperature of about 240 °C in the presence of a silica-alumina catalyst (Si/Al T-869, Süd-Chemie AG, Bruckmühl GE). Total conversion was 68%, with a selectivity to acrylates of 80%.

[00110] In another test, a source material comprising 3-hydroxypropionic acid amide (5 wt% in water) was introduced at a flow rate of about 0.1 WHSV. Results showed a selectivity of 67% to acrylate and a selectivity of 1.8% to acrylamide, indicating that hydrolysis reactions can occur through control of water concentration.

[00111] In another test, designed to show acrylamide can be formed from aqueous solutions of the source material comprising ammonium salts of 3-hydroxypropionic acid, an 8.7 wt% source material solution (comprising 27.73 g of ~15 wt% ammonium salt of 3-hydroxypropionic acid in water with 20.55 g concentrated ammonium hydroxide added) in the reactor. Ammonium hydroxide

was added to simulate ammonia vapor phase pressure in the reactor **12**. Reactor **12** was packed with 5.71 g Ti-0720® (Engelhard) catalyst. Temperature was selected in the range from about 200 °C and about 250 °C. Collected samples were analyzed by HPLC for acrylic acid (present as ammonium acrylates), 3-hydroxypropionic acid, and acrylamide. Results showed a significant quantity of the desired acrylamide product was formed (about 25%). Test further showed production of ammonium acrylates as a co-product at a molar yield of about 75%. Results are significant as they show acrylamide is produced in the instant process from an aqueous solution of the source material comprising the ammonium salt of 3-hydroxypropionic acid. Constant removal of the acrylamide product recovered provides a way to inhibit polymerization of the acrylamide under long reaction times. Hence, virtually the entire source material is converted to desirable products. Altering the water ratio and/or varying the ammonia pressure (e.g., using a direct ammonia gas feed at greater than atmospheric pressure), the ratio of acrylate to acrylamide can be expected to improve, providing options for tuning the reactor to achieve various desired ratios of the reaction products. No limitations are hereby intended.

[00112] Amide hydrolysis tends to occur in the absence of ammonia gas. In contrast, when ammonia is present, a dramatic increase in conversion of 3-hydroxypropionic acid salts to acrylamide occurs. Expectation is that optimum yields will be achieved through use of stabilizing agents, as described hereinabove. Results may be further optimized for conversion, yields, or recovery of products, through such conditions as temperature, water concentrations (e.g., up to about

80%), reactants (3-hydroxypropionic acid salts and acrylate salts), and ammonia gas pressure thereby optimizing yields of ammonium acrylate, acrylamide, and/or tunable mixtures thereof.

[00113] However, tests demonstrate the propensity for good outcomes using various conditions and parameters described herein, in particular, when optimized for the product of interest, as will be understood by those of skill in the art. Although some mass balance issues must be tackled when operating under extended reaction periods, the robustness of a continuous reactor has been demonstrated.

[00114] In sum, dehydration is required for conversion of ammonium salts of 3-hydroxypropionic acid to acrylamide via dehydration of the β -hydroxy group and amidation of the acid functionality. Formation of 3-hydroxypropionic acid amide followed by reactive distillation to acrylamide presents a plausible clean route to acrylamide. However, dehydration of the β -hydroxy functionality is at least competitive with amidation and hence direct amidation of acrylate is something to be considered. Another route for conversion of ammonium salts of 3-hydroxypropionic acid is via esterification, e.g., using an alcohol (e.g., R-OH), followed by aminolysis to yield the 3-hydroxypropionic acid amide (i.e., acrylamide).

EXAMPLE 3

[00115] Example 3 details conversion of salts of 3-hydroxypropionic acid without additional catalyst added. In an exemplary test, system **10** was configured as follows. Reactor **12** was packed with 5.51 g of crushed quartz glass in place of a

catalyst. An 8.86 wt% aqueous source material comprising an ammonium salt of 3-hydroxypropionic acid was employed. Temperature of operation was 180 °C. Flow rate was 0.2 (WHSV), based on quantity of quartz glass used. Reactor **12** was operated for a period exceeding 36 hours (~2207 minutes). In the absence of added catalyst, results showed an 84.4% conversion, a selectivity for acrylates of 71.9%, with an overall molar yield of acrylates of about 60% from ammonium 3-hydroxypropionate. Ammonia may play a potential role as a catalyst in the conversion process. Catalysts, including, e.g., basic catalysts, may further offer at least some limited improvement in conversion of ammonium salts of 3-hydroxypropionic acid to acrylates, but the invention is not limited thereto, as described and demonstrated herein. When utilized, choice for selected catalyst is not limited. For example, acidic catalysts can be completely defunctionalized in the presence of basic ammonia. Thus, basic catalysts may prove more beneficial in selective conversion and yields.

EXAMPLE 4

[00116] Example 4 details conversion of salts of 3-hydroxypropionic acid forming important conversion products, including, but not limited to, acrylates. The term "melt" or as used herein describes the state of a source material introduced to a reactor at a temperature near, greater than, or equal to the melting point temperature. In exemplary tests, the sodium salt of 3-hydroxypropionic acid was mixed with a dehydration catalyst, e.g., $Zr(OH)_4$, prepared internally, and a polymer

inhibitor, e.g., 2,6 dimethoxyphenol (DMP) (Sigma-Aldrich, St. Louis, MO) in a 1:1:1 (salt: catalyst: inhibitor) weight ratio and melted in vials in a batch reactor open to air atmosphere at 200 °C for 1, 2, 3, and 4 hours, respectively. Zr(OH)₄ was prepared via ammonium hydroxide precipitation of zirconyl nitrate (Spectrum Chemicals, Gardena, CA) followed by drying in a vacuum oven at 50 °C. Quantity of conversion products was determined by HPLC. Results are tabulated in Table 1.

Table 1. Yields for sodium acrylate formed in batch mode under catalytic conditions from a source material comprising a 1:1:1 weight ratio of a sodium salt of 3-hydroxypropionic acid (3HP), a dehydration catalyst Zr(OH)₄, and 2,6 dimethoxyphenol (DMP) polymer inhibitor.

Run	Conditions	Analyte	Mole%	Conversion	Selectivity
1	Na3HP Zr(OH) ₄ DMP* 1 hour	Na3HP NaAcrylate Dimer Polymer Mass Balance (wt%):	14.3 73.2 3.4 <u>9.1</u> 101.2	85.7	85.4 89.4**
2	Na3HP Zr(OH) ₄ DMP* 2 hour	Na3HP NaAcrylate Dimer Polymer Mass Balance (wt%):	13.6 68.9 3.4 <u>14.0</u> 102.4	86.4	79.8 83.8**
3	Na3HP Zr(OH) ₄ DMP* 3 hour	Na3HP NaAcrylate Dimer Polymer Mass Balance (wt%):	11.8 65.4 3.8 <u>19.0</u> 100.8	88.2	74.2 78.5**
4	Na3HP Zr(OH) ₄ DMP* 4 hour	Na3HP NaAcrylate Dimer Polymer Mass Balance (wt%):	10.5 61.8 3.8 <u>23.8</u> 103.4	89.5	69.1 73.3**

*DMP=2,6 dimethoxyphenol.

**Selectivity if ether dimers are converted.

[00117] Results for tests 1 through 4 showed an 86% conversion with 90% selectivity to sodium acrylate within 1 hour. Only slight increases in conversion were obtained at periods longer than 1 hour. Mass balances were approximately

100%. Results further showed that while dimers (e.g., ether and ester dimers of 3-hydroxypropionic acid) and polymers form during heating, these moieties are still converted to acrylate products. Rates for conversion of ether dimers and ester dimers to acrylates are lower than for conversion of the 3-hydroxypropionic acid monomer.

[00118] In other melt tests using ECS-3® catalyst (Engelhard, Iselin NJ), after 2 hours, combined yield of sodium acrylate and polymer was 91.2%, with a 94.5% conversion and a sodium acrylate selectivity of 96.4%.

[00119] Conversions in comparable aqueous preparations, which are equilibrium controlled, were about 50% of those involving melts with about 100% selectivity. Reactions proceed approximately halfway forming sodium acrylate exclusively, i.e., no polymer or ether dimer are formed. That reactions may be equilibrium-controlled should not be considered a limitation of the present invention, as optimum conversion of source materials has been demonstrated by various means including, e.g., selectively removing reaction products as they are formed. Further, in processes described herein in reference to **FIG. 5** and **FIG. 6**, for example, differences observed for aqueous and melt tests may be applied in commercial-scale applications by, e.g., sequentially combining both the solution phase and solid state aspects in processes. Conversions and selectivities higher than those from the individual processes are conceivable. For example, in the aqueous medium, 50% conversion of salts of 3-hydroxypropionic acid is achieved at ~100% selectivity (no polymer or ether dimer are formed). Water can then be removed and the conversion reactions resumed in the solid state. For this phase,

conversion and selectivities of greater than about 95% may be expected. Further, given the lower quantity of material remaining to be converted in the solid phase, reaction times may be further enhanced. Further improvements in yield may be obtained using shorter residence times at higher temperatures. Sodium acrylate is often sold commercially as an aqueous solution. Hence, to provide the aqueous solution in a commercial process, separation, e.g., of the recovered product and catalyst, can be achieved simply by dissolving the acrylate products in water and filtering the catalyst. All configurations as will be envisioned by those of skill in the art are within the scope of the invention.

[00120] Those of skill in the art will recognize that other suitable catalysts may be selected as described herein. No limitations are intended. For example, catalysts selected from among the various weak or strong acids, acidic catalysts and materials (e.g., acidic resins), or basic catalysts and materials, including solid acids and bases may be employed. In addition, solid catalysts will provide ease of product and catalyst separation. Thus, no limitations are hereby intended.

[00121] While the preferred embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its true scope and broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the spirit and scope of the invention.

CLAIMS

We claim:

1. A process, comprising the steps:

providing a material comprising an ammonium salt of a β -hydroxy carbonyl compound to a reactor in a substantially liquid form at a flow rate and a temperature whereby said material reacts substantially inside the reactor in the absence of a flow of inert gas; and

wherein said material is converted to one or more reaction products capable of vaporizing from the reactor at said temperature upon conversion, said reaction products comprising an α , β -unsaturated carbonyl compound and/or an ammonium salt of an α , β -unsaturated carbonyl compound recovered at a high molar yield.

2. A process of Claim 1, wherein said β -hydroxy carbonyl compound is selected from the group consisting of 3-hydroxypropionic acid, 3-hydroxypropionic acid ester dimers, 3-hydroxypropionic acid ether dimers, or combinations thereof.

3. A process of Claim 1, wherein said material is converted in conjunction with a catalyst.

4. A process of Claim 3, wherein said catalyst is a dehydration catalyst.

5. A process of Claim 3, wherein said catalyst is selected from the group consisting of solid oxides, solid acids, acidic catalysts, weakly acidic catalysts, strongly acidic catalysts, basic catalysts, ion-exchange resins, acidic gases, basic gases, or combinations thereof.
6. A process of Claim 3, wherein the solid oxide catalyst is selected from the group consisting of TiO_2 , ZrO_2 , Al_2O_3 , SiO_2 , ZnO_2 , SnO_2 , WO_3 , MnO_2 , Fe_2O_3 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, ZrO_2/WO_3 , $\text{ZrO}_2/\text{Fe}_2\text{O}_3$, $\text{ZrO}_2/\text{MnO}_2$, or combinations thereof.
7. A process of Claim 3, wherein the acidic or weakly acidic catalyst is selected from the group consisting of titanics acids, metal oxide hydrates, metal sulfates, metal oxide sulfates, metal phosphates, metal oxide phosphates, mineral acids, carboxylic acids, salts thereof, acidic resins, acidic zeolites, clays, carbon dioxide, or combinations thereof.
8. A process of Claim 3, wherein the acidic or weakly acidic catalyst is selected from the group consisting of Ti-0720®, $\text{SiO}_2/\text{H}_3\text{PO}_4$, fluorinated Al_2O_3 , $\text{Nb}_2\text{O}_3/\text{PO}_4^{-3}$, $\text{Nb}_2\text{O}_3/\text{SO}_4^{-2}$, $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$, phosphotungstic acids, phosphomolybdic acids, silicomolybdic acids, silicotungstic acids, carbon dioxide, salts thereof, PVPH^+Cl^- ®, ECS-3®, or combinations thereof.
9. A process of Claim 3, wherein the basic catalyst is selected from the group consisting of ammonia, polyvinylpyridine, metal hydroxides, $\text{Zr}(\text{OH})_4$, or amines of

the form $NR_1R_2R_3$, wherein R_1 , R_2 , and R_3 are selected from the group consisting of H, alkyl and aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

10. A process of Claim 1, further comprising addition of ammonia at a partial pressure and/or liquid concentration sufficient to promote amide formation.

11. A process of Claim 10, wherein the amide formation is formation of acrylamide.

12. A process of Claim 1, further comprising addition of amines having a general form NHR_1R_2 at a partial pressure and/or liquid concentration sufficient to promote amide formation, where R_1 and R_2 are independently selected from the group consisting of H, hydrocarbons containing from 1 to 20 carbon atoms, heteroatom substituted hydrocarbons containing from 1 to 20 carbon atoms, alkyl and/or aryl groups containing from 1 to 20 carbon atoms, or combinations thereof.

13. A process of Claim 1, further comprising addition of an inhibitor to minimize formation of polymers.

14. A process of Claim 1, wherein said providing comprises introducing said material to said reactor in a solvent at a concentration in the range from about 5% to about 50%.

15. A process of Claim 14, wherein said solvent is selected from the group consisting of donor solvents, non-donor solvents, non-protic solvents, acceptor solvents, protic solvents, or combinations thereof.
16. A process of Claim 15, wherein said protic solvents are selected from the group consisting of alcohols, water, or combinations thereof.
17. A process of Claim 16, wherein said alcohols are selected from the group of alkanols containing from 1 to 20 carbon atoms.
18. A process of Claim 1, wherein said providing comprises introducing said material to said reactor substantially continuously.
19. A process of Claim 18, wherein said reactor is a continuous flow reactor or a component of a continuous flow reactor system.
20. A process of Claim 18, wherein said reactor is selected from the group consisting of trickle-bed, fixed-bed, fluidized bed, stirred tank, continuous stirred tank, ebulating bed, membrane, Berty, plug-flow, bubble-column, reactive-distillation column, or combinations thereof.

21. A process of Claim 1, wherein said providing comprises introducing said material to said reactor at a rate in the range from about 0.05 WHSV to about 10 WHSV.

22. A process of Claim 1, wherein said providing comprises introducing said material to said reactor at a rate in the range from about 0.2 WHSV to about 0.4 WHSV.

23. A process of Claim 1, wherein said temperature is in the range from about 90 °C to about 250 °C.

24. A process of Claim 1, wherein said temperature is in the range from about 90 °C to about 220 °C with a partial vacuum in the range from about 0.1 mm Hg to about 760 mm Hg.

25. A process of Claim 1, wherein said temperature is in the range from about 180 °C to about 220 °C at atmospheric pressure.

26. A process of Claim 1, wherein said temperature is in the range from about 200 °C to about 500 °C with a pressure in the range from about 0 psig to about 500 psig.

27. A process of Claim 1, wherein said conversion is in the range from about 60 percent to about 100 percent.

28. A process of Claim 1, wherein said one or more reaction products is selected from the group consisting of acrylic acid, methacrylic acid, amides thereof, salts thereof, acrolein, water, or combinations thereof.

29. A process of Claim 1, wherein said one or more reaction products has a molar yield of up to about 100 percent, or alternatively in the range from about 80 percent to about 100 percent, or alternatively in the range from about 90 percent to about 100 percent.

30. A process of Claim 1, wherein one or more of said one or more reaction products formed from said conversion is recovered by removing from said reactor.

31. A process of Claim 30, wherein said removing comprises vaporization from said reactor for recovery of said one or more reaction products.

32. A process of Claim 31, wherein said one or more reaction products are recovered in a substantially neat form from said reactor.

33. A process of Claim 1, wherein said removing of said one or more reaction products is substantially continuous.

34. A process of Claim 1, wherein said removing comprises vaporization from said reactor for recovery of said one or more reaction products.

35. A process of Claim 34, wherein the vaporization comprises substantially continuous steam-stripping of said one or more reaction products in one or more effluent streams, whereby cooling and/or condensing of the one or more effluent streams recovers said one or more reaction products.

36. A process of Claim 35, wherein the condensing comprises isolating and recovering said one or more reaction products in separate product streams from the one or more effluent streams.

37. A process of Claim 35, wherein the condensing comprises isolating and recovering said one or more reaction products from said reactor in separate product streams.

38. A process of Claim 35, wherein said one or more reaction products has a molar yield of up to about 100 percent, or alternatively in the range from about 80 percent to about 100 percent, or alternatively in the range from about 90 percent to about 100 percent.

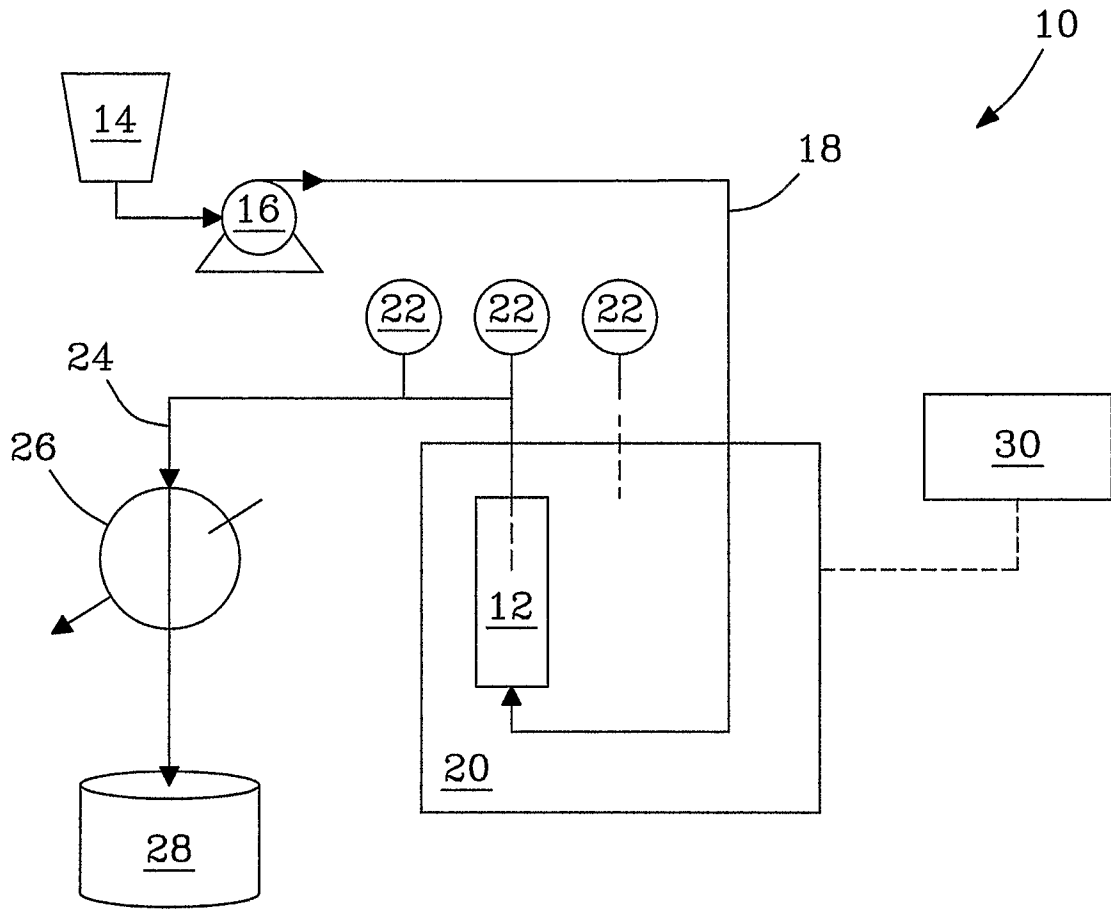


Fig. 1

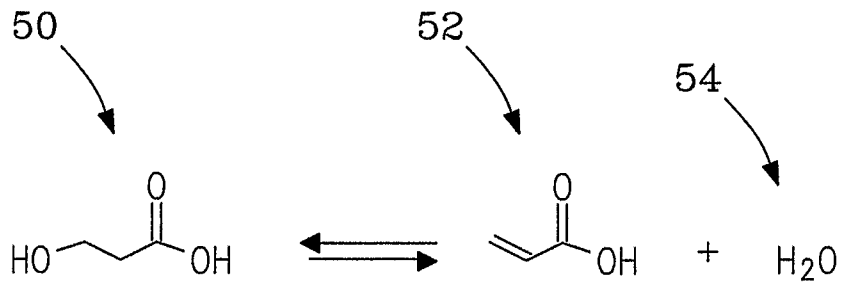
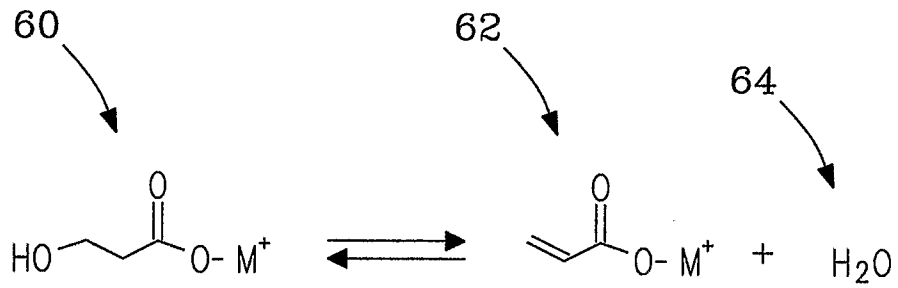


Fig. 2

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[M=Na⁺, alkali metal, alkaline-earth metal, Ca⁺⁺]

Fig. 3

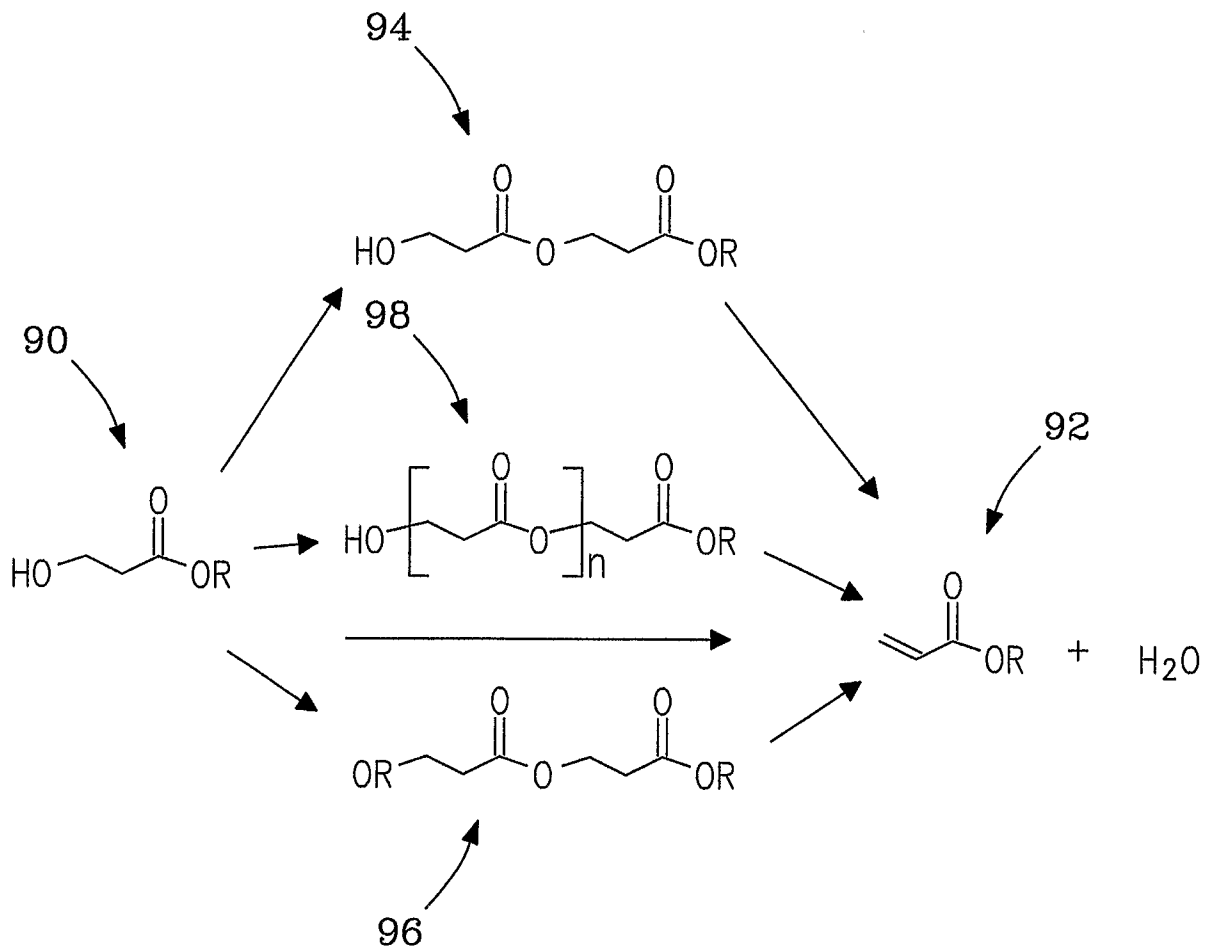


Fig. 4

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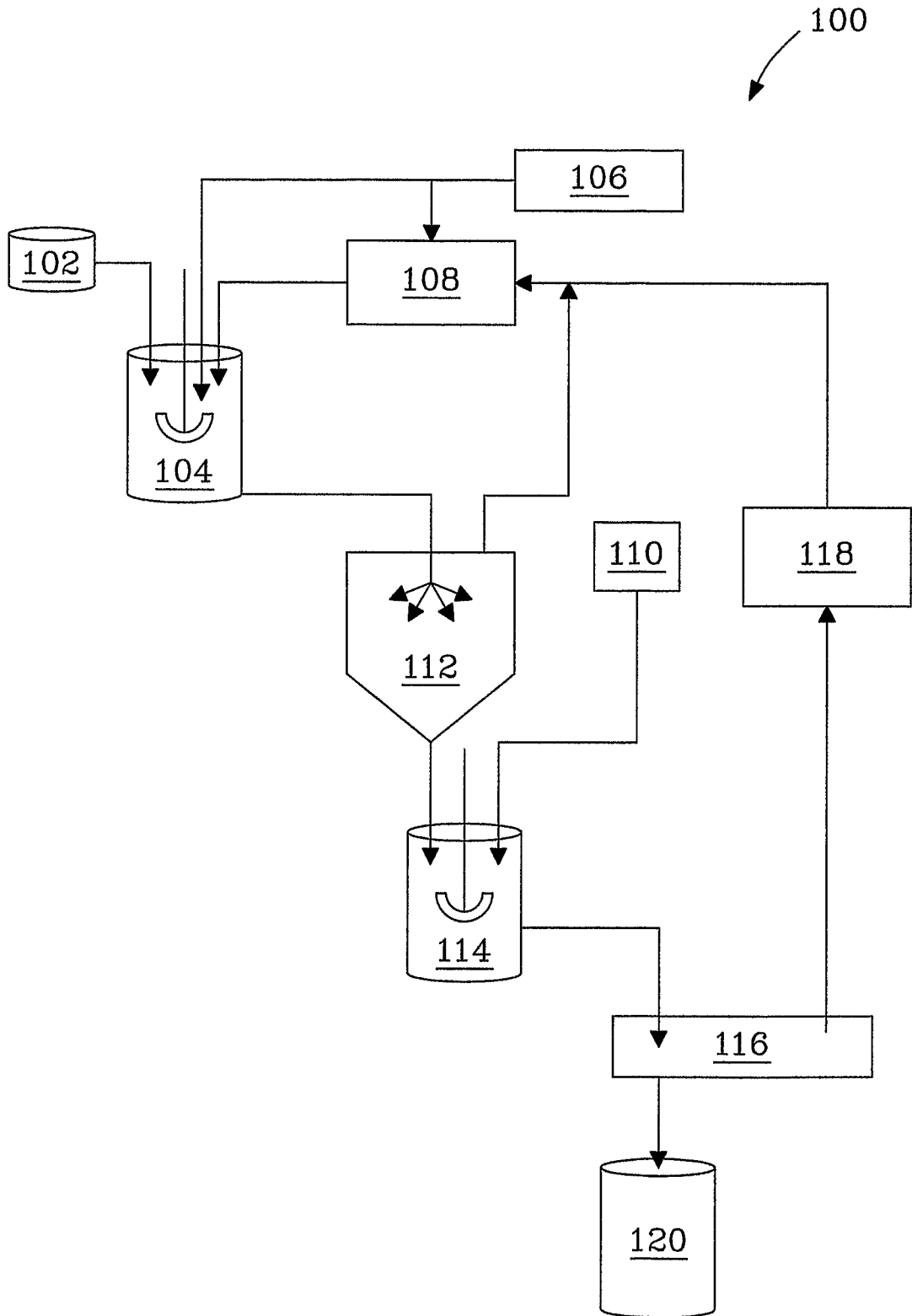


Fig. 5

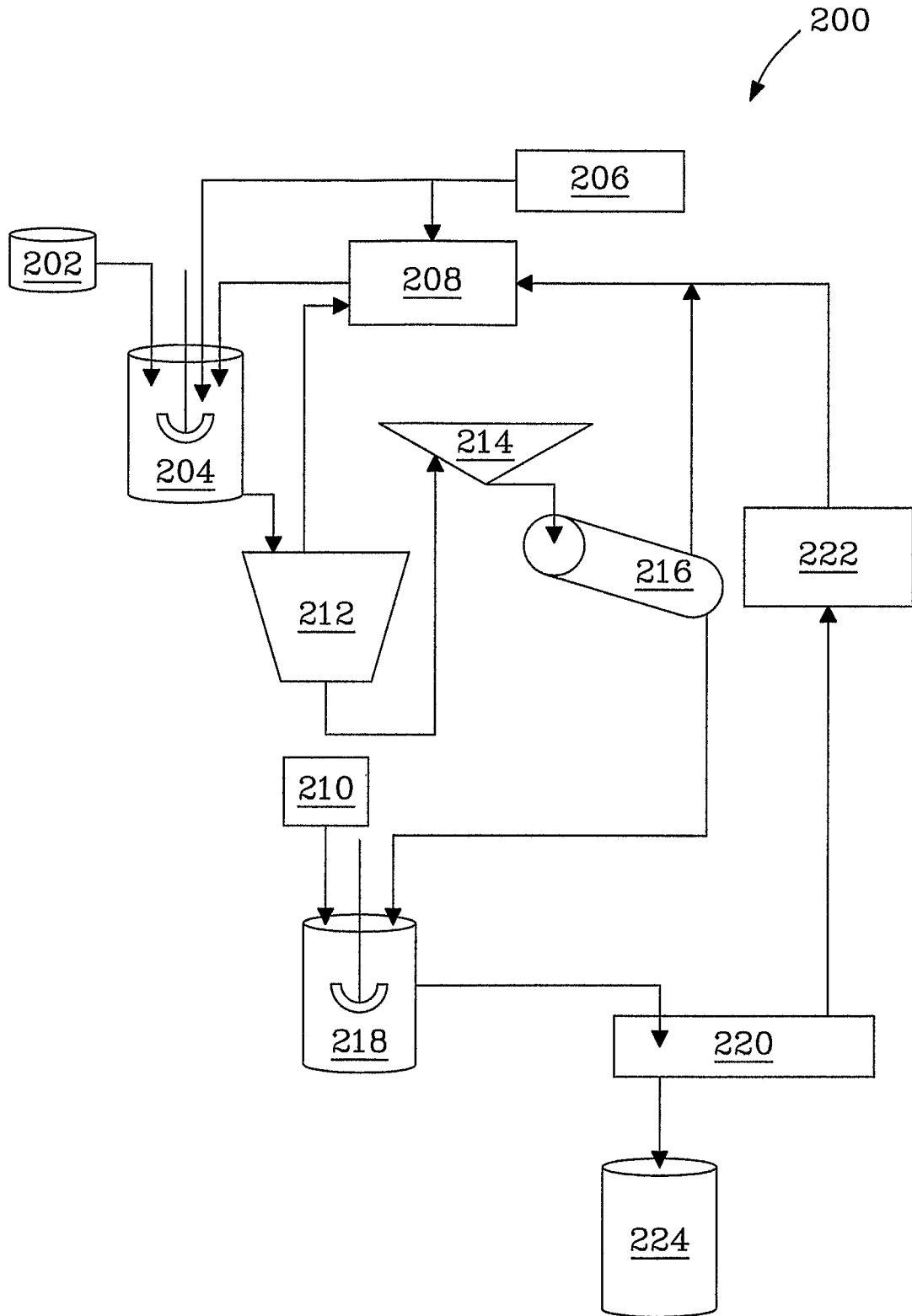
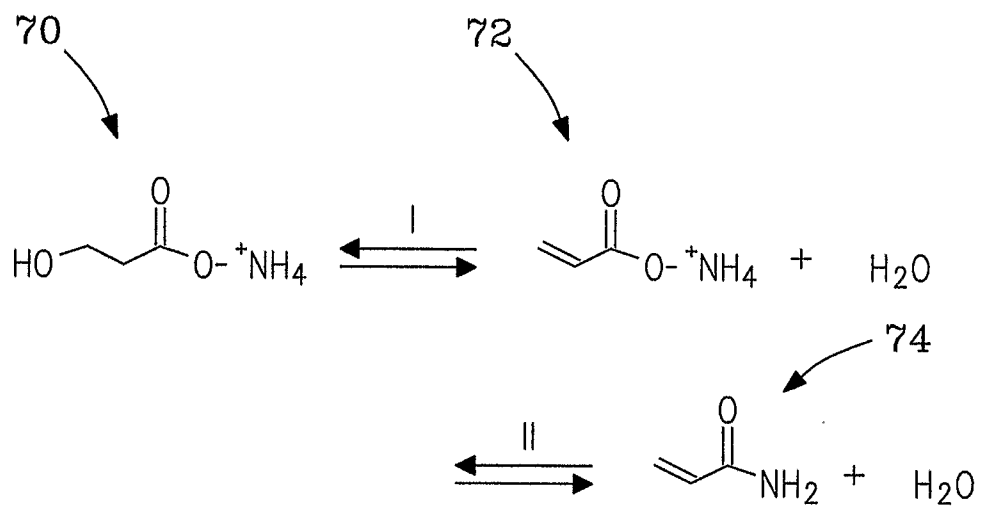


Fig. 6

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*Fig. 7*

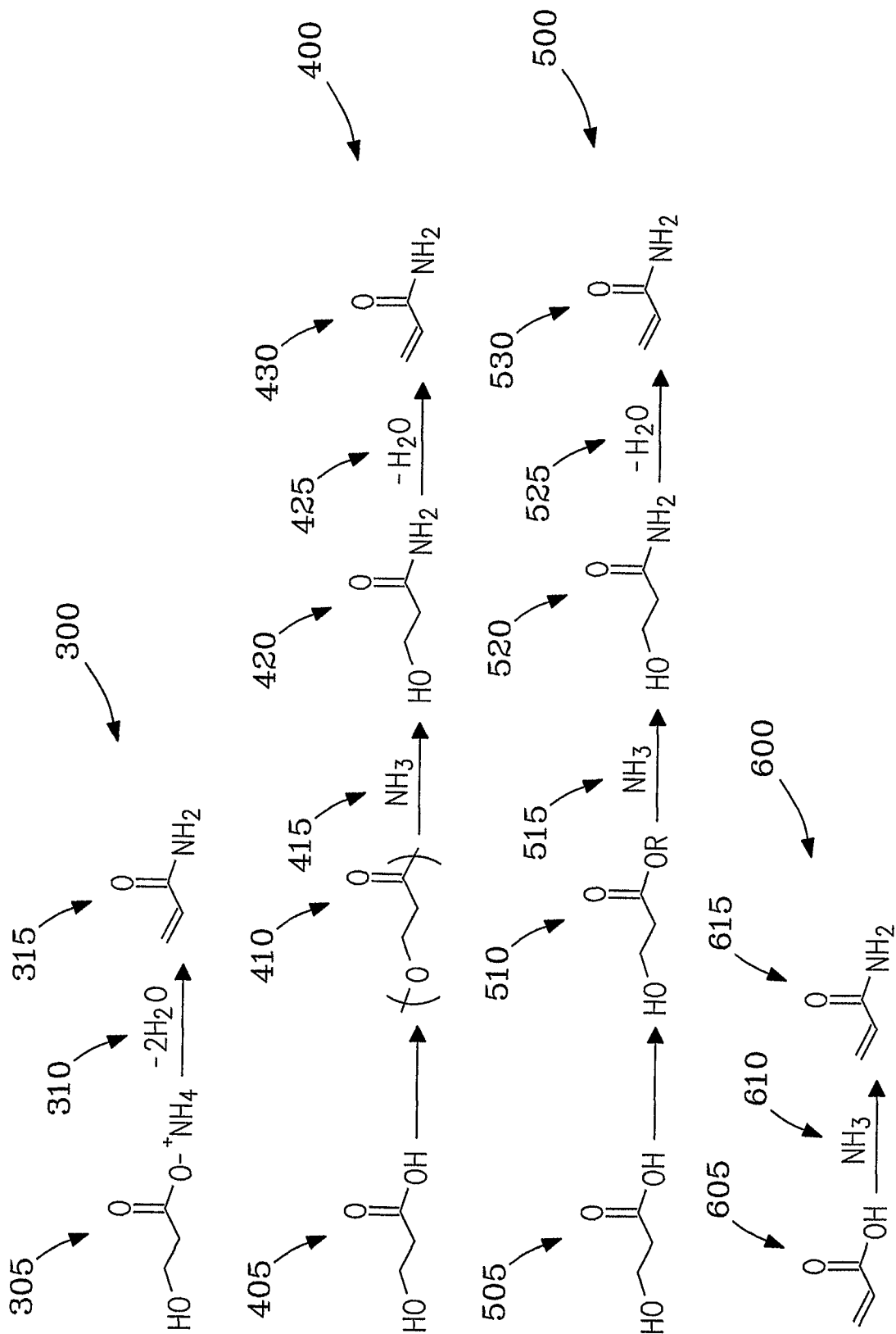


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/012696

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C51/377 C07C57/04		
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 practical, search terms used) EPO-Internal, CHEM ABS Data, BEILSTEIN Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/082795 A2 (CARGILL INC [US]; TSOBANAKIS PARASKEVAS [US]; MENG XIANGSHENG [US]; AB) 9 October 2003 (2003-10-09) claims 14,15,18,23,24,26; examples 6,9,11-13	1-38
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
12 January 2007		19/01/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Kleidernigg, Oliver

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2006/012696

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03082795	A2	09-10-2003	
		AU 2003223346 A1	13-10-2003
		BR 0308681 A	01-02-2005
		CA 2480152 A1	09-10-2003
		CN 1642897 A	20-07-2005
		CN 1789230 A	21-06-2006
		CN 1781897 A	07-06-2006
		CN 1800135 A	12-07-2006
		EP 1487775 A2	22-12-2004
		JP 2005521718 T	21-07-2005
