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INTEGRATED SYSTEMS AND PROCESSES FOR CHEMICAL PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application Nos. 62/673,638, filed May 18, 2018, and 62/690,782, filed June 27, 2018, which are each incorporated herein by reference in its entirety.

FIELD

[0002] The present invention is generally directed to integrated systems and processes for more efficient use of raw materials in chemical synthesis. Specifically, this disclosure relates to processing raw materials to produce molecular components that are integrated into chemical synthesis processes to produce biobased products.

BACKGROUND

[0003] There is growing worldwide interest in producing chemical products used plastics, fertilizers, carbon fiber, foams and superabsorbent materials in a sustainable and energy efficient manner. However, it is equally important to minimize waste and energy efficient in the production processes. To make sustainable chemical products, certain chemical processes may include gasification of carbonaceous material.

[0004] There is a need for industrial chemical synthesis systems and processes that reduce the environmental impact of the chemical synthesis. Provided herein are systems and processes that satisfy this need by providing for more efficient, sustainable, and economical integrated systems and processes.

BRIEF SUMMARY

[0005] The present invention is directed to integrated systems and processes for producing valuable chemical products. Advantageously, these systems and processes more efficiently and economically produce chemical products with reduced environmental impact. For example, the systems and processes herein can be more energy efficient and less wasteful while producing

chemical products with biobased characteristics. Furthermore, operations such as energy generation and maintenance as well as overall water use are improved by integrating and streamlining plant operations.

[0006] In some aspects, the systems comprise at least one operations unit, wherein each operations unit further comprises at least one reactor. In the systems of the present invention, each reactor generally comprises a wall configured as an enclosure. The size, shape, and configuration of each reactor may depend on many variables such as what materials or reagents will be added, what products or intermediates will be removed, and the rate at which reactions or other actions will be performed. For this reason, the disclosure of reactor limitations is not intended to be limiting where alternative configurations may be used, for example, to optimize conditions, processes, product properties, and/or product yield.

[0007] In certain embodiments, the systems comprise: a fermentation unit, a gasification unit, an air separation unit, a carbonylation unit, and a polymerization unit. In certain variations, the systems comprise: a fermentation unit, a gasification unit, an air separation unit, and a carbonylation unit.

[0008] In some embodiments, the processes comprise: separating air into an oxygen gas stream and a nitrogen gas stream; gasifying a carbonaceous material to produce a raw syngas stream comprising carbon monoxide, carbon dioxide and hydrogen gas; separating carbon monoxide from carbon dioxide and hydrogen gas; fermenting a nutrient to produce a biobased alcohol stream; dehydrating a portion of the biobased alcohol stream to produce a biobased alkene; oxidizing the biobased alkene with the oxygen stream to produce a biobased epoxide, and; carbonylating said biobased epoxide with carbon monoxide to produce a biobased carbonylation product, a hydrogen gas stream and carbon dioxide stream.

[0009] In certain embodiments, the processes produce a hydrogenation product such as ammonia. In some embodiments, the syngas is produced by gasification of a carbonaceous source or methane reforming. In some embodiments, the epoxide is carbonylated in the presence of the syngas and a carbonylation catalyst. In some embodiments, the epoxide is ethylene oxide. In some embodiments, the carbonylation product comprises a beta-lactone (such as beta-

propiolactone) or a cyclic anhydride (such as succinic anhydride), or any combination thereof. In some embodiments, the nitrogen gas is combined with the hydrogen-enriched syngas in the presence of an ammonification catalyst. In some embodiments, the carbon dioxide is produced by nutrient fermentation, alkene oxidation, produced by alkene oxidation, provided in syngas, or any combination thereof.

[0010] In some embodiments, the hydrogenation product is further combined with carbon dioxide to produce urea. In some embodiments, the yield of urea is at least about 65%. In some embodiments, the combining of the hydrogenation product with the carbon dioxide further produces ammonium carbamate. In some embodiments, the epoxide carbonylation product is further combined with glycerol for form a polyol copolymer. In some embodiments, the glycerol is derived from plant oil transesterification. In some embodiments, the epoxide is derived from oxidizing an alkene. In some embodiments, the alkene is derived from dehydrating an alcohol. In some embodiments, the alcohol is derived from fermenting a nutrient.

[0011] In other aspects, provided is a process of producing a bio-based hydrogenation product comprising: carbonylating an epoxide in the presence of a syngas to produce a carbonylation product and a hydrogen-enriched syngas, wherein the syngas comprises hydrogen and carbon monoxide; and combining a glycerol and the carbonylation product to produce a copolymer.

[0012] In some embodiments, the copolymer comprises polyols. In some embodiments, the carbonylation product comprises beta-propiolactone, polypropiolactone, succinic anhydride, a polyol, or any combination thereof. In some embodiments, the glycerol is derived from plant oil transesterification. In some embodiments, the plant oil is a vegetable oil such as corn oil. In some embodiments, the epoxide is ethylene oxide. In some embodiments, the glycerol and carbonylation product are combined in present of a catalyst, a chain transfer agent, or any mixture of the foregoing.

[0013] In some embodiments, the syngas is produced by gasification of a carbonaceous source or methane reforming. In some embodiments, the epoxide is derived from nutrient fermentation. In some embodiments, the hydrogen-enriched syngas is further combined with an

alkene and carbon monoxide to produce an aldehyde product. In some embodiments, the hydrogen-enriched syngas is further combined with a nitrogen gas to produce ammonia. In some embodiments, the ammonia is further combined with carbon dioxide to produce urea.

[0014] In yet other aspects, provided is a process comprising: fermenting a nutrient to produce an alcohol; hydrating the alcohol to produce an alkene; oxidizing the alkene with an oxygen gas to produce an epoxide; and carbonylating the epoxide with a syngas to produce a carbonylation product and a hydrogen-enriched syngas, wherein the syngas comprises hydrogen and carbon monoxide.

[0015] In some embodiments, the nutrient comprises plant based sugars, carbohydrates, polysaccharides, protein complexes, protein hydrolysates or a mixture of the foregoing. In some embodiments, the oxygen is derived from air separation. In some embodiments, the carbonylation product comprises beta-propiolactone, polypropiolactone, or a polyol, or any combination thereof. In some embodiments, the syngas is produced by gasification of a carbonaceous source or methane reforming. In some embodiments, the carbonylation product is further combined with glycerol to produce a copolymer. In some embodiments, the glycerol is derived from plant oil transesterification.

[0016] In some embodiments, the hydrogen-enriched syngas is combined with a nitrogen gas to produce ammonia. In some embodiments, the nitrogen gas is derived from air separation. In some embodiments, the ammonia is further combined with carbon dioxide to produce urea. In some embodiments, the hydrogen-enriched gas is used for energy production in hydrogen fuel cell. In some embodiments, the hydrogen-enriched gas is fed to a Fischer Tropsch reactor to produce a product. In some embodiments, the hydrogen-enriched gas is fed to a methanol synthesis reactor to produce methanol. In some embodiments, the methanol is further processed to produce methanol-derived products, such as dimethyl ether or olefins. In some embodiments, the hydrogen-enriched syngas is further combined with alkene and carbon monoxide to produce an aldehyde product. In some embodiments, the hydrogen-enriched syngas is again contacted with epoxide to further enrich the syngas and produce a second hydrogen-enriched syngas. In

some embodiments, the second hydrogen-enriched syngas is used in Fischer Tropsch reactions, ammonia synthesis, methanol synthesis or hydrogen fuel cells.

[0017] In some embodiments, the fermentation process produces an alcohol and carbon dioxide. In some embodiments, the carbon dioxide is electrolyzed to produce an oxygen gas and a carbon monoxide gas. In some embodiments, the oxygen gas is used in oxidizing alkene. In some embodiments, the carbon monoxide gas is used in carbonylating epoxide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The present application can be best understood by reference to the following description taken in conjunction with the accompanying figures, in which like parts may be referred to by like numerals.

[0019] FIG. 1 depicts a general scheme of an exemplary production system to produce ammonia, urea, and polymers from a syngas.

[0020] FIGS. 2A, 2B, 3A and 3B depict various exemplary configurations of the production system to produce ammonia and urea via the carbonylation of a syngas and air separation.

[0021] FIGS. 4 and 5 depict various exemplary configurations of the production system to produce a copolymer from a carbonylation product and a glycerol.

[0022] FIGS. 6-10, 11A and 11B depict various exemplary configurations of the production system to carbonylate a syngas with an epoxide derived from nutrient fermentation.

[0023] FIG. 12 depicts a general scheme of an exemplary integrated system to produce various chemical products.

DETAILED DESCRIPTION

[0024] The following description sets forth exemplary systems, methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

[0025] Provided herein are integrated systems and processes for producing a bio-based hydrogenation product. These processes generally can afford better economics through more efficient carbon utilization, improve the environmental footprint of chemical synthesis by reducing waste, reduce the overall greenhouse gas emissions of certain production facilities, and impart desirable properties such as bio-based content to chemical synthesis products.

Integrated Systems and Processes for Chemical Production

[0026] The present invention is directed to systems and processes for providing for more carbon-efficient and cost-effective production of chemical products. In some embodiments, the systems and processes integrate conventionally disregarded byproducts, molecular components and/or intermediates as reagents in chemical synthesis to produce the chemical products. For example, in one aspect, provided herein are processes that include transforming raw materials into molecular components such as hydrogen gas, oxygen gas, nitrogen gas, carbon monoxide, and carbon dioxide and integrating the molecular components into chemical synthesis to produce valuable chemicals.

[0027] In certain embodiments, the integrated processes of the present invention comprise:

- a) providing ethanol;
- b) converting at least a portion of the ethanol to ethylene oxide;
- c) providing a syngas comprising hydrogen, carbon monoxide, and carbon dioxide;
- d) carbonylating at least a portion of the ethylene oxide in the presence of the syngas and a carbonylation catalyst to produce beta-propiolactone, succinic anhydride, and an enriched syngas, wherein the enriched syngas comprises hydrogen and carbon dioxide;
- e) converting at least a portion of the beta-propiolactone to acrylic acid;
- f) polymerizing at least a portion of the acrylic acid, optionally in the presence of one or more crosslinkers, to produce an adsorbent polymer;
- g) converting at least a portion of the acrylic acid to an acrylate;
- h) converting at least a portion of the succinic anhydride to tetrahydrofuran;

- i) converting at least a portion of the succinic anhydride to 1,4-butanediol;
- j) converting at least a portion of the succinic anhydride to succinic acid;
- k) polymerizing at least a portion of the 1,4-butanediol and at least a portion of succinic anhydride to produce polybutylene succinate; providing a plant oil;
- l) transesterifying the plant oil, optionally in the presence of a catalyst or a chain transfer agent, to produce a glycerol;
- m) combining the glycerol and at least a portion of the beta-propiolactone or a portion of succinic anhydride to produce a polyol;
- n) converting at least a portion of the succinic acid to a succinate;
- o) converting at least a portion of the succinate to a diamide;
- p) converting at least a portion of the diamide to a diisocyanate;
- q) converting at least a portion of the beta-propiolactone to 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid;
- r) converting at least a portion of the 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid to benzoic acid;
- s) converting at least a portion of the benzoic acid to benzene; converting at least a portion of the benzene to styrene;
- t) providing a nitrogen gas;
- u) combining the enriched syngas comprising hydrogen and carbon dioxide with the nitrogen gas to produce ammonia;
- v) providing a carbon dioxide;
- w) combining the carbon dioxide and the ammonia to produce urea;
- x) combining at least a portion of the beta-propiolactone and at least a portion of the ammonia to produce beta-alanine, N-(3-hydroxy-1-oxopropyl), or 3-hydroxypropanamide;

- y) converting at least a portion of 3-hydroxypropanamide to acrylonitrile or acrylamide; polymerizing acrylamide to produce polyacrylamide;
- z) polymerizing acrylonitrile to produce polyacrylonitrile;
- aa) converting at least a portion of the polyacrylonitrile to a carbon fiber;
- bb) converting at least a portion of the ethanol to acetaldehyde;
- cc) converting at least a portion of the acetaldehyde to acetaldol;
- dd) converting at least a portion of the acetaldol to 1,3-butanediol;
- ee) converting at least a portion of the 1,3-butanediol to butadiene;
- ff) combining at least a portion of the acrylonitrile, at least a portion of butadiene, and at least a portion of the styrene to produce acrylonitrile butadiene styrene terpolymer;
- gg) combining at least a portion of butadiene and at least a portion of the styrene to produce styrenebutadiene copolymer;
- hh) polymerizing at least a portion of butadiene to produce polybutadiene;
- ii) combining at least a portion of polybutadiene and at least a portion of the styrene to produce styrenebutadiene block copolymer;
- jj) fermenting biomass to provide the ethanol;
- kk) gasifying a carbonaceous source or methane reforming to provide the syngas; and
- ll) separating air into oxygen and nitrogen.

[0028] It should be understood that in other exemplary embodiments, one or more of steps a)-ll) described above may be omitted or combined with each other in other configurations the same as if each and every combination were individually listed.

[0029] For example, in some variations, provided is an integrated process, comprising:

- separating air into an oxygen gas stream and nitrogen gas stream;
- gasifying a carbonaceous material to produce a raw syngas stream comprising carbon monoxide, carbon dioxide and hydrogen gas;

fermenting plant matter to produce a biobased alcohol stream;
reducing a portion of the biobased alcohol stream to produce a biobased alkene;
oxidizing the biobased alkene with the oxygen stream to produce a biobased epoxide, and;
carbonylating the biobased epoxide with the raw syngas stream to produce a biobased carbonylation product, a hydrogen gas stream and carbon dioxide stream.

[0030] In the foregoing variation, the biobased carbonylation product may comprise a beta-lactone stream and a succinic anhydride stream. In one variation, the succinic anhydride stream may be reduced to produce tetrahydrofuran. In another variation, the tetrahydrofuran may be reacted with a portion of the beta-lactone stream to produce a cyclohexene derivative. In yet another variation, the cyclohexene derivative may be used to produce a biobased styrene product. In other variations, the nitrogen gas stream may be hydrogenated by the hydrogen gas stream to produce an ammonia stream. In one variation, the ammonia stream may be reacted with a portion of the beta-lactone stream to produce 3-hydroxypropanamide. In another variation, the 3-hydroxypropanamide is dehydrated to produce a biobased acrylonitrile product. In yet other variations, a biobased 1,3-butadiene product is produced from the biobased alcohol stream.

[0031] In certain embodiments, the integrated systems of the present invention comprise:

- a) a beta-propiolactone production unit, comprising: a carbonylation catalyst source; a solvent source; a carbon monoxide source; an ethylene oxide source; a first carbonylation reactor, comprising: at least one inlet to receive a reaction stream comprising carbon monoxide from the carbon monoxide source, ethylene oxide from the ethylene oxide source, carbonylation catalyst from the carbonylation catalyst source, and solvent from the solvent source, and an outlet to output a beta-propiolactone product stream comprising beta-propiolactone;
- b) an acrylic acid production unit, comprising: a zeolite source; a polymerization inhibitor source; an acrylic acid reactor, comprising: at least one inlet to receive at least a portion of beta-propiolactone from the carbonylation reactor, zeolite from the zeolite source, and a polymerization inhibitor from the polymerization inhibitor source, and an outlet to output an acrylic acid product stream comprising acrylic acid; and a distillation column, comprising: an

inlet to receive the acrylic acid product stream from the acrylic acid reactor, and to isolate acrylic acid from the acrylic acid product stream; an outlet to output acrylic acid;

c) an acrylate production unit, comprising: a zeolite source; an alcohol source; a polymerization inhibitor source; an acrylate reactor, comprising: at least one inlet to receive at least a portion of beta-propiolactone from the carbonylation reactor, zeolite from the zeolite source, and a polymerization inhibitor from the polymerization inhibitor source, a C1-8 alcohol from the alcohol source, and an outlet to output an acrylate product stream comprising an acrylate; and a distillation column, comprising: an inlet to receive the acrylate product stream from the acrylate reactor, and to isolate acrylate from the acrylate product stream; an outlet to output acrylate;

d) an absorbent polymer production unit, comprising: a polymerization catalyst source; a solvent source; an absorbent polymer reactor, comprising: at least one inlet to receive at least a portion of beta-propiolactone from the carbonylation reactor, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output an absorbent polymer stream; and a distillation column, comprising an inlet to receive the absorbent polymer stream from the absorbent polymer reactor, and to isolate the absorbent polymer from the absorbent polymer product stream; an outlet to output the absorbent polymer;

e) a succinic anhydride production unit, comprising: a carbonylation catalyst source; a solvent source; a carbon monoxide source; a second carbonylation reactor, comprising: at least one inlet to receive at least a portion of beta-propiolactone from the first carbonylation reactor, carbon monoxide from the carbon monoxide source; carbonylation catalyst from the carbonylation catalyst source, and solvent from the solvent source; an outlet to output a succinic anhydride product stream comprising succinic anhydride; and a separation unit, comprising: an inlet to receive the succinic anhydride stream from the succinic anhydride reactor, and to isolate the succinic anhydride from the succinic anhydride stream; an outlet to output the succinic anhydride;

f) a succinic acid production unit, comprising: a water source; a heating source; a succinic acid reactor, comprising: at least one inlet to receive at least a portion of succinic

anhydride from the succinic anhydride reactor and water from the water source; an outlet to output a succinic acid product stream comprising succinic acid;

g) a 1,4-butanediol production unit, comprising: a hydrogen source; a hydrogenation catalyst source; a solvent source; a 1,4-butanediol reactor, comprising: at least one inlet to receive at least a portion of succinic anhydride from the succinic anhydride reactor, hydrogen from the hydrogen source, hydrogenation catalyst from the hydrogen catalyst source, and solvent from the solvent source; an outlet to output a 1,4-butanediol product stream comprising 1,4-butanediol;

h) a tetrahydrofuran production unit, comprising: a hydrogen source; a hydrogenation catalyst source; a solvent source; a tetrahydrofuran reactor, comprising: at least one inlet to receive at least a portion of succinic anhydride from the succinic anhydride reactor, hydrogen from the hydrogen source, hydrogenation catalyst from the hydrogenation catalyst source, and solvent from the solvent source; an outlet to output a tetrahydrofuran product stream comprising tetrahydrofuran;

i) a polybutylene succinate production unit, comprising: a polymerization catalyst source; a solvent source; a polybutylene succinate reactor, comprising: at least one inlet to receive at least a portion of succinic anhydride from the succinic anhydride reactor, 1,4-butanediol from the 1,4-butanediol reactor, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a polybutylene succinate product stream comprising polybutylene succinate;

j) a polyol production unit, comprising: a polymerization catalyst source; a solvent source; a glycerol source; a polyol reactor, comprising: at least one inlet to receive at least a portion of beta-propiolactone from the first carbonylation reactor or at least a portion of succinic anhydride from the succinic anhydride reactor, glycerol from the glycerol source, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a polyol product stream comprising polyol;

k) a diamide production unit, comprising: a catalyst source; a solvent source; a hydroxylamine source; an alcohol source; a succinate reactor, comprising: at least one inlet to receive at least a portion of succinic acid from the succinic acid reactor, catalyst from the catalyst source, alcohol from the alcohol source, and solvent from the solvent source; an outlet to output a succinate product stream comprising the succinate; a diamide reactor, comprising: at least one inlet to receive at least a portion of succinate from the succinate reactor, hydroxylamine from the hydroxylamine source, and solvent from the solvent source; an outlet to output a diamide product stream comprising the diamide;

l) a diisocyanate production unit, comprising: a catalyst source; a solvent source; an acetic anhydrite source; a heat source; a diisocyanate reactor, comprising: at least one inlet to receive at least a portion of diamide from the diamide reactor, catalyst from the catalyst source, acetic anhydrite from the acetic anhydrite source, and solvent from the solvent source; an outlet to output a diisocyanate product stream comprising the diisocyanate;

m) a 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid production unit, comprising: a catalyst source; a solvent source; a furan source; a 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid reactor, comprising: at least one inlet to receive at least a portion of beta-propiolactone from the diamide reactor, catalyst from the catalyst source, furan from the furan source, and solvent from the solvent source; an outlet to output a 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid product stream comprising the 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid;

n) a benzoic acid production unit, comprising: a hydrogenation catalyst source; a solvent source; a hydrogen source; a benzoic acid reactor, comprising: at least one inlet to receive at least a portion of 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid from the 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid reactor, hydrogenation catalyst from the hydrogenation catalyst source, hydrogen from the hydrogen source and solvent from the solvent source; an outlet to output a benzoic acid product stream comprising benzoic acid;

o) a benzene production unit, comprising: a hydrogenation catalyst source; a solvent source; a hydrogen source; a benzene reactor, comprising: at least one inlet to receive at least a portion of benzoic acid from the benzoic acid reactor, hydrogenation catalyst from the

hydrogenation catalyst source, hydrogen from the hydrogen source and solvent from the solvent source; an outlet to output a benzene product stream comprising benzene;

p) a styrene production unit, comprising: a catalyst source; a solvent source; an ethylene source; a styrene reactor, comprising: at least one inlet to receive at least a portion of benzene from the benzene reactor, catalyst from the catalyst source, ethylene from the ethylene source and solvent from the solvent source; an outlet to output a styrene product stream comprising styrene;

q) an ammonia production unit, comprising: a catalyst source; a nitrogen gas source; an ammonia reactor, comprising: at least one inlet to receive at least a portion of enriched syngas comprising hydrogen gas and carbon dioxide from the first or second carbonylation reactor, catalyst from the catalyst source, and nitrogen gas from the nitrogen gas source; an outlet to output an ammonia product stream comprising ammonia;

r) a urea production unit, comprising: a catalyst source; a carbon dioxide gas source; a urea reactor, comprising: at least one inlet to receive at least a portion of ammonia from the ammonia reactor, catalyst from the catalyst source, and carbon dioxide gas from the carbon dioxide gas source; an outlet to output a urea product stream comprising urea;

s) an alanine and derivative production unit, comprising: a catalyst source; a solvent source; an alanine and derivative reactor, comprising: at least one inlet to receive at least a portion of ammonia from the ammonia reactor, at least a portion of beta-propiolactone from the first carbonylation reactor, catalyst from the catalyst source, and solvent from the solvent source; an outlet to output an alanine product stream comprising beta-alanine, N-(3-hydroxy-1-oxopropyl), or 3-hydroxypropanamide; a separation unit, comprising: an inlet to receive the alanine product stream from the alanine and derivative reactor, and to isolate the 3-hydroxypropanamide from the alanine product stream; an outlet to output the 3-hydroxypropanamide;

t) an acrylonitrile and acrylamide production unit, comprising: a solvent source; a dehydration agent source; an acrylonitrile and acrylamide reactor, comprising: at least one inlet

to receive at least a portion of 3-hydroxypropanamide from the separation unit of the alanine and derivative production unit, dehydration agent from the dehydration agent source, and solvent from the solvent source; an outlet to output an acrylonitrile and acrylamide product stream comprising acrylonitrile and acrylamide; a separation unit, comprising: an inlet to receive the acrylonitrile and acrylamide product stream from the acrylonitrile and acrylamide reactor, and to isolate the acrylonitrile and acrylamide from the acrylonitrile and acrylamide product stream; an outlet to output the acrylonitrile; another outlet to output the acrylamide;

u) a polyacrylamide production unit, comprising: a solvent source; a polymerization catalyst source; a polyacrylamide reactor, comprising: at least one inlet to receive at least a portion of acrylamide from the separation unit of acrylonitrile and acrylamide production unit, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a polyacrylamide product stream comprising polyacrylamide;

v) a polyacrylonitrile production unit, comprising: a solvent source; a polymerization catalyst source; a polyacrylonitrile reactor, comprising: at least one inlet to receive at least a portion of acrylonitrile from the separation unit of acrylonitrile and acrylamide production unit, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a polyacrylonitrile product stream comprising polyacrylonitrile;

w) a carbon fiber production unit, comprising: a solvent source; a carbon fiber reactor, comprising: at least one inlet to receive at least a portion of polyacrylonitrile from the polyacrylonitrile reactor, and solvent from the solvent source; an outlet to output a carbon fiber product stream comprising carbon fiber;

x) an acetaldehyde production unit, comprising: an oxidation catalyst source; a solvent source; an ethanol source; an oxygen source; an acetaldehyde reactor, comprising: at least one inlet to receive ethanol from the ethanol source, oxidation catalyst from the oxidation catalyst source, oxygen from the oxygen source and solvent from the solvent source; an outlet to output an acetaldehyde product stream comprising acetaldehyde;

y) an acetaldol production unit, comprising: a solvent source; an acetaldol reactor, comprising: at least one inlet to receive at least portion of the acetaldehyde from the acetaldehyde reactor and solvent from the solvent source; an outlet to output an acetaldol product stream comprising acetaldol;

z) a 1,3-butanediol production unit, comprising: a hydrogenation catalyst source; a solvent source; a hydrogen source; a 1,3-butanediol reactor, comprising: at least one inlet to receive at least portion of acetaldol from the acetaldol reactor, hydrogenation catalyst from the hydrogenation catalyst source, hydrogen from the hydrogen source and solvent from the solvent source; an outlet to output a 1,3-butanediol product stream comprising 1,3-butanediol;

aa) a butadiene production unit, comprising: a solvent source; a catalyst source; a butadiene reactor, comprising: at least one inlet to receive at least portion of the 1,3-butanediol from the acetaldehyde reactor, catalyst from the catalyst source, and solvent from the solvent source; an outlet to output a butadiene product stream comprising butadiene;

bb) a polybutadiene production unit, comprising: a solvent source; a polymerization catalyst source; a polybutadiene reactor, comprising: at least one inlet to receive at least a portion of butadiene from the butadiene reactor, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a polybutadiene product stream comprising polybutadiene;

cc) an acrylonitrile butadiene styrene terpolymer production unit, comprising: a solvent source; a polymerization catalyst source; an acrylonitrile butadiene styrene terpolymer, comprising: at least one inlet to receive at least a portion of acrylonitrile from the separation unit of acrylonitrile and acrylamide production unit, at least a portion of styrene from the styrene reactor, at least a portion of the butadiene from the butadiene reactor, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a acrylonitrile butadiene styrene terpolymer product stream comprising acrylonitrile butadiene styrene terpolymer;

dd) a styrenebutadiene copolymer production unit, comprising: a solvent source; a polymerization catalyst source; a styrenebutadiene copolymer reactor, comprising: at least one inlet to receive at least a portion of butadiene from butadiene reactor and at least a portion of the styrene from the styrene reactor, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a styrenebutadiene copolymer product stream comprising styrenebutadiene copolymer;

ee) a styrenebutadiene block copolymer production unit, comprising: a solvent source; a polymerization catalyst source; a styrenebutadiene block copolymer reactor, comprising: at least one inlet to receive at least a portion of polybutadiene from the polybutadiene reactor and at least a portion of the styrene from the styrene reactor, polymerization catalyst from the polymerization catalyst source, and solvent from the solvent source; an outlet to output a styrenebutadiene block copolymer product stream comprising styrenebutadiene block copolymer.

[0032] It should be understood that in other exemplary embodiments, one or more of production units a)-ee) described above may be omitted or combined with each other in other configurations the same as if each and every combination were individually listed. For example, FIG. 12 depicts one exemplary configuration of the integrated system to produce various chemical products.

[0033] In some embodiments, the systems comprise at least one operations unit, wherein each operations unit further comprises at least one reactor. In the systems of the present invention, each reactor generally comprises a wall configured as an enclosure. The size, shape, and configuration of each reactor may depend on many variables such as what materials or reagents will be added, what products or intermediates will be removed, and the rate at which reactions or other actions will be performed. For this reason, the disclosure of reactor limitations is not intended to be limiting where alternative configurations is used, for example, to optimize conditions, processes, product properties, and/or product yield. In preferred embodiments, the systems comprise a fermentation unit, a gasification unit, an air separation unit, and a carbonylation unit.

[0034] In certain embodiments, the fermentation unit comprises a reactor configured to produce ethanol by fermentation of nutrients. The fermentation unit reactor comprises a nutrient inlet, fermentation reaction zone, heater, mixer, and ethanol outlet. The nutrient inlet is sized and shaped so that a nutrient feed stream is introduced to the fermentation unit reactor. The fermentation reaction zone is sized and shaped to receive the nutrient feed stream so that the nutrient feed stream is mixed by the mixer and heated by the heater during a fermentation reaction to produce ethanol. The ethanol outlet is sized and shaped so that ethanol is removed from the reactor.

[0035] In certain embodiments, the fermentation unit reactor may comprise a grinder, for example, to separate plant matter used for fermentation from plant matter used to produce glycerol. In some embodiments including a fermentation unit reactor comprising a grinder, the fermentation reactor may further comprise a filter, for example, to further separate plant matter used for fermentation from plant matter used to produce glycerol. In some embodiments including a fermentation unit reactor comprising a grinder, the fermentation reactor may further comprise a plant matter outlet, for example, to remove plant matter used to produce glycerol from a fermentation unit reactor. In certain preferred embodiments, the fermentation unit reactor is configured to separate ethanol from other fermentation reaction components such as water, for example, including a distillation zone. In some embodiments, a fermentation unit reactor including a distillation zone may comprise one or more distillation trays configured for facilitating phase separation, for example, of water from ethanol. In certain embodiments, the ethanol outlet of the fermentation unit reactor is in communication with a reactor configured for dehydration and oxidation to produce an epoxide. In some embodiments, the distillation zone of a fermentation unit reactor may terminate in an ethanol outlet which is in communication with a reactor configured for dehydration and oxidation of an alcohol to produce an epoxide.

[0036] In certain embodiments, the gasification unit comprises a reactor configured to produce syngas comprising carbon monoxide, carbon dioxide, and hydrogen gas. The fermentation unit reactor comprises a carbonaceous source inlet, oxygen gas inlet, gasification zone, heater, and syngas outlet. The carbonaceous source inlet is sized and shaped so that a

carbonaceous source feed stream is introduced to the gasification unit reactor. The gasification zone is sized and shaped to receive the carbonaceous source feed stream so that the carbonaceous source feed stream is mixed with oxygen gas from the oxygen gas inlet and heated by the heater to produce syngas. The syngas outlet is sized and shaped so that syngas comprising carbon monoxide, carbon dioxide, and hydrogen gas is removed from the reactor. In certain embodiments, the syngas outlet is in communication with a reactor configured for hydrogenation of nitrogen gas with the hydrogen gas to produce ammonia.

[0037] In certain embodiments, the air separation unit comprises a reactor configured to separate air into at least an oxygen gas stream and a hydrogen gas stream. The air separation unit reactor comprises an air source inlet, first air separation zone, second air separation zone, first molecular sieve, second molecular sieve, vacuum pump, and at least one gas outlet. The air source inlet is sized and shaped so that an air source feed stream is introduced to the first air separation zone of the air separation unit reactor. The first molecular sieve located in the first air separation zone adsorbs a first target gas with an affinity to the first molecular sieve and the air source feed stream continues to the second molecular sieve located in the second air separation zone where the second molecular sieve adsorbs a second target gas with an affinity to the second molecular sieve. The vacuum pump withdraws the first target gas from the first molecular sieve through the at least one gas outlet and then the vacuum pump is used to withdraw the second target gas from the second molecular sieve through the at least one gas outlet. In certain preferred embodiments, the first target gas and second target gas are nitrogen gas and oxygen gas respectively or oxygen gas and nitrogen gas respectively. In certain embodiments the at least one gas outlet is in communication with a reactor configured for dehydration and oxidation of an alcohol to produce an epoxide.

[0038] In certain embodiments, the carbonylation unit comprises a reactor configured to produce at least one carbonylation product from an epoxide and carbon monoxide such as beta-lactone, acid anhydride, and/or polylactone. The air separation unit reactor comprises an epoxide source inlet, carbon monoxide source inlet, carbonylation zone, heater, mixer, and carbonylation product outlet. The epoxide source inlet is sized and shaped so an epoxide source feed stream is

introduced to the carbonylation unit reactor. The carbon monoxide source inlet is sized and shaped so a carbon monoxide source feed stream is introduced to the carbonylation unit reactor. The carbonylation zone is sized and shaped to receive the carbon monoxide source feed stream, epoxide source feed stream and a carbonylation catalyst for a carbonylation reaction. The heater may heat the contents of the carbonylation zone sufficient for a carbonylation reaction. The mixer may mix the contents of the carbonylation zone sufficient for a carbonylation reaction. The carbonylation product outlet is sized and shaped so that at least one carbonylation product is removed from the carbonylation unit reactor. In certain preferred embodiments the carbonylation unit reactor is in communication with the gasification unit reactor to received the carbon monoxide feed stream.

[0039] Conventional systems and processes used to produce ammonia typically require separation of carbon monoxide and carbon dioxide from hydrogen to produce ammonia. This is often because carbon monoxide and carbon dioxide deactivate the catalysts typically used in convention processes. In contrast, the processes herein use the hydrogen/carbon dioxide-enriched syngas to produce ammonia because it has less deleterious effect due to the lack of carbon monoxide. For embodiments including separation, rather than hydrogen being separated such as through an expensive membrane, carbon dioxide can be removed to achieve a less deleterious effect, for example, via separation by solvating the carbon dioxide.

[0040] In some embodiments, provided are processes for producing a chemical product comprising: gasifying a carbonaceous material to produce a syngas; carbonylating an epoxide with the syngas in the presence of a carbonylation catalyst to produce a beta-lactone and a hydrogen-enriched syngas; and carbonylating the beta-lactone with the carbon dioxide enriched syngas in the presence of a second carbonylation catalyst to produce a succinic anhydride carbonylation product. In some embodiments, air may be separated to produce a nitrogen feed stream and/or an oxygen feed stream which may be integrated into the processes to produce carbonylation products and derivatives thereof, such as ammonia and urea. In some embodiments, raw materials may be integrated into the processes of the present disclosure to produce copolymers with carbonylation products and derivatives thereof.

[0041] With reference to **FIG. 1**, process **100** is an exemplary process to produce chemical products including ammonia, urea, monomers, and polymers. In process **100**, carbonaceous source **102** undergoes gasification **104** to produce a syngas **106**. Then, carbonylation **122** of first reagent **116** with syngas **106** produces a carbonylation product **132** and a hydrogen-enriched syngas **142**. The contact of hydrogen-enriched syngas **142** with a second reagent produces synthesis product **162**. Hydrogen-enriched syngas **142** may be combined with a nitrogen gas derived from air separation **152** to produce ammonia **162**. Ammonia **162** may be further combined with carbon dioxide to produce urea **172**. Carbonylation product **132** may be combined with diols, triols or a mixture of the foregoing (element **182**) to form heterogeneous copolymers **192**. In some embodiments, first reagent **116** described above may be made up of an epoxide derived from fermentation **114** of nutrient **112**. In some embodiments, air separation **152** produces a nitrogen stream and an oxygen stream. In some embodiments, the oxygen stream can be used in fermentation **114** of nutrient **112**. Fermentation **114** of nutrient **112** may further produce a carbon dioxide stream. In some embodiments, the carbon dioxide stream is combined with ammonia **162** to produce urea **172**.

[0042] The exemplary process described above may be performed using one or more reactors, also termed reaction zones, reaction vessels or process vessels, suitable for fermentation, dehydration, oxidation, gasification, carbonylation, and/or electrolysis. The one or more process vessels may include an enclosed volume sized and shaped to retain a volume of matter with one or more barriers comprised of stainless steel. The one or more process vessels may be configured as a batch reactor, fixed bed reactor, packed column reactor, fluidized bed reactor, laminar flow reactor, plug flow reactor, and/or continuous stirred-tank reactor.

[0043] The exemplary process described above may reduce the environmental footprint of chemical synthesis and increase carbon efficiency through incorporation of conventionally unused carbon atoms into final products. The integrated processes may emit less carbon dioxide to the atmosphere compared to conventional chemical production plants. The integrated processes may result in improved carbon efficiencies for processes using biomass or fossil-fuel-

based sources or from steam methane reforming, while producing valuable commodity chemicals instead of emitting a significant portion of the carbon as carbon dioxide to the atmosphere.

Integrated Process for Synthesis of Ammonia and Urea

[0044] In one aspect, provided herein is a process for synthesizing ammonia, urea, or a mixture of the foregoing. With reference to **FIG. 2A**, process **200** is an exemplary process to produce ammonia and urea via the carbonylation of a syngas and air separation. In process **200**, carbonaceous source **202** undergoes gasifying **204** to produce syngas **206**. The syngas may be made up of carbon monoxide, hydrogen, and carbon dioxide. Then, epoxide **216** undergoes carbonylation **222** with the syngas **206** to produce carbonylation product **232**. A nitrogen gas is derived from air separation **252**, and the nitrogen gas is contacted with hydrogen-enriched syngas **242** to produce ammonia **262**, which may be combined with carbon dioxide to produce urea **272**.

[0045] In some embodiments, the process depicted in **FIG. 2A** comprises multiple carbonaceous sources. For example, with reference to **FIG. 2B**, petroleum and/or fossil-fuel **201**, municipal solid waste (MSW) **205**, and biomass **203** are non-limiting exemplary carbonaceous sources. In some embodiments, epoxide **216** in the process depicted in **FIG. 2A** can be produced by oxidizing an ethylene **215**, as shown in **FIG. 2B**. Ethylene can be produced from naphtha **217**. In some embodiments, sugar is used to produce ethanol **214**, which can then react with corn oil **212** for making biodiesel **211** and glycerol **210**. Ethanol **214** can also be used to produce ethylene **215**. In some embodiments, O₂ produced from air separation **252** in the process of **FIG. 2A** can be used to oxidize ethylene **215** to produce epoxide **216** as shown in **FIG. 2B**.

[0046] In some embodiments, the processes described herein may more efficiently use raw materials to produce carbonylation products. For example, with reference to **FIG. 3A**, process **300** involves gasifying biomass, MSW, and/or fossil-fuel-based sources **302** to produce syngas **304**. The syngas may be made up of carbon monoxide, hydrogen gas and carbon dioxide. Nutrients **312** may be fermented to produce an alcohol and carbon dioxide **314**. The alcohol may be dehydrated to produce alkene **316**, which may then be oxidized with the oxygen from an air separation unit **352** in the presence of a catalyst to produce an epoxide and carbon dioxide.

Epoxide **322** may undergo carbonylation with the carbon monoxide in the presence of a carbonylation catalyst to produce an epoxide carbonylation product. Exemplary carbonylation products may include beta-propiolactone (BPL), succinic anhydride, polypropiolactone (PPL) and polyols, or any mixtures thereof. A hydrogen-enriched syngas stream with $H_2:CO \sim 2$ may be recovered. Nitrogen may be combined with the hydrogen-enriched syngas in a catalytic reaction to produce ammonia **362**; which may then be reacted with carbon dioxide to produce urea **372**.

[0047] In some embodiments, the process depicted in **FIG. 3A** further comprises converting petroleum **313** to produce ethylene **315**, which can then be oxidized to produce epoxide used in the carbonylation process **322** as shown in **FIG. 3B**.

[0048] In some variations, the systems and processes described herein comprise separation of syngas into molecular components of carbon monoxide, hydrogen gas, and carbon dioxide. In certain variations, separation provides a higher purity stream of carbon monoxide, higher purity stream of hydrogen gas, and/or higher purity stream of carbon dioxide. In some variations of the systems and processes, carbonylation using syngas produces an enriched syngas. However, in other variations of the systems and processes described herein, carbonylation may not be required to enrich syngas. Rather, the molecular components of syngas may be separated using suitable methods and techniques known in the art. For example, syngas may be separated into its molecular components by use of membrane filtration.

Syngas

[0049] Synthesis gas may be referred to as “syngas” in the processes described herein. In some variations, the syngas includes a mixture of hydrogen and carbon monoxide gases. In certain variations, the syngas further contains carbon dioxide. In some embodiments, syngas comprises the molecular components produced by gasification of carbonaceous sources, such as carbon monoxide, hydrogen, and carbon dioxide.

[0050] Generally, syngas may be derived from the gasification of carbonaceous sources, including biomass, landfill gas, natural gas, coal, coke oven gas, steel mill gas, petroleum, and

petroleum-based products. Conventional industrial processes to produce syngas include gasification of biomass, coal, petroleum, and petroleum-derived materials. The processes of the present disclosure comprise gasification that includes heating carbonaceous materials to produce molecular components. Any suitable methods known in the art for gasification may be employed.

[0051] In certain embodiments, gasification of the carbonaceous material occurs in the presence of an alkali metal catalyst source and steam at elevated temperatures and pressures produces syngas.

[0052] In some variations of the processes herein, biomass and petroleum-based feedstock flexibility can present certain advantages. This is due to the cost of feedstocks and the location and distribution channels required to supply raw materials to the plant. In some embodiments, biomass is used to produce syngas and includes, for example, wood, bagasse, corn stover, switchgrass, agricultural waste, and municipal solid waste. In some embodiments, biomass-derived carbon constitutes at least 10% of the carbon content of the final chemical products. In certain embodiments, biomass-derived carbon constitutes 100% of the carbon content of the final chemical products. In certain embodiments, fossil-fuel-based raw material sources are used. These include, for example, landfill gas, natural gas, coal, petroleum and petroleum-based products. In certain embodiments, fossil-fuel-based raw material sources constitute at least 10% of the carbon content of the final chemical products. In certain embodiments, petroleum-based raw material sources constitute 100% of the carbon content of the final chemical products. In certain embodiments, the nutrients used in the fermentation to produce alcohol can come from a variety of sources. These include, for example, corn, beet, and date.

[0053] Steam methane reforming of natural gas is also commonly used to generate a hydrogen-enriched syngas. In certain embodiments, it may be desirable to use steam-methane reforming to yield a syngas whose ratio of hydrogen-to-carbon monoxide is about 2 or greater. Advantageously, steam-methane reforming replaces the water-gas shift reaction requirement needed to produce a syngas with a high hydrogen-to-carbon monoxide ratio to perform a variety of downstream chemical production processes. In some embodiments, the hydrogen-enriched

syngas used for ammonia production is derived by reacting methane with water in a steam methane reforming process. In certain embodiments, before the steam methane reforming process can be carried out, all sulfurous compounds must be removed from the natural gas to prevent catalyst poisoning. For example, a conventional industrial method to remove sulfur compounds from natural gas is to heat it to 400 °C in the presence of zinc oxide.

[0054] In some embodiments, the purified natural gas is sent to a steam methane reformer where it is mixed with superheated steam and reformed at above 750 °C in the presence of a nickel catalyst. At the high temperature, the methane is converted to hydrogen, carbon dioxide and small amounts of carbon monoxide forming a syngas whose ratio of hydrogen-to-carbon monoxide is about 2 or greater.

[0055] In certain embodiments, the syngas stream has a hydrogen-to-carbon monoxide ratio of less than one. Syngas streams of this ratio tend to be typical of biomass and solids gasification which produce carbon-rich streams. In some embodiments, the syngas stream has a hydrogen-to-carbon monoxide ratio of at least 1, at least 1.5, at least 2.0, at least 2.5, at least 3.0, at least 3.5, at least 4.0, at least 4.5, or at least 5.0. In some embodiments, the syngas stream has a hydrogen-to-carbon monoxide ratio of about 0.5-1.0, about 1.0-1.5, about 1.5-2.0, about 2.0-2.5, about 2.5-3.0, about 3.0-3.5, about 3.5-4.0, about 4.0-4.5, about 4.5-5.0, about 1.0-2.0, about 2.0-3.0, about 3.0-4.0, or about 4.0-5.0. In some embodiments, the syngas stream has a hydrogen-to-carbon monoxide ratio of about 1.5-3.0. These hydrogen-rich syngas streams may be the result of steam methane reforming of natural gas and other light aliphatic compounds. In some embodiments, a hydrogen-enriched syngas is derived from the off gas of the carbonylation reactions between an epoxide and the carbon monoxide contained in the syngas from gasification as described herein.

[0056] Syngas derived from gasification of carbonaceous biomass may contain significant amounts of carbon dioxide. In some variations, the syngas may have more than 20 percent mole volume of carbon dioxide. In certain variations, the carbonylation catalyst used in the processes herein are not inhibited by high levels of carbon dioxide in the syngas stream. In some

embodiments, the systems and processes herein may include separation of carbon dioxide from syngas, for example, by using a membrane filter.

[0057] In some embodiments, the syngas stream used in the carbonylation reaction contains carbon dioxide in the range of 1 mole percent to 30 mole percent. In some embodiments, the excess carbon dioxide is diverted for downstream chemical production uses. In certain embodiments, a syngas stream containing little or no carbon dioxide is desirable for downstream chemical production processes.

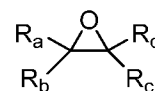
[0058] Depending on the carbonaceous source, the syngas may comprise trace components such as carbonyl sulfide, hydrogen sulfide, nitrogen, water vapor, and ash. In some embodiments, the syngas stream contains contaminants such as sulfurous compounds, hydrogen cyanide, and nitrogenous compounds that may be inhibitory to the catalysts used in the processes described in this disclosure. Therefore, in some embodiments, the syngas stream may require a conditioning process before being used in downstream chemical production processes. In some embodiments, the syngas stream is substantially free of inhibitory contaminants.

[0059] Production of syngas can use a diverse array of feedstocks with various process conditions and operations. Similar, a variety of apparatus and methods for the handling and purification of syngas suitable for practicing the processes described in this disclosure are available.

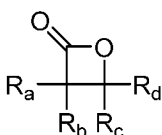
Carbonylation

[0060] Carbonylation may include converting an alkene oxide or epoxide, such as ethylene oxide, to a carbonylation product, such as a beta-lactone and/or succinic anhydride with syngas comprising carbon monoxide and or carbon dioxide.

[0061] In certain embodiments, carbonylation of an epoxide of formula



produces a beta-lactone of formula



[0062] In certain embodiments, each R_a, R_b, R_c, and R_d is independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, or optionally substituted aryl. It should be understood that the epoxides and beta-lactones may have asymmetric centers, and exist in different enantiomeric or diastereomeric forms. All optical isomers and stereoisomers of the compounds of the general formula, and mixtures thereof in any ratio, are considered within the scope of the formula. Thus, any formula provided herein may include (as the case may be) a racemate, one or more enantiomeric forms, one or more diastereomeric forms, one or more atropisomeric forms, and mixtures thereof in any ratio.

[0063] “Alkyl” refers to a monoradical unbranched or branched saturated hydrocarbon chain. In some embodiments, alkyl has 1 to 10 carbon atoms (*i.e.*, C₁₋₁₀ alkyl), 1 to 9 carbon atoms (*i.e.*, C₁₋₉ alkyl), 1 to 8 carbon atoms (*i.e.*, C₁₋₈ alkyl), 1 to 7 carbon atoms (*i.e.*, C₁₋₇ alkyl), 1 to 6 carbon atoms (*i.e.*, C₁₋₆ alkyl), 1 to 5 carbon atoms (*i.e.*, C₁₋₅ alkyl), 1 to 4 carbon atoms (*i.e.*, C₁₋₄ alkyl), 1 to 3 carbon atoms (*i.e.*, C₁₋₃ alkyl), or 1 to 2 carbon atoms (*i.e.*, C₁₋₂ alkyl). Examples of alkyl include methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, 2-pentyl, isopentyl, neopentyl, hexyl, 2-hexyl, 3-hexyl, 3-methylpentyl, and the like. When an alkyl residue having a specific number of carbon atoms is named, all geometric isomers having that number of carbon atoms may be encompassed; thus, for example, “butyl” can include n-butyl, sec-butyl, isobutyl and t-butyl; “propyl” can include n-propyl and isopropyl.

[0064] “Alkenyl” refers to an unsaturated linear or branched monovalent hydrocarbon chain or combination thereof, having at least one site of olefinic unsaturation (*i.e.*, having at least one moiety of the formula C=C). In some embodiments, alkenyl has 2 to 10 carbon atoms (*i.e.*, C₂₋₁₀ alkenyl). The alkenyl group may be in “cis” or “trans” configurations, or alternatively in “E” or “Z” configurations. Examples of alkenyl include ethenyl, allyl, prop-1-enyl, prop-2-enyl, 2-methylprop-1-enyl, but-1-enyl, but-2-enyl, but-3-enyl, isomers thereof, and the like.

[0065] “Cycloalkyl” refers to a carbocyclic non-aromatic group that is connected via a ring carbon atom. Examples of cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like.

[0066] “Aryl” refers to a monovalent aromatic carbocyclic group of from 6 to 18 annular carbon atoms having a single ring or a ring system having multiple condensed rings. Examples of aryl include phenyl, naphthyl and the like.

[0067] The term “optionally substituted” means that the specified group is unsubstituted or substituted by one or more substituent groups. Examples of substituents may include halo, -OSO₂R₂, -OSiR₄, -OR, C=CR₂, -R, -OC(O)R, -C(O)OR, and -C(O)NR₂, wherein R is independently H, optionally substituted alkyl, optionally substituted alkenyl, or optionally substituted aryl. In some embodiments, R is independently unsubstituted alkyl, unsubstituted alkenyl, or unsubstituted aryl. In some embodiments, R is independently H, methyl (Me), ethyl (Et), propyl (Pr), butyl (Bu), benzyl (Bn), allyl, phenyl (Ph), or a haloalkyl. In certain embodiments, substituents may include F, Cl, -OSO₂Me, -OTBS (where “TBS” is tert-butyl(dimethyl)silyl), -OMOM, -OMe, -OEt, -OiPr, -OPh, -OCH₂CHCH₂, -OBn, -OCH₂(furyl), -OCF₂CHF₂, -C=CH₂, -OC(O)Me, -OC(O)*n*Pr, -OC(O)Ph, -OC(O)C(Me)CH₂, -C(O)OMe, -C(O)OnPr, -C(O)NMe₂, -CN, -Ph, -C₆F₅, -C₆H₄OMe, and -OH.

[0068] In one variation, three of R_a, R_b, R_c, and R_d are H, and the remaining R_a, R_b, R_c, and R_d is optionally substituted alkyl, optionally substituted alkenyl, optionally substituted cycloalkyl, or optionally substituted aryl. In one variation, three of R_a, R_b, R_c, and R_d are H, and the remaining R_a, R_b, R_c, and R_d is unsubstituted alkyl, or alkyl substituted with a substituent selected from the group consisting of halo, -OSO₂R₂, -OSiR₄, -OR, C=CR₂, -R, -OC(O)R, -C(O)OR, and -C(O)NR₂, wherein R is independently H, Me, Et, Pr, Bu, Bn, allyl, and Ph.

[0069] In one variation, two of R_a, R_b, R_c, and R_d are H, and the remaining two of R_a, R_b, R_c, and R_d are optionally substituted alkyl. In one variation, two of R_a, R_b, R_c, and R_d are H, one of the remaining R_a, R_b, R_c, and R_d is optionally substituted alkyl, and one of the remaining R_a, R_b, R_c, and R_d is optionally substituted aryl. In one variation, two of R_a, R_b, R_c, and R_d are H, one of the remaining R_a, R_b, R_c, and R_d is optionally substituted alkyl, and one of the remaining R_a, R_b, R_c, and R_d is optionally substituted alkenyl. In one variation, two of R_a, R_b, R_c, and R_d are H, one of the remaining R_a, R_b, R_c, and R_d is optionally substituted alkyl, and one of the remaining R_a, R_b, R_c, and R_d is optionally substituted cycloalkyl. In one variation, two of R_a, R_b, R_c, and R_d are

H, one of the remaining R_a , R_b , R_c , and R_d is optionally substituted alkenyl, and one of the remaining R_a , R_b , R_c , and R_d is optionally substituted aryl.

0069.1 In certain embodiments, R_a , R_b , R_c , and R_d are H. In certain embodiments, R_a , R_b , and R_c are H, and R_d is optionally substituted alkyl. In certain embodiments, R_d , R_b , and R_c are H, and R_a is optionally substituted alkyl. In certain embodiments, R_a , R_b , and R_c are H, and R_d is optionally substituted alkenyl. In certain embodiments, R_d , R_b , and R_c are H, and R_a is optionally substituted alkenyl. In certain embodiments, R_a , R_b , and R_c are H, and R_d is optionally substituted cycloalkyl. In certain embodiments, R_d , R_b , and R_c are H, and R_a is optionally substituted cycloalkyl. In certain embodiments, R_a , R_b , and R_c are H, and R_d is optionally substituted aryl. In certain embodiments, R_d , R_b , and R_c are H, and R_a is optionally substituted aryl.

[0070] In certain embodiments, R_a and R_b are optionally substituted alkyl, and R_c and R_d are H. In certain embodiments, R_c and R_d are optionally substituted alkyl, and R_a and R_b are H. In certain embodiments, R_a and R_b are taken together to form an optionally substituted ring. In certain embodiments, R_c and R_d are taken together to form an optionally substituted ring. In certain embodiments, the optionally substituted ring is a carbocyclic non-aromatic ring containing from 3 to 10 carbon atoms. In certain embodiments, the carbocyclic non-aromatic ring contains at least one site of olefinic unsaturation.

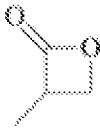
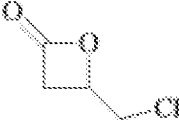
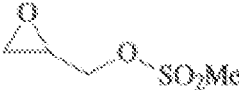
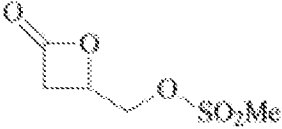
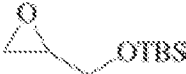
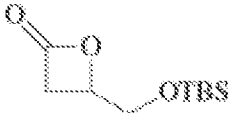
[0071] In certain embodiments, R_a and R_d are taken together to form an optionally substituted ring. In certain embodiments, the optionally substituted ring is a carbocyclic non-aromatic ring containing from 3 to 10 carbon atoms. In certain embodiments, the carbocyclic non-aromatic ring contains at least one site of olefinic unsaturation.

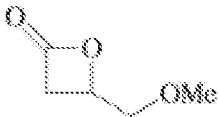
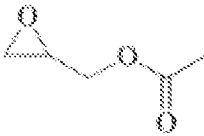
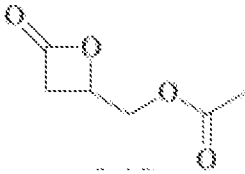
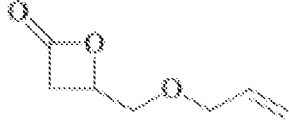
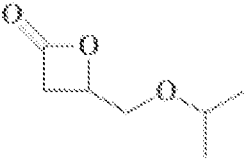
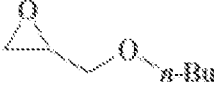
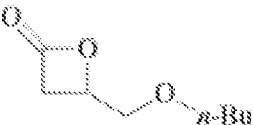
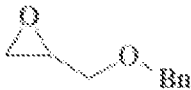
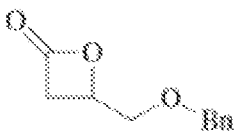
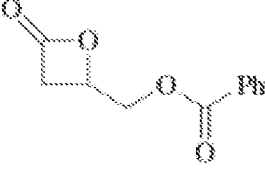
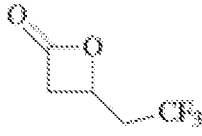
[0072] In certain embodiments, R_a and R_d are each independently optionally substituted alkyl, and R_b and R_c are H. In certain embodiments, R_a is optionally substituted alkyl, R_d is optionally substituted aryl, and R_b and R_c are H. In certain embodiments, R_d is optionally substituted alkyl, R_a is optionally substituted aryl, and R_b and R_c are H. In certain embodiments, R_a is optionally substituted alkenyl, R_d is optionally substituted aryl, and R_b and R_c are H. In certain embodiments, R_d is optionally substituted alkenyl, R_a is optionally substituted aryl, and

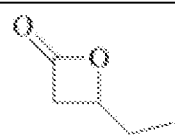
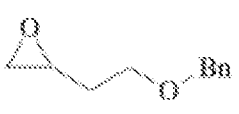
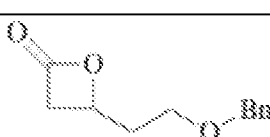
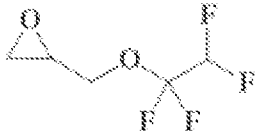
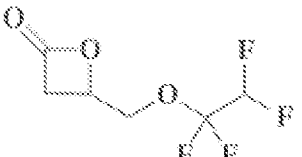
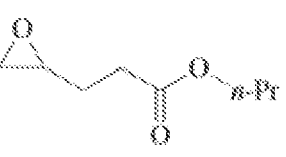
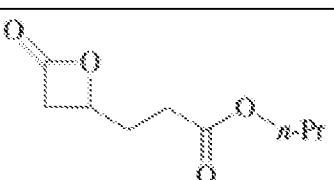
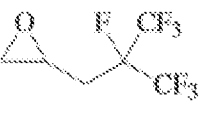
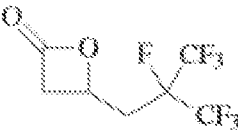
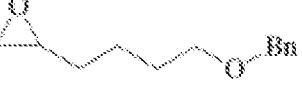
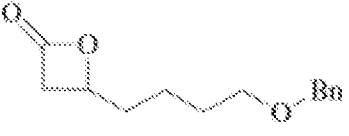
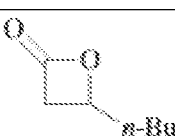
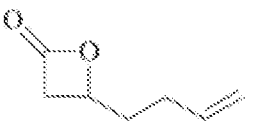
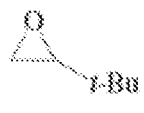
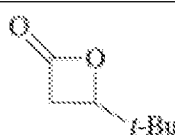
R_b and R_c are H. In certain embodiments, R_a is optionally substituted alkyl, R_d is optionally substituted alkenyl, and R_b and R_c are H. In certain embodiments, R_d is optionally substituted alkyl, R_a is optionally substituted alkenyl, and R_b and R_c are H.

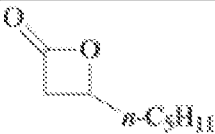
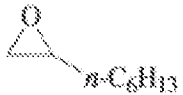
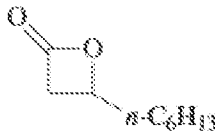
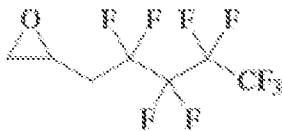
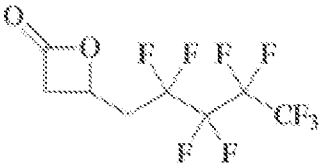
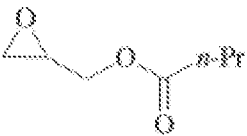
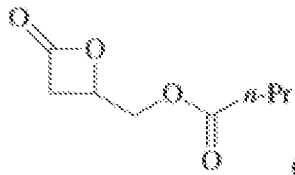
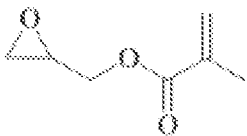
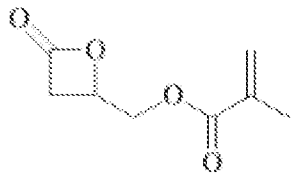
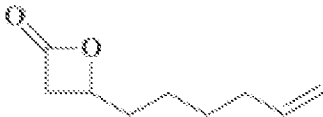
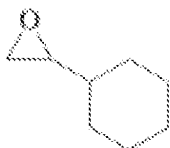
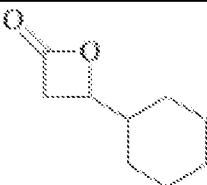
[0073] In Table A below, Column A includes epoxides which undergo carbonylation and Column B includes the respective beta-lactones produced by carbonylation of the epoxides.

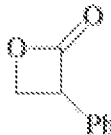
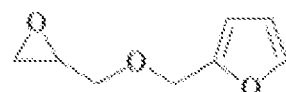
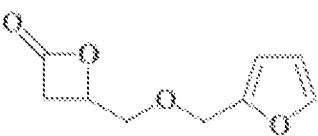
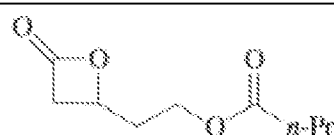
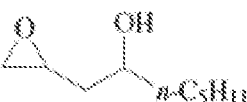
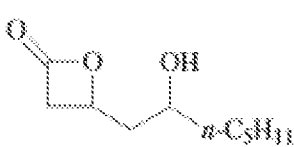
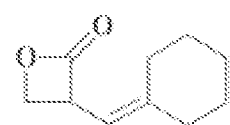
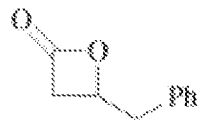
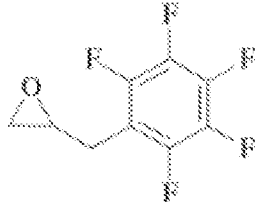
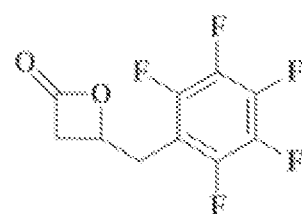
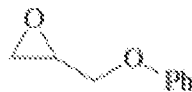
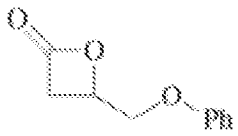
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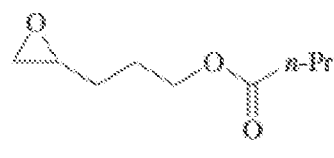
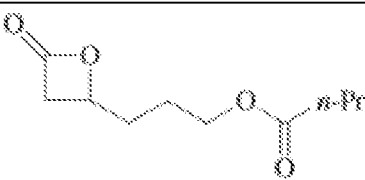
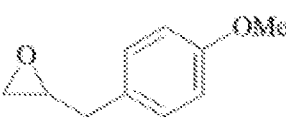
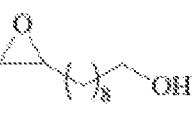
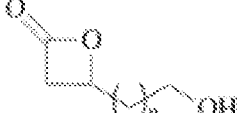
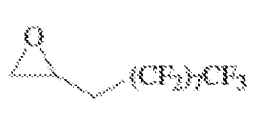
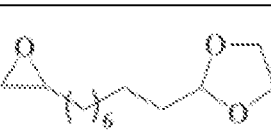
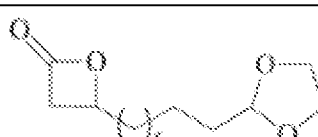
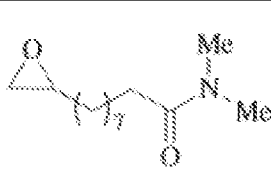
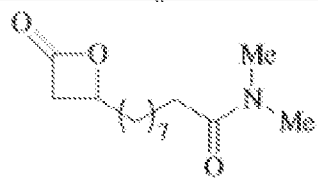
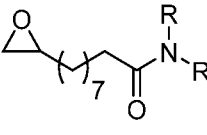
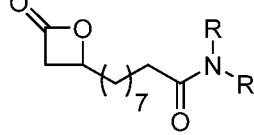
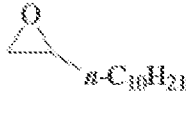
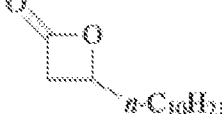
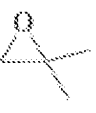
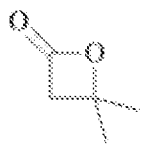
Column A	Column B
	
	 or/and 
	
	
	
	

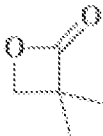
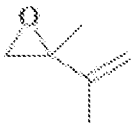
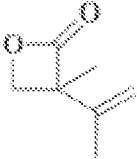
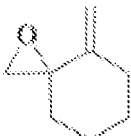
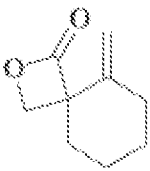
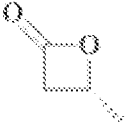
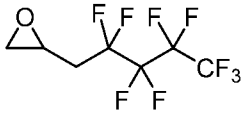
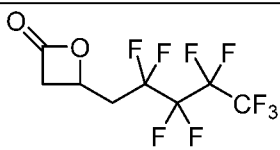
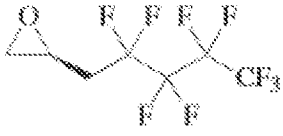
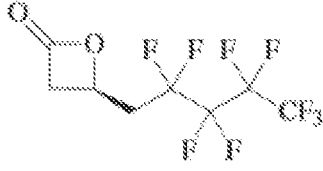
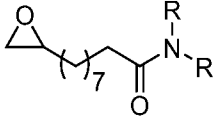
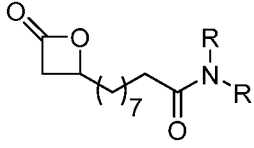
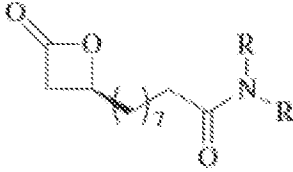
	
	
	
	
	
	
	
	
	

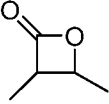
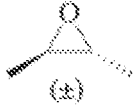
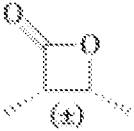
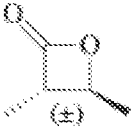
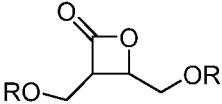
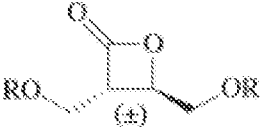
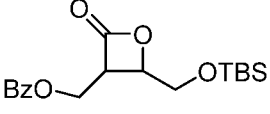
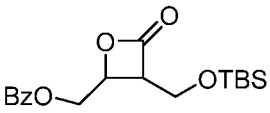
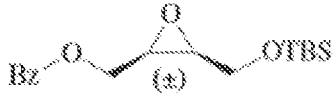
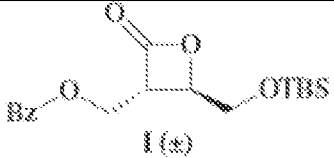
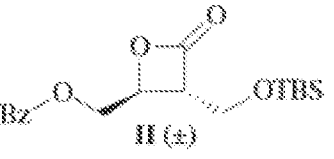
	
	
	
	
	
	
	
	
	

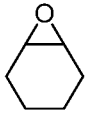
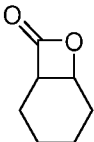
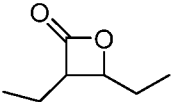
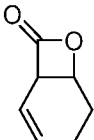
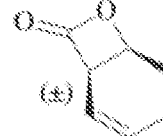
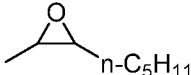
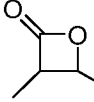
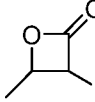
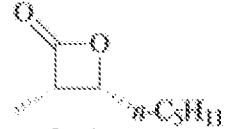
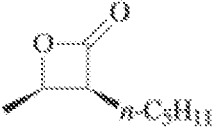
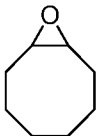
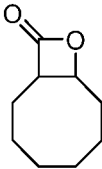
	
	
	
	
	
	
	
	

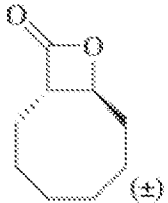
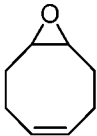
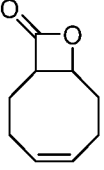
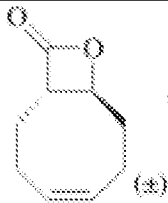
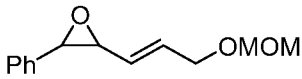
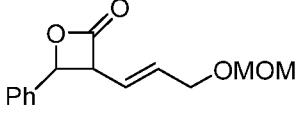
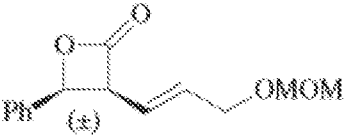
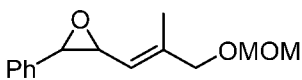
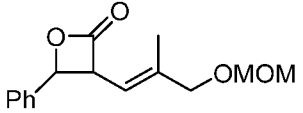
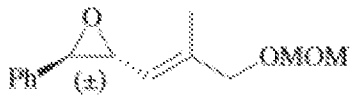
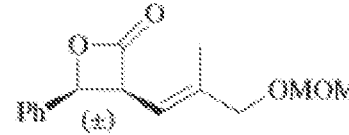
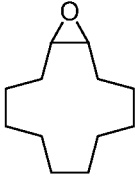
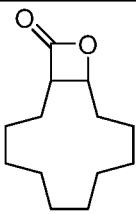
	
	
	
	
	
	
	
	

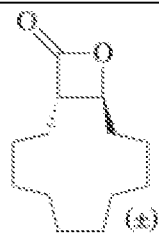
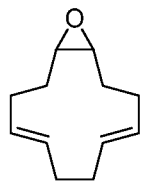
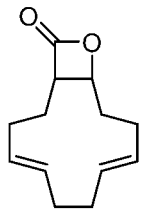
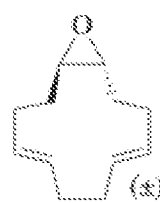
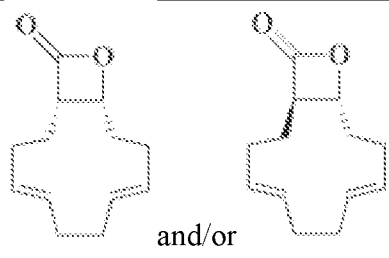
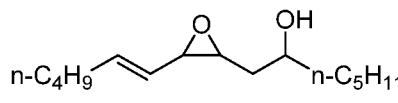
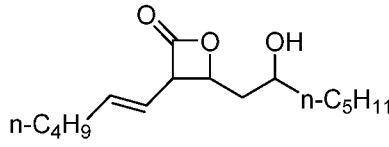
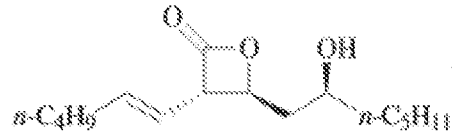
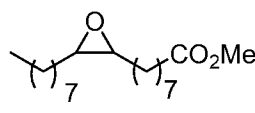
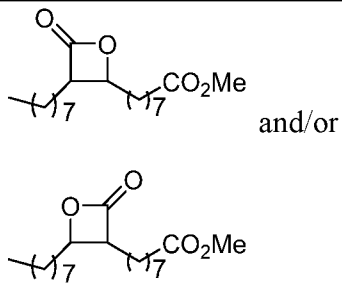
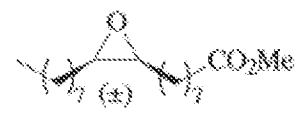
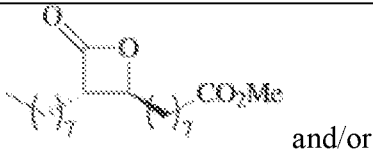
	
	
	
	
	
	
	
	
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[0074] The methods suitable for carbonylation of an epoxide and/or succinic anhydride with syngas include use of a carbonylation catalyst. In some embodiments, the carbonylation catalyst comprises a metal carbonyl Lewis acid moiety. In some embodiments, the carbonylation catalyst is selective towards carbonylation with carbon monoxide or carbon dioxide.

[0075] In some embodiments, the carbonylation catalyst is utilized in any of the methods described herein and the carbonylation catalyst comprises a metal carbonyl compound in combination with a cationic Lewis acid, the Lewis acid has a formula $[(L^c)_v M_b]^{z+}$, wherein:

L^c is a ligand where, when two or more L^c are present, each may be the same or different;

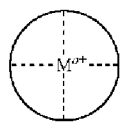
M is a metal atom where, when two M are present, each may be the same or different;

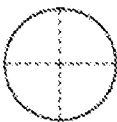
v is an integer from 1 to 4 inclusive;

b is an integer from 1 to 2 inclusive; and

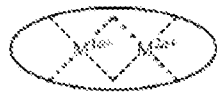
z is an integer greater than 0 that represents the cationic charge on the metal complex.

[0076] In some embodiments, the Lewis acids has structure I:



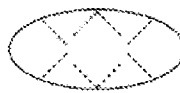
, wherein  is a multidentate ligand; M is a metal coordinated to the multidentate ligand; and a is the charge of the metal atom and ranges from 0 to 2.

[0077] In some embodiments, the Lewis acids has structure II



, wherein a is as defined above (each a might be different or same), M^1 is a

first metal atom; M^2 is a second metal atom; and



comprises a multidentate ligand system capable of coordinating both metal atoms.

[0078] In some embodiments, the enriched syngas has a hydrogen-to-carbon monoxide ratio of at least 1.5, at least 2, at least 2.5, at least 3.0, at least 3.5, at least 4.0, at least 4.5, at least 5.0, at least 5.5, at least 6.0, at least 6.5, at least 7.0, at least 7.5, at least 8.0, at least 8.5, at least 9.0, at least 9.5, or at least 10 depending on how much carbon monoxide is fed to the carbonylation reaction and used during the carbonylation reaction process. In some embodiments, the enriched syngas has a hydrogen-to-carbon monoxide ratio of about 1.5-3.0, about 3.0-4.5, about 4.5-6.0, about 6.0-7.5, about 7.5-9.0, or about 9.0-10.0.

[0079] In some embodiments, the carbonylation product is a beta -lactone. In certain embodiments, the beta-lactone may be beta-butyrolactone, beta-valerolactone, beta-heptanolactone, beta-tridecanolactone, cis-3,4-dimethyloxetan-2-one, 4-(but-3-en-1-yl)oxetan-2-one, 4-(butoxymethyl)-2-oxetanone, 4-[[[(1,1-dimethylethyl)dimethylsilyl]oxy] methyl]- 2-oxetanone, 4-[(2-propen-1-yloxy)methyl]- 2-oxetanone, 4-[(benzoyloxy)methyl]-2-Oxetanone. In some embodiments, the processes produce beta-propiolactone.

Air Separation

[0080] In another aspect, the integrated ammonia and urea synthesis process comprises separating air into a nitrogen stream and an oxygen stream. In some embodiments, the nitrogen stream is contacted with the hydrogen-enriched syngas stream to form ammonia. In certain some

embodiments, the ammonia is contacted with carbon dioxide to form urea. In some embodiments, the oxygen stream is contacted with an alkene in the presence of a catalyst in an oxidation step to produce an epoxide and carbon dioxide.

Ammonia Synthesis

[0081] In some embodiments, the ammonia synthesis process comprises mixing nitrogen gas and hydrogen-enriched syngas in a pressure vessel using an iron catalyst to produce ammonia. In some embodiments, a ruthenium catalyst can be used. In some embodiments, the ammonia synthesis process comprising mixing nitrogen gas and hydrogen-enriched syngas at about 100-150 °C, about 150-200 °C, about 200-250 °C, about 250-300 °C, about 300-350, about 350-400 °C, about 400-450 °C, about 450-500 °C, about 500-550 °C, about 550-600 °C, about 600-700 °C, about 700-800 °C, or about 800-900°C. In some embodiments, the ammonia synthesis process comprising mixing nitrogen gas and hydrogen-enriched syngas at about 400-450 °C. In some embodiments, the ammonia synthesis process comprising mixing nitrogen gas and hydrogen-enriched syngas at about 50-100 atm, about 100-150 atm, about 150-200 atm, about 200-250 atm, about 250-300 atm, about 300-350 atm, or about 350-400 atm. In some embodiments, the ammonia synthesis process comprising mixing nitrogen gas and hydrogen-enriched syngas at about 200 atm.

[0082] In some embodiments, the ammonia synthesis process is about 10-20 minutes, about 20-30 minutes, about 30-40 minutes, about 40-50 minutes, about 50-60 minutes, about 1-2 hours, about 2-3 hours, or about 3-4 hours.

[0083] In some embodiments, the hydrogen-enriched syngas and nitrogen gas pass over the catalyst bed more than one time, more than two times, more than three times, more than four times, more than five times, more than six times, more than seven times, more than eight times, more than nine times, more than ten times, more than 15 times, more than 20 times, more than 25 times, or more than 30 times.

[0084] In some embodiments, the conversion rate for each passing of catalyst bed is in the range of about 5-10%, about 10-15%, about 15-20%, about 20-25%, about 25-30%, about 30-

35%, about 35-40%, about 40-45%, or about 45-50%. In some embodiments, the conversion rate for each passing of catalyst bed is about 15%. By the end of the process, in some embodiments, conversion of nitrogen and hydrogen to ammonia is more than about 50%, more than about 55%, more than about 60%, more than about 65%, more than about 70%, more than about 80%, more than about 85%, more than about 90%, more than about 95%, or more than about 97%. In some embodiments, conversion of nitrogen and hydrogen to ammonia is about 97%. In some embodiments, upon cooling, the ammonia turns to liquid and the unreacted gases are recycled back into the ammonification process.

Urea Synthesis

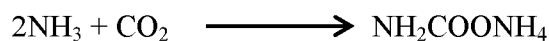
[0085] In another aspect, the ammonia product can be carbonylated using excess carbon dioxide generated during alcohol fermentation, alkene oxidation and syngas production to produce a nitrogenous compound such as urea. In some embodiments, the carbon dioxide is derived from the alcohol fermentation process. In some embodiments, the carbon dioxide is derived from the alkene oxidation process. In some embodiments, the carbon dioxide is derived from the syngas. In some embodiments, the carbon dioxide is derived from alcohol fermentation, alkene oxidation, and syngas or combinations thereof. In some embodiments, the carbon dioxide may be derived from alkene oxidation and/or from fermentation and/or from syngas for use in downstream chemical processes.

[0086] In some embodiments, the carbon dioxide used in the urea production process is derived from gasification of biomass. In certain embodiments, the carbon dioxide used in the urea production process is derived from gasification of petroleum and petroleum-based sources. In some embodiments, the carbon dioxide reacted with ammonia in the urea production process is derived from a mixture of alcohol fermentation, alkene oxidation, and gasification. In some embodiments, the carbon dioxide reacted with ammonia in the urea production process is derived from at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% bio-based sources. In some embodiments, the carbon dioxide reacted with ammonia in the urea production process is derived from about 100% bio-based sources.

[0087] In some embodiments, carbon dioxide is reacted with ammonia at high pressure to form ammonium carbamate. In some embodiments, carbon dioxide is reacted with ammonia at about 50-100 atm, about 100-150 atm, about 150-200 atm, about 200-250 atm, about 250-300 atm, about 300-350 atm, about 350-400 atm, or about 400-500 atm. In some embodiments, carbon dioxide is reacted with ammonia at about 250 atm. Because the reaction is exothermic, the heat is recovered by a boiler which produces steam. In some embodiments, the initial reaction achieves more than 50%, more than 55%, more than 60%, more than 65%, more than 70%, more than 75%, more than 80%, more than 85%, more than 90%, or more than 95% conversion of the carbon dioxide to urea. In some embodiments, the initial reaction achieves more than 75% conversion of the carbon dioxide to urea.

[0088] A three-step purification process is performed to remove water and the unconsumed reactants ammonia, carbon dioxide and ammonium carbamate to yield a urea product. In some embodiments, the urea product comprises about 30-40%, about 40-50%, about 50-60%, about 60-70%, about 70-75%, about 75-80%, about 80-85%, about 85-90%, or about 90-95% urea. In some embodiments, the urea product comprises about 5-10%, about 10-15%, about 15-20%, about 20-25%, about 25-30%, about 30-35%, about 35-40%, about 45-50%, or about 50-55% urea. In some embodiments, the urea product comprises about 75-80% urea, with about 20% ammonia.

[0089] Without being bound by theory, in some embodiments, urea is produced from ammonia and carbon dioxide via an ammonium carbamate intermediate in two equilibrium reactions:



[0090] In comparison, the industrial synthesis of urea using two urea molecules to form biuret and ammonia is undesirable, not only because it lowers the yield of urea, but also because biuret is toxic to plants, making it unsuitable for use as a fertilizer.

Integrated Systems and Process for Synthesis of Copolymers

[0091] In another aspect, provided are systems and processes that integrate raw materials to produce copolymers with carbonylation products. In some embodiments, the process transforms plant matter into triglycerides, transesterificates the triglycerides to produce glycerol, and copolymerizes the glycerol with a carbonylation product, such as a beta-lactone. In some embodiments, the process comprises copolymerization of beta-lactones and glycerol. In some embodiments, the process comprises copolymerization of succinic anhydride with glycerol.

[0092] With reference to **FIG. 4**, process **400** is an exemplary process that involves processing plants **482** to extract the plant oil from the plant. Exemplary plants may include corn, beet, and date. The plant oil may be treated with methanol and the hydrogen-enriched syngas, which undergoes chemical modification in a transesterification zone **484** to produce glycerol **486**. Carbonaceous source **402** is undergoes gasification **404** to produce syngas stream **406**. Then, carbonylation **422** of the epoxide with the syngas stream produces epoxide carbonylation product **432**. Carbonylation product **432** may be combined with glycerol **486** to produce copolymer and/or polyol **492**.

Plant Oil Transesterification

[0093] Plant fats and oils are composed of triglycerides, which are esters formed by the reactions of three free fatty acids and the triol, glycerol. Without being bound by theory, in the transesterification process, the added alcohol is deprotonated with a base to make it a stronger nucleophile. The reaction has no other inputs other than the triglyceride and the alcohol. In some embodiments, catalysts (acid and/or base) are used in the transesterification reaction. In some embodiments, triglyceride and the alcohol are heated during the transesterification reaction. Common base catalysts for transesterification include sodium hydroxide, potassium hydroxide, and sodium methoxide.

[0094] In certain embodiments, the transesterification reaction involves reacting vegetable oils or fats with short-chain alcohols, such as methanol and ethanol. In some embodiments, the transesterification process necessitates the use of low-molecular weight

alcohols, with ethanol the most often used due to low cost. However, greater conversions into biodiesel can be reached using methanol.

[0095] In some embodiments, the transesterification reaction uses ethanol generated by the alcohol fermentation processes described herein. In some embodiments, the transesterification reaction is catalyzed by acids. In some embodiments, the transesterification reaction is base-catalyzed because this path has shorter reaction times and lower catalyst cost than those used in acid-catalyzed reactions.

[0096] In some embodiments, a base-catalyzed transesterification reaction is carried out with an alcohol to produce biodiesel and glycerol (which may be a byproduct of this reaction). Transesterification products include biodiesel, soap, glycerol, excess alcohol, and trace amounts of water. In some embodiments, the glycerol is separated from the biodiesel and the other products, processed, and purified for use in downstream chemical production. In some embodiments, the glycerol is separated from the biodiesel based on density differences. In some embodiments, the residual methanol is recovered by distillation and reused and soaps can be removed or converted into acids. In some variations, the glycerol may be integrated back into the systems and processes described herein.

[0097] In some embodiments, the extracted vegetable oils can be used for producing a valuable biofuel, biodiesel, through the chemical reactions of transesterification. In the present disclosure, there is no restriction as to the vegetable oil that may be used in biodiesel production. Exemplary feedstocks may include, but are not limited, to corn, beet, date, safflower, cottonseed, and any high oil content vegetable. Impure and recycled plant oil is processed to remove impurities derived from storage, handling, and processing. Regardless of the feedstock, water is removed as its presence during base-catalyzed transesterification causes the triglycerides to hydrolyze, giving salts of the fatty acids (soaps) instead of producing biodiesel.

[0098] In some embodiments, the plant oil used for the production of biodiesel is derived from corn, since the integrated processes described in this disclosure may use corn sugar as a nutrient source in the alcohol fermentation. In some embodiments, the plant oil(s) used in biodiesel production in the present disclosure will be derived from processing the plant matter

used as the nutrient source for fermentation. In some embodiments, the plant oil(s) used in biodiesel production in the present disclosure will be derived from plant matter obtained from other sources such as agricultural waste. The plant oil extraction process may produce a substantially pure oil free of any contaminants.

[0099] In some embodiments, the pure plant oil stream is reacted with an alcohol stream and a syngas stream to initiate the transesterification reaction. In some embodiments, the alcohol used in the transesterification process comprises ethanol. In some embodiments, the alcohol used in the transesterification process comprises methanol. In some embodiments, the syngas stream has a hydrogen to carbon monoxide ratio of less than one. In some embodiments, the syngas stream has a hydrogen to carbon monoxide ratio of greater than one. In some embodiments, the transesterification reaction is base-catalyzed.

[0100] In some embodiments, the plant oil comprises small amounts of moisture and free fatty acids. In some embodiments, the plant oil comprises less than 10%, less than 5%, less than 4%, less than 3%, less than 2%, or less than 1% moisture (w/w). In some embodiments, the plant oil comprises less than 30%, less than 25%, less than 20%, less than 15%, less than 10%, less than 5%, or less than 1% free fatty acids (w/w).

[0101] In some embodiments, the transesterification reaction has a conversion rate of about more than 50%, more than 55%, more than 60%, more than 65%, more than 70%, more than 75%, more than 80%, more than 85%, more than 90%, more than 95%, or more than 98%. In some embodiments, the transesterification reaction has a conversion rate of more than 98%.

Polymerization

[0102] In some embodiments, copolymerization proceeds in the presence of a metal complex including a permanent ligand set with at least one ligand that is a polymerization initiator, and a chain transfer agent having a plurality of sites capable of initiating polymer chains. In some embodiments, a ligand that is a polymerization initiator has a plurality of polymer initiation sites. Chain transfer agents suitable for the present disclosure comprise any compound having two or more sites capable of initiating chain growth in the co-polymerization of an epoxide and

glycerol. In some embodiments, such compounds do not have other functional groups that interfere with the polymerization. In some embodiments, copolymerization of glycerol and an epoxide may be performed in the presence of a catalyst. In some embodiments, a polymerization system further includes a co-catalyst.

[0103] In some embodiments, chain transfer agents may have a broad array of chemical structures. In some embodiments, each molecule of the chain transfer agent is capable of initiating two or more polycarbonate chains. Without being bound by theory, this can occur by several mechanisms including, for example: by ring-opening an epoxide monomer, by reacting with carbon dioxide molecules to yield a moiety capable of sustaining polymer chain growth, or by a combination of these. In some embodiments, a chain transfer agent comprises two or more functional groups independently capable of reacting with carbon dioxide or an epoxide. Examples of these include molecules such as diacids, glycols, diols, triols, hydroxyacids, amino acids, amino alcohols, dithiols, mercapto alcohols, saccharides, catechols, polyethers, etc. In some embodiments, the chain transfer agent comprises a multiply active functional group that is itself able to react multiple times to initiate more than one polymer chain. Examples of the latter include functional groups having a single atom capable of reacting multiple times such as ammonia, primary amines and water, as well as functional groups having more than one nucleophilic atom such as amidines, guanidines, urea, boronic acids, etc.

[0104] In some embodiments, without wishing to be bound by any theory, the copolymerization of glycerol and a carbonylation product may comprise ring-opening polymerization. In some embodiments, beta-lactones and/or succinic anhydride undergo a ring-opening polymerization reaction in the presence of a compound having a hydroxyl group such as glycerol. In some embodiments, the copolymerization comprises anionic polymerization with alkali hydroxides, (*e.g.*, sodium hydroxide or potassium hydroxide), or alkali alcoholates (*e.g.*, sodium methylate, sodium ethylate, potassium ethylate or potassium isopropylate) as catalysts with the addition of at least one initiator molecule containing 2 to 8 reactive hydrogens. In some embodiments, the copolymerization comprises cationic polymerization with Lewis acids (*e.g.*, antimony pentachloride or boron trifluoride etherate). In some embodiments, the

copolymerization comprises bleaching earth as catalysts from one or more alkylene oxides comprising 2 to 4 carbons in the alkylene radical.

[0105] In some embodiments, the polyol product contains at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% bio-based content. In some embodiments, the polyol product contains about 100% bio-based content. The polyol bio-based content may derive from any of the chemical processes leading up to co-polymerization of the epoxide carbonylation products and glycerol, including the plant matter processing generating the glycerol, epoxide production, and syngas generation.

[0106] With reference to **FIG. 5**, process **500** is an exemplary process to produce polyol. Process **500** involves providing conditioned syngas **504** derived from gasification of biomass or fossil-fuel-based sources **502**; providing nutrients for fermentation **512** to produce alcohol and carbon dioxide **514**; dehydrating alcohol **516** to produce an alkene; oxidizing the alkene in catalytic reaction **518** to produce an epoxide and carbon dioxide; reacting the epoxide from with the carbon monoxide in the presence of carbonylation catalyst **522** to produce a beta-lactone product; recovering a hydrogen-enriched syngas stream; processing **582** and extracting **584** a plant oil; subjecting the plant oil to a transesterification process with alcohol and hydrogen-enriched syngas stream **586** to produce biodiesel and glycerol; processing the long-chain alkyl esters and the glycerol by-product into separate streams **588**; and copolymerizing the beta-lactone with the processed glycerol in the presence of catalyst **592** to produce a polyol copolymer product.

Carbonylation of Epoxide Derived from Nutrient Fermentation in the Integrated Process

[0107] In another aspect, provided herein is carbonylation of an epoxide derived from fermenting nutrients in an integrated process. With reference to **FIG. 6**, process **600** is an exemplary process that includes fermenting nutrient medium **612** to produce an alcohol. For example, a suitable nutrient medium may contain a metabolizable sugar and energy sources, protein complexes, vitamins, and minerals well known to those having ordinary skill with fermentation. The alcohol is separated from the fermentation zone and dehydrated to produce alkene **614**. The alkene is then oxidized to produce epoxide **618**, which then reacts with a syngas

606 in carbonylation unit **622** to produce carbonylation product **632** and hydrogen-enriched syngas **642**. In some embodiments, the hydrogen-enriched syngas **642** is used in ammonia formation **644**. In some embodiments, the syngas **606** is derived from gasification **604** of a carbonaceous source **602**, including for example, biomass, methane, and petroleum-based materials.

Nutrients

[0108] In some embodiments, the nutrient comprises simple sugars, complex sugars, complex carbohydrates, polysaccharides, protein complexes, protein hydrolysates or a mixture of the foregoing. Any suitable methods for the maintenance and growth of bacterial cells may be used for fermentation. For example, fermentation conditions may include a suitable temperature. In some variations, fermentation may be performed at a temperature between about 250°C and about 600°C, or between about 300°C and about 400°C.

Alcohol Dehydration

[0109] In some embodiments, the dehydration comprises removal of a hydroxyl group and a hydrogen atom from an alcohol to produce an alkene. Any suitable methods for dehydration of the alcohol to the corresponding unsaturated hydrocarbon may be used.

[0110] In some variations, dehydration comprises passing vaporized alcohol through a tube packed with coarse granules of alumina and maintained at a temperature of about 250-300 °C, 300-350 °C, about 350-400 °C, about 400-450 °C, or about 450-500 °C. In some embodiments, the alcohol is dehydrated at about 50-100 °C, about 100-150 °C, about 150-200 °C, about 200-250 °C, or about 250-300 °C, with use of chemical dehydrating agents. In some embodiments, the dehydration agent comprises sulfuric acid. In some embodiments, the process produces methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, or a mixture of the foregoing. In some embodiments, the process produces ethanol.

[0111] Integrated chemical dehydration processes such as alcohol dehydration to form an alkene may therefore become a critical process operations factor in maintaining efficient water usage throughout the plant under such conditions as described above.

Alkene Oxidation

[0112] Alkene oxidation comprises converting an alkene to an alkene oxide or epoxide, such as ethylene oxide. Suitable methods for oxidation of an alkene to produce an epoxide may be used. For example, such methods include the use of silver epoxidation catalysts and/or promoted silver epoxidation catalysts.

[0113] In some embodiments, the process produces an epoxide selected from the group consisting of ethylene oxide, propylene oxide, 1,2-butene oxide, 2,3-butene oxide, cyclohexene oxide, 3-vinyl cyclohexene oxide, epichlorohydrin, glycidyl esters, glycidyl ethers, styrene oxides, and epoxides of higher alpha olefins. In some embodiments, the process produces ethylene oxide.

[0114] In some embodiments, the alkene is oxidized by an oxygen gas. In some embodiments, the oxygen gas is derived from air separation. In some embodiments, the oxygen is derived from carbon dioxide electrolysis. Carbon dioxide electrolysis or conversion as used below refers to any electrochemical process where carbon dioxide, carbonate, or bicarbonate is converted into another chemical substance in any step of the electrolysis process.

[0115] An electrochemical cell typically contains an anode, a cathode and an electrolyte. Catalysts can be placed on the anode, at both the anode and cathode, or just the cathode. Moreover, the catalysts can be placed in the electrolyte or in combinations with the anode and cathode to promote desired electrochemical reactions. In some embodiments, the catalyst comprises one or more of the following: Ni, Cu, Au, Ru, Rh, Hg, Sn, Zr, Al, Co, Fe, Cr, Mn, V, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Si, Ti, Pb, Bi, Sb, Te, U, Sm, La, Ce and Nd.

[0116] In some embodiments, the catalysts enhance the carbon dioxide conversion rate or conversion of other chemical compounds. These may include, for example, catalytically active elements, helper catalysts, which are any organic molecule or ion, or a mixture of organic molecules and/or ions, that does at least one of the following: a) speeds up a chemical reaction or b) lowers the overpotential of the reaction, without being substantially consumed in the process; and helper polymers, which refers to a polymer that does at least one of the following: a) speeds

up a chemical reaction; b) increases the current seen in an electrochemical reaction at a given potential; or c) increases the selectivity of a reaction. Reaction types involved in carbon dioxide conversion to other chemicals include homogeneously catalyzed reactions, heterogeneously catalyzed reactions, chemical reactions in power plants, chemical reactions in chemical plants, and chemical reactions in fuel cells.

[0117] When an electrochemical cell is used as a carbon dioxide conversion system, a reactant comprising carbon dioxide, carbonate or bicarbonate is fed into the cell. A voltage is applied and the carbon dioxide reacts to form new chemical compounds. In some embodiments, the carbon dioxide used in the electrochemical reaction is derived from an alcohol fermentation. In some embodiments, the carbon dioxide used in the electrochemical reaction is derived from the alkene oxidation process. In some embodiments, the carbon dioxide used in the electrochemical reaction is derived from syngas. In some embodiments, the carbon dioxide used in the electrochemical reaction is derived from a nutrient fermentation, an alkene oxidation process, and syngas or combinations thereof. In some embodiments, the electrochemical reaction consumes carbon dioxide to form oxygen and carbon monoxide. In some embodiments, the electrochemical reaction converts carbon dioxide, carbonate and bicarbonate or mixtures thereof to oxygen and carbon monoxide.

[0118] Carbon dioxide electrolysis can help with reducing carbon dioxide emission from large scale industrial facilities and eliminate the need for an air separation unit to supply oxygen gas.

[0119] A nutrient fermentation process can be used to produce an epoxide in all integrated processes described herein.

Downstream Reactions with Hydrogen-Enriched Syngas

[0120] In some embodiments, the hydrogen-enriched syngas is integrated into the downstream chemical production processes to make a variety of valuable products. In some embodiments, the hydrogen-enriched syngas has a $H_2:CO$ ratio of at least 1.5, at least 2, at least 2.5, at least 3.0, at least 3.5, at least 4.0, at least 4.5, at least 5.0, at least 5.5, at least 6.0, at least

6.5, at least 7.0, at least 7.5, at least 8.0, at least 8.5, at least 9.0, at least 9.5, or at least 10. In some embodiments, the hydrogen-enriched syngas is integrated into a Fischer-Tropsch process to produce Fischer-Tropsch products. The high purity stream of hydrogen gas produced in the systems and processes herein may be directed to a hydrogen fuel cell for energy consumption. In some embodiments, the hydrogen-enriched syngas can react with a hydrogen fuel cell to generate electrical energy. In some embodiments, the hydrogen-enriched syngas can react with a nitrogen gas to produce ammonia. In some embodiments, the ammonia can further react with carbon dioxide to produce urea.

[0121] In some embodiments, the hydrogen-enriched syngas can be further fed to a reactor configured for Fischer-Tropsch process 744, as depicted exemplary process 700 in FIG. 7. In some embodiments, the hydrogen-enriched syngas can be further fed to a cell configured as a hydrogen fuel cell power source 742, as depicted again in process 700. Again with reference to FIG. 7, process 700 may also include fermenting nutrients in step 712 to produce alcohol 714; dehydrating the alcohol to produce alkene 716; oxidizing the alkene with oxygen to produce epoxide 718; gasifying 702 a carbonaceous source to produce a syngas stream with $H_2:CO < 1$; conditioning syngas 704; carbonylation of the epoxide with syngas stream 722 to produce carbonylation product 732; and utilizing the epoxide carbonylation product in downstream chemical production processes to make derivatives. For example, in some variations, such downstream processes may include reacting with glycerol to produce polyols. In some embodiments, the alcohol may be separated from other fermentation byproducts prior to dehydrating the alcohol. In some embodiments, a hydrogen-enriched syngas stream is diverted for non-chemical synthesis uses such as for sale in the fuel or power industries or for sale as a commodity chemical.

[0122] In some embodiments, the hydrogen-enriched syngas derived from a carbonylation reaction is used to carbonylate an epoxide in a second carbonylation reaction. With reference to FIG. 8, process 800 is an exemplary process wherein the epoxide is carbonated with syngas 804 in first carbonylation unit 822 and second carbonylation unit 824. The first hydrogen-enriched gas is combined with carbon dioxide to produce methanol 842. The methanol is then subjected

to methanol-to-olefins process **844** where an alkene product stream is generated. The alkene product stream is subjected to alkene oxidation process **818** generating an epoxide stream. In certain embodiments, oxygen may be obtained from the separation of air. The second hydrogen-enriched syngas can be used for further hydrogenation reactions **846**. In some embodiments, carbon monoxide is added downstream to the first carbonylation unit. A second carbonylation reaction is performed with the beta-lactone produced in second carbonylation **826**. Such a reaction yields an anhydride product stream which may be used as an intermediate in downstream chemical production processes. In some embodiments, the anhydride product stream is subjected to hydrogenation process **846** for conversion to valuable chemicals. Depending on the type of catalyst used and the anhydride chemical structure produced in step **846**, a variety of hydrogenated products is produced. For example, such hydrogenated products may include tetrahydrofuran, butanediol, and gamma butyrolactone.

[0123] The second carbonylation process may be used in all integrated processes described herein to increase the $H_2:CO$ ratio in the syngas.

[0124] In some embodiments, a process comprises gasifying carbonaceous material to produce syngas comprising the molecular component carbon monoxide; carbonylating a first reagent comprising ethylene oxide with the syngas to produce a carbonylation product comprising beta-propiolactone and a hydrogen-enriched syngas; and reacting the enriched syngas comprising hydrogen with a second reagent comprising an alkene to produce an aldehyde or an isoaldehyde. With reference to **FIG. 9**, process **900** is an exemplary process that involves producing aldehydes and isoaldehydes. In some embodiments, the integrated aldehyde and isoaldehyde production process **900** occurs when alkenes **918** derived from alcohol dehydration are contacted with syngas where and undergo hydroformylation **942** in the presence of a catalyst to produce an aldehyde and isoaldehyde stream.

[0125] In some embodiments, processes are provided for integrating plant operations using a carbon dioxide electrolyzer for the generation of higher value chemicals. With reference to **FIG. 10**, process **1000** is an exemplary process that involves electrolyzing the carbon dioxide to produce oxygen and carbon monoxide **1002**; fermenting nutrients to produce an alcohol and

carbon dioxide **1012**; dehydrating the alcohol to produce alkene **1014**; oxidizing the alkene with the oxygen to produce epoxide **1016**; and carbonylating the epoxide with the carbon monoxide in the presence of a carbonylation catalyst to produce beta-lactone product **1022**. In one variation, the electrolyzing step may be performed in a solid oxide electrolyser. In some embodiments, the processes include an alcohol separation step comprising distillation. In some embodiments, the processes include a dehydration step such as using molecular sieve and pervaporation. In some embodiments, the carbon dioxide sources used in electrolysis is derived from alcohol fermentation **1012**, alkene oxidation **1016**, a syngas production stream containing carbon dioxide, or a mixture of the foregoing. The oxygen stream **1004** is processed and optionally purified.

[0126] In some embodiments, the optionally purified oxygen stream **1004** is used in alkene oxidation **1016** thus creating an alternative or concurrent stream to alcohol dehydration for epoxide production. In some embodiments, the carbon monoxide stream **1006** is processed and optionally purified. In some embodiments, the optionally purified carbon monoxide stream **1006** is mixed with epoxides from alkene oxidation **1016** in carbonylation unit **1022** where epoxide carbonylation products are produced. Carbonylation products made by certain embodiments of the processes in this disclosure include, for example, beta-lactones and beta-lactone polymers **1032**.

[0127] With reference to **FIG. 11A**, process **1100** is an exemplary process to produce ammonia, urea, and a copolymer. The process comprises providing syngas **1106** derived from gasification of biomass or fossil-fuel-based sources **1104**; providing a nutrient for fermentation to produce an alcohol and carbon dioxide **1112**; dehydrating the alcohol to produce alkene **1114**; providing nitrogen and oxygen from air separation unit **1152**; combining the oxygen with the alkene in a catalytic reaction to produce an epoxide and carbon dioxide **1116**; reacting the epoxide with the syngas in the presence of carbonylation catalyst **1122** to produce beta-lactone product **1132**; recovering a hydrogen-enriched syngas stream which has a higher hydrogen-to-carbon monoxide ratio than starting syngas stream **1142**; purifying a plant oil during processing **1182**; subjecting the plant oil to a transesterification process with alcohol and the hydrogen-

enriched syngas stream to generate long-chain alkyl esters and glycerol **1184**; processing the long-chain alkyl esters and the glycerol by-product into separate streams **1186**; and copolymerizing the beta-lactone with the processed glycerol in the presence of a catalyst to produce a polyol copolymer product **1192**. In some embodiments, alcohol **1113** produced from nutrient fermentation **1112** can be used in the plant oil extraction process **1182** as shown in **FIG. 11B**. In some embodiments, gas produced from the gasification **1104** of carbonaceous sources **1102** can be directly used for producing ammonia **1162** by reacting with N₂ from the air separation **1152** without going through the carbonylation reaction **1122** as shown in **FIG. 11B**.

Integrated Process for Production of Monomers and Polymers

[0128] Provided herein are systems and methods to produce monomer, polymer, copolymer and/or terpolymer products. Preferred embodiments of the present invention are directed to integrated processes for producing monomers including acrylonitrile, butadiene, and styrene. In certain preferred embodiments, the present invention is directed to integrated processes for producing polymers, copolymers and terpolymers including polyacrylonitriles, styrene butadiene copolymers, styrene butadiene block copolymers, and acrylonitrile styrene butadiene terpolymers.

[0129] In certain embodiments, acrylonitrile compounds and other nitrile compounds that may be produced from beta-hydroxy amides and/or beta-lactones. In certain embodiments, the processes include the steps: separating air into an oxygen gas and a nitrogen gas; gasifying a carbonaceous material to produce a raw syngas stream comprising carbon monoxide, carbon dioxide and hydrogen gas; fermenting a nutrient to produce a biobased alcohol; dehydrating a portion of the biobased alcohol to produce a biobased alkene; oxidizing the biobased alkene with the oxygen to produce a biobased epoxide; carbonylating said biobased epoxide with said raw syngas to produce a biobased beta-lactone, a hydrogen stream and carbon dioxide stream; hydrogenating the nitrogen gas with the hydrogen gas to produce ammonia; reacting the biobased beta-lactone with the ammonia to produce beta-alanine-n-3-hydroxy-1-oxypropyl, beta-alanine, and 3-hydroxypropanamide; and dehydrating 3-hydroxypropanamide to produce acrylamide and acrylonitrile. In certain embodiments, 3-hydroxypropanamide is combined with

ammonia in water. In certain embodiments, 3-hydroxypropanamide is combined with ammonium hydroxide in water. In certain embodiments, 3-hydroxypropanamide is combined with ammonia and a dehydration agent. In some embodiments, the dehydration agent may be phosphorous pentoxide, an organophosphorous compound, a carbodiimide compound, a triazine compound, an organosilicon compound, a transition metal complex, or an aluminum complex.

[0130] The acrylonitrile compounds and other nitrile compounds produced according to the methods described herein may, in some variations, be used as a monomer for the industrial production of polymers, copolymers, and/or terpolymers.

[0131] For example, acrylonitrile produced according to the methods described herein may be used in the production of polyacrylonitrile. In some aspects, provided is a method of producing polyacrylonitrile, comprising: producing acrylonitrile according to any of the methods described herein; and polymerizing the acrylonitrile under suitable conditions to produce polyacrylonitrile

[0132] Certain embodiments of the present invention are directed to a process to produce ammonia, monomers, copolymer, and terpolymer products. The process comprises gasification of carbonaceous material for providing syngas comprising carbon monoxide and hydrogen gas; separating air to produce oxygen gas and nitrogen gas; fermenting a nutrient to produce ethanol; producing butadiene from a portion of the ethanol; dehydrating a portion of the ethanol to produce ethylene; oxidizing the ethylene with the oxygen gas in a catalytic reaction to produce an epoxide; carbonylating the epoxide with the syngas to produce a carbonylation product comprising beta-lactone, succinic anhydride, and hydrogen-enriched syngas; dehydrating the succinic anhydride to produce tetrahydrofuran; reacting the tetrahydrofuran with the beta-lactone to produce a cyclohexene; producing styrene from the cyclohexene; catalytically reducing the nitrogen gas with the hydrogen-enriched syngas to produce ammonia; reacting the beta-lactone with ammonia to produce 3-hydroxypropanamide; and dehydrating the 3-hydroxypropanamide to produce acrylonitrile. In certain embodiments, the processes include the steps: dehydrating the cyclohexene to produce benzoic acid; dehydration of the benzoic acid to produce benzene; and reacting the benzene with the ethylene to produce styrene. In certain embodiments the

cyclohexene is 7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid. In certain preferred embodiments, the butadiene and styrene may be copolymerized to produce styrene-butadiene copolymer products. In certain preferred embodiments, the acrylonitrile, styrene and butadiene may be polymerized to produce acrylonitrile-styrene-butadiene terpolymer products.

[0133] In certain embodiments, the processes include a step of coupled dehydration and dehydrogenation of ethanol to produce butadiene. In certain preferred embodiments, ethanol may be fed to a fixed-bed reactor charged with a metal oxide catalyst to catalyze coupled dehydration and dehydrogenation. In some embodiments, the metal oxide may be a single oxide from the group including Al_2O_3 , Fe_2O_3 , ArO_3 , and ThO_2 . In some embodiments, the metal oxide may be a binary oxide from the group including $\text{Al}_2\text{O}_3\text{:ZnO}$, $\text{Al}_2\text{O}_3\text{:Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{:MgO}$, $\text{Al}_2\text{O}_3\text{:CaO}$. In some embodiments, the metal oxide may be a ternary oxide such as $\text{Al}_2\text{O}_3\text{:Fe}_2\text{O}_3\text{:Cr}_2\text{O}_3$.

[0134] In certain embodiments, the processes include a reaction of furan with beta-propiolactone comprising a cycloaddition reaction where the two methylene carbons of the lactone ring react. In certain embodiments, the beta-propiolactone undergoes rearrangement to form acrylic acid which then undergoes cycloaddition. On the other hand, it is also possible that the propiolactone reacts directly with the furan in a concerted fashion.

[0135] In certain embodiments, the reaction of beta-propiolactone with furan is promoted by introducing heat. In certain embodiments, the cycloaddition reaction is promoted by contacting a mixture of the furan and the beta propiolactone with a catalyst. In certain embodiments, the cycloaddition reaction is promoted by contacting a mixture of the furan and the beta propiolactone with a Lewis acid catalyst. In certain embodiments, the cycloaddition reaction is conducted in a solvent. In certain embodiments, the cycloaddition reaction is conducted in the gas phase. In certain embodiments, the cycloaddition reaction is conducted in the presence of a solid catalyst. In certain embodiments, the cycloaddition reaction is conducted in by heating a mixture of the furan and the beta propiolactone in the presence of a solid Lewis acid catalyst. In certain embodiments, the cycloaddition reaction is conducted in by heating a mixture of the furan and the beta propiolactone in a solvent in the presence of a homogeneous Lewis acid catalyst in a continuous stirred tank reactor. In certain embodiments, the cycloaddition reaction is conducted

in by flowing a mixture of the furan and the beta propiolactone through a plug flow reactor in a solvent in the presence of a homogeneous Lewis acid catalyst.

[0136] In certain embodiments, the step of dehydrating the cyclohexene comprises heating the cyclohexene compound in the presence of a dehydrating agent. In certain embodiments, the step includes continuously removing water vapor from a reaction zone where the dehydration reaction is performed. In certain embodiments, the dehydration reaction is acid catalyzed. In certain embodiments, the dehydration reaction is acid catalyzed by phosphoric or sulfuric acid. In certain embodiments, the dehydration reaction is acid catalyzed. In certain embodiments, the dehydration reaction is acid catalyzed by a solid supported acid catalyst. In certain embodiments, the dehydration reaction is performed by heating the cyclohexene ring-containing compound in the presence of sulfuric acid. In certain embodiments, the dehydration reaction is performed by heating the cyclohexene ring-containing compound in the presence of sulfonic acid resin. In certain embodiments where the cyclohexene ring-containing compound comprises an ester, the dehydration step results in hydrolysis of the ester group. In certain embodiments where the cyclohexene ring-containing compound comprises an ester, the dehydration conditions promote ester hydrolysis and the product is an acid. In certain embodiments, where the cyclohexene ring-containing compound is an acid or an ester, the dehydration step results in formation a carboxylate salt.

[0137] In certain embodiments, the dehydration reaction is catalyzed by reaction with a strong base. In certain embodiments, where the cyclohexene compound comprises a substituent that is a carboxylate ester, the dehydration reaction comprises treating the ester with a strong base in the presence of water to form a salt of an aromatic acid. In certain embodiments, the salt formed comprises potassium benzoate. In certain embodiments, the potassium benzoate from the dehydration step is continuously fed to the disproportionation reaction. In certain embodiments, the alcohol liberated by the ester hydrolysis is recovered and used to generate additional acrylate ester from beta propiolactone or acrylic acid formed during an earlier step in the process.

[0138] In certain embodiments, the product of the dehydration reaction comprises benzoic acid, a salt of benzoic acid, an ester of benzoic acid, benzoic anhydride or a mixture of any two

or more of these. In certain embodiments, the product of the dehydration reaction comprises benzoic acid. In certain embodiments, the product of the dehydration reaction comprises a compound selected from the group consisting of: methyl benzoate, ethyl benzoate, butyl benzoate, 2-ethylhexylbenzoate, a benzoic ester of a C.sub.3-12 alcohol, and a mixture of any two or more of these. In certain embodiments, the product of the dehydration reaction comprises potassium benzoate. In certain embodiments, the product of the dehydration reaction comprises sodium benzoate. In certain embodiments, the product of the dehydration reaction comprises benzoic acid anhydride.

[0139] In certain embodiments, the processes include a step of disproportionating a product of the dehydration of a cyclohexene. In certain embodiments, the dehydration of a cyclohexene produces a monosubstituted benzene compound such as benzoic acid. In certain embodiments, the processes include a step of converting the monosubstituted benzene compound to a metal benzoate salt. In certain embodiments, the processes include a step of treating the metal benzoate salt with a suitable catalyst. In certain embodiments, the step of treating the metal benzoate salt with a catalyst is performed at a temperature above about 200°C.

[0140] In certain embodiments, the catalyst utilized for the disproportionation comprises a transition metal. In certain embodiments, the disproportionation is performed in the presence of a catalyst comprising a Group 10-12 transition metal. In certain embodiments, the disproportionation is performed in the presence of a catalyst comprising a Group 12 transition metal. In certain embodiments, the disproportionation is performed in the presence of a catalyst comprising cadmium. In certain embodiments, the disproportionation is performed in the presence of a catalyst comprising zinc. In certain embodiments, the disproportionation is performed in the presence of a catalyst comprising mercury.

[0141] In certain embodiments, the process further includes continuously withdrawing a stream containing benzene from the disproportionation reaction zone. In certain embodiments, the process further includes a step of purifying the benzene withdrawn from the reaction zone. In certain embodiments, the purification includes distillation, extraction, crystallization or combinations of these.

[0142] In certain embodiments, the benzene from the disproportionation reaction is treated to convert it to styrene. This transformation is readily accomplished using known processes, for example, by reaction of the benzene with ethylene to produce ethyl benzene which is then oxidatively dehydrogenated to provide styrene. In certain embodiments, where either or both of the ethylene oxide and furan feeds to the process are derived from biomass, the resulting benzene contains 2, 4, or 6 biobased carbon atoms. This product can be reacted with ethylene derived from bio ethanol to provide biobased styrene thereby providing an opportunity to make biobased polystyrene and related products. The styrene thereby produced may contain 2, 4, 6, or 8 biobased carbon atoms. In certain embodiments, the styrene produced has the novel attribute of containing four carbon atoms derived from ethanol. The integrated process to biobased terephthalic acid and styrene is remarkably carbon efficient since each step is high yielding and every carbon atom in the feedstocks is incorporated into useful final products.

[0143] As used herein, in some variations, the term “about” preceding one or more numerical values means the numerical value $\pm 5\%$. It should be understood that reference to “about” a value or parameter herein includes (and describes) embodiments that are directed to that value or parameter per se. For example, description referring to “about x” includes description of “x” per se.

CLAIMS

What is claimed:

1. A process for producing a bio-based hydrogenation product comprising:
providing an epoxide;
providing a syngas comprising hydrogen and carbon monoxide;
carbonylating the epoxide in the presence of the syngas to produce a carbonylation product and a hydrogen-enriched syngas;
separating air to produce a nitrogen gas and an oxygen gas; and
combining the nitrogen gas with the hydrogen-enriched syngas to produce a hydrogenation product.
2. The process of claim 1, wherein the hydrogenation product comprises ammonia.
3. The process of claim 1 or 2, further comprising combining the hydrogenation product with carbon dioxide to produce urea.
4. The process of claim 3, wherein the carbon dioxide is produced by alcohol fermentation, produced by alkene oxidation, provided in syngas, or any combination thereof.
5. The process of claim 3 or 4, wherein the yield of urea is at least about 65%.
6. The process of any one of claims 3 to 5, wherein the combining of the hydrogenation product with the carbon dioxide further produces ammonium carbamate.
7. The process of any one of claims 1 to 6, wherein the syngas is produced by gasification of a carbonaceous source or methane reforming.
8. The process of any one of claims 1 to 7, wherein the epoxide is carbonylated in the presence of the syngas and a carbonylation catalyst.
9. The process of any one of claims 1 to 8, wherein the epoxide is ethylene oxide.
10. The process of any one of claims 1 to 9, wherein the carbonylation product comprises beta-propiolactone, polypropiolactone, a polyol, or any combination thereof.

11. The process of any one of claims 1 to 10, further comprising contacting the carbonylation product with a glycerol to form a polyol copolymer.
12. The process of claim 11, wherein the glycerol is derived from plant oil transesterification.
13. The process of any one of claims 1 to 12, wherein the epoxide is derived from oxidizing an alkene.
14. The process of claim 13, wherein the alkene is derived from dehydrating an alcohol.
15. The process of claim 14, wherein the alcohol is derived from fermenting a nutrient.
16. A process of producing a bio-based hydrogenation product comprising:
providing an epoxide;
providing a syngas comprising hydrogen and carbon monoxide;
carbonylating the epoxide in the presence of the syngas to produce a carbonylation product and a hydrogen-enriched syngas;
combining a glycerol and the carbonylation product to produce a copolymer.
17. The process of claim 16, wherein the carbonylation product comprises beta-lactone, polypropiolactone, a polyol, or any combination thereof.
18. The process of claim 16 or 17, wherein the epoxide is ethylene oxide.
19. The process of any one of claims 16 to 18, wherein the epoxide is carbonylated with the syngas in the presence of a carbonylation catalyst.
20. The process of any one of claims 16 to 19, wherein the epoxide is derived from oxidizing an alkene.
21. The process of claim 20, wherein the alkene is derived from dehydrating an alcohol.
22. The process of claim 21, wherein the alcohol is derived from fermenting a nutrient.

23. The process of any one of claims 16 to 21, wherein the syngas is produced by gasification of a carbonaceous source or methane reforming.
24. The process of any one of claims 16 to 23, further comprising contacting the hydrogen-enriched syngas with an alkene and carbon monoxide to produce an aldehyde product.
25. The process of claim 24, wherein the alkene is produced by dehydrating an alcohol.
26. The process of claim 24 or 25, wherein the carbon monoxide is derived from syngas.
27. The process of any one of claims 16 to 26, further comprising contacting the hydrogen-enriched syngas with a nitrogen gas to produce ammonia.
28. The process of claim 27, further comprising combining the ammonia with carbon dioxide to produce urea.
29. The process of any one of claims 16 to 28, wherein the glycerol is derived from transesterifying a plant oil.
30. The process of claim 29, wherein the plant oil is a vegetable oil.
31. The process of claim 29 or 30, wherein the glycerol is derived from transesterifying a plant oil in the presence of a catalyst, a chain transfer agent, or a mixture of the foregoing.
32. A process comprising:
providing a syngas comprising hydrogen and carbon monoxide;
fermenting a nutrient to produce an alcohol;
hydrating the alcohol to produce an alkene;
oxidizing the alkene with an oxygen gas to produce an epoxide; and
carbonylating the epoxide with the syngas to produce a carbonylation product and a hydrogen-enriched syngas.
33. The process of claim 32, further comprising combining the hydrogen-enriched syngas with a nitrogen gas to produce a hydrogenation product.
34. The process of claim 33, wherein the hydrogenation product comprises ammonia.

35. The process of claim 33 or 34, further comprising combining the hydrogenation product with carbon dioxide to produce urea.
36. The process of any one of claims 32 to 35, wherein the carbonylation product comprises beta-propiolactone, polypropiolactone, a polyol, or any combination thereof.
37. The process of any one of claims 32 to 36, wherein fermenting a nutrient further produces a carbon dioxide gas.
38. The process of claim 37, wherein the carbon dioxide gas is combined with the ammonia to produce urea.
39. The process of claim 37, wherein the carbon dioxide gas is electrolyzed to produce oxygen and carbon monoxide.
40. The process of any one of claims 32 to 39, further comprising contacting the hydrogen-enriched syngas with an alkene and carbon monoxide to produce an aldehyde product.
41. The process of any one of claims 32 to 40, further comprising feeding the hydrogen-enriched syngas into a methanol synthesis reactor.
42. The process of any one of claims 32 to 41, further comprising contacting the carbonylation product with a glycerol to produce a copolymer.
43. The process of claim 42, wherein the glycerol is derived from transesterifying a plant oil.
44. The process of claim 43, wherein the plant oil is a vegetable oil.
45. The process of any one of claims 32 to 44, wherein the nutrient comprises a sugar, a carbohydrate, a polysaccharide, a protein complex, a protein hydrolysate, or any combination thereof.
46. An integrated process, comprising:
separating air into an oxygen gas stream and nitrogen gas stream;
gasifying a carbonaceous material to produce a raw syngas stream comprising carbon monoxide, carbon dioxide and hydrogen gas;

fermenting plant matter to produce a biobased alcohol stream;
reducing a portion of the biobased alcohol stream to produce a biobased alkene;
oxidizing the biobased alkene with the oxygen stream to produce a biobased epoxide, and;
carbonylating the biobased epoxide with the raw syngas stream to produce a biobased carbonylation product, a hydrogen gas stream and carbon dioxide stream.

47. The process of claim 46, wherein the biobased carbonylation product comprises a beta-lactone stream and a succinic anhydride stream.

48. The process of claim 47, wherein the succinic anhydride stream is reduced to produce tetrahydrofuran.

49. The process of claim 48, wherein the tetrahydrofuran is reacted with a portion of the beta-lactone stream to produce a cyclohexene derivative.

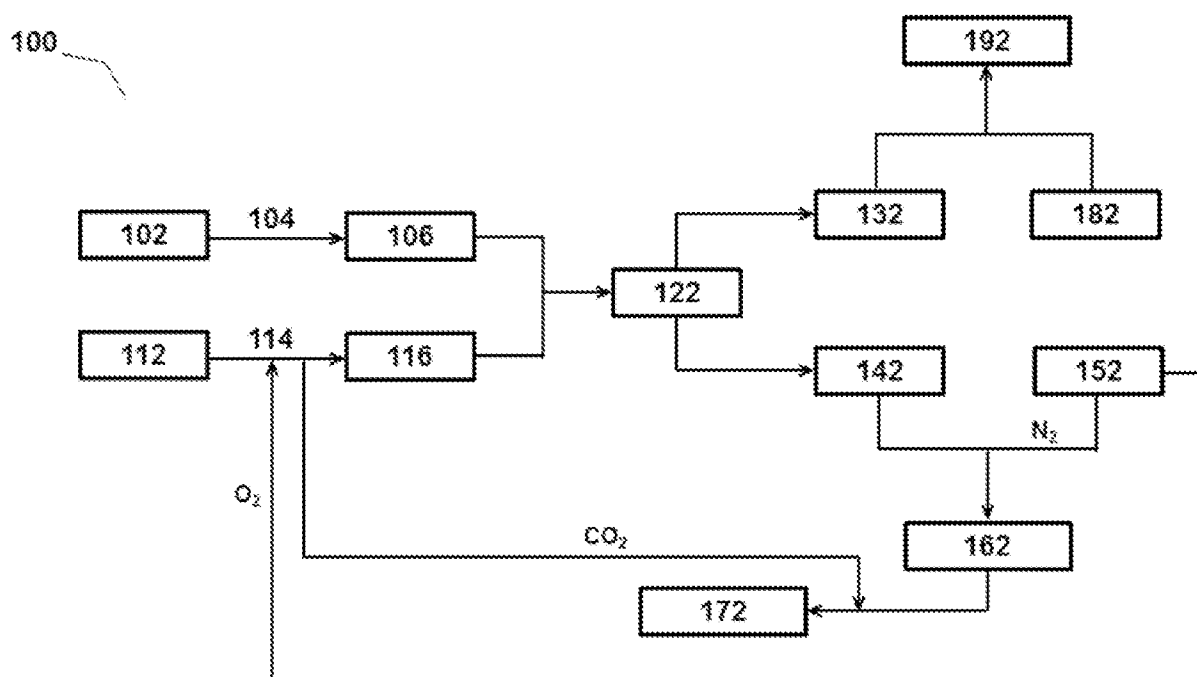
50. The process of claim 49, wherein the cyclohexene derivative is used to produce a biobased styrene product.

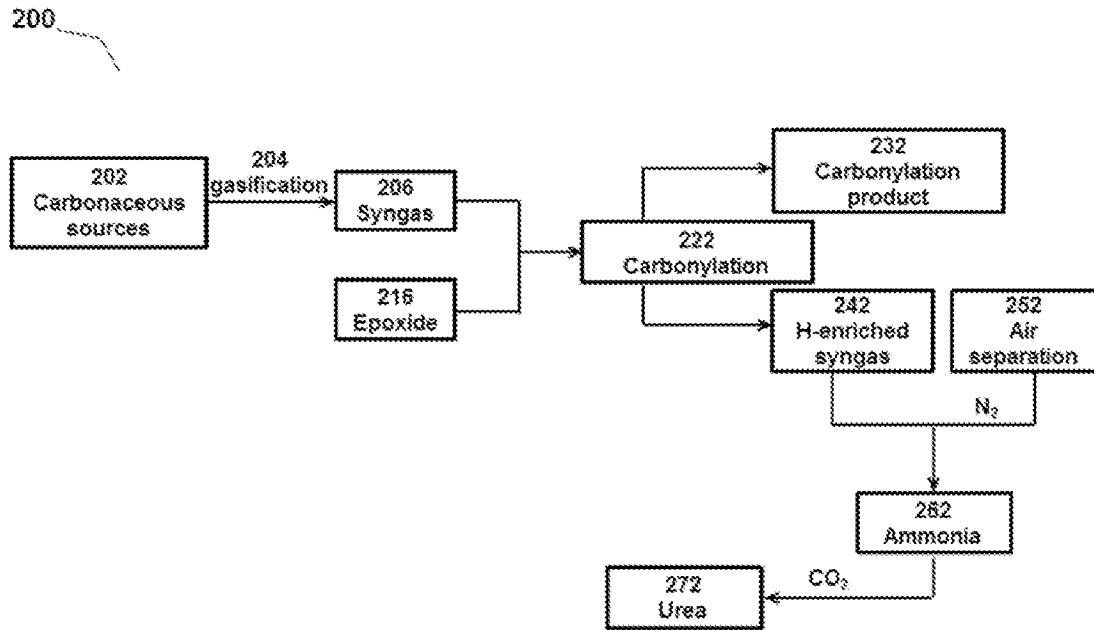
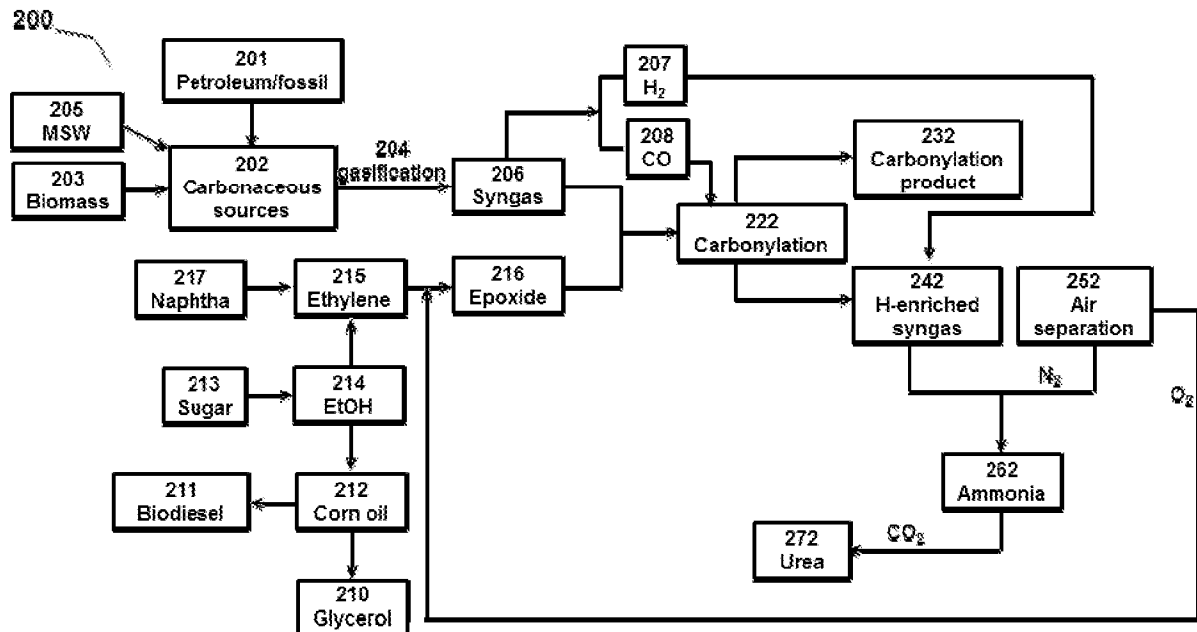
51. The process of any one of claims 46 to 50, wherein the nitrogen gas stream is hydrogenated by the hydrogen gas stream to produce an ammonia stream.

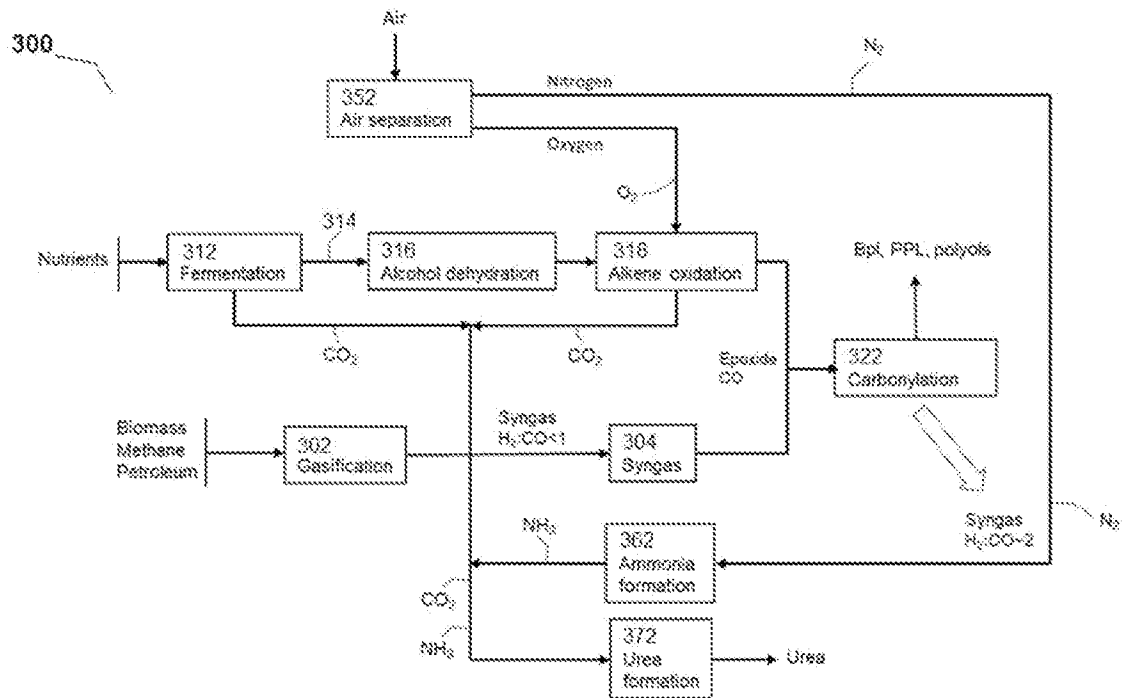
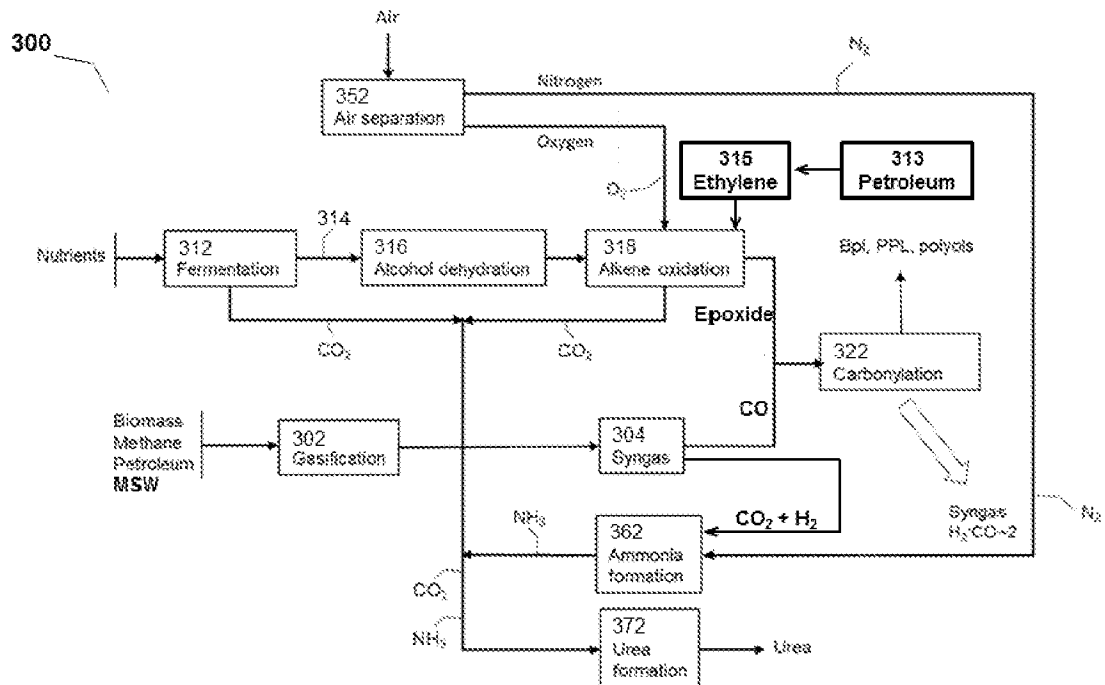
52. The process of claim 51, wherein the ammonia stream is reacted with a portion of the beta-lactone stream to produce 3-hydroxypropanamide.

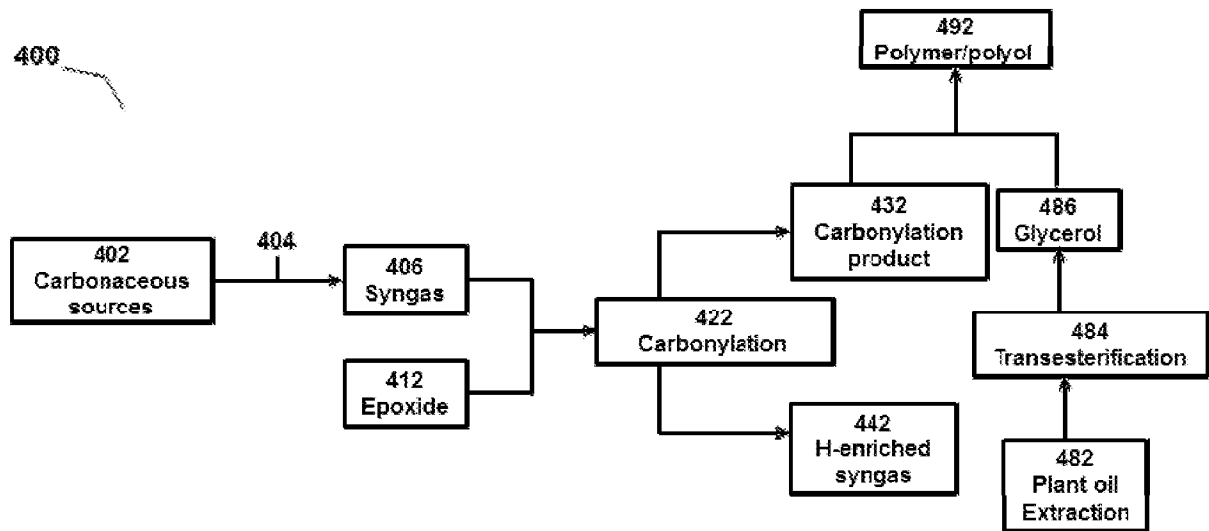
53. The process of claim 52, wherein the 3-hydroxypropanamide is dehydrated to produce a biobased acrylonitrile product.

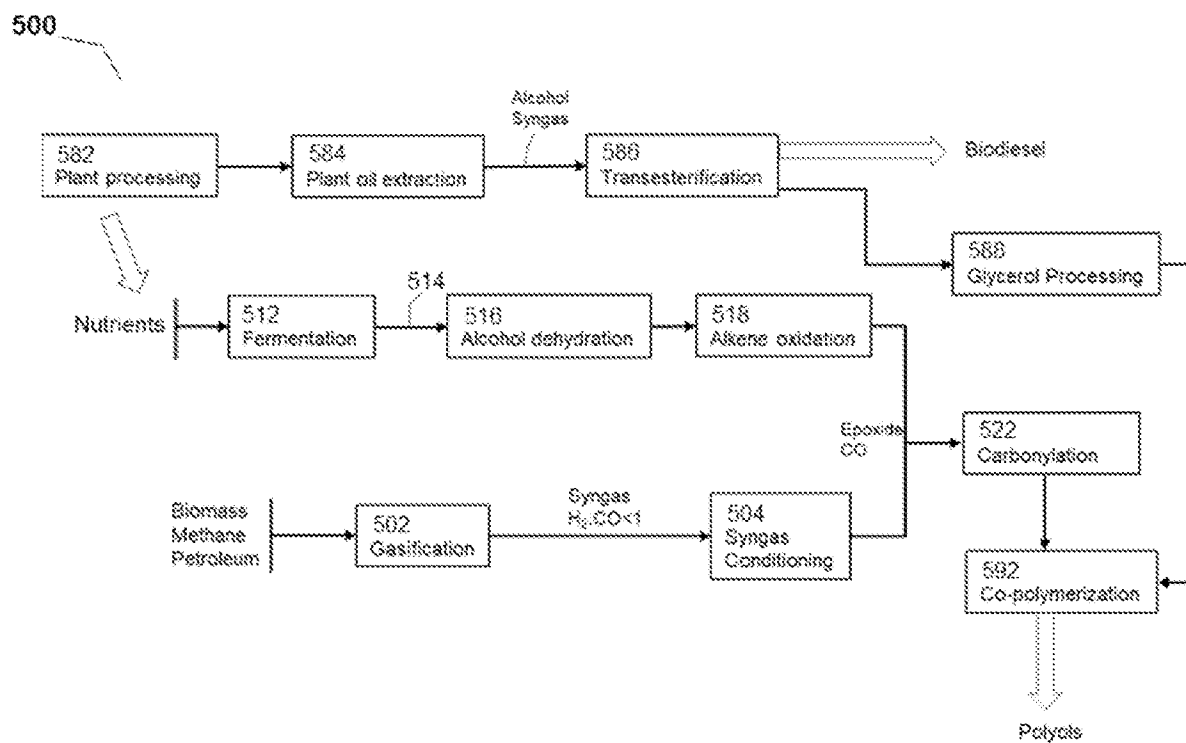
54. The process of any one of claims 46 to 53, wherein a biobased 1,3-butadiene product is produced from the biobased alcohol stream.

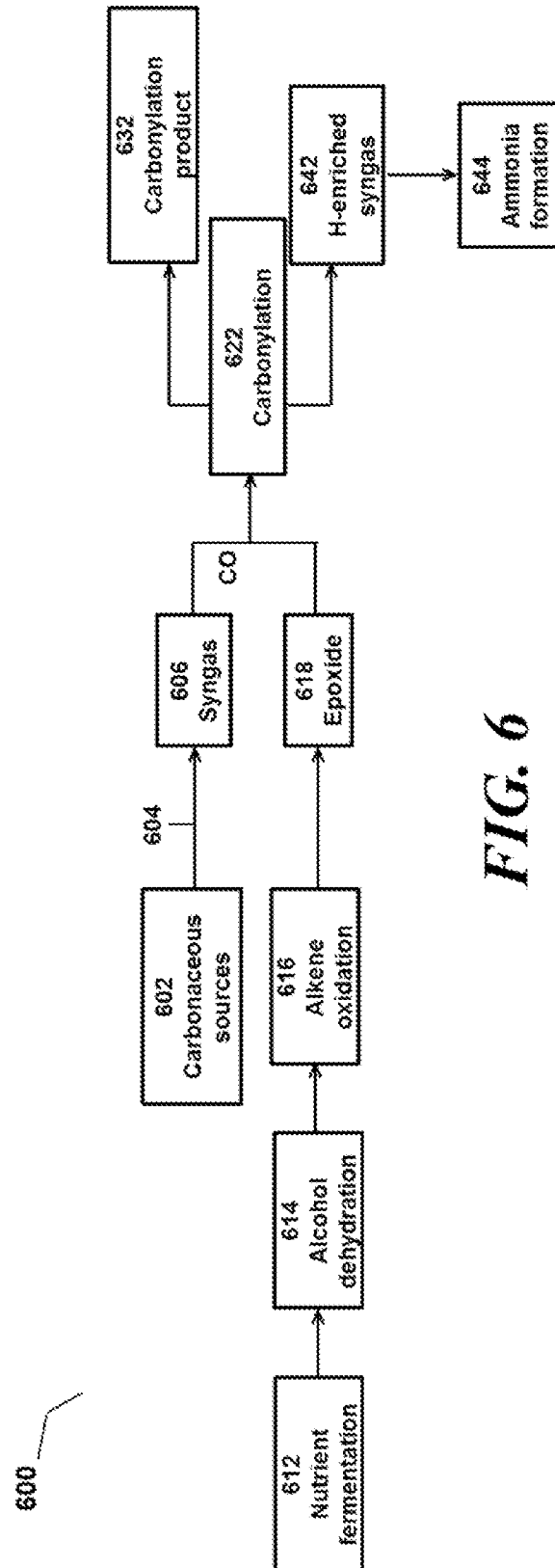
**FIG. 1**

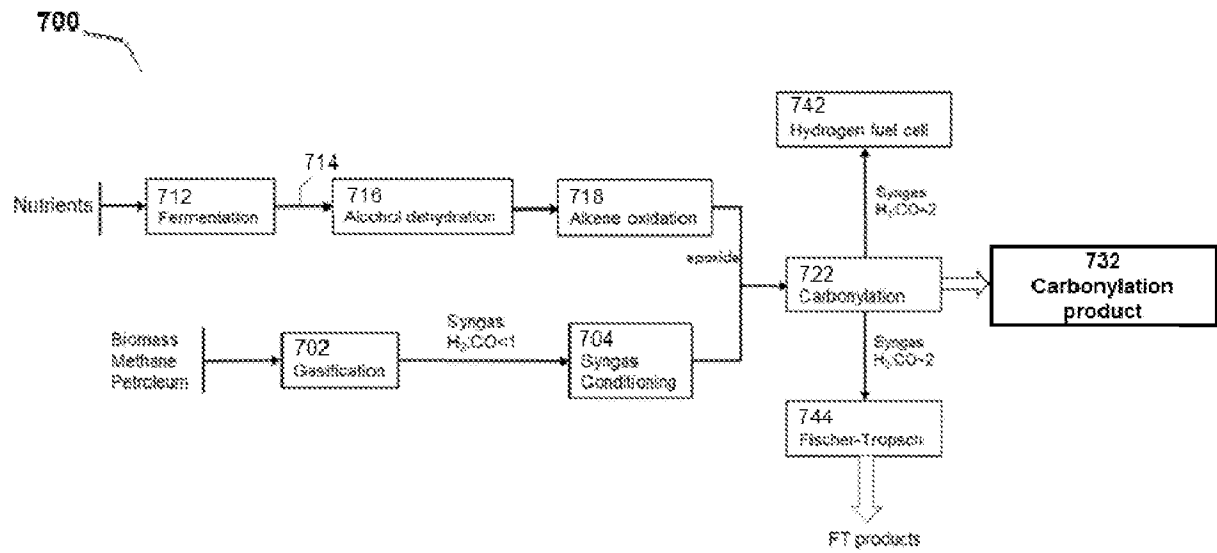
**FIG. 2A****FIG. 2B**

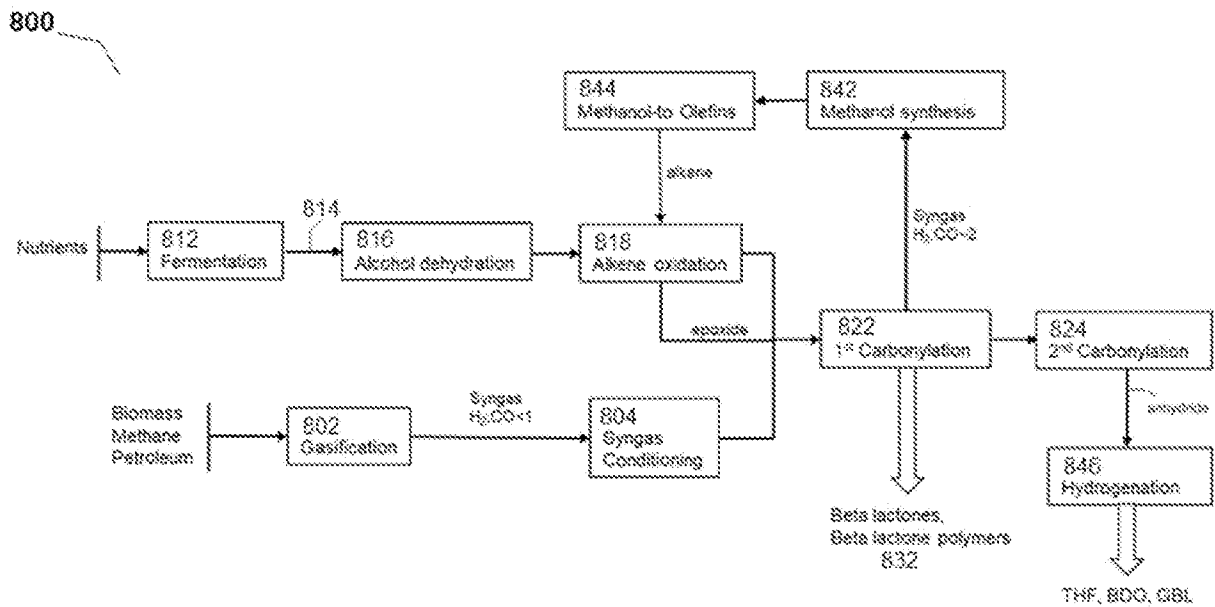
**FIG. 3A****FIG. 3B**

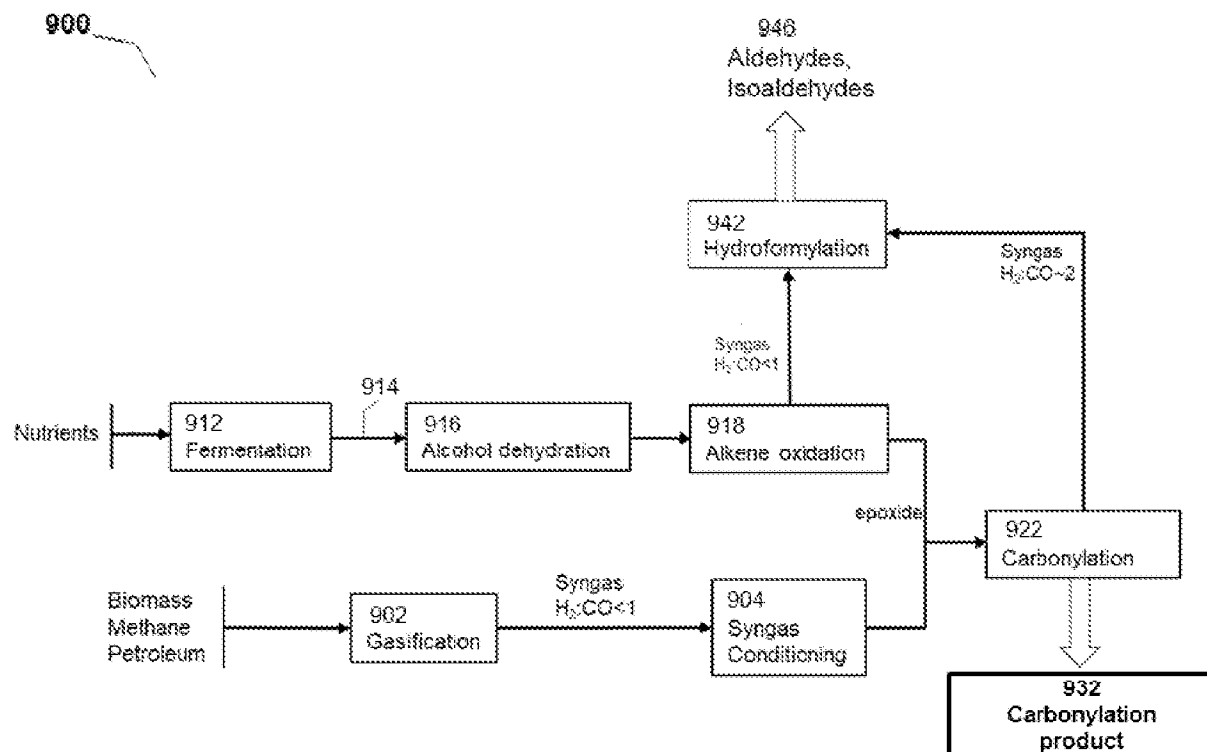
**FIG. 4**

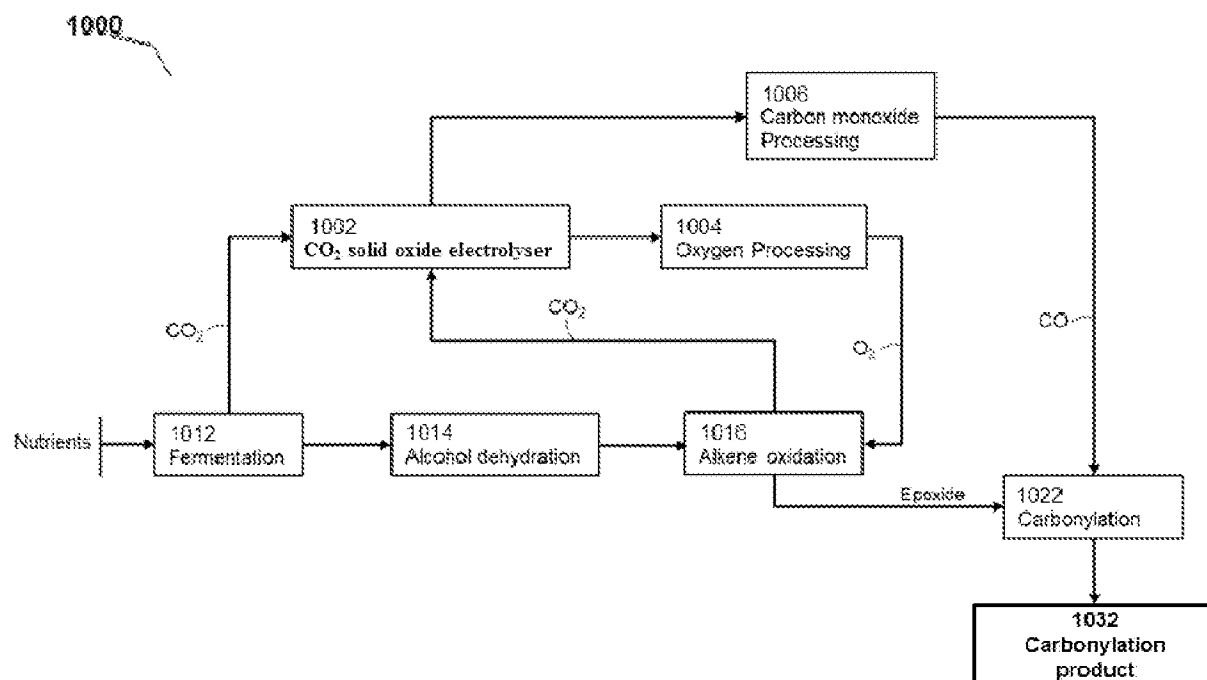
**FIG. 5**

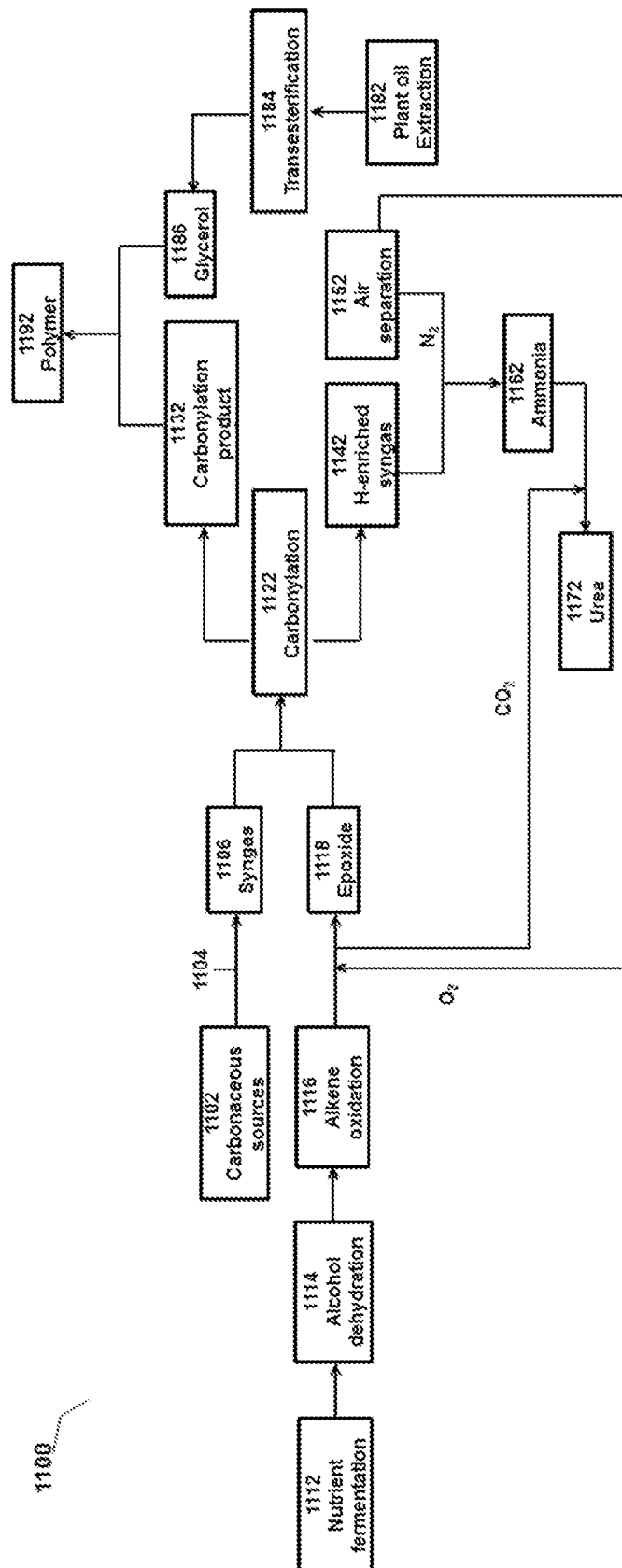
**FIG. 6**

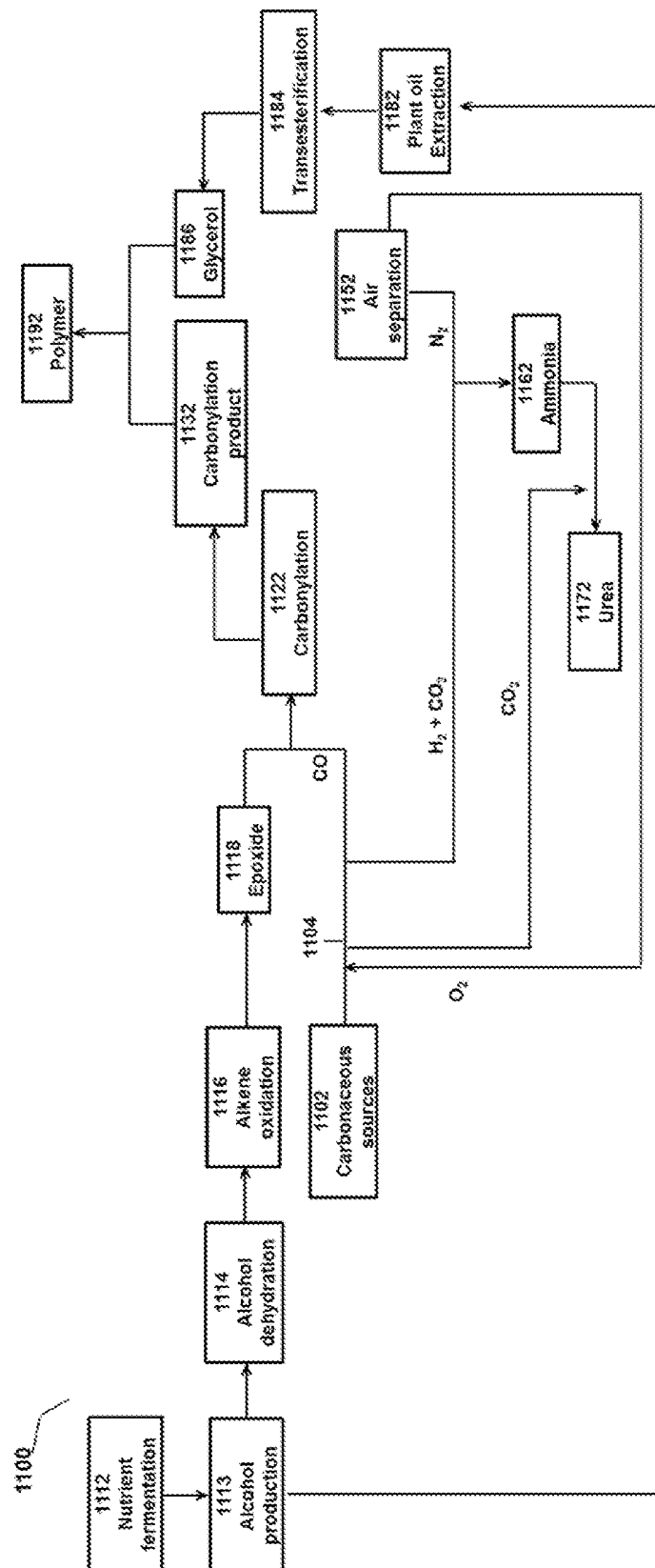
**FIG. 7**

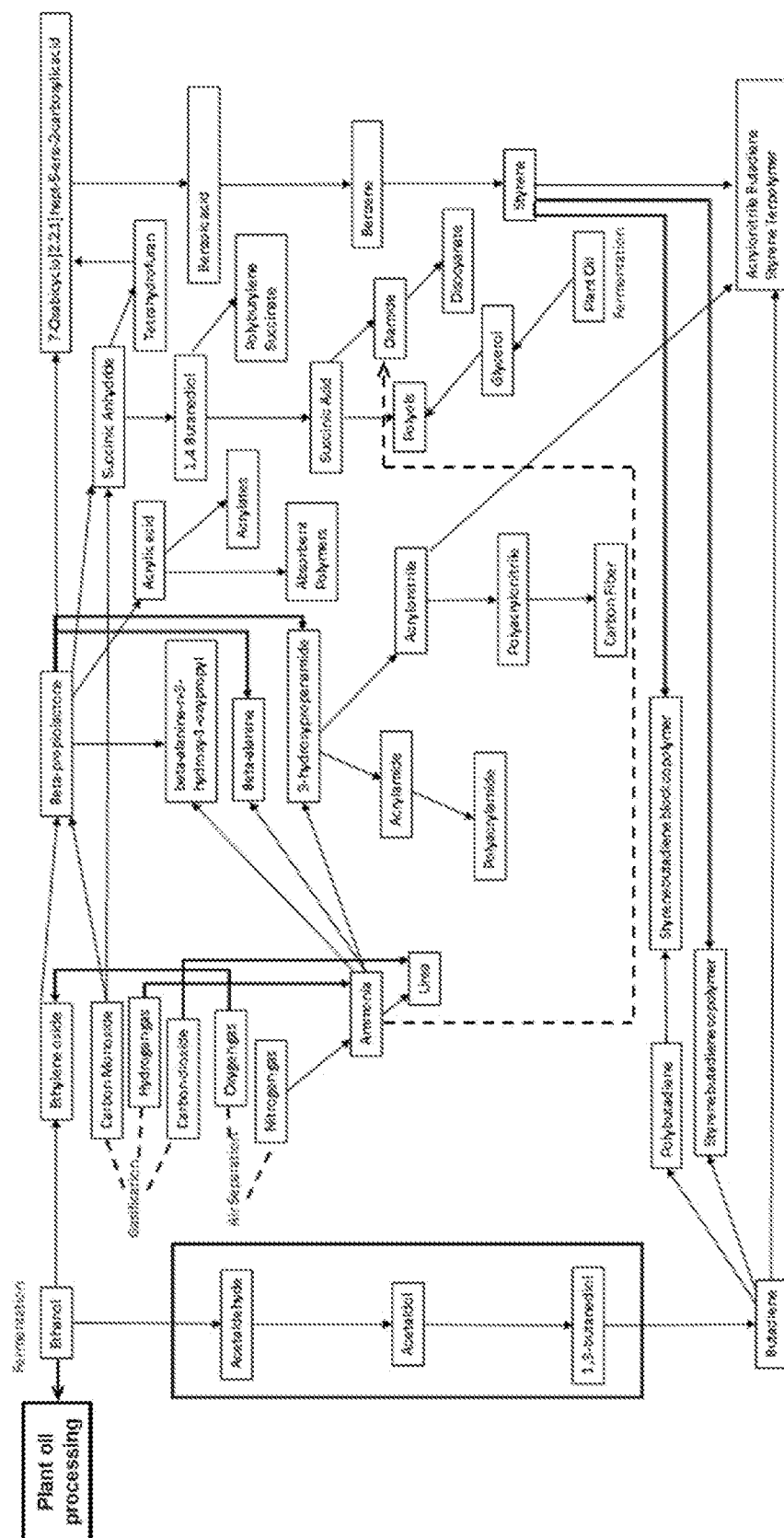
**FIG. 8**

**FIG. 9**

**FIG. 10**







INTERNATIONAL SEARCH REPORT

International application No.

PCT/US19/30468

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C01B 3/50; C07C 233/02, 235/02, 255/08; C07D 305/12; H01M 8/0612, 8/0668 (2019.01)

CPC - B01J 31/00; C07C 233/02, 235/02, 255/08; C07D 305/12; C10G 2/00; H01M 8/0612, 8/0668

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2017/0107103 A1 (NOVOMER INC.) 20 April 2017; abstract; figure 3; paragraphs [0007], [0016], [0041], [0064], [0077], [0082], [0096], [0123], [0126], [0160], [0183], [0205]; claim 1	1-2, 3/1-2, 4/3/1-2, 16-17, 18/16-17, 32-34, 35/33-34, 46-50, 51/46-50
Y	US 2,936,593 A (GRUNBERG) 17 May 1960; column 2, lines 38-42; claim 1	1-2, 3/1-2, 4/3/1-2, 46-50, 51/46-50
Y	US 2007/0287863 A1 (ROMITI) 13 December 2007; abstract	3/1-2, 4/3/1-2, 35/33-34
Y	US 2011/0092743 A1 (LI et al.) 21 April 2011; paragraphs [0015], [0023]	16-17, 18/16-17
Y	US 2011/0112315 A1 (KUNG et al.) 12 May 2011; paragraph [0023]	32-34, 35/33-34, 46-50, 51/46-50
Y	US 2017/0001939 A1 (SOOKRAJ et al.) 05 January 2017; paragraphs [0015], [0023]	32-34, 35/33-34, 46-50, 51/46-50
A	US 2005/0101760 A1 (ZHONG et al.) 12 May 2005; paragraph [0092]	52/51/46-50, 53/52/51/46-50

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

14 June 2019 (14.06.2019)

Date of mailing of the international search report

09 JUL 2019

Name and mailing address of the ISA/

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P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US19/30468

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-15, 19-31, 36-45, 54
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.