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(54) **Title:** PROCESS FOR SEPARATING ETHANOL HAVING LOW ACID

(57) **Abstract:** A process for operating a distillation column to separate an ethanol mixture comprising ethanol and acetic acid where the recovered ethanol comprises less than 700 wppm acetic acid. The operating conditions for the column may vary depending on the feed composition. In particular the process provides energy efficient recovery of ethanol with low concentration acetic acid.



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PROCESS FOR SEPARATING ETHANOL HAVING LOW ACID

FIELD OF THE INVENTION

[0001] The present invention relates generally to processes for producing ethanol and, in particular, to separating ethanol from a crude product containing acetic acid in an energy efficient manner.

BACKGROUND OF THE INVENTION

[0002] 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. Starchy materials, as well as cellulose material, are converted to ethanol by fermentation. However, fermentation is typically used for consumer production of ethanol, which is suitable for fuels or human consumption. In addition, fermentation of starchy or cellulose materials competes with food sources and places restraints on the amount of ethanol that can be produced for industrial use.

[0003] Ethanol production via the reduction of alkanoic 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 alkanoic acid, e.g., acetic acid, other compounds are formed with ethanol or are formed in side reactions. These impurities limit the production and recovery of ethanol from such reaction mixtures. For example, during hydrogenation, esters are produced that together with ethanol and/or water form azeotropes, which are difficult to separate. In addition when conversion is incomplete, unreacted acid remains in the crude ethanol product, which must be removed to recover ethanol.

[0004] EP02060553 describes a process for converting hydrocarbons to ethanol involving converting the hydrocarbons to ethanoic acid and hydrogenating the ethanoic acid to ethanol. The stream from the hydrogenation reactor is separated to obtain an ethanol product and a stream of acetic acid and ethyl acetate, which is recycled to the hydrogenation reactor.

[0005] The need remains for improved processes for recovering ethanol from a crude product obtained by reducing alkanolic acids, such as acetic acid, and/or other carbonyl group-containing compounds.

SUMMARY OF THE INVENTION

[0006] In a first embodiment, the present invention is directed to a process for producing ethanol comprising hydrogenating a feed stream comprising alkanolic acid and/or esters thereof in a reactor in the presence of a catalyst to produce a crude ethanol mixture comprising ethanol, water, and acetic acid; separating at least a portion of the crude ethanol mixture in a distillation column operated at a reflux ratio from 1:1.8 to 1.5:1 to yield a distillate comprising at least 90% of the ethanol from the crude ethanol mixture and less than 600 wppm acetic acid and a residue comprising acetic acid, wherein the distillate to feed flow ratio is less than 0.5; and recovering ethanol from the distillate.

[0007] In a second embodiment, the present invention is directed to a process for producing ethanol comprising hydrogenating a feed stream comprising alkanolic acid and/or esters thereof in a reactor in the presence of a catalyst to produce a crude ethanol mixture comprising ethanol, water, and acetic acid; separating at least a portion of the crude ethanol mixture in a distillation column having more than 55 stages and operated at a reflux ratio of greater than 1.5:1 to yield a distillate comprising at least 90% of the ethanol from the crude ethanol mixture and less than 600 wppm acetic acid and a residue comprising acetic acid, wherein the distillate to feed flow ratio is less than 0.5; and recovering ethanol from the distillate.

[0008] In a third embodiment, the present invention is directed to a process for producing ethanol comprising hydrogenating a feed stream comprising alkanolic acid and/or esters thereof in a reactor in the presence of a catalyst to produce a crude ethanol mixture comprising ethanol, water, and acetic acid; separating at least a portion of the crude ethanol mixture in a distillation column operated at a reflux ratio from 1:10 to 1:1 to yield a distillate comprising at least 90% of

the ethanol from the crude ethanol mixture and less than 700 wppm acetic acid and a residue comprising acetic acid and a substantial portion of the water fed to the distillation column, wherein the distillate to feed flow ratio is from 0.6 to 0.8; and recovering ethanol from the distillate.

BRIEF DESCRIPTION OF DRAWINGS

[0009] The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts.

[0010] FIG. 1 is a schematic diagram of a hydrogenation process having four columns in accordance with an embodiment of the present invention.

[0011] FIG. 2 is a schematic diagram of another hydrogenation process having two columns in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

[0012] The present invention relates to processes for producing ethanol by separating the ethanol from a crude mixture that also comprises acetic acid. In one embodiment the ethanol may be produced by hydrogenating alkanoic acids, such as acetic acid, in the presence of a catalyst. The pH of recovered ethanol is important and acidic ethanol may be disadvantageous in many ethanol applications. Thus, when ethanol is produced from acetic acid, the remaining acid should be efficiently separated from the ethanol. The present invention relates to the distillation system that separates acetic acid from the crude ethanol product. In addition to separating acetic acid, the present invention advantageously provides an energy efficient process for operating the distillation system.

[0013] Distillation systems are mechanisms to facilitate mass transfer between opposite phases moving in a counter-current fashion. The mechanism provides vapor rich overhead comprising the more volatile components a liquid rich residue comprising the less volatile components. The functions of the system are performed by a column, a reboiler, and a condenser/stream splitter. The control of the system may vary depending on the composition of the feed to the column and the operating parameters. Operating parameters refers to how the system separates the feed into

two or more stream, for example, which compounds are separated into the distillate, side, and/or residue streams.

[0014] The operating conditions, feed location, number of stages, feed location, distillate to feed flow ratios, and/or reflux ratio, may change the energy efficiency in recovering ethanol. Typically in distillation systems, as the reflux ratio increases, the amount of acetic acid in the distillate decreases. However, increasing the reflux ratio typically requires an increase of energy. Also, as the distillate to feed flow ratio increases, the amount of acetic acid in the distillate increases as well as the energy requirements. However, lower distillate to feed flow ratios may not provide sufficient ethanol recovery. Lowering the feed location may also decrease the energy requirements. In addition, in a distillation system the volatility of both liquid and vapor streams increases with number of stages and the temperature decreases with number of stages.

[0015] Embodiments of the present invention provide operating conditions for separation columns that surprisingly and unexpectedly achieve high ethanol recovery with low acid concentration. In addition, the embodiments of the present invention advantageously achieve energy efficient operating conditions. In one aspect, the embodiments of the present invention may recover at least 90% of the ethanol fed to the first distillation column, e.g., at least 95% or at least 98%. Additional columns, membranes, adsorption units, molecular sieves, and combinations thereof may be further used to purify the ethanol as necessary.

[0016] The embodiments of the present invention maintain low concentrations of acetic acid in the recovered ethanol. The initial removal of acetic acid from the recovered ethanol is preferably achieved in one distillation column. Depending on the column operating parameters, the concentration of acetic acid in the distillate may be less than 700 wppm, e.g., less than 600 wppm, or more preferably less than 400 wppm. Although substantially complete separation of the acetic acid from the recovered ethanol may be achievable by the present invention, there may be some trace amounts of acetic acid in the recovered ethanol, e.g., more than 10 wppm acetic acid or more than 50 wppm acetic acid.

[0017] In a first embodiment of the present invention shown in FIG. 1, the crude mixture or a liquid portion of the crude mixture from a reactor 103 having an acetic acid conversion from 40% to 70%, e.g., from 50% to 60%, is fed to a distillation column 120. Distillation column 120 is the first column in the purification system and may also be referred to as the acid column. The

operating parameters of the column 120 are such that ethanol is primarily separated in a distillate stream 122 and acetic acid is recovered in a residue stream 121. The distillate to feed flow ratio may be less than 0.5, and preferably from 0.3 to 0.5, and most preferably about 0.4. This distillate to feed flow ratio range provides sufficient ethanol recovery of at least 90%. In addition, the acetic acid concentration may be less than 600 wppm. Increasing the distillate to feed flow ratio may adversely increase acetic acid concentrations above 600 wppm. In addition, the distillation column 120 is operated with a reflux ratio of 1:1.8 to 1.5:1, e.g., from 1:1.6 to 1.2:1 or from 1:1.4 to 1:1. When the reflux ratio is decreased outside of this range, then the energy requirements increase in a similar manner as the predicted energy increase with a higher reflux ratio.

[0018] Although the size of feed location of the column 120 in the first embodiment may vary, it is preferable that when the number of stages is less than 60, the crude mixture is fed to the lower portion of the column 120. When the number of stages is more than 60, the feed location may be below the 30th stage. The distillation column 120 preferably has from 40 to 120 stages, e.g., from 45 to 115 or from 50 to 90 stages.

[0019] In one embodiment, higher reflux ratio, e.g. greater than 1.5:1, may be used in combination with a larger column at least 55 stages, provided that the feed point is below the 30th stage. For example a reflux ratio of 2:1 may be used in such columns to achieve low acetic acid concentrations and high ethanol recovery rates.

[0020] When column 120 is operated under standard atmospheric pressure, the temperature of the residue exiting in line 121 preferably is from 95°C to 120°C, e.g., from 110°C to 117°C or from 111°C to 115°C. The temperature of the distillate exiting in line 122 preferably is from 70°C to 110°C, e.g., from 75°C to 95°C or from 80°C to 90°C. Column 120 preferably operates at ambient pressure. In other embodiments, the pressure of first column 120 may range from 0.1 kPa to 510 kPa, e.g., from 1 kPa to 475 kPa or from 1 kPa to 375 kPa.

[0021] In a second embodiment of the present invention, the crude mixture or a liquid portion via line 112 of the crude mixture, is fed to a first distillation column 150 in FIG. 2. For purposes of convenience, the columns in each exemplary separation process, may be referred as the first, second, third, etc., columns, but it is understood that first column 150 in FIG. 2 operates

differently than the first column 120 of FIG. 1. First column 150 in FIG. 2 is also referred to as an acid column, but may remove more water in the residue than acid column 120 of FIG. 1.

[0022] The acetic acid conversion in the second embodiment may be greater than 70%, e.g., greater than 85% or greater than 90%. The operating parameters of the column 150 are such that ethanol is primarily separated in a distillate stream 152, and a substantial portion of the water and acetic acid is recovered in a residue stream. In one embodiment, 30 to 90% of the water in the crude ethanol product is removed in the residue, e.g., from 40 to 88% of the water or from 50 to 84% of the water. To achieve at least 90% ethanol recovery, the distillate to feed flow ratio may be from 0.6 to 0.8, and most preferably from 0.65 to 0.75 or about 0.7. Increasing the distillate to feed flow ratio tends to increase acetic acid concentrations above 700 wppm. In addition, the distillation column 150 is operated with a reflux ratio of 1:10 to 1:1, e.g., from 1:5 to 1:1.1 or from 1:5 to 1:2.

[0023] In the second embodiment the number of stages in first column 150 may be less than 60 stages, e.g., less than 55 stages or less than 40 stages. Preferably, from 50 to 55 stages are suitable for the second embodiment of the present invention. Increasing the number of stages over 60 stages may decrease the energy efficiency in recovering ethanol. The feed location may vary, but typically may be in the upper or middle portion of first column 150.

[0024] When column 150 is operated under about 170 kPa, the temperature of the residue exiting in line 151 preferably is from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting in line 152 preferably is from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. In some embodiments, the pressure of first column 150 may range from 0.1 kPa to 510 kPa, e.g., from 1 kPa to 475 kPa or from 1 kPa to 375 kPa.

Hydrogenation

[0025] 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.

[0026] The raw materials, acetic acid and hydrogen, fed to the reactor 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] The acetic acid fed to the hydrogenation reactor may also comprise other carboxylic acids and anhydrides, as well as aldehydes and/or ketones, such 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.

[0033] 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 hydrogenation reactor without the need for condensing the acetic acid and light ends or removing water, saving overall processing costs.

[0034] 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.

[0035] The reactor, in some embodiments, 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 as the reactor, 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.

[0036] 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.

[0037] The hydrogenation in the reactor 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.

[0038] 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.

[0039] 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.

[0040] 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.

[0041] The hydrogenation of acetic acid to form ethanol is preferably conducted in the presence of a hydrogenation catalyst in the reactor. 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.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] 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.

[0046] 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.%.

[0047] 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.

[0048] 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.

[0049] 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.

[0050] 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.

[0051] 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 those selected from the group consisting of WO_3 , MoO_3 , Fe_2O_3 , Cr_2O_3 , V_2O_5 , MnO_2 , CuO , Co_2O_3 , and Bi_2O_3 .

[0052] 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 metal 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.

[0053] 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 $250 \text{ m}^2/\text{g}$; median pore diameter of about 12 nm; average pore volume of about $1.0 \text{ cm}^3/\text{g}$ as measured by mercury intrusion porosimetry and a packing density of about 0.352 g/cm^3 (22 lb/ft^3).

[0054] 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 $0.583 \text{ g H}_2\text{O/g}$ support, a surface area of about 160 to $175 \text{ m}^2/\text{g}$, and a pore volume of about 0.68 ml/g .

[0055] 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.

[0056] In particular, the hydrogenation of acetic acid may achieve favorable conversion of acetic acid and favorable selectivity and productivity to ethanol in the reactor. 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. As indicated above, the conversion for the first embodiment is from 40% to 70%, and the conversion for the second embodiment is greater than 85%.

[0057] 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, in the reactor, 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.

[0058] 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.

[0059] 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.

[0060] In various embodiments of the present invention, the crude ethanol product produced by the reactor, 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	5 to 70	5 to 50
Water	5 to 30	5 to 28	10 to 26	10 to 22
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	--

[0061] In one embodiment, the crude ethanol product may comprise acetic acid in an amount less than 20 wt.%, e.g., of 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 greater than 75%, e.g., greater than 85% or greater than 90%.

Ethanol Separation

[0062] Ethanol produced may be recovered using several different techniques. In FIG. 1, the separation of the crude ethanol product may use four columns. In FIG. 2, the crude ethanol product is separated in two columns with an intervening water separation. Other separation systems may also be used with embodiments of the present invention.

[0063] Hydrogenation system 100 includes a reaction zone 101 and separation zone 102. Hydrogen and acetic acid via lines 104 and 105, respectively, are fed to a vaporizer 106 to create a vapor feed stream in line 107 that is directed to reactor 103. In one embodiment, lines 104 and 105 may be combined and jointly fed to the vaporizer 106. The temperature of the vapor feed stream in line 107 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 106 and may be recycled or discarded thereto. In addition, although line 107 is shown as being directed to the top of reactor 103, line 107 may be directed to the side, upper portion, or bottom of reactor 103.

[0064] 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 upstream of the reactor, optionally upstream of the vaporizer 106, 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 may include, for example, carbon, silica, alumina, ceramic, or resins. In one aspect, the guard bed media is functionalized, e.g., silver functionalized, to trap particular species such as sulfur or halogens. During the hydrogenation process, a crude ethanol product stream is withdrawn, preferably continuously, from reactor 103 via line 109.

[0065] The crude ethanol product stream in line 109 may be condensed and fed to a separator 110, which, in turn, provides a vapor stream 111 and a liquid stream 112. In some embodiments, separator 110 may comprise a flasher or a knockout pot. The separator 110 may operate at a temperature of from 20°C to 250°C, e.g., from 30°C to 225°C or from 60°C to 200°C. The pressure of separator 110 may be from 50 kPa to 2000 kPa, e.g., from 75 kPa to 1500 kPa or from 100 kPa to 1000 kPa. Optionally, the crude ethanol product in line 109 may pass through one or more membranes to separate hydrogen and/or other non-condensable gases.

[0066] The vapor stream 111 exiting separator 110 may comprise hydrogen and hydrocarbons, and may be purged and/or returned to reaction zone 101. When returned to reaction zone 101, vapor stream 111 is combined with the hydrogen feed 104 and co-fed to vaporizer 106. In some embodiments, the returned vapor stream 111 may be compressed before being combined with hydrogen feed 104.

[0067] In FIG. 1, the liquid stream 112 from separator 110 is withdrawn and pumped to the side of first column 120, also referred to as an “acid separation column.” In one embodiment, the contents of liquid stream 112 are substantially similar to the crude ethanol product obtained from the reactor, except that the composition has been depleted of hydrogen, carbon dioxide, methane and/or ethane, which are removed by separator 110. Accordingly, liquid stream 112 may also be referred to as a crude ethanol product. Exemplary components of liquid stream 112

are provided in Table 2. It should be understood that liquid stream 112 may contain other components, not listed in Table 2.

TABLE 2
COLUMN FEED COMPOSITION
(Liquid Stream 112)

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	5 to 70	10 to 60	15 to 50
Acetic Acid	< 90	5 to 80	5 to 70
Water	5 to 30	5 to 28	10 to 26
Ethyl Acetate	< 30	0.001 to 20	1 to 12
Acetaldehyde	< 10	0.001 to 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

[0068] The amounts indicated as less than (<) in the tables throughout the present specification are preferably not present and if present may be present in trace amounts or in amounts greater than 0.0001 wt.%.

[0069] 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 liquid stream 112 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.

[0070] Optionally, crude ethanol product in line 109 or in liquid stream 112 may be further fed to an esterification reactor, hydrogenolysis reactor, or combination thereof. An esterification reactor may be used to consume residual acetic acid present in the crude ethanol product to further reduce the amount of acetic acid that would otherwise need to be removed.

Hydrogenolysis may be used to convert ethyl acetate in the crude ethanol product to ethanol.

[0071] The operation parameters and conditions for first column 120 in FIG. 1, are provided above. Exemplary components of the distillate and residue compositions for first column 120 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
ACID COLUMN 120 (FIG. 1)

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	20 to 75	30 to 70	40 to 65
Water	10 to 40	15 to 35	20 to 35
Ethyl Acetate	< 60	5.0 to 40	10 to 30
Acetaldehyde	< 10	0.001 to 5	0.01 to 4
Acetal	< 0.1	< 0.1	< 0.05
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	< 0.07

[0072] In preferred embodiments, first column 120 is operated to maintain an acetic acid concentration in the first distillate of less than less than 600 wppm, e.g., less than 400 wppm or less than 200 wppm. In terms of ranges, the amount of acetic acid may be from 0.01 wppm to 600 wppm, e.g., from 0.1 to 400 wppm or from 0.1 to 200 wppm. In some embodiments, the first distillate may comprise substantially no acetic acid.

[0073] As shown in Table 3, without being bound by theory, it has surprisingly and unexpectedly been discovered that when any amount of acetal is fed to the acid separation column 120, the acetal appears to decompose in the column such that less or even no detectable amounts are present in the distillate and/or residue.

[0074] The distillate in line 122 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. To further separate distillate, line 122 is introduced to the second column 123, also referred to as the “light ends column,” preferably in the middle part of column 123, e.g., middle half or middle third. Preferably the second column 123 is an extractive distillation column, and an extraction agent is added thereto via lines 124 and/or 125. Extractive distillation is a method of separating close boiling components, such as azeotropes, by distilling the feed in the presence of an extraction agent. The extraction agent preferably has a boiling point that is higher than the compounds being separated in the feed. In preferred embodiments, the extraction agent is comprised primarily of water. As indicated above, the first distillate in line 122 that is fed to the second column 123 comprises ethyl acetate, ethanol, and water. These compounds tend to form binary and ternary azeotropes, which decrease separation efficiency. As shown, in one embodiment the extraction agent comprises the third residue in line 124. Preferably, the recycled third residue in line 124 is fed to second column 123 at a point higher than the first distillate in line 122. In one embodiment, the recycled third residue in line 124 is fed near the top of second column 123 or fed, for example, above the feed in line 122 and below the reflux line from the condensed overheads. In a tray column, the third residue in line 124 is continuously added near the top of the second column 123 so that an appreciable amount of the third residue is present in the liquid phase on all of the trays below. In another embodiment, the extraction agent is fed from a source outside of the process 100 via line 125 to second column 123. Preferably this extraction agent comprises water.

[0075] The molar ratio of the water in the extraction agent to the ethanol in the feed to the second column is preferably at least 0.5:1, e.g., at least 1:1 or at least 3:1. In terms of ranges, preferred molar ratios may range from 0.5:1 to 8:1, e.g., from 1:1 to 7:1 or from 2:1 to 6.5:1. Higher molar ratios may be used but with diminishing returns in terms of the additional ethyl acetate in the second distillate and decreased ethanol concentrations in the second column distillate.

[0076] In one embodiment, an additional extraction agent, such as water from an external source, dimethylsulfoxide, glycerine, diethylene glycol, 1-naphthol, hydroquinone, N,N'-dimethylformamide, 1,4-butanediol; ethylene glycol-1,5-pentanediol; propylene glycol-

tetraethylene glycol-polyethylene glycol; glycerine-propylene glycol-tetraethylene glycol-1,4-butanediol, ethyl ether, methyl formate, cyclohexane, N,N'-dimethyl-1,3-propanediamine, N,N'-dimethylethylenediamine, diethylene triamine, hexamethylene diamine and 1,3-diaminopentane, an alkylated thiopene, dodecane, tridecane, tetradecane and chlorinated paraffins, may be added to second column 123. Some suitable extraction agents include those described in U.S. Patent Nos. 4,379,028, 4,569,726, 5,993,610 and 6,375,807, the entire contents and disclosure of which are hereby incorporated by reference. The additional extraction agent may be combined with the recycled third residue in line 124 and co-fed to the second column 123. The additional extraction agent may also be added separately to the second column 123. In one aspect, the extraction agent comprises an extraction agent, e.g., water, derived from an external source via line 125 and none of the extraction agent is derived from the third residue.

[0077] Second column 123 may be a tray or packed column. In one embodiment, second column 123 is a tray column having from 5 to 70 trays, e.g., from 15 to 50 trays or from 20 to 45 trays. Although the temperature and pressure of second column 123 may vary, when at atmospheric pressure the temperature of the second residue exiting in line 126 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 127 from second column 123 preferably is from 50°C to 90°C, e.g., from 60°C to 80°C or from 60°C to 70°C. Column 123 may operate at atmospheric pressure. In other embodiments, the pressure of second column 123 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 123 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 123 (FIG. 1)

	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	40 to 85	50 to 85
Ethanol	10 to 75	15 to 60	20 to 50
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

[0078] In preferred embodiments, the recycling of the third residue promotes the separation of ethyl acetate from the residue of the second column 123. For example, the weight ratio of ethyl acetate in the second residue to 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 distillation column with water as an extraction agent as the second column 123, the weight ratio of ethyl acetate in the second residue to ethyl acetate in the second distillate approaches zero.

[0079] The weight ratio of ethanol in the second residue to 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. All or a portion of the third residue is recycled to the second column. In one embodiment, all of the third residue may be recycled until process 100 reaches a steady state and then a portion of the third residue is recycled with the remaining portion being purged from the system 100. The composition of the second residue will tend to have lower amounts of ethanol than when the third residue is not recycled. As the third residue is recycled, the composition of the second residue, as provided in Table 5, comprises less than 30 wt.% of ethanol, e.g., less than 20 wt.% or less than 15 wt.%. The majority of the second residue preferably comprises water. Notwithstanding this effect, the extractive distillation step advantageously also reduces the amount of ethyl acetate that is sent to the third column, which is highly beneficial in ultimately forming a highly pure ethanol product.

[0080] As shown, the second residue from second column 123, which comprises ethanol and water, is fed via line 126 to third column 128, also referred to as the “product column.” More

preferably, the second residue in line 126 is introduced in the lower part of third column 128, e.g., lower half or lower third. Third column 128 recovers ethanol, which preferably is substantially pure with respect to organic impurities and other than the azeotropic water content, as the distillate in line 129. The distillate of third column 128 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 124, which comprises primarily water, preferably is returned to the second column 123 as an extraction agent as described above. In one embodiment, a first portion of the third residue in line 124 is recycled to the second column and a second portion is purged and removed from the system via line 130. In one embodiment, once the process reaches steady state, the second portion of water to be purged is substantially similar to the amount water formed in the hydrogenation of acetic acid. In one embodiment, a portion of the third residue may be used to hydrolyze any other stream, such as one or more streams comprising ethyl acetate.

[0081] Although FIG. 1 show third residue being directly recycled to second column 123, third residue may also be returned indirectly, for example, by storing a portion or all of the third residue in a tank (not shown) or treating the third residue to further separate any minor components such as aldehydes, higher molecular weight alcohols, or esters in one or more additional columns (not shown).

[0082] Third column 128 is preferably a tray column as described above and operates at atmospheric pressure or optionally at pressures above or below atmospheric pressure. The temperature of the third distillate exiting in line 129 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 in line 124 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 105°C. Exemplary components of the distillate and residue compositions for third column 128 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 128 (FIG. 1)

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	75 to 96	80 to 96	85 to 96
Water	< 12	1 to 9	3 to 8
Acetic Acid	< 12	0.0001 to 0.1	0.005 to 0.05
Ethyl Acetate	< 12	0.0001 to 0.05	0.005 to 0.025
Acetaldehyde	< 12	0.0001 to 0.1	0.005 to 0.05
Diethyl Acetal	< 12	0.0001 to 0.05	0.005 to 0.025
<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

[0083] In one embodiment, the third residue in line 124 is withdrawn from third column 128 at a temperature higher than the operating temperature of the second column 123. Preferably, the third residue in line 124 is integrated to heat one or more other streams or is reboiled prior to be returned to the second column 123.

[0084] 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 in the system 100. Preferably at least one side stream is used to remove impurities from the third column 128. The impurities may be purged and/or retained within the system 100.

[0085] The third distillate in line 129 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, adsorption units, membranes, or molecular sieves. Suitable adsorption units include pressure swing adsorption units and thermal swing adsorption unit.

[0086] Returning to second column 123, the second distillate preferably is refluxed as shown in FIG. 1, optionally at a reflux ratio of 1:10 to 10:1, e.g., from 1:5 to 5:1 or from 1:3 to 3:1. The second distillate in line 127 may be purged or recycled to the reaction zone. In one embodiment,

the second distillate in line 127 is further processed in a fourth column 131, also referred to as the “acetaldehyde removal column.” In fourth column 131 the second distillate is separated into a fourth distillate, which comprises acetaldehyde, in line 132 and a fourth residue, which comprises ethyl acetate, in line 133. 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, and a portion of the fourth distillate is returned to the reaction zone 101. For example, the fourth distillate may be combined with the acetic acid feed, added to the vaporizer 106, or added directly to the reactor 103. The fourth distillate preferably is co-fed with the acetic acid in feed line 105 to vaporizer 106. 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 byproduct and waste generation. In another embodiment, the acetaldehyde may be collected and utilized, with or without further purification, to make useful products including but not limited to n-butanol, 1,3-butanediol, and/or crotonaldehyde and derivatives.

[0087] The fourth residue of fourth column 131 may be purged via line 133. 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 131 such that no detectable amount of acetaldehyde is present in the residue of column 131.

[0088] Fourth column 131 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 131 may operate at a pressure that is higher than the pressure of the other columns.

[0089] The temperature of the fourth distillate exiting in line 132 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 in line 133 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 131 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 131 (FIG. 1)

	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	0.01 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

[0090] In one embodiment, a portion of the third residue in line 124 is recycled to second column 123. In one embodiment, recycling the third residue further reduces the aldehyde components in the second residue and concentrates these aldehyde components in second distillate in line 127 and thereby sent to the fourth column 131, wherein the aldehydes may be more easily separated. The third distillate, e.g. intermediate stream, in line 129 may have lower concentrations of aldehydes and esters due to the recycling of third residue in line 124.

[0091] FIG. 2 illustrates another exemplary separation system that has a similar reaction zone 101 as FIG. 1 and produces a liquid stream 112, e.g., crude ethanol product, for further separation. In one preferred embodiment, the reaction zone 101 of FIG. 2 operates at above 70% acetic acid conversion, e.g., above 85% conversion or above 90% conversion. Thus, the acetic acid concentration in the liquid stream 112, as shown in Table 2, may be low.

[0092] Liquid stream 112 is fed to the first column 150. The operation parameters and conditions for first column 150 in FIG. 2 are provided above. In some embodiments, it is preferred to remove water from the first distillate in line 152.

[0093] The first distillate in line 152 comprises water, in addition to ethanol and other organics. In terms of ranges, the concentration of water in the first distillate in line 152 preferably is from 4 wt.% to 38 wt.%, e.g., from 7 wt.% to 32 wt.%, or from 7 to 25 wt.%. A portion of first distillate in line 153 may be condensed and refluxed, for example, at a ratio as described above,

e.g., from 10:1 to 1:1. The condensed portion of the first distillate may also be fed to a second column 154.

[0094] The remaining portion of the first distillate in 155 is fed to a water separation unit 156. Water separation unit 156 may be an adsorption unit, membrane, molecular sieves, extractive column distillation, or a combination thereof. A membrane or an array of membranes may also be employed to separate water from the distillate. The membrane or array of membranes may be selected from any suitable membrane that is capable of removing a permeate water stream from a stream that also comprises ethanol and ethyl acetate.

[0095] In a preferred embodiment, water separator 156 is a pressure swing adsorption (PSA) unit. The PSA unit is optionally operated at a temperature from 30°C to 160°C, e.g., from 80°C to 140°C, and a pressure of from 0.01 kPa to 550 kPa, e.g., from 1 kPa to 150 kPa. The PSA unit may comprise two to five beds. Water separator 156 may remove at least 95% of the water from the portion of first distillate in line 155, and more preferably from 99% to 99.99% of the water from the first distillate, in a water stream 157. All or a portion of water stream 157 may be returned to column 150 in line 158, where the water preferably is ultimately recovered from column 150 in the first residue in line 151. Additionally or alternatively, all or a portion of water stream 157 may be purged via line 159. The remaining portion of first distillate exits the water separator 156 as ethanol mixture stream 160. Ethanol mixture stream 160 may have a low concentration of water of less than 10 wt.%, e.g., less than 6 wt.% or less than 2 wt.%. Exemplary components of ethanol mixture stream 160 and first residue in line 151 are provided in Table 7 below. It should also be understood that these streams may also contain other components, not listed, such as components derived from the feed.

TABLE 7
FIRST COLUMN 150 WITH PSA (FIG. 2)

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Ethanol Mixture Stream</u>			
Ethanol	20 to 95	30 to 95	40 to 95
Water	< 10	0.01 to 6	0.1 to 2
Ethyl Acetate	< 60	1 to 55	5 to 55
Acetaldehyde	< 10	0.001 to 5	0.01 to 4
Acetal	< 0.1	< 0.1	< 0.05
Acetone	< 0.05	0.001 to 0.03	0.01 to 0.025
<u>Residue</u>			
Acetic Acid	< 90	1 to 50	2 to 35
Water	30 to 100	45 to 95	60 to 90
Ethanol	< 1	< 0.9	< 0.3

[0096] In preferred embodiments, first column 150 is operated to maintain an acetic acid concentration in the first distillate of less than less than 700 wppm, e.g., less than 600 wppm or less than 200 wppm. In terms of ranges, the amount of acetic acid may be from 0.01 wppm to 700 wppm, e.g., from 0.1 to 600 wppm or from 0.1 to 200 wppm. In some embodiments, the first distillate may comprise substantially no acetic acid.

[0097] Preferably, ethanol mixture stream 160 is not returned or refluxed to first column 150. The condensed portion of the first distillate in line 153 may be combined with ethanol mixture stream 160 to control the water concentration fed to the second column 154. For example, in some embodiments the first distillate may be split into equal portions, while in other embodiments, all of the first distillate may be condensed or all of the first distillate may be processed in the water separation unit. In FIG. 2, the condensed portion in line 153 and ethanol mixture stream 160 are co-fed to second column 154. In other embodiments, the condensed portion in line 153 and ethanol mixture stream 160 may be separately fed to second column 154. The combined distillate and ethanol mixture has a total water concentration of greater than 0.5 wt.%, e.g., greater than 2 wt.% or greater than 5 wt.%. In terms of ranges, the total water concentration of the combined distillate and ethanol mixture may be from 0.5 to 15 wt.%, e.g., from 2 to 12 wt.%, or from 5 to 10 wt.%.

[0098] The second column 154 in FIG. 2, also referred to as the “light ends column,” removes ethyl acetate and acetaldehyde from the first distillate in line 153 and/or ethanol mixture stream

160. Ethyl acetate and acetaldehyde are removed as a second distillate in line 161 and ethanol is removed as the second residue in line 162. Second column 154 may be a tray column or packed column. In one embodiment, second column 154 is a tray column having from 5 to 70 trays, e.g., from 15 to 50 trays or from 20 to 45 trays.

[0099] Second column 154 operates at a pressure ranging from 0.1 kPa to 510 kPa, e.g., from 10 kPa to 450 kPa or from 50 kPa to 350 kPa. Although the temperature of second column 154 may vary, when at about 20 kPa to 70 kPa, the temperature of the second residue exiting in line 162 preferably is from 30°C to 75°C, e.g., from 35°C to 70°C or from 40°C to 65°C. The temperature of the second distillate exiting in line 161 preferably is from 20°C to 55°C, e.g., from 25°C to 50°C or from 30°C to 45°C.

[0100] The total concentration of water fed to second column 154 preferably is less than 10 wt.%, as discussed above. When first distillate in line 153 and/or ethanol mixture stream 160 comprises minor amounts of water, e.g., less than 1 wt.% or less than 0.5 wt.%, additional water may be fed to the second column 154 as an extractive agent in the upper portion of the column. A sufficient amount of water is preferably added via the extractive agent such that the total concentration of water fed to second column 154 is from 1 to 10 wt.% water, e.g., from 2 to 6 wt.%, based on the total weight of all components fed to second column 154. If the extractive agent comprises water, the water may be obtained from an external source or from an internal return/recycle line from one or more of the other columns or water separators.

[0101] Suitable extractive agents may also include, for example, dimethylsulfoxide, glycerine, diethylene glycol, 1-naphthol, hydroquinone, N,N'-dimethylformamide, 1,4-butanediol; ethylene glycol-1,5-pentanediol; propylene glycol-tetraethylene glycol-polyethylene glycol; glycerine-propylene glycol-tetraethylene glycol-1,4-butanediol, ethyl ether, methyl formate, cyclohexane, N,N'-dimethyl-1,3-propanediamine, N,N'-dimethylethylenediamine, diethylene triamine, hexamethylene diamine and 1,3-diaminopentane, an alkylated thiopene, dodecane, tridecane, tetradecane, chlorinated paraffins, or a combination thereof. When extractive agents are used, a suitable recovery system, such as a further distillation column, may be used to recycle the extractive agent.

[0102] Exemplary components for the second distillate and second residue compositions for the second column 154 are provided in Table 8, below. It should be understood that the distillate and residue may also contain other components, not listed in Table 8.

TABLE 8
SECOND COLUMN 154 (FIG. 2)

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Second Distillate</u>			
Ethyl Acetate	5 to 90	10 to 80	15 to 75
Acetaldehyde	< 60	1 to 40	1 to 35
Ethanol	< 45	0.001 to 40	0.01 to 35
Water	< 20	0.01 to 10	0.1 to 5
<u>Second Residue</u>			
Ethanol	80 to 99.5	85 to 99.5	90 to 99.5
Water	< 20	0.001 to 15	0.01 to 10
Ethyl Acetate	< 1	0.001 to 2	0.001 to 0.5
Acetic Acid	< 0.5	< 0.01	0.001 to 0.01

[0103] The second distillate in line 161, which comprises ethyl acetate and/or acetaldehyde, preferably is refluxed as shown in FIG. 2, for example, at a reflux ratio of from 1:30 to 30:1, e.g., from 1:10 to 10:1 or from 1:3 to 3:1. In one aspect, not shown, the second distillate 161 or a portion thereof may be returned to reactor 103.

[0104] In one embodiment, the second distillate in line 161 and/or a refined second distillate, or a portion of either or both streams, may be further separated to produce an acetaldehyde-containing stream and an ethyl acetate-containing stream. This may allow a portion of either the resulting acetaldehyde-containing stream or ethyl acetate-containing stream to be recycled to reactor 103 while purging the other stream. The purge stream may be valuable as a source of either ethyl acetate and/or acetaldehyde.

[0105] Some of the residues withdrawn from the separation zone 102 comprise acetic acid and water. Depending on the amount of water and acetic acid contained in the residue of first column, e.g., 120 in FIG. 1, or 150 in FIG. 2, the residue may be treated in one or more of the following processes. The following are exemplary processes for further treating the residue and it should be understood that any of the following may be used regardless of acetic acid concentration. When the residue comprises a majority of acetic acid, e.g., greater than 70 wt.%,

the residue may be recycled to the reactor without any separation of the water. In one embodiment, the residue may be separated into an acetic acid stream and a water stream when the residue comprises a majority of acetic acid, e.g., greater than 50 wt.%. Acetic acid may also be recovered in some embodiments from the residue having a lower acetic acid concentration. The residue may be separated into the acetic acid and water streams by a distillation column or one or more membranes. If a membrane or an array of membranes is employed to separate the acetic acid from the water, the membrane or array of membranes may be selected from any suitable acid resistant membrane that is capable of removing a permeate water stream. The resulting acetic acid stream optionally is returned to the reactor 103. The resulting water stream may be used as an extractive agent or to hydrolyze an ester-containing stream in a hydrolysis unit.

[0106] In other embodiments, for example, where the residue comprises less than 50 wt.% acetic acid, possible options include one or more of: (i) returning a portion of the residue to reactor 103, (ii) neutralizing the acetic acid, (iii) reacting the acetic acid with an alcohol, or (iv) disposing of the residue in a waste water treatment facility. It also may be possible to separate a residue comprising less than 50 wt.% acetic acid using a weak acid recovery distillation column to which a solvent (optionally acting as an azeotroping agent) may be added. Exemplary solvents that may be suitable for this purpose include ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, vinyl acetate, diisopropyl ether, carbon disulfide, tetrahydrofuran, isopropanol, ethanol, and C₃-C₁₂ alkanes. When neutralizing the acetic acid, it is preferred that the residue comprises less than 10 wt.% acetic acid. Acetic acid may be neutralized with any suitable alkali or alkaline earth metal base, such as sodium hydroxide or potassium hydroxide. When reacting acetic acid with an alcohol, it is preferred that the residue comprises less than 50 wt.% acetic acid. The alcohol may be any suitable alcohol, such as methanol, ethanol, propanol, butanol, or mixtures thereof. The reaction forms an ester that may be integrated with other systems, such as carbonylation production or an ester production process. Preferably, the alcohol comprises ethanol and the resulting ester comprises ethyl acetate. Optionally, the resulting ester may be fed to the hydrogenation reactor.

[0107] In some embodiments, when the residue comprises very minor amounts of acetic acid, e.g., less than 5 wt.%, the residue may be disposed of to a waste water treatment facility without

further processing. The organic content, e.g., acetic acid content, of the residue beneficially may be suitable to feed microorganisms used in a waste water treatment facility.

[0108] The columns shown in figures may comprise any distillation column capable of performing the desired separation and/or purification. For example, other than the acid columns describe above, the other columns preferably are a tray column 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.

[0109] 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 the figures. 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. The heat that is provided to the 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 the figures, additional reactors, flashers, condensers, heating elements, and other components may be used in various 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.

[0110] The temperatures and pressures employed in 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 or superatmospheric pressures may be employed. 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. As will be recognized by those skilled in the art, 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.

[0111] The final ethanol product produced by the processes of the present invention may be taken from a stream that primarily comprises ethanol from FIGS. 1 and 2. The ethanol product may be an industrial grade ethanol comprising 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 ethanol product. Exemplary finished ethanol compositional ranges are provided below in Table 9.

TABLE 9
FINISHED ETHANOL COMPOSITIONS

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	75 to 99.9	80 to 99.5	85 to 96
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

[0112] 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 composition 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 is substantially free of acetaldehyde, optionally comprising less than 8 wppm acetaldehyde, e.g., less than 5 wppm or less than 1 wppm.

[0113] In some embodiments, when further water separation is used, the ethanol product may be withdrawn as a stream from the water separation unit as discussed above. In such embodiments, the ethanol concentration of the ethanol product may be greater than indicated in Table 9, and preferably is greater than 97 wt.% ethanol, e.g., greater than 98 wt.% or greater than 99.5 wt.%. The ethanol product in this aspect preferably comprises less than 3 wt.% water, e.g., less than 2 wt.% or less than 0.5 wt.%.

[0114] The finished ethanol composition produced by the embodiments of the present invention may be used in a variety of applications including 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.

[0115] 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, ethyl benzene, aldehydes, butadiene, 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.

[0116] 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

[0117] The following examples were prepared with ASPEN Plus 7.1 simulation software to test various feed composition and separation systems. Several runs were conducted to determine the effect of reflux ratio (R/D), distillate to feed flow (D/TOF) ratios, feed stage and

number of stages. Runs where the acetic acid concentration in the first distillate is less than 700 wppm and the ethanol recovery was at least 98% demonstrated energy efficient operating conditions. Energy is relative and based on million btu per ton of ethanol refined in the column.

Example 1

[0118] A liquid portion of a crude ethanol mixture obtained by converting from 40 to 70% acetic acid is fed to an acid column as shown in FIG. 1. Each run for this example was at 1:2 R/D. The DTOF between Run 1-A and Run 1-B, indicates higher acetic acid concentration in the distillate with increased a larger DTOF along with energy. The number of stages and feed location was varied in Runs 1-C through 1-I. In each of these runs the concentration of acetic acid exceeded 600 wppm. The results are shown in Table 10.

Table 10

Run	Energy (MMBtu/ton)	DTOF	R/D	[HOAc] Distillate (wppm)	EtOH Recovery (%)	Feed Stage	Number of Stages
1-A	2.83	0.4	1:2	25,094	83.51%	30	40
1-B	3.22	0.5	1:2	98,348	93.97%	30	40
1-C	2.98	0.4	1:2	44,900	79.58%	35	40
1-D	2.54	0.4	1:2	12,954	89.84%	22	55
1-E	2.55	0.4	1:2	5,166	90.36%	30	55
1-F	2.55	0.4	1:2	2,974	90.40%	35	55
1-G	2.54	0.4	1:2	12,837	89.90%	22	70
1-H	2.54	0.4	1:2	4,935	90.55%	30	70
1-I	2.54	0.4	1:2	2,691	90.72%	35	70

Example 2

[0119] Using a similar crude ethanol mixture as Example 1, the reflux ratio was changed to 1:1. Runs 2-E, 2-H, 2-L, and 2-O demonstrated low acetic acid concentration and high ethanol recoveries. The results are shown in Table 11.

Table 11

Run	Energy (MMBtu/ton)	DTOF	R/D	[HOAc] Distillate (wppm)	EtOH Recovery (%)	Feed Stage	Number of Stages
2-A	3.10	0.4	1:1	5,521	94.32%	22	40
2-B	3.36	0.4	1:1	4,052	90.43%	30	40
2-C	3.65	0.4	1:1	5,235	86.29%	35	40
2-D	2.82	0.4	1:1	1,888	99.32%	22	55
2-E	2.85	0.4	1:1	502	99.00%	30	55
2-F	4.34	0.5	1:1	26,343	99.99%	30	55
2-G	4.85	0.6	1:1	166,668	99.99%+	30	55
2-H	2.87	0.4	1:1	234	98.64%	35	55
2-I	4.39	0.5	1:1	19,486	99.98%	35	55
2-J	4.85	0.6	1:1	166,684	99.99%+	35	55
2-K	2.79	0.4	1:1	1,588	99.98%	22	70
2-L	2.80	0.4	1:1	361	99.97%	30	70
2-M	4.34	0.5	1:1	26,367	99.99%+	30	70
2-N	4.85	0.6	1:1	166,662	99.99%+	30	70
2-O	2.80	0.4	1:1	145	99.95%	35	70
2-P	4.38	0.5	1:1	19,431	99.99%+	35	70
2-Q	4.85	0.6	1:1	166,669	99.99%+	35	70

Example 3

[0120] Using a similar crude ethanol mixture as Example 1, the reflux ratio was change to 2:1. Runs 3-F and 3-I demonstrated low acetic acid concentration and high ethanol recoveries. The results are shown in Table 12.

Table 12

Run	Energy (MMBtu/ton)	DTOF	R/D	[HOAc] Distillate (wppm)	EtOH Recovery (%)	Feed Stage	Number of Stages
3-A	4.41	0.4	2:1	1,846	96.69%	30	40
3-B	6.55	0.5	2:1	32,777	98.54%	30	40
3-C	4.76	0.4	2:1	2,086	92.82%	35	40
3-D	4.12	0.4	2:1	2,484	99.99%+	22	55
3-E	4.13	0.4	2:1	809	99.99%	30	55
3-F	4.14	0.4	2:1	379	99.98%	35	55
3-G	4.12	0.4	2:1	2,490	99.99%+	22	70
3-H	4.13	0.4	2:1	810	99.99%+	30	70
3-I	4.14	0.4	2:1	379	99.99%+	35	70

[0121] The results in Table 12, that used higher reflux ratio, expectedly consumed a larger amount of energy than the results in Table 11. Using less energy with a lower reflux ratio, as shown in Table 10, was unable to achieve low acetic acid concentrations. What is surprising and unexpected is that the acetic acid concentration may be reduced at lower energies in Table 11.

Example 4

[0122] A liquid portion of a crude ethanol mixture obtained by converting more than 90% acetic acid is fed to an acid column as shown in FIG. 2. The acid column of FIG. 2 operates to remove acetic acid and a substantial portion of water in the residue. Each run for this example was at 1:5 R/D. The number of stages in the column was 50. Although low acetic acid concentration may be achieved at low DTOF, the ethanol recovery was poor. Runs 4-C, 4-F, and 4-I demonstrated low acetic acid concentration and high ethanol recoveries at DTOF of 0.7. The results are shown in Table 13.

Table 13

Run	Energy (MMBtu/ton)	DTOF	R/D	[HOAc] Distillate (wppm)	EtOH Recovery (%)	Feed Stage
4-A	1.79	0.5	1:5	273	61.43%	15
4-B	1.74	0.6	1:5	298	80.00%	15
4-C	1.73	0.7	1:5	324	98.48%	15
4-D	2.25	0.8	1:5	5,914	99.99%+	15
4-E	1.74	0.6	1:5	131	80.06%	19
4-F	1.73	0.7	1:5	158	98.36%	19
4-G	2.25	0.8	1:5	5,490	99.99%+	19
4-H	1.75	0.6	1:5	52	79.86%	24
4-I	1.76	0.7	1:5	100	97.40%	24
4-J	2.25	0.8	1:5	5,432	99.99%+	24

Example 5

[0123] Using a similar crude ethanol mixture as Example 4, the reflux ratio was change to 1:1. The runs that demonstrated low acetic acid and high ethanol recovery at a DTOF of 0.7 were similar to Table 13. The results are shown in Table 14.

Table 14

Run	Energy (MMBtu/ton)	DTOF	R/D	[HOAc] Distillate (wppm)	EtOH Recovery (%)	Feed Stage
5-A	2.66	0.5	1:1	100	65.61%	15
5-B	2.57	0.6	1:1	99	85.49%	15
5-C	2.81	0.7	1:1	684	99.99%+	15
5-D	3.77	0.8	1:1	4,427	99.99%+	15
5-E	2.51	0.6	1:1	25	86.56%	19
5-F	2.81	0.7	1:1	399	99.99%+	19
5-G	3.77	0.8	1:1	3,318	99.99%+	19
5-H	2.46	0.6	1:1	4	87.37%	24
5-I	2.81	0.7	1:1	185	99.99%+	24
5-J	3.78	0.8	1:1	2,429	99.99%+	24

Example 6

[0124] Using a similar crude ethanol mixture as Example 4, the reflux ratio was change to 3:1. The results are shown in Table 15.

Table 15

Run	Energy (MMBtu/ton)	DTOF	R/D	[HOAc] Distillate (wppm)	EtOH Recovery (%)	Feed Stage
6-A	5.10	0.5	3:1	54	67.38%	15
6-B	4.90	0.6	3:1	49	87.88%	15
6-C	5.62	0.7	3:1	771	99.99%+	15
6-D	7.59	0.8	3:1	3406	99.99%+	15
6-E	4.76	0.6	3:1	12	89.11%	19
6-F	5.63	0.7	3:1	510	99.99%+	19
6-G	7.59	0.8	3:1	2574	99.99%+	19
6-H	4.65	0.6	3:1	2	90.11%	24
6-I	5.63	0.7	3:1	287	99.99%+	24
6-J	7.59	0.8	3:1	1913	99.99%+	24

[0125] 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.

What is claimed is:

1. A process for producing ethanol comprising:
hydrogenating a feed stream comprising alkanoic acid and/or esters thereof in a reactor in the presence of a catalyst to produce a crude ethanol mixture comprising ethanol, water, and acetic acid;
separating at least a portion of the crude ethanol mixture in a distillation column operated at a reflux ratio from 1:1.8 to 1.5:1 to yield a distillate comprising at least 90% of the ethanol from the crude ethanol mixture and less than 600 wppm acetic acid and a residue comprising acetic acid, wherein the distillate to feed flow ratio is less than 0.5; and
recovering ethanol from the distillate.
2. The process of claim 1, wherein the conversion of acetic acid is from 40% to 70%.
3. The process of claim 1, wherein the distillate to feed flow ratio is from 0.4 to 0.5.
4. The process of claim 1, wherein the distillate comprises at least 98% of the ethanol from the crude ethanol mixture.
5. The process of claim 1, wherein the distillation column comprises from 40 to 120 stages.
6. The process of claim 1, wherein the at least a portion of the crude ethanol mixture is fed to the distillation column in a lower portion, when the distillation column comprises less than 60 stages.
7. The process of claim 1, wherein the at least a portion of the crude ethanol mixture is fed to the distillation column below a 30th stage, when the distillation column comprises more than 60 stages.
8. The process of claim 1, further comprising separating at least a portion of the distillate in

a second column to yield a second distillate comprising ethyl acetate and a second residue comprising ethanol and water.

9. The process of claim 8, further comprising separating at least a portion of the second residue in a third column to yield a third distillate comprising ethanol and a third residue comprising water.

10. The process of claim 9, wherein a portion of the third residue is returned to the second column.

11. A process for producing ethanol comprising:

hydrogenating a feed stream comprising alkanoic acid and/or esters thereof in a reactor in the presence of a catalyst to produce a crude ethanol mixture comprising ethanol, water, and acetic acid;

separating at least a portion of the crude ethanol mixture in a distillation column having more than 55 stages and operated at a reflux ratio of greater than 1.5:1 to yield a distillate comprising at least 90% of the ethanol from the crude ethanol mixture and less than 600 wppm acetic acid and a residue comprising acetic acid, wherein the distillate to feed flow ratio is less than 0.5; and

recovering ethanol from the distillate.

12. The process of claim 11, wherein the reflux ratio is 2:1.

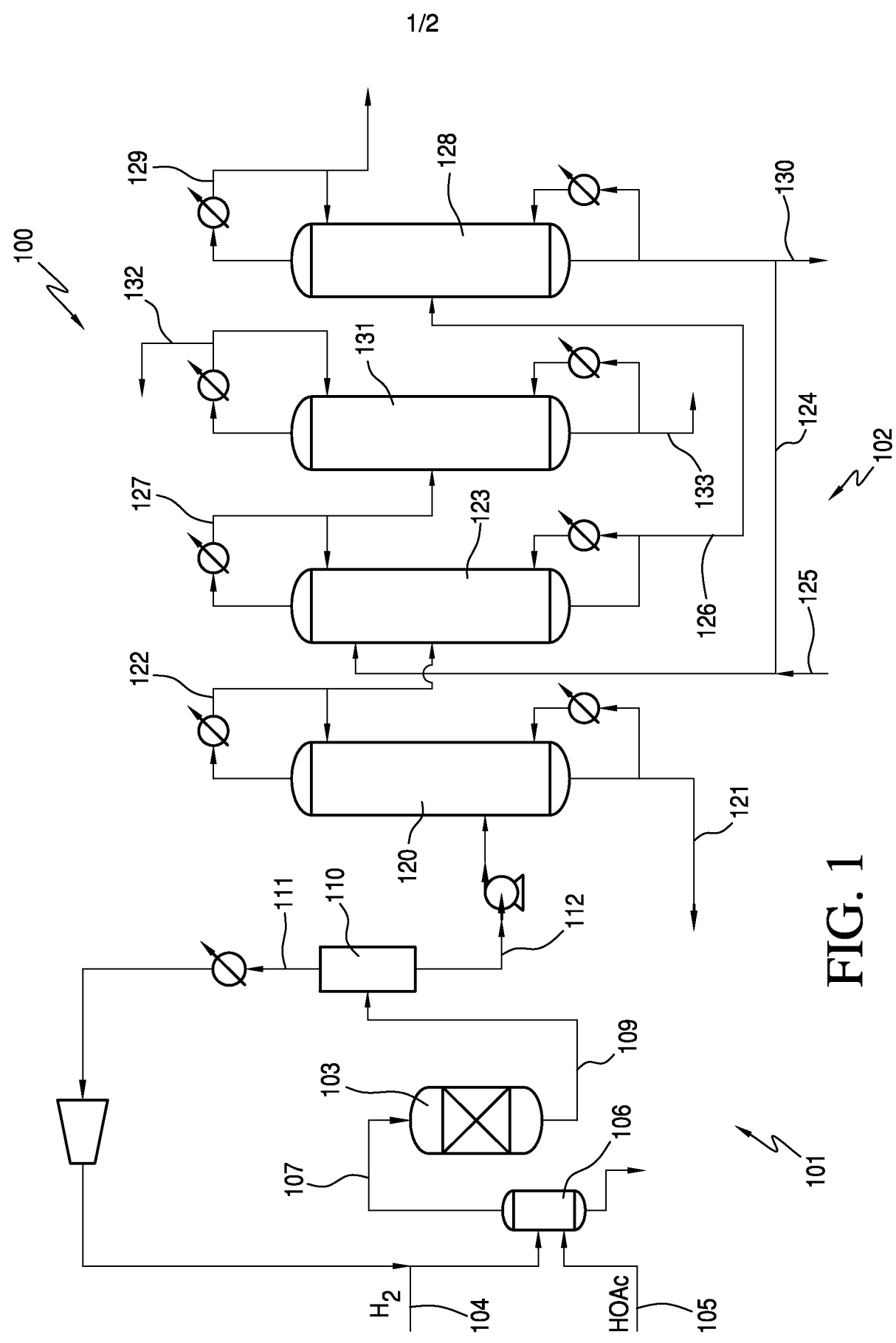
13. The process of claim 11, wherein the distillation comprises from 55 to 120 stages.

14. A process for producing ethanol comprising:

hydrogenating a feed stream comprising alkanoic acid and/or esters thereof in a reactor in the presence of a catalyst to produce a crude ethanol mixture comprising ethanol, water, and acetic acid;

separating at least a portion of the crude ethanol mixture in a distillation column operated at a reflux ratio from 1:10 to 1:1 to yield a distillate comprising at least 90% of the ethanol from the crude ethanol mixture and less than 700 wppm acetic acid and a residue comprising acetic acid and a substantial portion of the water fed to the distillation column, wherein the distillate to feed flow ratio is from 0.6 to 0.8; and
recovering ethanol from the distillate.

15. The process of claim 14, wherein the conversion of acetic acid is greater than 70%.
16. The process of claim 14, wherein the distillate to feed flow ratio is about 0.7.
17. The process of claim 14, wherein the distillate comprises at least 98% of the ethanol from the crude ethanol mixture.
18. The process of claim 14, wherein the substantial portion of water is from 30 to 90% of the water fed to the distillation column.
19. The process of claim 14, further comprising removing water in a water separation unit to yield an ethanol mixture, wherein the water separation unit is selected from the group consisting of extractive distillation columns, adsorption units, membranes, and molecular sieves.
20. The process of claim 19, further comprising separating at least a portion of the ethanol mixture in a second distillation column to yield a second distillate comprising ethyl acetate and second residue comprising ethanol.



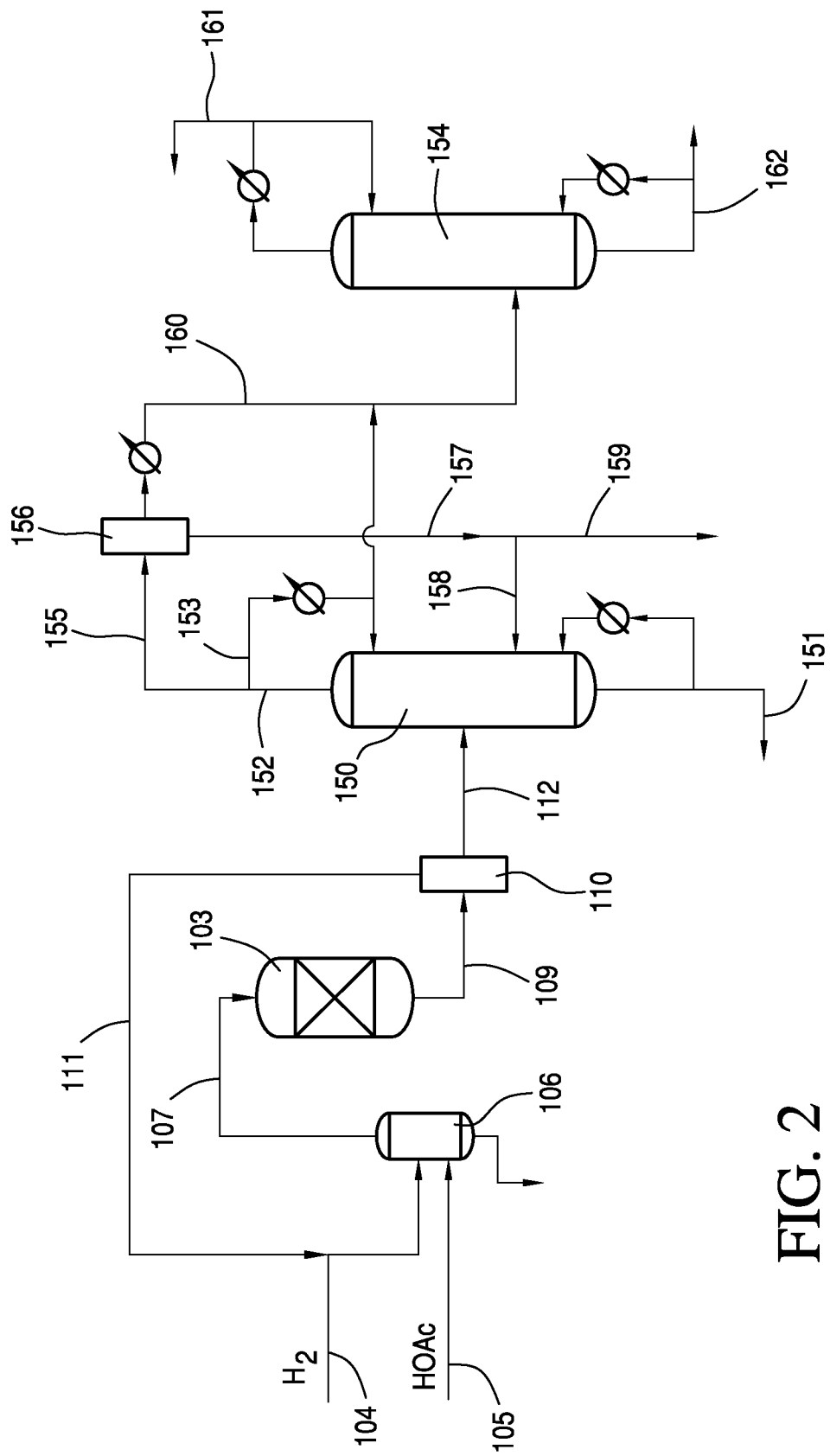


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/046487

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C29/149 C07C29/80 C07C31/08 B01D3/14
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C B01D

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

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

EPO-Internal, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/056597 A2 (CELANESE INT CORP [US]; JEVTIC RADMILA [US]; JOHNSTON VICTOR J [US]; W) 12 May 2011 (2011-05-12) paragraphs [0002], [0004], [0009], [0058] - [0059], [0064] - [0066]; tables paragraphs [0072] - [0075] -----	1-20
Y	US 3 404 186 A (BAILEY WALTON W ET AL) 1 October 1968 (1968-10-01) the whole document -----	1-20
X	EP 0 053 917 A1 (BP CHEM INT LTD [GB]) 16 June 1982 (1982-06-16) the whole document ----- -/--	1-20



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

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

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

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

"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

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"&" document member of the same patent family

Date of the actual completion of the international search

10 August 2012

Date of mailing of the international search report

21/08/2012

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/046487

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	ROSENDO VARGAS VALLE ET AL: "Control of an azeotropic distillation process for anhydrous ethanol production", ELECTRICAL COMMUNICATIONS AND COMPUTERS (CONIELECOMP), 2011 21ST INTERNATIONAL CONFERENCE ON, IEEE, 28 February 2011 (2011-02-28), pages 88-93, XP031937762, DOI: 10.1109/CONIELECOMP.2011.5749345 ISBN: 978-1-4244-9558-0 the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

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