

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 February 2012 (09.02.2012)

PCT

(10) International Publication Number
WO 2012/018961 A2

(51) International Patent Classification:
C07C 29/149 (2006.01)

77059 (US). PAN, Tianshu [CN/US]; 4115 Crimson Oak Court, Houston, Texas 77059 (US).

(21) International Application Number:
PCT/US2011/046504

(74) Agents: GENDZWILL, Jeffrey T. et al.; ROBERTS MLOTKOWSKI SAFRAN & COLE, 7918 Jones Branch Drive, Suite 500, McLean, Virginia 22102 (US).

(22) International Filing Date:
3 August 2011 (03.08.2011)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/852,269 6 August 2010 (06.08.2010) US

(71) Applicant (for all designated States except US):
CELANESE INTERNATIONAL CORPORATION
[US/US]; 1601 West LBJ Freeway, Dallas, Texas 75234 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SARAGER, Lincoln [US/US]; 16110 La Cabana Drive, Houston, Texas 77062 (US). WARNER, R., Jay [US/US]; 3507 East Pine Brook Way, Houston, Texas 77062 (US). WEINER, Heiko [DE/US]; 4827 Baywood Drive, Pasadena, Texas 77505 (US). CHAPMAN, Josefina [US/US]; 15427 Rocky Oak Court, Houston, Texas 77059 (US). CUNNINGHAM, Robert [US/US]; 5952 Portman Place, Palinfeld, Indiana 46168 (US). GRUSENDORF, Gerald [US/US]; 14003 Savannah Landing Lane, Rosharon, Texas 77583 (US). HORTON, Trinity [US/US]; 322 Remington Green Court, Houston, Texas 77073 (US). JEVTIC, Radmila [RS/US]; 7033 Red Coral Drive, Pasadena, Texas 77505 (US). JOHNSTON, Victor J. [US/US]; 3234 Pleasant Cove Court, Houston, Texas

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))



WO 2012/018961 A2

(54) Title: PROCESS FOR PURIFYING ETHANOL

(57) Abstract: In one embodiment, the invention is to a process for producing ethanol. The process comprises the step of hydro-generating an acetic acid feed stream in a first reactor to form a crude ethanol product. The crude ethanol product may comprise, among other components, ethanol, acetaldehyde, and residual acetic acid. The process further comprises the step of recovering acetaldehyde from the crude ethanol product. The process further comprises the steps of feeding a first portion of the recovered acetaldehyde to the first reactor and reacting the first portion of the recovered acetaldehyde in the first reactor to form additional ethanol. In addition, the inventive process may comprise the steps of feeding a second portion of the recovered acetaldehyde to a second reactor and reacting the second portion of the recovered acetaldehyde in the second reactor to form an additional product.

PROCESS FOR PURIFYING ETHANOL

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Utility Application No. 12/852,269 filed on August 6, 2010, which claims priority to U.S. Provisional Application No. 61/300,815, filed on February 2, 2010, and to U.S. Provisional Application No. 61/332,699, filed on May 7, 2010, the entire contents and disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for producing and/or purifying ethanol and, in particular, to processes for producing and/or purifying ethanol from the hydrogenation of acetic acid.

BACKGROUND OF THE INVENTION

[0003] Ethanol for industrial use is conventionally produced from petrochemical feed stocks, such as oil, natural gas, or coal, from feed stock intermediates, such as syngas, or from starchy materials or cellulose materials, such as corn or sugar cane. Conventional methods for producing ethanol from petrochemical feed stocks, as well as from cellulose materials, include the acid-catalyzed hydration of ethylene, methanol homologation, direct alcohol synthesis, and Fischer-Tropsch synthesis. Instability in petrochemical feed stock prices contributes to fluctuations in the cost of conventionally produced ethanol, making the need for alternative sources of ethanol production all the greater when feed stock prices rise. In addition to petrochemical feed stocks synthesis methods, starchy materials, as well as cellulose materials, may be converted to ethanol by fermentation. Fermentation methods are typically employed for production of consumable ethanol, although the ethanol thus produced may also be suitable for fuels. Fermentation of starchy or cellulose materials also competes with food sources and places restraints on the amount of ethanol that can be produced for industrial use.

[0004] Ethanol production via the reduction of alkanolic acids and/or other carbonyl group-containing compounds has been widely studied, and a variety of combinations of catalysts, supports, and operating conditions have been mentioned in the literature. During the reduction of alkanolic acid, e.g., acetic acid, other compounds are formed with ethanol or are formed in side

reactions. These impurities 1) limit the production of ethanol; and 2) impede the purification of the ethanol in the crude reaction product.

[0005] In view of these shortcomings, a need remains for improved separation schemes, which provide the ability to more effectively separate and/or utilize the ethanol impurities.

SUMMARY OF THE INVENTION

[0006] In one embodiment, the present invention is to a process for producing ethanol. The process comprises the step of hydrogenating an acetic acid feed stream in a first reactor to form a crude ethanol product. The crude ethanol product may comprise, among other components, ethanol, acetaldehyde, and residual acetic acid. The process further comprises the step of recovering acetaldehyde from the crude ethanol product. The process further comprises the steps of feeding a first portion of the recovered acetaldehyde to the first reactor and reacting the first portion of the recovered acetaldehyde in the first reactor to form additional ethanol. In addition, the inventive process may comprise the steps of feeding a second portion of the recovered acetaldehyde to a second reactor and reacting the second portion of the recovered acetaldehyde in the second reactor to form an additional product. Preferably, the additional product comprises at least one of n-butanol, 1,3-butanediol, crotonaldehyde, and derivatives thereof.

BRIEF DESCRIPTION OF DRAWINGS

[0007] The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts.

[0008] FIG. 1 is a schematic diagram of a hydrogenation system in accordance with one embodiment of the present invention.

[0009] FIG. 2 is a schematic diagram of the reaction zone in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The present invention relates to processes for recovering ethanol produced by a hydrogenation process comprising hydrogenating acetic acid in a first reactor in the presence of a catalyst. In particular, the present invention relates to recovering acetaldehyde from the crude ethanol and utilizing the recovered acetaldehyde to produce ethanol and additional valuable

commercial products, e.g., n-butanol, 1,3-butanediol, crotonaldehyde, and derivatives thereof. The process includes the step of separating acetaldehyde from the crude ethanol product and feeding a first portion of the separated acetaldehyde back to the first reaction zone, preferably to the acetic acid feed, to the vaporizer, or to the first hydrogenation reactor. The first portion of returned acetaldehyde may be reacted under hydrogenation conditions in the first reactor to form additional ethanol, e.g., ethanol in addition to the ethanol formed via the initial acetic acid hydrogenation reaction. The process further comprises the step of feeding a second portion of the separated acetaldehyde to a second reactor. The second reactor is different from the first reactor. For example, the second reactor may employ a different catalyst than the first reactor. The process also comprises the step of reacting the second portion of the recovered acetaldehyde in the second reactor to form an additional product. Because the second reactor is different from the first reactor, the additional product formed by the second reactor may be entirely different from the crude ethanol product formed in the first reactor. As a result, the processes of the present invention advantageously provide for 1) more efficient use of existing feed stocks; and 2) the production of different products from the same feed stocks. Beneficially, the acetaldehyde, which is conventionally an impurity that is typically wasted, is utilized to produce both additional ethanol and other commercial products, e.g., n-butanol, 1,3-butanediol, and crotonaldehyde.

[0011] In a preferred embodiment, the acetaldehyde is separated from a crude ethanol product derivative stream that comprises both the acetaldehyde and ethyl acetate. This beneficially allows a major portion of the ethyl acetate in the derivative stream to be removed without allowing the same to build up throughout the separation process. Embodiments of the present invention beneficially may be used in applications for recovering and/or purifying ethanol on an industrial scale.

Hydrogenation Process

[0012] The process of the present invention may be used with any hydrogenation process for producing ethanol. The materials, catalysts, reaction conditions, and separation processes that may be used in the hydrogenation of acetic acid are described further below.

[0013] The raw materials, acetic acid and hydrogen, used in connection with the process of this invention may be derived from any suitable source including natural gas, petroleum, coal, biomass, and so forth. As examples, acetic acid may be produced via methanol carbonylation,

acetaldehyde oxidation, ethylene oxidation, oxidative fermentation, and anaerobic fermentation. Methanol carbonylation processes suitable for production of acetic acid are described in U.S. Pat. Nos. 7,208,624; 7,115,772; 7,005,541; 6,657,078; 6,627,770; 6,143,930; 5,599,976; 5,144,068; 5,026,908; 5,001,259; and 4,994,608, the entire disclosures of which are incorporated herein by reference. Optionally, the production of ethanol may be integrated with such methanol carbonylation processes.

[0014] As petroleum and natural gas prices fluctuate becoming either more or less expensive, methods for producing acetic acid and intermediates such as methanol and carbon monoxide from alternate carbon sources have drawn increasing interest. In particular, when petroleum is relatively expensive, it may become advantageous to produce acetic acid from synthesis gas (“syngas”) that is derived from more available carbon sources. U.S. Pat. No. 6,232,352, the entirety of which is incorporated herein by reference, for example, teaches a method of retrofitting a methanol plant for the manufacture of acetic acid. By retrofitting a methanol plant, the large capital costs associated with CO generation for a new acetic acid plant are significantly reduced or largely eliminated. All or part of the syngas is diverted from the methanol synthesis loop and supplied to a separator unit to recover CO, which is then used to produce acetic acid. In a similar manner, hydrogen for the hydrogenation step may be supplied from syngas.

[0015] In some embodiments, some or all of the raw materials for the above-described acetic acid hydrogenation process may be derived partially or entirely from syngas. For example, the acetic acid may be formed from methanol and carbon monoxide, both of which may be derived from syngas. The syngas may be formed by partial oxidation reforming or steam reforming, and the carbon monoxide may be separated from syngas. Similarly, hydrogen that is used in the step of hydrogenating the acetic acid to form the crude ethanol product may be separated from syngas. The syngas, in turn, may be derived from variety of carbon sources. The carbon source, for example, may be selected from the group consisting of natural gas, oil, petroleum, coal, biomass, and combinations thereof. Syngas or hydrogen may also be obtained from bio-derived methane gas, such as bio-derived methane gas produced by landfills or agricultural waste.

[0016] In another embodiment, the acetic acid used in the hydrogenation step may be formed from the fermentation of biomass. The fermentation process preferably utilizes an acetogenic process or a homoacetogenic microorganism to ferment sugars to acetic acid producing little, if any, carbon dioxide as a by-product. The carbon efficiency for the fermentation process

preferably is greater than 70%, greater than 80% or greater than 90% as compared to conventional yeast processing, which typically has a carbon efficiency of about 67%. Optionally, the microorganism employed in the fermentation process is of a genus selected from the group consisting of Clostridium, Lactobacillus, Moorella, Thermoanaerobacter, Propionibacterium, Propionispora, Anaerobiospirillum, and Bacteriodes, and in particular, species selected from the group consisting of Clostridium formicoaceticum, Clostridium butyricum, Moorella thermoacetica, Thermoanaerobacter kivui, Lactobacillus delbrukii, Propionibacterium acidipropionici, Propionispora arboris, Anaerobiospirillum succinicproduces, Bacteriodes amylophilus and Bacteriodes ruminicola. Optionally in this process, all or a portion of the unfermented residue from the biomass, e.g., lignans, may be gasified to form hydrogen that may be used in the hydrogenation step of the present invention. Exemplary fermentation processes for forming acetic acid are disclosed in U.S. Pat. Nos. 6,509,180; 6,927,048; 7,074,603; 7,507,562; 7,351,559; 7,601,865; 7,682,812; and 7,888,082, the entireties of which are incorporated herein by reference. See also U.S. Pub. Nos. 2008/0193989 and 2009/0281354, the entireties of which are incorporated herein by reference.

[0017] Examples of biomass include, but are not limited to, agricultural wastes, forest products, grasses, and other cellulosic material, timber harvesting residues, softwood chips, hardwood chips, tree branches, tree stumps, leaves, bark, sawdust, off-spec paper pulp, corn, corn stover, wheat straw, rice straw, sugarcane bagasse, switchgrass, miscanthus, animal manure, municipal garbage, municipal sewage, commercial waste, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, grass pellets, hay pellets, wood pellets, cardboard, paper, plastic, and cloth. See, e.g., U.S. Pat. No. 7,884,253, the entirety of which is incorporated herein by reference. Another biomass source is black liquor, a thick, dark liquid that is a byproduct of the Kraft process for transforming wood into pulp, which is then dried to make paper. Black liquor is an aqueous solution of lignin residues, hemicellulose, and inorganic chemicals.

[0018] U.S. Pat. No. RE 35,377, also incorporated herein by reference, provides a method for the production of methanol by conversion of carbonaceous materials such as oil, coal, natural gas and biomass materials. The process includes hydrogasification of solid and/or liquid carbonaceous materials to obtain a process gas which is steam pyrolyzed with additional natural gas to form synthesis gas. The syngas is converted to methanol which may be carbonylated to acetic acid. The method likewise produces hydrogen which may be used in connection with this

invention as noted above. U.S. Pat. No. 5,821,111, which discloses a process for converting waste biomass through gasification into synthesis gas, and U.S. Pat. No. 6,685,754, which discloses a method for the production of a hydrogen-containing gas composition, such as a synthesis gas including hydrogen and carbon monoxide, are incorporated herein by reference in their entireties.

[0019] The acetic acid fed to the hydrogenation reaction may also comprise other carboxylic acids and anhydrides, as well as acetaldehyde and acetone. Preferably, a suitable acetic acid feed stream comprises one or more of the compounds selected from the group consisting of acetic acid, acetic anhydride, acetaldehyde, ethyl acetate, and mixtures thereof. These other compounds may also be hydrogenated in the processes of the present invention. In some embodiments, the presence of carboxylic acids, such as propanoic acid or its anhydride, may be beneficial in producing propanol. Water may also be present in the acetic acid feed.

[0020] Alternatively, acetic acid in vapor form may be taken directly as crude product from the flash vessel of a methanol carbonylation unit of the class described in U.S. Pat. No. 6,657,078, the entirety of which is incorporated herein by reference. The crude vapor product, for example, may be fed directly to the ethanol synthesis reaction zones of the present invention without the need for condensing the acetic acid and light ends or removing water, saving overall processing costs.

[0021] The acetic acid may be vaporized at the reaction temperature, following which the vaporized acetic acid may be fed along with hydrogen in an undiluted state or diluted with a relatively inert carrier gas, such as nitrogen, argon, helium, carbon dioxide and the like. For reactions run in the vapor phase, the temperature should be controlled in the system such that it does not fall below the dew point of acetic acid. In one embodiment, the acetic acid may be vaporized at the boiling point of acetic acid at the particular pressure, and then the vaporized acetic acid may be further heated to the reactor inlet temperature. In another embodiment, the acetic acid is mixed with other gases before vaporizing, followed by heating the mixed vapors up to the reactor inlet temperature. Preferably, the acetic acid is transferred to the vapor state by passing hydrogen and/or recycle gas through the acetic acid at a temperature at or below 125°C, followed by heating of the combined gaseous stream to the reactor inlet temperature.

[0022] Some embodiments of the process of hydrogenating acetic acid to form ethanol may include a variety of configurations using a fixed bed reactor or a fluidized bed reactor. In many

embodiments of the present invention, an “adiabatic” reactor can be used; that is, there is little or no need for internal plumbing through the reaction zone to add or remove heat. In other embodiments, a radial flow reactor or reactors may be employed, or a series of reactors may be employed with or without heat exchange, quenching, or introduction of additional feed material. Alternatively, a shell and tube reactor provided with a heat transfer medium may be used. In many cases, the reaction zone may be housed in a single vessel or in a series of vessels with heat exchangers therebetween.

[0023] In preferred embodiments, the catalyst is employed in a fixed bed reactor, e.g., in the shape of a pipe or tube, where the reactants, typically in the vapor form, are passed over or through the catalyst. Other reactors, such as fluid or ebullient bed reactors, can be employed. In some instances, the hydrogenation catalysts may be used in conjunction with an inert material to regulate the pressure drop of the reactant stream through the catalyst bed and the contact time of the reactant compounds with the catalyst particles.

[0024] The hydrogenation reaction may be carried out in either the liquid phase or vapor phase. Preferably, the reaction is carried out in the vapor phase under the following conditions. The reaction temperature may range from 125°C to 350°C, e.g., from 200°C to 325°C, from 225°C to 300°C, or from 250°C to 300°C. The pressure may range from 10 kPa to 3000 kPa, e.g., from 50 kPa to 2300 kPa, or from 100 kPa to 1500 kPa. The reactants may be fed to the reactor at a gas hourly space velocity (GHSV) of greater than 500 hr⁻¹, e.g., greater than 1000 hr⁻¹, greater than 2500 hr⁻¹ or even greater than 5000 hr⁻¹. In terms of ranges the GHSV may range from 50 hr⁻¹ to 50,000 hr⁻¹, e.g., from 500 hr⁻¹ to 30,000 hr⁻¹, from 1000 hr⁻¹ to 10,000 hr⁻¹, or from 1000 hr⁻¹ to 6500 hr⁻¹.

[0025] The hydrogenation optionally is carried out at a pressure just sufficient to overcome the pressure drop across the catalytic bed at the GHSV selected, although there is no bar to the use of higher pressures, it being understood that considerable pressure drop through the reactor bed may be experienced at high space velocities, e.g., 5000 hr⁻¹ or 6,500 hr⁻¹.

[0026] Although the reaction consumes two moles of hydrogen per mole of acetic acid to produce one mole of ethanol, the actual molar ratio of hydrogen to acetic acid in the feed stream may vary from about 100:1 to 1:100, e.g., from 50:1 to 1:50, from 20:1 to 1:2, or from 12:1 to 1:1. Most preferably, the molar ratio of hydrogen to acetic acid is greater than 2:1, e.g., greater than 4:1 or greater than 8:1.

[0027] Contact or residence time can also vary widely, depending upon such variables as amount of acetic acid, catalyst, reactor, temperature, and pressure. Typical contact times range from a fraction of a second to more than several hours when a catalyst system other than a fixed bed is used, with preferred contact times, at least for vapor phase reactions, of from 0.1 to 100 seconds, e.g., from 0.3 to 80 seconds or from 0.4 to 30 seconds.

[0028] The hydrogenation of acetic acid to form ethanol is preferably conducted in the presence of a hydrogenation catalyst. Suitable hydrogenation catalysts include catalysts comprising a first metal and optionally one or more of a second metal, a third metal or any number of additional metals, optionally on a catalyst support. The first and optional second and third metals may be selected from Group IB, IIB, IIIB, IVB, VB, VIB, VIIB, VIII transition metals, a lanthanide metal, an actinide metal or a metal selected from any of Groups IIIA, IVA, VA, and VIA. Preferred metal combinations for some exemplary catalyst compositions include platinum/tin, platinum/ruthenium, platinum/rhenium, palladium/ruthenium, palladium/rhenium, cobalt/palladium, cobalt/platinum, cobalt/chromium, cobalt/ruthenium, cobalt/tin, silver/palladium, copper/palladium, copper/zinc, nickel/palladium, gold/palladium, ruthenium/rhenium, and ruthenium/iron. Exemplary catalysts are further described in U.S. Pat. No. 7,608,744 and U.S. Pub. No. 2010/0029995, the entireties of which are incorporated herein by reference. In another embodiment, the catalyst comprises a Co/Mo/S catalyst of the type described in U.S. Pub. No. 2009/0069609, the entirety of which is incorporated herein by reference.

[0029] In one embodiment, the catalyst comprises a first metal selected from the group consisting of copper, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, titanium, zinc, chromium, rhenium, molybdenum, and tungsten. Preferably, the first metal is selected from the group consisting of platinum, palladium, cobalt, nickel, and ruthenium. More preferably, the first metal is selected from platinum and palladium. In embodiments of the invention where the first metal comprises platinum, it is preferred that the catalyst comprises platinum in an amount less than 5 wt.%, e.g., less than 3 wt.% or less than 1 wt.%, due to the high commercial demand for platinum.

[0030] As indicated above, in some embodiments, the catalyst further comprises a second metal, which typically would function as a promoter. If present, the second metal preferably is selected from the group consisting of copper, molybdenum, tin, chromium, iron, cobalt,

vanadium, tungsten, palladium, platinum, lanthanum, cerium, manganese, ruthenium, rhenium, gold, and nickel. More preferably, the second metal is selected from the group consisting of copper, tin, cobalt, rhenium, and nickel. More preferably, the second metal is selected from tin and rhenium.

[0031] In certain embodiments where the catalyst includes two or more metals, e.g., a first metal and a second metal, the first metal is present in the catalyst in an amount from 0.1 to 10 wt.%, e.g., from 0.1 to 5 wt.%, or from 0.1 to 3 wt.%. The second metal preferably is present in an amount from 0.1 to 20 wt.%, e.g., from 0.1 to 10 wt.%, or from 0.1 to 5 wt.%. For catalysts comprising two or more metals, the two or more metals may be alloyed with one another or may comprise a non-alloyed metal solution or mixture.

[0032] The preferred metal ratios may vary depending on the metals used in the catalyst. In some exemplary embodiments, the mole ratio of the first metal to the second metal is from 10:1 to 1:10, e.g., from 4:1 to 1:4, from 2:1 to 1:2, from 1.5:1 to 1:1.5 or from 1.1:1 to 1:1.1.

[0033] The catalyst may also comprise a third metal selected from any of the metals listed above in connection with the first or second metal, so long as the third metal is different from the first and second metals. In preferred aspects, the third metal is selected from the group consisting of cobalt, palladium, ruthenium, copper, zinc, platinum, tin, and rhenium. More preferably, the third metal is selected from cobalt, palladium, and ruthenium. When present, the total weight of the third metal preferably is from 0.05 to 4 wt.%, e.g., from 0.1 to 3 wt.%, or from 0.1 to 2 wt.%.

[0034] In addition to one or more metals, in some embodiments of the present invention the catalysts further comprise a support or a modified support. As used herein, the term “modified support” refers to a support that includes a support material and a support modifier, which adjusts the acidity of the support material.

[0035] The total weight of the support or modified support, based on the total weight of the catalyst, preferably is from 75 to 99.9 wt.%, e.g., from 78 to 97 wt.%, or from 80 to 95 wt.%. In preferred embodiments that utilize a modified support, the support modifier is present in an amount from 0.1 to 50 wt.%, e.g., from 0.2 to 25 wt.%, from 0.5 to 15 wt.%, or from 1 to 8 wt.%, based on the total weight of the catalyst. The metals of the catalysts may be dispersed throughout the support, layered throughout the support, coated on the outer surface of the support (i.e., egg shell), or decorated on the surface of the support.

[0036] As will be appreciated by those of ordinary skill in the art, support materials are selected such that the catalyst system is suitably active, selective and robust under the process conditions employed for the formation of ethanol.

[0037] Suitable support materials may include, for example, stable metal oxide-based supports or ceramic-based supports. Preferred supports include siliceous supports, such as silica, silica/alumina, a Group IIA silicate such as calcium metasilicate, pyrogenic silica, high purity silica, and mixtures thereof. Other supports may include, but are not limited to, iron oxide, alumina, titania, zirconia, magnesium oxide, carbon, graphite, high surface area graphitized carbon, activated carbons, and mixtures thereof.

[0038] As indicated, the catalyst support may be modified with a support modifier. In some embodiments, the support modifier may be an acidic modifier that increases the acidity of the catalyst. Suitable acidic support modifiers may be selected from the group consisting of: oxides of Group IVB metals, oxides of Group VB metals, oxides of Group VIB metals, oxides of Group VIIB metals, oxides of Group VIIIB metals, aluminum oxides, and mixtures thereof. Acidic support modifiers include those selected from the group consisting of TiO_2 , ZrO_2 , Nb_2O_5 , Ta_2O_5 , Al_2O_3 , B_2O_3 , P_2O_5 , and Sb_2O_3 . Preferred acidic support modifiers include those selected from the group consisting of TiO_2 , ZrO_2 , Nb_2O_5 , Ta_2O_5 , and Al_2O_3 . The acidic modifier may also include WO_3 , MoO_3 , Fe_2O_3 , Cr_2O_3 , V_2O_5 , MnO_2 , CuO , Co_2O_3 , and Bi_2O_3 .

[0039] In another embodiment, the support modifier may be a basic modifier that has a low volatility or no volatility. Such basic modifiers, for example, may be selected from the group consisting of: (i) alkaline earth oxides, (ii) alkali metal oxides, (iii) alkaline earth metal metasilicates, (iv) alkali metal metasilicates, (v) Group IIB metal oxides, (vi) Group IIB metal metasilicates, (vii) Group IIIB metal oxides, (viii) Group IIIB metal metasilicates, and mixtures thereof. In addition to oxides and metasilicates, other types of modifiers including nitrates, nitrites, acetates, and lactates may be used. Preferably, the support modifier is selected from the group consisting of oxides and metasilicates of any of sodium, potassium, magnesium, calcium, scandium, yttrium, and zinc, as well as mixtures of any of the foregoing. More preferably, the basic support modifier is a calcium silicate, and even more preferably calcium metasilicate (CaSiO_3). If the basic support modifier comprises calcium metasilicate, it is preferred that at least a portion of the calcium metasilicate is in crystalline form.

[0040] A preferred silica support material is SS61138 High Surface Area (HSA) Silica Catalyst

Carrier from Saint Gobain NorPro. The Saint-Gobain NorPro SS61138 silica exhibits the following properties: contains approximately 95 wt.% high surface area silica; surface area of about 250 m²/g; median pore diameter of about 12 nm; average pore volume of about 1.0 cm³/g as measured by mercury intrusion porosimetry and a packing density of about 0.352 g/cm³ (22 lb/ft³).

[0041] A preferred silica/alumina support material is KA-160 silica spheres from Sud Chemie having a nominal diameter of about 5 mm, a density of about 0.562 g/ml, an absorptivity of about 0.583 g H₂O/g support, a surface area of about 160 to 175 m²/g, and a pore volume of about 0.68 ml/g.

[0042] The catalyst compositions suitable for use with the present invention preferably are formed through metal impregnation of the modified support, although other processes such as chemical vapor deposition may also be employed. Such impregnation techniques are described in U.S. Pat. Nos. 7,608,744 and 7,863,489 and U.S. Pub. No. 2010/0197485 referred to above, the entireties of which are incorporated herein by reference.

[0043] In particular, the hydrogenation of acetic acid may achieve favorable conversion of acetic acid and favorable selectivity and productivity to ethanol. For purposes of the present invention, the term "conversion" refers to the amount of acetic acid in the feed that is converted to a compound other than acetic acid. Conversion is expressed as a mole percentage based on acetic acid in the feed. The conversion may be at least 10%, e.g., at least 20%, at least 40%, at least 50%, at least 60%, at least 70% or at least 80%. Although catalysts that have high conversions are desirable, such as at least 80% or at least 90%, in some embodiments a low conversion may be acceptable at high selectivity for ethanol. It is, of course, well understood that in many cases, it is possible to compensate for conversion by appropriate recycle streams or use of larger reactors, but it is more difficult to compensate for poor selectivity.

[0044] Selectivity is expressed as a mole percent based on converted acetic acid. It should be understood that each compound converted from acetic acid has an independent selectivity and that selectivity is independent from conversion. For example, if 60 mole % of the converted acetic acid is converted to ethanol, we refer to the ethanol selectivity as 60%. Preferably, the catalyst selectivity to ethoxylates is at least 60%, e.g., at least 70%, or at least 80%. As used herein, the term "ethoxylates" refers specifically to the compounds ethanol, acetaldehyde, and ethyl acetate. Preferably, the selectivity to ethanol is at least 80%, e.g., at least 85% or at least

88%. Preferred embodiments of the hydrogenation process also have low selectivity to undesirable products, such as methane, ethane, and carbon dioxide. The selectivity to these undesirable products preferably is less than 4%, e.g., less than 2% or less than 1%. More preferably, these undesirable products are present in undetectable amounts. Formation of alkanes may be low, and ideally less than 2%, less than 1%, or less than 0.5% of the acetic acid passed over the catalyst is converted to alkanes, which have little value other than as fuel.

[0045] The term “productivity,” as used herein, refers to the grams of a specified product, e.g., ethanol, formed during the hydrogenation based on the kilograms of catalyst used per hour. A productivity of at least 100 grams of ethanol per kilogram of catalyst per hour, e.g., at least 400 grams of ethanol per kilogram of catalyst per hour or at least 600 grams of ethanol per kilogram of catalyst per hour, is preferred. In terms of ranges, the productivity preferably is from 100 to 3,000 grams of ethanol per kilogram of catalyst per hour, e.g., from 400 to 2,500 grams of ethanol per kilogram of catalyst per hour or from 600 to 2,000 grams of ethanol per kilogram of catalyst per hour.

[0046] Operating under the conditions of the present invention may result in ethanol production on the order of at least 0.1 tons of ethanol per hour, e.g., at least 1 ton of ethanol per hour, at least 5 tons of ethanol per hour, or at least 10 tons of ethanol per hour. Larger scale industrial production of ethanol, depending on the scale, generally should be at least 1 ton of ethanol per hour, e.g., at least 15 tons of ethanol per hour or at least 30 tons of ethanol per hour. In terms of ranges, for large scale industrial production of ethanol, the process of the present invention may produce from 0.1 to 160 tons of ethanol per hour, e.g., from 15 to 160 tons of ethanol per hour or from 30 to 80 tons of ethanol per hour. Ethanol production from fermentation, due the economies of scale, typically does not permit the single facility ethanol production that may be achievable by employing embodiments of the present invention.

[0047] In various embodiments of the present invention, the crude ethanol product produced by the hydrogenation process, before any subsequent processing, such as purification and separation, will typically comprise unreacted acetic acid, ethanol and water. As used herein, the term “crude ethanol product” refers to any composition comprising from 5 to 70 wt.% ethanol and from 5 to 40 wt.% water. Exemplary compositional ranges for the crude ethanol product are provided in Table 1. The “others” identified in Table 1 may include, for example, esters, ethers, aldehydes, ketones, alkanes, and carbon dioxide.

TABLE 1
CRUDE ETHANOL PRODUCT COMPOSITIONS

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	5 to 70	15 to 70	15 to 50	25 to 50
Acetic Acid	0 to 90	0 to 50	15 to 70	20 to 70
Water	5 to 40	5 to 30	10 to 30	10 to 26
Ethyl Acetate	0 to 30	0 to 20	1 to 12	3 to 10
Acetaldehyde	0 to 10	0 to 3	0.1 to 3	0.2 to 2
Others	0.1 to 10	0.1 to 6	0.1 to 4	--

[0048] In one embodiment, the crude ethanol product comprises acetic acid in an amount less than 20 wt.%, e.g., less than 15 wt. %, less than 10 wt.% or less than 5 wt.%. In embodiments having lower amounts of acetic acid, the conversion of acetic acid is preferably greater than 75%, e.g., greater than 85% or greater than 90%. In addition, the selectivity to ethanol may also be preferably high, and is preferably greater than 75%, e.g., greater than 85% or greater than 90%.

Ethanol Recovery

[0049] FIG. 1 shows hydrogenation system 100, which is suitable for the hydrogenation of acetic acid and separation ethanol from the crude reaction mixture according to some embodiments of the invention. System 100 comprises reaction zone 101 and distillation zone 102. Reaction zone 101 comprises first reactor 103, hydrogen feed line 104 and acetic acid feed line 105. Distillation zone 102 comprises flasher 106, first column 107, second column 108, third column 109, and fourth column 123. Hydrogen and acetic acid are fed to a vaporizer 110 via lines 104 and 105, respectively, to create a vapor feed stream in line 111 that is directed to first reactor 103. In one embodiment, lines 104 and 105 may be combined and jointly fed to vaporizer 110, e.g., in one stream containing both hydrogen and acetic acid. The temperature of the vapor feed stream in line 111 is preferably from 100°C to 350°C, e.g., from 120°C to 310°C or from 150°C to 300°C. Any feed that is not vaporized is removed from vaporizer 110, as shown in FIG. 1, and may be recycled thereto (not shown). In addition, although FIG. 1 shows line 111 being directed to the top of reactor 103, line 111 may be directed to the side, upper portion, or bottom of reactor 103. Further modifications and additional components to reaction

zone 101 are described below in FIG. 2.

[0050] First reactor 103 contains the catalyst that is used in the hydrogenation of the carboxylic acid, preferably acetic acid. In one embodiment, one or more guard beds (not shown) may be used to protect the catalyst from poisons or undesirable impurities contained in the feed or return/recycle streams. Such guard beds may be employed in the vapor or liquid streams. Suitable guard bed materials are known in the art and include, for example, carbon, silica, alumina, ceramic, or resins. In one aspect, the guard bed media is functionalized to trap particular species such as sulfur or halogens. During the hydrogenation process, a crude ethanol product is withdrawn, preferably continuously, from reactor 103 via line 112. The crude ethanol product may be condensed and fed to flasher 106, which, in turn, provides a vapor stream and a liquid stream. The flasher 106 in one embodiment preferably operates at a temperature of from 50°C to 500°C, e.g., from 70°C to 400°C or from 100°C to 350°C. In one embodiment, the pressure of flasher 106 preferably is from 50 KPa to 2000 KPa, e.g., from 75 KPa to 1500 KPa or from 100 to 1000 KPa. In one preferred embodiment the temperature and pressure of the flasher is similar to the temperature and pressure of the reactor 103.

[0051] The vapor stream exiting the flasher 106 may comprise hydrogen and hydrocarbons, which may be purged and/or returned to reaction zone 101 via line 113. As shown in FIG. 1, the returned portion of the vapor stream passes through compressor 114 and is combined with the hydrogen feed and co-fed to vaporizer 110.

[0052] The liquid from flasher 106 is withdrawn and pumped as a feed composition via line 115 to the side of first column 107, also referred to as the acid separation column. The contents of line 115 typically will be substantially similar to the product obtained directly from the reactor, and may, in fact, also be characterized as a crude ethanol product. However, the feed composition in line 115 preferably has substantially no hydrogen, carbon dioxide, methane or ethane, which are removed by flasher 106. Exemplary components of liquid in line 115 are provided in Table 2. It should be understood that liquid line 115 may contain other components, not listed, such as components in or derived from the feed.

TABLE 2
FEED COMPOSITION

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	5 to 70	10 to 70	15 to 50
Acetic Acid	< 90	50 to 80	15 to 70
Water	5 to 40	5 to 30	10 to 30
Ethyl Acetate	< 30	< 20	1 to 12
Acetaldehyde	< 10	< 3	0.1 to 3
Acetal	< 5	0.001 to 2	0.005 to 1
Acetone	< 5	0.0005 to 0.05	0.001 to 0.03
Other Esters	< 5	< 0.005	< 0.001
Other Ethers	< 5	< 0.005	< 0.001
Other Alcohols	< 5	< 0.005	< 0.001

[0053] The amounts indicated as less than (<) in the tables throughout present application are preferably not present and if present may be present in trace amounts or in amounts greater than 0.0001 wt.%.

[0054] The “other esters” in Table 2 may include, but are not limited to, ethyl propionate, methyl acetate, isopropyl acetate, n-propyl acetate, n-butyl acetate or mixtures thereof. The “other ethers” in Table 2 may include, but are not limited to, diethyl ether, methyl ethyl ether, isobutyl ethyl ether or mixtures thereof. The “other alcohols” in Table 2 may include, but are not limited to, methanol, isopropanol, n-propanol, n-butanol or mixtures thereof. In one embodiment, the feed composition, e.g., line 115, may comprise propanol, e.g., isopropanol and/or n-propanol, in an amount from 0.001 to 0.1 wt.%, from 0.001 to 0.05 wt.% or from 0.001 to 0.03 wt.%. It should be understood that these other components may be carried through in any of the distillate or residue streams described herein and will not be further described herein, unless indicated otherwise.

[0055] When the content of acetic acid in line 115 is less than 5 wt.%, the acid separation column 107 may be skipped and line 115 may be introduced directly to second column 108, also referred to herein as a light ends column.

[0056] In the embodiment shown in FIG. 1, line 115 is introduced in the lower part of first column 107, e.g., lower half or lower third. In first column 107, unreacted acetic acid, a portion of the water, and other heavy components, if present, are removed from the composition in line 115 and are withdrawn, preferably continuously, as residue. Some or all of the residue may be returned and/or recycled back to reaction zone 101 via line 116. First column 107 also forms an

overhead distillate, which is withdrawn in line 117, and which may be condensed and refluxed, for example, at a ratio of from 10:1 to 1:10, e.g., from 3:1 to 1:3 or from 1:2 to 2:1.

[0057] Any of columns 107, 108, 109, or 123 may comprise any distillation column capable of separation and/or purification. The columns preferably comprise tray columns having from 1 to 150 trays, e.g., from 10 to 100 trays, from 20 to 95 trays or from 30 to 75 trays. The trays may be sieve trays, fixed valve trays, movable valve trays, or any other suitable design known in the art. In other embodiments, a packed column may be used. For packed columns, structured packing or random packing may be employed. The trays or packing may be arranged in one continuous column or they may be arranged in two or more columns such that the vapor from the first section enters the second section while the liquid from the second section enters the first section, etc.

[0058] The associated condensers and liquid separation vessels that may be employed with each of the distillation columns may be of any conventional design and are simplified in FIG. 1. As shown in FIG. 1, heat may be supplied to the base of each column or to a circulating bottom stream through a heat exchanger or reboiler. Other types of reboilers, such as internal reboilers, may also be used in some embodiments. The heat that is provided to reboilers may be derived from any heat generated during the process that is integrated with the reboilers or from an external source such as another heat generating chemical process or a boiler. Although one reactor and one flasher are shown in FIG. 1, additional reactors, flashers, condensers, heating elements, and other components may be used in embodiments of the present invention. As will be recognized by those skilled in the art, various condensers, pumps, compressors, reboilers, drums, valves, connectors, separation vessels, etc., normally employed in carrying out chemical processes may also be combined and employed in the processes of the present invention.

[0059] The temperatures and pressures employed in any of the columns may vary. As a practical matter, pressures from 10 KPa to 3000 KPa will generally be employed in these zones although in some embodiments subatmospheric pressures may be employed as well as superatmospheric pressures. Temperatures within the various zones will normally range between the boiling points of the composition removed as the distillate and the composition removed as the residue. It will be recognized by those skilled in the art that the temperature at a given location in an operating distillation column is dependent on the composition of the material at that location and the pressure of column. In addition, feed rates may vary depending on the size

of the production process and, if described, may be generically referred to in terms of feed weight ratios.

[0060] When column 107 is operated under standard atmospheric pressure, the temperature of the residue exiting in line 116 from column 107 preferably is from 95°C to 120°C, e.g., from 105°C to 117°C or from 110°C to 115°C. The temperature of the distillate exiting in line 117 from column 107 preferably is from 70°C to 110°C, e.g., from 75°C to 95°C or from 80°C to 90°C. In other embodiments, the pressure of first column 107 may range from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa. Exemplary components of the distillate and residue compositions for first column 107 are provided in Table 3 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed. For convenience, the distillate and residue of the first column may also be referred to as the “first distillate” or “first residue.” The distillates or residues of the other columns may also be referred to with similar numeric modifiers (second, third, etc.) in order to distinguish them from one another, but such modifiers should not be construed as requiring any particular separation order.

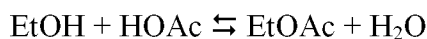
TABLE 3
FIRST COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	20 to 95	30 to 95	40 to 95
Water	10 to 40	15 to 35	20 to 35
Acetic Acid	< 2	0.001 to 0.5	0.01 to 0.2
Ethyl Acetate	< 60	1 to 55	5 to 55
Acetaldehyde	< 10	0.001 to 5	0.01 to 4
Acetal	< 0.1	< 0.05	< 0.01
Acetone	< 0.05	0.001 to 0.03	0.01 to 0.025
<u>Residue</u>			
Acetic Acid	60 to 100	70 to 95	85 to 92
Water	< 30	1 to 20	1 to 15
Ethanol	< 1	< 0.9	< 0.5

[0061] As shown in Table 3, without being bound by theory, it has surprisingly and unexpectedly been discovered that when any amount of acetal is detected in the feed that is introduced to the acid separation column (first column 107), the acetal appears to decompose in

the column such that less or even no detectable amounts are present in the distillate and/or residue.

[0062] Depending on the reaction conditions, the crude ethanol product exiting reactor 103 in line 112 may comprise ethanol, acetic acid (unconverted), ethyl acetate, and water. After exiting reactor 103, a non-catalyzed equilibrium reaction may occur between the components contained in the crude ethanol product until it is added to flasher 106 and/or first column 107. This equilibrium reaction tends to drive the crude ethanol product to an equilibrium between ethanol/acetic acid and ethyl acetate/water, as shown below.



[0063] In the event the crude ethanol product is temporarily stored, e.g., in a holding tank, prior to being directed to distillation zone 102, extended residence times may be encountered. Generally, the longer the residence time between reaction zone 101 and distillation zone 102, the greater the formation of ethyl acetate. For example, when the residence time between reaction zone 101 and distillation zone 102 is greater than 5 days, significantly more ethyl acetate may form at the expense of ethanol. Thus, shorter residence times between reaction zone 101 and distillation zone 102 are generally preferred in order to maximize the amount of ethanol formed. In one embodiment, a holding tank (not shown), is included between the reaction zone 101 and distillation zone 102 for temporarily storing the liquid component from line 115 for up to 5 days, e.g., up to 1 day, or up to 1 hour. In a preferred embodiment no tank is included and the condensed liquids are fed directly to the first distillation column 107. In addition, the rate at which the non-catalyzed reaction occurs may increase as the temperature of the crude ethanol product, e.g., in line 115, increases. These reaction rates may be particularly problematic at temperatures exceeding 30°C, e.g., exceeding 40°C or exceeding 50°C. Thus, in one embodiment, the temperature of liquid components in line 115 or in the optional holding tank is maintained at a temperature less than 40°C, e.g., less than 30°C or less than 20°C. One or more cooling devices may be used to reduce the temperature of the liquid in line 115.

[0064] As discussed above, a holding tank (not shown) may be included between the reaction zone 101 and distillation zone 102 for temporarily storing the liquid component from line 115, for example from 1 to 24 hours, optionally at a temperature of about 21°C, and corresponding to

an ethyl acetate formation of from 0.01 wt.% to 1.0 wt.% respectively. In addition, the rate at which the non-catalyzed reaction occurs may increase as the temperature of the crude ethanol product is increased. For example, as the temperature of the crude ethanol product in line 115 increases from 4°C to 21°C, the rate of ethyl acetate formation may increase from about 0.01 wt.% per hour to about 0.005 wt.% per hour. Thus, in one embodiment, the temperature of liquid components in line 115 or in the optional holding tank is maintained at a temperature less than 21°C, e.g., less than 4°C or less than -10°C.

[0065] In addition, it has now been discovered that the above-described equilibrium reaction may also favor ethanol formation in the top region of first column 107.

[0066] The distillate, e.g., overhead stream, of column 107 optionally is condensed and refluxed as shown in FIG. 1, preferably, at a reflux ratio of 1:5 to 10:1. The distillate in line 117 preferably comprises ethanol, ethyl acetate, and water, along with other impurities, which may be difficult to separate due to the formation of binary and tertiary azeotropes.

[0067] The first distillate in line 117 is introduced to the second column 108, also referred to as the “light ends column,” preferably in the middle part of column 108, e.g., middle half or middle third. As one example, when a 25 tray column is utilized in a column without water extraction, line 117 is introduced at tray 17. In one embodiment, the second column 108 may be an extractive distillation column. In such embodiments, an extraction agent, such as water, may be added to second column 108. If the extraction agent comprises water, it may be obtained from an external source or from an internal return/recycle line from one or more of the other columns.

[0068] Second column 108 may be a tray column or packed column. In one embodiment, second column 108 is a tray column having from 5 to 70 trays, e.g., from 15 to 50 trays or from 20 to 45 trays.

[0069] Although the temperature and pressure of second column 108 may vary, when at atmospheric pressure the temperature of the second residue exiting in line 118 from second column 108 preferably is from 60°C to 90°C, e.g., from 70°C to 90°C or from 80°C to 90°C. The temperature of the second distillate exiting in line 120 from second column 108 preferably is from 50°C to 90°C, e.g., from 60°C to 80°C or from 60°C to 70°C. Column 108 may operate at atmospheric pressure. In other embodiments, the pressure of second column 108 may range from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa. Exemplary components for the distillate and residue compositions for second column 108 are provided in

Table 4 below. It should be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 4
SECOND COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethyl Acetate	10 to 99	25 to 95	50 to 93
Acetaldehyde	< 25	0.5 to 15	1 to 8
Water	< 25	0.5 to 20	4 to 16
Ethanol	< 30	0.001 to 15	0.01 to 5
Acetal	< 5	0.001 to 2	0.01 to 1
<u>Residue</u>			
Water	30 to 90	30 to 85	30 to 85
Ethanol	10 to 75	15 to 70	20 to 70
Ethyl Acetate	< 3	0.001 to 2	0.001 to 0.5
Acetic Acid	< 0.5	0.001 to 0.3	0.001 to 0.2

[0070] The weight ratio of ethanol in the second residue to ethanol in the second distillate preferably is at least 3:1, e.g., at least 6:1, at least 8:1, at least 10:1 or at least 15:1. The weight ratio of ethyl acetate in the second residue to ethyl acetate in the second distillate preferably is less than 0.4:1, e.g., less than 0.2:1 or less than 0.1:1. In embodiments that use an extractive column with water as an extraction agent as the second column 108, the weight ratio of ethyl acetate in the second residue to ethyl acetate in the second distillate approaches zero.

[0071] As shown, the second residue from the bottom of second column 108, which comprises ethanol and water, is fed via line 118 to third column 109, also referred to as the “product column.” More preferably, the second residue in line 118 is introduced in the lower part of third column 109, e.g., lower half or lower third. Third column 109 recovers ethanol, which preferably is substantially pure other than the azeotropic water content, as the distillate in line 119. The distillate of third column 109 preferably is refluxed as shown in FIG. 1, for example, at a reflux ratio of from 1:10 to 10:1, e.g., from 1:3 to 3:1 or from 1:2 to 2:1. The third residue in line 121, which preferably comprises primarily water, preferably is removed from the system 100 or may be partially returned to any portion of the system 100. Third column 109 is preferably a tray column as described above and preferably operates at atmospheric pressure. The temperature of the third distillate exiting in line 119 from third column 109 preferably is

from 60°C to 110°C, e.g., from 70°C to 100°C or from 75°C to 95°C. The temperature of the third residue exiting from third column 109 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 105°C, when the column is operated at atmospheric pressure. Because most if not all of the acetaldehyde that is contained in line 117 is separated into the second distillate, very little acetaldehyde is conveyed to third column 109. As such the third distillate in third column 109 comprises little if any acetaldehyde. For example, the third distillate in line 119 may comprise less than 8 wppm acetaldehyde, e.g., less than 5 wppm. In a preferred embodiment, third distillate in line 119 is substantially free of acetaldehyde. Exemplary components of the distillate and residue compositions for third column 109 are provided in Table 5 below. It should be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

**TABLE 5
THIRD COLUMN**

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	75 to 99	80 to 99	85 to 99
Water	< 12	1 to 9	3 to 8
Acetic Acid	< 1	0.001 to 0.1	0.005 to 0.01
Ethyl Acetate	< 5	0.001 to 4	0.01 to 3
<u>Residue</u>			
Water	75 to 100	80 to 100	90 to 100
Ethanol	< 0.8	0.001 to 0.5	0.005 to 0.05
Ethyl Acetate	< 1	0.001 to 0.5	0.005 to 0.2
Acetic Acid	< 2	0.001 to 0.5	0.005 to 0.2

[0072] Any of the compounds that are carried through the distillation process from the feed or crude reaction product generally remain in the third distillate in amounts of less 0.1 wt.%, based on the total weight of the third distillate composition, e.g., less than 0.05 wt.% or less than 0.02 wt.%. In one embodiment, one or more side streams may remove impurities from any of the columns 107, 108 and/or 109 in the system 100. Preferably at least one side stream is used to remove impurities from the third column 109. The impurities may be purged and/or retained within the system 100.

[0073] The third distillate in line 119 may be further purified to form an anhydrous ethanol product stream, i.e., “finished anhydrous ethanol,” using one or more additional separation systems, such as, for example, distillation columns (e.g., a finishing column) or molecular sieves.

[0074] Returning to second column 108, the second distillate preferably is refluxed as shown in FIG. 1, for example, at a reflux ratio of from 1:10 to 10:1, e.g., from 1:5 to 5:1 or from 1:3 to 3:1. The second distillate is fed via line 120 to fourth column 123, also referred to as the “acetaldehyde removal column.” In fourth column 123 the second distillate is separated into a fourth distillate, which comprises acetaldehyde, in line 124 and a fourth residue, which comprises ethyl acetate, in line 125. The fourth distillate preferably is refluxed at a reflux ratio of from 1:20 to 20:1, e.g., from 1:15 to 15:1 or from 1:10 to 10:1. At least a portion of the fourth distillate may be returned to reaction zone 101 via line 124. For example, a first portion of the fourth distillate may be returned to first reactor 103 via line 126. The fourth distillate may be combined with the acetic acid feed, added to the vaporizer 110, or added directly to first reactor 103. In this case, the fourth distillate may be co-fed with the acetic acid in feed line 105 to vaporizer 110. Without being bound by theory, since acetaldehyde may be hydrogenated to form ethanol, the recycling of a stream that contains acetaldehyde to the reaction zone increases the yield of ethanol and decreases by-product and waste generation.

[0075] As shown in FIG. 1, a second portion of the fourth distillate may be directed to second reactor 127 via line 128. In this case line 124 provided the acetaldehyde stream for lines 126 and 128. Preferably, the second portion of acetaldehyde in line 128 is conveyed directly to second reactor 127, e.g., without further purification. In doing so, the production of additional product is achieved without the need for costly separation processes. Second reactor 127 may comprise a second catalyst, which is suitable for catalyzing the formation of the additional product. The selection of a suitable catalyst is well within the ordinary skill in the art. Exemplary catalysts include, but are not limited to those discussed above with respect to the first reactor. The second catalyst, in preferred embodiments, is selected such that it differs from the catalyst selected as the first catalyst.

[0076] The fourth residue of fourth column 123 may be purged via line 125. The fourth residue primarily comprises ethyl acetate and ethanol, which may be suitable for use as a solvent mixture or in the production of esters. In one preferred embodiment, the acetaldehyde is

removed from the second distillate in fourth column 123 such that no detectable amount of acetaldehyde is present in the residue of column 123.

[0077] Fourth column 123 is preferably a tray column as described above and preferably operates above atmospheric pressure. In one embodiment, the pressure is from 120 KPa to 5,000 KPa, e.g., from 200 KPa to 4,500 KPa, or from 400 KPa to 3,000 KPa. In a preferred embodiment the fourth column 123 may operate at a pressure that is higher than the pressure of the other columns.

[0078] The temperature of the fourth distillate exiting in line 124 from fourth column 123 preferably is from 60°C to 110°C, e.g., from 70°C to 100°C or from 75°C to 95°C. The temperature of the residue exiting from fourth column 125 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 110°C. Exemplary components of the distillate and residue compositions for fourth column 123 are provided in Table 6 below. It should be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 6
FOURTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Acetaldehyde	2 to 80	2 to 50	5 to 40
Ethyl Acetate	< 90	30 to 80	40 to 75
Ethanol	< 30	0.001 to 25	0.01 to 20
Water	< 25	0.001 to 20	0.01 to 15
<u>Residue</u>			
Ethyl Acetate	40 to 100	50 to 100	60 to 100
Ethanol	< 40	0.001 to 30	0 to 15
Water	< 25	0.001 to 20	2 to 15
Acetaldehyde	< 1	0.001 to 0.5	Not detectable
Acetal	< 3	0.001 to 2	0.01 to 1

[0079] Although a first reactor, a second reactor, and one flasher are shown in FIG. 1, additional reactors and/or components may be included in various optional embodiments of the present invention. FIG. 2 represents a hydrogenation system 100' that comprises dual reactors 103, 103', dual flashers 106, 106', heat exchanger 130, and pre-heater 131. In this embodiment, acetic acid in line 105, along with the recycled acetic acid in line 116 and recycled acetaldehyde

from line 124, are heated in a heat exchanger 130 and sent to vaporizer 110 via line 132. The temperature of the contents of line 132 preferably is from 30°C to 150°C, e.g., from 50°C to 130°C or from 75°C to 120°C. Hydrogen is fed via line 104 to vaporizer 110, which forms vaporized stream 111. Vaporized stream 111 passes through pre-heater 131, which further heats stream 111 to a temperature of preferably from 200°C to 300°C, e.g., from 210°C to 275°C or from 220°C to 260°C. The heated stream is then fed to first reactor 103. In order to control the reaction exotherm, the crude reaction mixture is removed from first reactor 103 via line 133 and cooled before being fed to a second reactor 103', such that the temperature of the reactants and products in contact with the catalyst is maintained at or below 310°C in order to minimize the formation of undesired byproducts including methane, ethane, carbon dioxide, and/or carbon monoxide. Additionally, above about 320°C corrosion can become severe necessitating the use of exotic and expensive alloy materials. The temperature of the contents in line 133 after cooling preferably is from 200°C to 300°C, e.g., from 210°C to 275°C or from 220°C to 260°C. The reactors 103 and 103' may be the same size and configuration or they may be of different size and configuration. Each reactor preferably contains the same type of catalyst, although additional and/or different catalysts may be used for each reactor. As an example, the catalysts mentioned above may be utilized. Also, mixtures of catalysts, mixtures of catalysts and inert materials, and/or catalysts with differing active metal concentrations may be utilized. For example, the catalyst may include the same types of metal in varying metal ratios. A crude ethanol product is withdrawn, preferably continuously, from reactor 103' via line 112 and passes as a heating medium through heat exchanger 130 before being condensed and fed to first flasher 106. Thus, heat from the crude ethanol product advantageously may be employed to preheat the acetic acid feed prior to its introduction into vaporizer 110. Conversely, the acetic acid feed may be used as a cooling medium to cool the crude ethanol product prior to its introduction to first flasher 106. The vapor stream exiting the first flasher comprises hydrogen and hydrocarbons, which may be purged and/or returned to reaction zone 101 via line 113. As shown in FIG. 2, at least a portion of the recycled vapor stream passes through compressor 114 and is co-fed with the hydrogen (or combined with hydrogen and then co-fed) to vaporizer 110.

[0080] The remaining liquid in flasher 106 is withdrawn via line 134 and fed to a second flasher 106' to remove any residual vapor that is dissolved in the liquid. Second flasher 106' may operate at a lower temperature and/or pressure than the first flasher 106. In one

embodiment, the temperature of second flasher 106' preferably is from 20°C to 100°C, e.g., from 30°C to 85°C or from 40°C to 70°C. In one embodiment, the temperature of second flasher 106' preferably is at least 50°C lower than first flasher 106, e.g., at least 75°C lower or at least 100°C lower. The pressure of second flasher 106' preferably is from 0.1 KPa to 1000 KPa, e.g., from 0.1 KPa to 500 KPa or from 0.1 KPa to 100 KPa. In one embodiment, the pressure of second flasher 106' preferably is at least 50 KPa lower than first flasher 106, e.g., at least 100 KPa lower or at least 200 KPa lower. The vapor stream 135 exiting the second flasher may comprise hydrogen and hydrocarbons, which may be purged and/or returned to the reaction zone in a manner similar to that of the first flasher 106. The remaining liquid in flasher 106' is withdrawn and pumped via line 115 to the side of the first column (not shown in FIG. 2) and is further purified to form an ethanol product stream, i.e., "finished ethanol," as described, for example, in connection with FIG. 1.

Finished Ethanol

[0081] The finished ethanol composition obtained by the processes of the present invention preferably comprises from 75 to 96 wt.% ethanol, e.g., from 80 to 96 wt.% or from 85 to 96 wt.% ethanol, based on the total weight of the finished ethanol composition. Exemplary finished ethanol compositional ranges are provided below in Table 7.

TABLE 7
FINISHED ETHANOL COMPOSITIONS

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	75 to 99	80 to 99	85 to 99
Water	< 12	1 to 9	3 to 8
Acetic Acid	< 1	< 0.1	< 0.01
Ethyl Acetate	< 2	< 0.5	< 0.05
Acetal	< 0.05	< 0.01	< 0.005
Acetone	< 0.05	< 0.01	< 0.005
Isopropanol	< 0.5	< 0.1	< 0.05
n-propanol	< 0.5	< 0.1	< 0.05

[0082] The finished ethanol composition of the present invention preferably contains very low amounts, e.g., less than 0.5 wt.%, of other alcohols, such as methanol, butanol, isobutanol, isoamyl alcohol and other C₄-C₂₀ alcohols. In one embodiment, the amount of isopropanol in the finished ethanol is from 80 to 1,000 wppm, e.g., from 95 to 1,000 wppm, from 100 to 700 wppm, or from 150 to 500 wppm. In one embodiment, the finished ethanol composition preferably is

substantially free of acetaldehyde and may comprise less than 8 wppm of acetaldehyde, e.g., less than 5 wppm or less than 1 wppm.

[0083] The finished ethanol composition produced by the embodiments of the present invention may be used in a variety of applications including applications as fuels, solvents, chemical feedstocks, pharmaceutical products, cleansers, sanitizers, hydrogenation transport or consumption. In fuel applications, the finished ethanol composition may be blended with gasoline for motor vehicles such as automobiles, boats and small piston engine aircraft. In non-fuel applications, the finished ethanol composition may be used as a solvent for toiletry and cosmetic preparations, detergents, disinfectants, coatings, inks, and pharmaceuticals. The finished ethanol composition may also be used as a processing solvent in manufacturing processes for medicinal products, food preparations, dyes, photochemicals and latex processing.

[0084] The finished ethanol composition may also be used as a chemical feedstock to make other chemicals such as vinegar, ethyl acrylate, ethyl acetate, ethylene, glycol ethers, ethylamines, aldehydes, and higher alcohols, especially butanol. In the production of ethyl acetate, the finished ethanol composition may be esterified with acetic acid. In another application, the finished ethanol composition may be dehydrated to produce ethylene. Any known dehydration catalyst can be employed to dehydrate ethanol, such as those described in copending U.S. Pub. Nos. 2010/0030002 and 2010/0030001, the entire contents and disclosures of which are hereby incorporated by reference. A zeolite catalyst, for example, may be employed as the dehydration catalyst. Preferably, the zeolite has a pore diameter of at least about 0.6 nm, and preferred zeolites include dehydration catalysts selected from the group consisting of mordenites, ZSM-5, a zeolite X and a zeolite Y. Zeolite X is described, for example, in U.S. Pat. No. 2,882,244 and zeolite Y in U.S. Pat. No. 3,130,007, the entireties of which are hereby incorporated herein by reference.

[0085] In order that the invention disclosed herein may be more efficiently understood, an example is provided below. It should be understood that these examples are for illustrative purposes only and is not to be construed as limiting the invention in any manner.

Examples

Example 1

[0086] A crude ethanol product comprising ethanol, acetic acid, water and ethyl acetate was produced by reacting a vaporized feed comprising 95.2 wt.% acetic acid and 4.6 wt.% water with

hydrogen in the presence of a catalyst comprising 1.6 wt.% platinum and 1 wt.% tin supported on 1/8 inch calcium silicate modified silica extrudates at an average temperature of 291°C, an outlet pressure of 2,063 KPa. Unreacted hydrogen was recycled back to the inlet of the reactor such that the total H₂/acetic acid molar ratio was 5.8 at a GHSV of 3,893 hr⁻¹. Under these conditions, 42.8% of the acetic acid was converted, and the selectivity to ethanol was 87.1%, selectivity to ethyl acetate was 8.4%, and selectivity to acetaldehyde was 3.5%. The crude ethanol product was purified using a separation scheme having distillation columns as shown in FIG. 1.

[0087] The crude ethanol product was fed to the first column at a feed rate of 20 g/min. The composition of the liquid feed is provided in Table 8. The first column is a 2 inch diameter Oldershaw with 50 trays. The column was operated at a temperature of 115°C at atmospheric pressure. Unless otherwise indicated, a column operating temperature is the temperature of the liquid in the reboiler and the pressure at the top of the column is ambient (approximately one atmosphere). The column differential pressure between the trays in the first column was 7.4 KPa. The first residue was withdrawn at a flow rate of 12.4 g/min and returned to the hydrogenation reactor.

[0088] The first distillate was condensed and refluxed at a 1:1 ratio at the top of the first column, and a portion of the distillate was introduced to the second column at a feed rate of 7.6 g/min. The second column is a 2 inch diameter Oldershaw design equipped with 25 trays. The second column was operated at a temperature of 82°C at atmospheric pressure. The column differential pressure between the trays in the second column was 2.6 KPa. The second residue was withdrawn at a flow rate of 5.8 g/min and directed to the third column. The second distillate was refluxed at a ratio of 4.5:0.5 and the remaining distillate was collected for analysis.

[0089] The fourth column is a 1 inch diameter Oldershaw column containing 25 trays and designed to operate at elevated pressures. The fourth column was operated at a pressure of 25 psig, and the differential pressure between the trays in the fourth column was 2.2 KPa. The fourth distillate was refluxed at a ratio of 28:1 and returned to the hydrogenation reactor. The residue of the fourth column was withdrawn at a flow rate of 1.6 g/min. The compositions of the feed, distillates, and residues are provided in Table 8.

TABLE 8

Component	Feed (wt.%)	First Column		Second Column		Fourth Column	
		Distillate (wt.%)	Residue (wt.%)	Distillate (wt.%)	Residue (wt.%)	Distillate (wt.%)	Residue (wt.%)
Water	13.8	24.7	5.6	5.1	30.8	2.1	4.7
Acetaldehyde	nd	1.8	nd	8.3	nd	61.5	nd
Acetic Acid	55.0	0.08	93.8	0.03	0.1	0.02	0.03
Ethanol	23.4	57.6	0.06	12.4	67.6	5.4	14.3
Ethyl Acetate	6.5	15.1	nd	76.0	nd	39.8	80.5
Acetal	0.7	0.1	nd	0.006	0.03	0.001	0.017
Acetone	nd	0.01	nd	0.03	nd	0.08	0.01

[0090] Residue from the second column was collected from several runs and introduced above the 25 tray to the third column, a 2 inch Oldershaw containing 60 trays, at a rate of 10 g/min. The third column was operated at a temperature of 103°C at standard pressure. The column differential pressure between the trays in the third column was 6.2 KPa. The third residue was withdrawn at a flow rate of 2.7 g/min. The third distillate was condensed and refluxed at a 3:1 ratio at the top of the third column, and recovered an ethanol composition as shown in Table 9. The ethanol composition also contained 10 ppm of n-butyl acetate.

TABLE 9

Component	Feed (wt.%)	Third Column	
		Distillate (wt.%)	Residue (wt.%)
Acetic Acid	0.098	0.001	0.4
Ethanol	65.7	93.8	0.004
Water	35.5	6.84	98
Ethyl Acetate	1.37	1.8	--
Acetal	0.02	0.03	--
Isopropanol	0.004	0.005	--
n-propanol	0.01	0	--

Example 2

[0091] A crude ethanol product comprising ethanol, acetic acid, water and ethyl acetate was produced by reacting a vaporized feed comprising 96.3 wt.% acetic acid and 4.3 wt.% water with hydrogen in the presence of a catalyst comprising 1.6 wt.% platinum and 1% tin supported on 1/8 inch calcium silicate modified silica extrudates at an average temperature of 290 °C, an outlet

pressure of 2,049 kPa. Unreacted hydrogen was recycled back to the inlet of the reactor such that the total H₂/acetic acid molar ratio was 10.2 at a GHSV of 1,997 hr⁻¹. Under these conditions, 74.5% of the acetic acid was converted, and the selectivity to ethanol was 87.9%, selectivity to ethyl acetate was 9.5%, and selectivity to acetaldehyde was 1.8%. The crude ethanol product was purified using a separation scheme having distillation columns as shown in FIG. 1.

[0092] The crude ethanol product was fed to the first column at a feed rate of 20 g/min. The composition of the liquid feed is provided in Table 10. The first column is a 2 inch diameter Oldershaw with 50 trays. The column was operated at a temperature of 116 °C at atmospheric pressure. The column differential pressure between the trays in the first column was 8.1 KPa. The first residue was withdrawn at a flow rate of 10.7 g/min and returned to the hydrogenation reactor.

[0093] The first distillate was condensed and refluxed at a 1:1 ratio at the top of the first column, and a portion of the distillate was introduced to the second column at a feed rate of 9.2 g/min. The second column is a 2 inch diameter Oldershaw design equipped with 25 trays. The second column was operated at a temperature of 82°C at atmospheric pressure. The column differential pressure between the trays in the second column was 2.4 KPa. The second residue was withdrawn at a flow rate of 7.1 g/min and directed to the third column. The second distillate was refluxed at a ratio of 4.5:0.5 and the remaining distillate was collected for analysis.

[0094] The fourth column is a 1 inch diameter Oldershaw column containing 25 trays and designed to operate at elevated pressures. The fourth column was operated at a pressure of 25 psig, and the differential pressure between the trays in the fourth column was 1.2 KPa. The fourth distillate was refluxed and returned to the hydrogenation reactor. The residue of the fourth column was withdrawn at a flow rate of 1.4 g/min. The compositions of the feed, distillates, and residues are provided in Table 10.

TABLE 10

Component	Feed (wt.%)	First Column		Second Column		Fourth Column	
		Distillate (wt.%)	Residue (wt.%)	Distillate (wt.%)	Residue (wt.%)	Distillate (wt.%)	Residue (wt.%)
Water	14.6	27.2	3.7	3.0	36.2	0.5	7.4
Acetaldehyde	nd	1.5	nd	10.3	nd	>40.00	nd
Acetic Acid	49.1	0.2	98.2	0.04	0.3	0.05	0.04
Ethanol	27.6	54.5	0.04	13.3	64.4	1.9	16.4
Ethyl Acetate	7.9	15.2	nd	75.7	1.8	8.3	79.9
Acetal	0.7	0.1	nd	0.01	0.02	0.01	0.03
Acetone	nd	0.01	nd	0.03	nd	0.02	0.03

[0095] Residue from the second column was collected from several runs and introduced above the 25 tray to the third column, a 2 inch Oldershaw containing 60 trays, at a rate of 10 g/min. The third column was operated at a temperature of 103°C at standard pressure. The column differential pressure between the trays in the third column was 6.5 KPa. The third residue was withdrawn at a flow rate of 2.8 g/min. The third distillate was condensed and refluxed at a 3:1 ratio at the top of the third column, and recovered an ethanol composition as shown in Table 11. The ethanol composition also contained 86 ppm of isopropanol and 2.3 ppm of n-propyl acetate.

TABLE 11

Component	Third Column		
	Feed (wt.%)	Distillate (wt.%)	Residue (wt.%)
Acetic Acid	0.16	0.0028	0.77
Ethanol	64.4	92.3	0.8
Water	35.8	6.3	98.0
Ethyl Acetate	0.9	0.45	0.0007

[0096] While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference. In addition, it should be understood that aspects of the invention and portions of various embodiments and various features recited below and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions

of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one of skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

We claim:

1. A process for producing ethanol, comprising the steps of:
 - (a) hydrogenating an acetic acid feed stream in a first reactor to form a crude ethanol product;
 - (b) separating acetaldehyde from the crude ethanol product;
 - (c) feeding a first portion of the separated acetaldehyde to the first reactor;
 - (d) reacting the first portion of the separated acetaldehyde in the first reactor to form additional ethanol; and
 - (e) feeding a second portion of the separated acetaldehyde to a second reactor; and
 - (f) reacting the second portion of the separated acetaldehyde in the second reactor to form an additional product.

2. The process of claim [0006], wherein the first reactor comprises a first catalyst and wherein the second reactor comprises a second catalyst different from the first catalyst.

3. The process of claim [0006], wherein the additional product is different from the crude ethanol product.

4. The process of claim [0006], wherein the additional product comprises at least one of n-butanol, 1,3-butanediol, crotonaldehyde, and derivatives thereof.

5. The process of claim [0006], wherein the second portion of the separated acetaldehyde is conveyed directly to the second reactor.

6. The process of claim [0006], wherein step (b) comprises:
 - separating at least a portion of the crude ethanol product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid;
 - separating at least a portion of the first distillate in a second column into a second distillate comprising ethyl acetate and a second residue comprising ethanol and water;
 - optionally separating at least a portion of the second residue in a third column into a third distillate comprising ethanol and a third residue comprising water; and

separating at least a portion of the second distillate in a fourth column into a fourth distillate comprising acetaldehyde and a fourth residue comprising ethyl acetate.

7. The process of claim 6, wherein the first portion of separated acetaldehyde comprises a first portion of the fourth distillate and wherein the second portion of separated acetaldehyde comprises a second portion of the fourth distillate.

8. The process of claim 6, wherein the third distillate is substantially free of acetaldehyde.

9. The process of claim 6, wherein the third distillate comprises less than 8 wppm acetaldehyde.

10. The process of claim [0006] , wherein the recovered acetaldehyde stream comprises from 2 to 80 wt.% of acetaldehyde.

11. The process of claim [0006] , wherein the acetic acid is formed from methanol and carbon monoxide, wherein each of the methanol, the carbon monoxide, and hydrogen for the hydrogenating step is derived from syngas, and wherein the syngas is derived from a carbon source selected from the group consisting of natural gas, oil, petroleum, coal, biomass, and combinations thereof.

12. A process for producing ethanol, comprising the steps of:
(a) providing a crude ethanol product comprising ethanol, acetaldehyde and acetic acid;
(b) separating acetaldehyde from the crude ethanol product;
(c) feeding a first portion of the separated acetaldehyde to a first reactor;
(d) reacting the first portion of the separated acetaldehyde in the first reactor to form additional ethanol; and
(e) feeding a second portion of the separated acetaldehyde to a second reactor; and
(f) reacting the second portion of the separated acetaldehyde in the second reactor to form an additional product.

13. A process for producing ethanol, comprising the steps of:
 - (a) providing a crude ethanol product comprising ethanol, acetaldehyde and acetic acid;
 - (b) separating acetaldehyde from the crude ethanol product;
 - (c) feeding at least a portion of the separated acetaldehyde to a first reactor; and
 - (d) reacting the at least a portion of the separated acetaldehyde in the first reactor to form ethanol.

14. A process for producing ethanol, comprising the steps of:
 - (a) hydrogenating an acetic acid feed stream in a first reactor to form a crude ethanol product;
 - (b) separating acetaldehyde from the crude ethanol product;
 - (c) feeding at least a portion of the separated acetaldehyde to a second reactor; and
 - (d) reacting the at least a portion of the separated acetaldehyde in the second reactor.

15. The process of claim 14, wherein step (d) comprises reacting the at least a portion of the separated acetaldehyde in the second reactor to form additional ethanol.

16. The process of claim 14, wherein step (d) comprises reacting the at least a portion of the separated acetaldehyde in the second reactor to form an additional product.

17. The process of claim 14, wherein an additional portion of the separated acetaldehyde is reacted in the first reactor to form an ethanol product.

18. The process of claim 14, wherein an additional portion of the separated acetaldehyde is reacted in the first reactor to form an additional product.

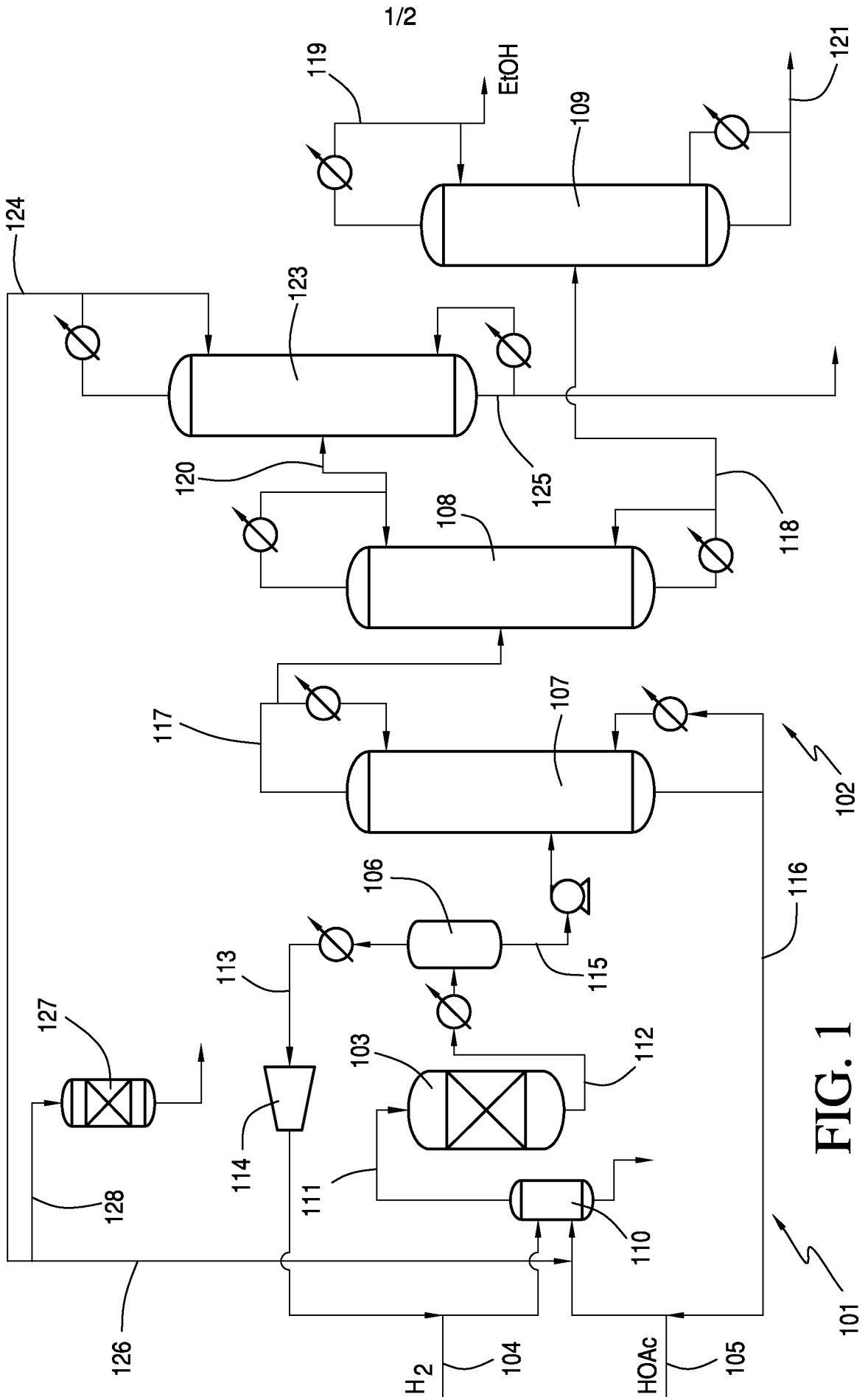


FIG. 1

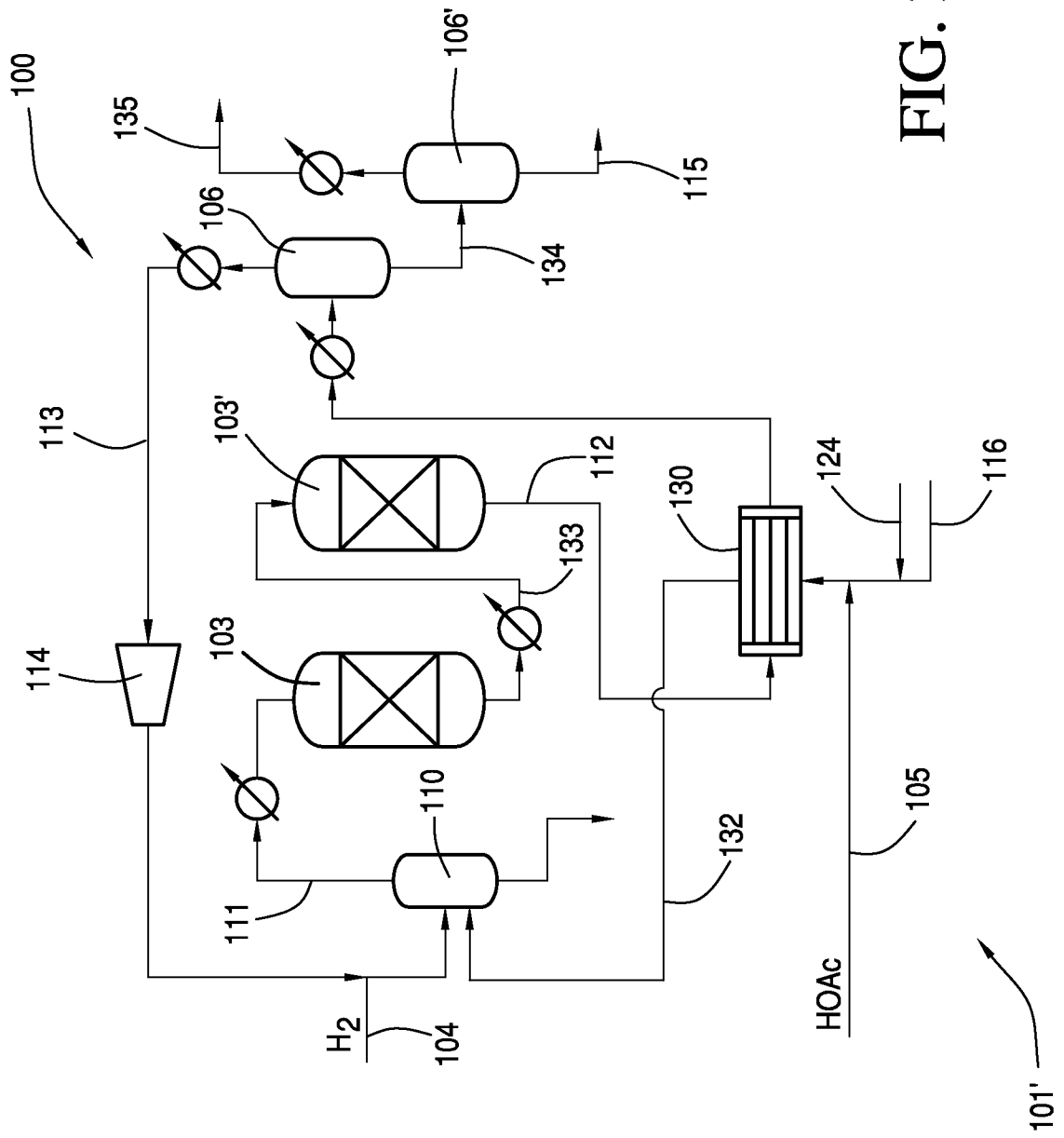


FIG. 2