

PROCESS FOR PRODUCING AN ETHYL ACETATE SOLVENT AND CO-PRODUCTION OF ETHANOL

PRIORTY CLAIM

[0001] This application claims priority to U.S. Provisional App. No. 61/300,815, filed on February 2, 2010; U.S. Provisional App. No. 61/332,696, U.S. Provisional App. No. 61/332,699, and U.S. Provisional App. No. 61/332,728, each filed on May 7, 2010; U.S. Provisional App. No. 61/346,344, filed on May 19, 2010; and U.S. App. No. 12/833,809, filed on July 9, 2010, the entireties of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for producing an ethyl acetate solvent and, in particular, to processes for producing an ethyl acetate solvent from the hydrogenation of acetic acid.

BACKGROUND OF THE INVENTION

[0003] Ethyl acetate is commonly used as an industrial solvent used for paints, coatings, wood stains, oil-based lacquers and enamels, adhesives, cellulose, inks, plastics, or fats. In addition ethyl acetate may be used in the preparation of photographic films and plates, in as a drug intermediate or in nail polish removers. Ethyl acetate is a moderately polar solvent that has the advantages of being volatile, relatively non-toxic, and non-hygroscopic.

[0004] Ethyl acetate is commonly prepared by esterification of ethanol and acetic acid. Ethanol for use in production of ethyl acetate 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 for fuels or 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.

[0005] Ethanol production via the reduction of alkanolic acids and/or other carbonyl group-containing compounds has been widely studied, and a variety of combinations of catalysts, supports, and operating conditions have been mentioned in the literature. During the reduction of alkanolic acid, e.g., acetic acid, other compounds are formed with ethanol or are formed in side reactions. These impurities 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.

[0006] Therefore, a need remains for improving the recovery of 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

[0007] In a first embodiment the present invention is directed to a process for recovering an ethyl acetate solvent, comprising the steps of hydrogenating acetic acid in a reactor in the presence of a catalyst to form a crude product, separating at least a portion of the crude product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, wherein the first residue comprises substantially all of the acetic acid from the at least a portion of the crude product, and separating at least a portion of the first distillate to form the ethyl acetate solvent comprising ethyl acetate and ethanol.

[0008] In one aspect the process recovers ethanol and ethyl acetate solvent, comprising the steps of hydrogenating acetic acid in the presence of a catalyst to form a crude product, separating at least a portion of the crude product stream in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, separating at least a portion of the first distillate in a second column into a second distillate comprising the ethyl acetate solvent and a second residue comprising ethanol and water, and separating at least a portion of the second residue in a third column into a third distillate

comprising ethanol and a third residue comprising water.

[0009] In another aspect of the present invention, the process recovers ethanol and ethyl acetate solvent, comprising the steps of hydrogenating acetic acid in a reactor in the presence of a catalyst to form a crude product stream, separating at least a portion of the crude product stream in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, separating at least a portion of the first distillate in a second column into a second distillate comprising ethyl acetate and a second residue comprising ethanol and water, separating at least a portion of the second residue in a third column into a third distillate comprising ethanol and a third residue comprising water, and separating at least a portion of the second distillate in a fourth column into a fourth distillate comprising acetaldehyde and a fourth residue comprising the ethyl acetate solvent.

[0010] In a further aspect of the present invention, the process recovers ethyl acetate solvent comprising the steps of hydrogenating acetic acid in the presence of a catalyst to form a crude product, separating at least a portion of the crude product in a distillation column into a residue comprising acetic acid and a distillate comprising ethyl acetate, ethanol, water, and acetaldehyde, and condensing the distillate and biphasically separating the condensed distillate to form a heavy phase comprising water and a light phase comprising the ethyl acetate solvent.

[0011] In yet another aspect of the present invention, the process recovers ethyl acetate solvent comprising the steps of hydrogenating acetic acid in the presence of a catalyst to form a crude product, separating at least a portion of the crude product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, and separating at least a portion of the first distillate in a second column into a second distillate comprising the ethyl acetate solvent and a second residue comprising water.

[0012] In a second embodiment of the present invention is directed to a process for recovering an ethyl acetate solvent comprising providing a crude product comprising ethanol, ethyl acetate, water, and acetic acid, separating at least a portion of the crude product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, wherein the first residue comprises substantially all of the acetic acid from the at least a portion of the crude product, and separating at least a portion of the first distillate to form the ethyl acetate solvent comprising ethyl acetate and ethanol.

[0013] In a third embodiment of the present invention is directed to a process for recovering

an ethyl acetate solvent, comprising the steps of hydrogenating acetic acid in a reactor in the presence of a catalyst to form a crude product, and separating at least a portion of the crude product in a distillation column into a distillate comprising acetaldehyde and a residue comprising the ethyl acetate solvent, wherein the ethyl acetate solvent comprises ethyl acetate, acetic acid, water and ethanol.

[0014] In a fourth embodiment of the present invention is directed to a process for recovering an ethyl acetate solvent, comprising the steps of providing a crude product comprising ethanol, ethyl acetate, water, acetaldehyde, and acetic acid, and separating at least a portion of the crude product in a distillation column into a distillate comprising acetaldehyde and a residue comprising the ethyl acetate solvent, wherein the ethyl acetate solvent comprises ethyl acetate, acetic acid, water and ethanol.

BRIEF DESCRIPTION OF DRAWINGS

[0015] The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts.

[0016] FIG. 1 is a schematic diagram of a hydrogenation system for co-production of ethanol and an ethyl acetate solvent in accordance with one embodiment of the present invention.

[0017] FIG. 2 is a schematic diagram of a hydrogenation system for co-production of ethanol and an ethyl acetate solvent in accordance with one embodiment of the present invention.

[0018] FIG. 3 is a schematic diagram of a hydrogenation system for production of an ethyl acetate solvent in accordance with one embodiment of the present invention.

[0019] FIG. 4 is a schematic diagram of a hydrogenation system for production of an ethyl acetate solvent in accordance with one embodiment of the present invention.

[0020] FIG. 5 is a schematic diagram of a hydrogenation system for production of an ethyl acetate solvent in accordance with one embodiment of the present invention.

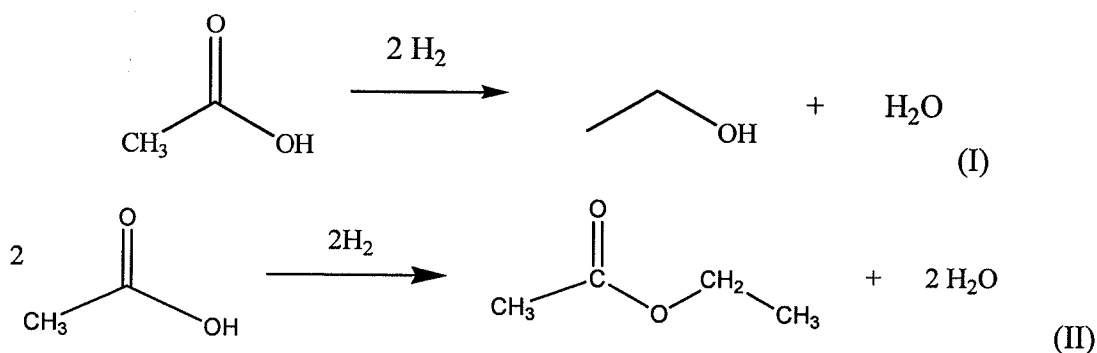
DETAILED DESCRIPTION OF THE INVENTION

[0021] The present invention relates to processes for recovering an ethyl acetate solvent. The ethyl acetate solvent is derived from a crude product produced by a hydrogenation process comprising hydrogenating acetic acid in the presence of a catalyst. In one embodiment, ethyl acetate solvent may comprise ethyl acetate and ethanol in a weight ratio of 5:1 to 1:5, e.g., from

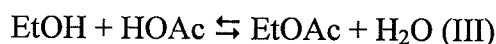
3:1 to 1:3 or from 1.5:1 to 1:1.5. In one embodiment, the ethyl acetate solvent is co-produced with an ethanol stream, which also is derived from the crude product.

[0022] The composition of the ethyl acetate solvent may vary widely, depending, for example, on the catalyst employed and reaction conditions among other factors, and may contain one or more additional compounds, such as ethanol, water, acetic acid and acetaldehyde. Although water and acetaldehyde may be present in the ethyl acetate solvent, it is desirable that these compounds are present, if at all, in a minor amount. For example, the ethyl acetate solvent may comprise water in an amount less than 10 wt.%, e.g., less than 8 wt.%, or less than 5 wt.%, and may comprise acetaldehyde in an amount less than 1 wt.%, e.g., less than 0.5 wt.%, or less than 0.25 wt.%. The acetaldehyde may be present in the form of free acetaldehyde or as diethyl acetal. When co-produced with ethanol, the ethyl acetate solvent and the ethanol stream preferably are respectively separated from the crude product.

[0023] The hydrogenation of acetic acid to form ethanol, ethyl acetate and water is represented by reactions I and II:



[0024] Ethyl acetate may also be formed through esterification of acetic acid and ethanol as shown in reaction III:



[0025] Suitable hydrogenation catalysts include catalysts comprising a first metal and optionally one or more of a second metal, a third metal or 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 transitional 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, silver/palladium, copper/palladium, nickel/palladium, gold/palladium, ruthenium/rhenium, and ruthenium/iron. Exemplary catalysts are further described in U.S. Patent Nos. 7,608,744, and 7,863,489, and U.S. Publication No. 2010/0197485, the entireties of which are incorporated herein by reference.

[0026] In one exemplary 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. When 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 demand for platinum.

[0027] As indicated above, the catalyst optionally 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.

[0028] If the catalyst includes two or more metals, e.g., a first metal and a second metal, the first metal optionally 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 and 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.

[0029] 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.

[0030] 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 and 4 wt.%, e.g., from 0.1 to 3 wt.%, or from 0.1 to 2 wt.%.

[0031] In addition to one or more metals, the exemplary catalysts further comprise a support or a modified support, meaning a support that includes a support material and a support modifier, which adjusts the acidity of the support material. The total weight of the support or modified support, based on the total weight of the catalyst, preferably is from 75 wt.% to 99.9 wt.%, e.g., from 78 wt.% to 97 wt.%, or from 80 wt.% to 95 wt.%. In preferred embodiments that use a modified support, the support modifier is present in an amount from 0.1 wt.% to 50 wt.%, e.g., from 0.2 wt.% to 25 wt.%, from 0.5 wt.% to 15 wt.%, or from 1 wt.% to 8 wt.%, based on the total weight of the catalyst.

[0032] 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.

[0033] In the production of ethanol, the catalyst support may be modified with a support modifier. Preferably, the support modifier is a basic modifier that has a low volatility or no volatility. Such basic modifiers, for example, may be selected from the group consisting of: (i) alkaline earth oxides, (ii) alkali metal oxides, (iii) alkaline earth metal metasilicates, (iv) alkali metal metasilicates, (v) Group IIB metal oxides, (vi) Group IIB metal metasilicates, (vii) Group IIIB metal oxides, (viii) Group IIIB metal metasilicates, and mixtures thereof. In addition to oxides and metasilicates, other types of modifiers including nitrates, nitrites, acetates, and lactates may be used. Preferably, the support modifier is selected from the group consisting of oxides and metasilicates of any of sodium, potassium, magnesium, calcium, scandium, yttrium, and zinc, as well as mixtures of any of the foregoing. Preferably, the support modifier is a calcium silicate, and more preferably calcium metasilicate (CaSiO_3). If the support modifier comprises calcium metasilicate, it is preferred that at least a portion of the calcium metasilicate is in crystalline form.

[0034] A preferred silica support material is SS61138 High Surface Area (HSA) Silica Catalyst Carrier from Saint Gobain NorPro. The Saint-Gobain NorPro SS61138 silica contains approximately 95 wt.% high surface area silica; a surface area of about 250 m²/g; a median pore diameter of about 12 nm; an average pore volume of about 1.0 cm³/g as measured by mercury intrusion porosimetry and a packing density of about 0.352 g/cm³ (22 lb/ft³).

[0035] A preferred silica/alumina support material is KA-160 (Sud Chemie) silica spheres having a nominal diameter of about 5 mm, a density of about 0.562 g/ml, in absorptivity of about 0.583 g H₂O/g support, a surface area of about 160 to 175 m²/g, and a pore volume of about 0.68 ml/g.

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

[0037] The metals of the catalysts may be dispersed throughout the support, coated on the outer surface of the support (egg shell) or decorated on the surface of the support.

[0038] 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. Patent Nos. 7,608,744, and 7,863,489, and U.S. Publication No. 2010/0197485, the entireties of which are incorporated herein by reference.

[0039] Some embodiments of the process of hydrogenating acetic acid to form ethanol according to one embodiment of the invention may include a variety of configurations using a fixed bed reactor or a fluidized bed reactor, as one of skill in the art will readily appreciate. 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, radial flow reactor or reactors may be employed, or a series of reactors may be employed with or without heat exchange, quenching, or introduction of additional feed material. Alternatively, a shell and tube reactor provided with a heat transfer medium may be used. In many cases, the reaction zone may be housed in a single vessel or in a series of vessels with heat exchangers therebetween.

[0040] 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.

[0041] The hydrogenation reaction may be carried out in either the liquid phase or vapor phase. Preferably, the reaction is carried out in the vapor phase under the following conditions. The reaction temperature may range from 125°C to 350°C, e.g., from 200°C to 325°C, from 225°C to 300°C, or from 250°C to 300°C. The pressure may range from 10 KPa to 3000 KPa (about 1.5 to 435 psi), 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.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] The raw materials, acetic acid and hydrogen, used in connection with the process of this invention may be derived from any suitable source including natural gas, petroleum, coal, biomass, and so forth. As examples, acetic acid may be produced via methanol carbonylation, acetaldehyde oxidation, ethylene oxidation, oxidative fermentation, and anaerobic

fermentation. 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 compared to natural gas, it may become advantageous to produce acetic acid from synthesis gas ("syn gas") that is derived from any available carbon source. United States Patent No. 6,232,352, the disclosure 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 syn gas is diverted from the methanol synthesis loop and supplied to a separator unit to recover CO and hydrogen, which are then used to produce acetic acid. In addition to acetic acid, such a process can also be used to make hydrogen which may be utilized in connection with this invention.

[0046] Methanol carbonylation processes suitable for production of acetic acid are described in U.S. Patent 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 disclosure of which is incorporated herein by reference. Optionally, the production of ethanol may be integrated with such methanol carbonylation processes.

[0047] U.S. Patent 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 syn gas 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. Patent No. 5,821,111, which discloses a process for converting waste biomass through gasification into synthesis gas as well as U.S. Patent No. 6,685,754, the disclosures of which are incorporated herein by reference.

[0048] In one optional embodiment, the acetic acid fed to the hydrogenation reaction may also comprise other carboxylic acids and anhydrides, as well as acetaldehyde and acetone. 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.

[0049] 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. Patent No. 6,657,078, the entirety of which is incorporated herein by reference. The crude vapor product, for example, may be fed directly to the ethanol synthesis reaction zones of the present invention without the need for condensing the acetic acid and light ends or removing water, saving overall processing costs.

[0050] The acetic acid may be vaporized at the reaction temperature, following which the vaporized acetic acid can 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 transferred to the vapor state by passing hydrogen, recycle gas, another suitable gas, or mixtures thereof through the acetic acid at a temperature below the boiling point of acetic acid, thereby humidifying the carrier gas with acetic acid vapors, followed by heating the mixed vapors up to the reactor inlet temperature. Preferably, the acetic acid is transferred to the vapor 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.

[0051] In particular, the hydrogenation of acetic acid may achieve favorable conversion of acetic acid and favorable selectivity and productivity to ethanol. For purposes of the present invention, the term “conversion” refers to the amount of acetic acid in the feed that is converted to a compound other than acetic acid. Conversion is expressed as a mole percentage based on acetic acid in the feed. The conversion may be at least 10%, e.g., at least 20%, at least 40%, at least 50%, at least 60%, at least 70% or at least 80%. Although catalysts that have high conversions are desirable, such as at least 80% or at least 90%, in some embodiments a low conversion may be acceptable at high selectivity for ethanol. It is, of course, well understood

that in many cases, it is possible to compensate for conversion by appropriate recycle streams or use of larger reactors, but it is more difficult to compensate for poor selectivity.

[0052] 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 50 mole % of the converted acetic acid is converted to ethanol, we refer to the ethanol selectivity as 50%. Preferably, the catalyst selectivity to ethoxylates is at least 60%, e.g., at least 70%, or at least 80%. As used herein, the term “ethoxylates” refers specifically to the compounds ethanol, acetaldehyde, and ethyl acetate. Preferably, the selectivity to ethanol is at least 80%, e.g., at least 85% or at least 88%. Preferred embodiments of the hydrogenation process also have low selectivity to undesirable products, such as methane, ethane, and carbon dioxide. The selectivity to these undesirable products preferably is less than 4%, e.g., less than 2% or less than 1%. More preferably, these undesirable products are not detectable. 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.

[0053] 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 200 grams of ethanol per kilogram catalyst per hour, e.g., at least 400 or at least 600 is preferred. In terms of ranges, the productivity preferably is from 200 to 3,000 grams of ethanol per kilogram catalyst per hour, e.g., from 400 to 2,500 or from 600 to 2,000.

[0054] In various embodiments, the crude product produced by the hydrogenation process, before any subsequent processing, such as purification and separation, will typically comprise unreacted acetic acid, ethanol and water. The crude product may also be referred to as the crude ethanol product. As used herein, the term “crude product” refers to any composition comprising from 5 to 70 wt.% ethanol and from 5 to 35 wt.% water. In some exemplary embodiments, the crude product comprises ethanol in an amount from 5 wt.% to 70 wt.%, e.g., from 10 wt.% to 60 wt.%, or from 15 wt.% to 50 wt.%, based on the total weight of the crude product. Preferably, the crude product contains at least 10 wt.% ethanol, at least 15 wt.% ethanol or at least 20 wt.% ethanol. The crude product typically will further comprise unreacted acetic acid, depending on conversion, for example, in an amount of less than 90

wt.%, e.g., less than 80 wt.% or less than 70 wt.%. In terms of ranges, the unreacted acetic acid is preferably from 0 to 90 wt.%, e.g., from 5 to 80 wt.%, from 15 to 70 wt.%, from 20 to 70 wt.% or from 25 to 65 wt.%. As water is formed in the reaction process, water will generally be present in the crude product, for example, in amounts ranging from 5 to 35 wt.%, e.g., from 10 to 30 wt.% or from 10 to 26 wt.%. Ethyl acetate may also be produced during the hydrogenation of acetic acid or through side reactions and may be present, for example, in amounts ranging from 0 to 20 wt.%, e.g., from 0 to 15 wt.%, from 1 to 12 wt.% or from 3 to 10 wt.%. Acetaldehyde may also be produced through side reactions and may be present, for example, in amounts ranging from 0 to 10 wt.%, e.g., from 0 to 3 wt.%, from 0.1 to 3 wt.% or from 0.2 to 2 wt.%. Other components, such as, for example, esters, ethers, aldehydes, ketones, alkanes, and carbon dioxide, if detectable, collectively may be present in amounts less than 10 wt.%, e.g., less than 6 wt.% or less than 4 wt.%. In terms of ranges, other components may be present in an amount from 0.1 to 10 wt.%, e.g., from 0.1 to 6 wt.%, or from 0.1 to 4 wt.%. Exemplary embodiments of crude ethanol compositional ranges are provided in Table 1.

TABLE 1
CRUDE PRODUCT COMPOSITIONS

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	5 to 70	10 to 60	15 to 50	25 to 50
Acetic Acid	0 to 90	5 to 80	15 to 70	20 to 70
Water	5 to 35	5 to 30	10 to 30	10 to 26
Ethyl Acetate	0 to 20	0 to 15	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	--

[0055] FIGS. 1 and 2 show hydrogenation systems 100 suitable for the hydrogenation of acetic acid and separating ethanol and an ethyl acetate solvent from the crude reaction mixture according to one embodiment of the invention. In FIG. 1, system 100 comprises reaction zone 101 and distillation zone 102. Reaction zone 101 comprises reactor 103, hydrogen feed line 104 and acetic acid feed line 105. Distillation zone 102 comprises flasher 106, first column 107, second column 108, and third column 109. FIG. 2 includes a fourth column 123 in the distillation zone for further processing the ethyl acetate solvent.

[0056] In both FIGS. 1 and 2, hydrogen and acetic acid are fed to a vaporizer 110 via lines 104 and 105, respectively, to create a vapor feed stream in line 111 that is directed to reactor 103. In one embodiment, lines 104 and 105 may be combined and jointly fed to the vaporizer 110, e.g., in one stream containing both hydrogen and acetic acid. The temperature of the vapor feed stream in line 111 is preferably from 100°C to 350°C, e.g., from 120°C to 310°C or from 150°C to 300°C. Any feed that is not vaporized is removed from vaporizer 110, as shown in FIG. 1, and may be recycled thereto. In addition, although FIG. 1 shows line 111 being directed to the top of reactor 103, line 111 may be directed to the side, upper portion, or bottom of reactor 103. Further modifications and additional components to reaction zone 101 are described below.

[0057] Reactor 103 contains the catalyst that is used in the hydrogenation of the carboxylic acid, preferably acetic acid. In one embodiment, one or more guard beds (not shown) may be used to protect the catalyst from poisons or undesirable impurities contained in the feed or return/recycle streams. Such guard beds may be employed in the vapor or liquid streams. Suitable guard bed materials are known in the art and include, for example, carbon, silica, alumina, ceramic, or resins. In one aspect, the guard bed media is functionalized to trap particular species such as sulfur or halogens. During the hydrogenation process, a crude product is withdrawn, preferably continuously, from reactor 103 via line 112. The crude product may be condensed and fed to flasher 106, which, in turn, provides a vapor stream and a liquid stream. The flasher 106 in one embodiment preferably operates at a temperature of from 50°C to 500°C, e.g., from 70°C to 400°C or from 100°C to 350°C. In one embodiment, the pressure of flasher 106 preferably is from 50 KPa to 2000 KPa, e.g., from 75 KPa to 1500 KPa or from 100 to 1000 KPa. In one preferred embodiment the temperature and pressure of the flasher is similar to the temperature and pressure of the reactor 103.

[0058] The vapor stream exiting the flasher 106 may comprise hydrogen and hydrocarbons, which may be purged and/or returned to reaction zone 101 via line 113. As shown in FIG. 1, the returned portion of the vapor stream passes through compressor 114 and is combined with the hydrogen feed and co-fed to vaporizer 110.

[0059] The liquid from flasher 106 is withdrawn and pumped as a feed composition via line 115 to the side of first column 107, also referred to as the acid separation column. The contents of line 115 typically will be substantially similar to the product obtained directly from the

reactor, and may, in fact, also be characterized as a crude product. However, the feed composition in line 115 preferably has substantially no hydrogen, carbon dioxide, methane or ethane, which are removed by flasher 106. Exemplary compositions of line 115 are provided in Table 2.

TABLE 2
FEED COMPOSITION

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	5 to 70	10 to 60	15 to 50
Acetic Acid	< 90	5 to 80	15 to 70
Water	5 to 35	5 to 30	10 to 30
Ethyl Acetate	< 20	0.001 to 15	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

[0060] The amounts indicated as less than (<) in the tables throughout present application are preferably not present and if present may be present in trace amounts or in amounts greater than 0.0001 wt.%.

[0061] The “other esters” in Table 2 may include, but are not limited to, ethyl propionate, methyl acetate, isopropyl acetate, n-propyl acetate, n-butyl acetate or mixtures thereof. The “other ethers” in Table 2 may include, but are not limited to, diethyl ether, methyl ethyl ether, isobutyl ethyl ether or mixtures thereof. The “other alcohols” in Table 2 may include, but are not limited to, methanol, isopropanol, n-propanol, n-butanol or mixtures thereof. In one embodiment, the feed composition, e.g., line 115, may comprise propanol, e.g., isopropanol and/or n-propanol, in an amount from 0.001 to 0.1 wt.%, from 0.001 to 0.05 wt.% or from 0.001 to 0.03 wt.%. It should be understood that these other components may be carried through in any of the distillate or residue streams described herein and will not be further described herein, unless indicated otherwise.

[0062] When the content of acetic acid in line 115 is less than 5 wt.%, the acid separation column 107 may be skipped and line 115 may be introduced directly to second column 108, also referred to herein as a light ends column.

[0063] In the embodiment shown in FIG. 1, line 115 is introduced in the lower part of first column 107, e.g., lower half or lower third. In first column 107, unreacted acetic acid, a portion of the water, and other heavy components, if present, are removed from the composition in line 115 and are withdrawn, preferably continuously, as residue. Some or all of the residue may be returned and/or recycled back to reaction zone 101 via line 116. Recycling the acetic acid in line 116 to the vaporizer 110 may reduce the amount of heavies that need to be purged from vaporizer 110. Reducing the amount of heavies to be purged may improve efficiencies of the process while reducing byproducts.

[0064] First column 107 also forms an overhead distillate, which is withdrawn in line 117, and which may be condensed and refluxed, for example, at a ratio of from 10:1 to 1:10, e.g., from 3:1 to 1:3 or from 1:2 to 2:1.

[0065] Any of columns 107, 108, 109, or 123 may comprise any distillation column capable of separation and/or purification. The columns preferably comprise tray columns having from 1 to 150 trays, e.g., from 10 to 100, 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.

[0066] 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 FIGS. 1 and 2. As shown in FIGS. 1 and 2, heat may be supplied to the base of each column or to a circulating bottom stream through a heat exchanger or reboiler. Other types of reboilers, such as internal reboilers, may also be used in some embodiments. The heat that is provided to reboilers may be derived from any heat generated during the process that is integrated with the reboilers or from an external source such as another heat generating chemical process or a boiler. Although one reactor and flasher are shown in FIGS. 1 and 2, additional reactors, flashers, condensers, heating elements, and other components may be used in embodiments of the present invention. As will be recognized by those skilled in the art, various condensers, pumps, compressors, reboilers, drums, valves, connectors, separation vessels, etc., normally

employed in carrying out chemical processes may also be combined and employed in the processes of the present invention.

[0067] The temperatures and pressures employed in any of the columns may vary. As a practical matter, pressures from 10 KPa to 3000 KPa will generally be employed in these zones although in some embodiments subatmospheric pressures may be employed as well as superatmospheric pressures. Temperatures within the various zones will normally range between the boiling points of the composition removed as the distillate and the composition removed as the residue. It will be recognized by those skilled in the art that the temperature at a given location in an operating distillation column is dependent on the composition of the material at that location and the pressure of column. In addition, feed rates may vary depending on the size of the production process and, if described, may be generically referred to in terms of feed weight ratios.

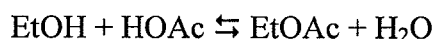
[0068] When column 107 is operated under standard atmospheric pressure, the temperature of the residue exiting in line 116 from column 107 preferably is from 95°C to 120°C, e.g., from 105°C to 117°C or from 110°C to 115°C. The temperature of the distillate exiting in line 117 from column 107 preferably is from 70°C to 110°C, e.g., from 75°C to 95°C or from 80°C to 90°C. Column 107 may operate at atmospheric pressure. In other embodiments, the pressure of first column 107 may range from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa. Exemplary components of the distillate and residue compositions for first column 107 are provided in Table 3 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed. For convenience, the distillate and residue of the first column may also be referred to as the “first distillate” or “first residue.” The distillates or residues of the other columns may also be referred to with similar numeric modifiers (second, third, etc.) in order to distinguish them from one another, but such modifiers should not be construed as requiring any particular separation order.

TABLE 3
FIRST COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	20 to 75	30 to 70	40 to 65
Water	10 to 40	15 to 35	20 to 35
Acetic Acid	< 2	0.001 to 0.5	0.01 to 0.2
Ethyl Acetate	< 60	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

[0069] As shown in Table 3, without being bound by theory, it has surprisingly and unexpectedly been discovered that when any amount of acetal is detected in the feed that is introduced to the acid separation column (first column 107), the acetal appears to decompose in the column such that no lesser or even no detectable amounts are present in the distillate and/or residue.

[0070] Depending on the reaction conditions, the crude product exiting reactor 103 in line 112 may comprise ethanol, acetic acid (unconverted), ethyl acetate, and water. After exiting reactor 103, a non-catalyzed equilibrium reaction may occur between the components contained in the crude product until it is added to flasher 106 and/or first column 107. This equilibrium reaction tends to drive the crude product to an equilibrium between ethanol/acetic acid and ethyl acetate/water, as shown below.



[0071] In the event the crude product is temporarily stored, e.g., in a holding tank, prior to being directed to distillation zone 102, extended residence times may be encountered. Generally, the longer the residence time between reaction zone 101 and distillation zone 102, the greater the formation of ethyl acetate. For example, when the residence time between reaction zone 101 and distillation zone 102 is greater than 5 days, significantly more ethyl

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

[0072] As discussed above, a holding tank (not shown) may be included between the reaction zone 101 and distillation zone 102 for temporarily storing the liquid component from line 115, for example from 1 to 24 hours, optionally at a temperature of about 21°C, and corresponding to an ethyl acetate formation of from 0.01 wt.% to 1.0 wt.% respectively. In addition, the rate at which the non-catalyzed reaction occurs may increase as the temperature of the crude product is increased. For example, as the temperature of the crude product in line 115 increases from 4°C to 21°C, the rate of ethyl acetate formation may increase from about 0.01 wt.% per hour to about 0.005 wt.% per hour. Thus, in one embodiment, the temperature of liquid components in line 115 or in the optional holding tank is maintained at a temperature less than 21°C, e.g., less than 4°C or less than -10°C.

[0073] In addition, it has now been discovered that the above-described equilibrium reaction may also favor ethanol formation in the top region of first column 107.

[0074] The distillate, e.g., overhead stream, of column 107 optionally is condensed and refluxed as shown in FIG. 1, preferably, at a reflux ratio of 5:1 to 10:1. The distillate in line 117 preferably comprises ethanol, ethyl acetate, and water, along with other impurities, which may be difficult to separate due to the formation of binary and tertiary azeotropes.

[0075] The first distillate in line 117 is introduced to the second column 108, also referred to as the "light ends column," preferably in the middle part of column 108, e.g., middle half or middle third. As one example, when a 25 tray column is utilized in a column without water

extraction, line 117 is introduced at tray 17. In one embodiment, the second column 108 may be an extractive distillation column. In such embodiments, an extraction agent, such as water, may be added to second column 108. If the extraction agent comprises water, it may be obtained from an external source or from an internal return/recycle line from one or more of the other columns.

[0076] Second column 108 may be a tray column or packed column. In one embodiment, second column 108 is a tray column having from 5 to 70 trays, e.g., from 15 to 50 trays or from 20 to 45 trays.

[0077] Although the temperature and pressure of second column 108 may vary, when at atmospheric pressure the temperature of the second residue exiting in line 118 from second column 108 preferably is from 60°C to 90°C, e.g., from 70°C to 90°C or from 80°C to 90°C. The temperature of the second distillate exiting in line 120 from second column 108 preferably is from 50°C to 90°C, e.g., from 60°C to 80°C or from 60°C to 70°C. In other embodiments, the pressure of second column 108 may be from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa.

[0078] The system shown in FIG. 1 yields an ethyl acetate solvent through second distillate (line 120). The second distillate may be further processed, as shown in FIG. 2 and described below, to form another ethyl acetate solvent having a more desirable composition. Exemplary components of the second distillate and residue compositions for second column 108 are provided in Table 4 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 4
SECOND COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethyl Acetate	10 to 90	25 to 90	50 to 90
Acetaldehyde	1 to 25	1 to 15	1 to 8
Water	1 to 25	1 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 70	30 to 60	30 to 50
Ethanol	20 to 75	30 to 70	40 to 70
Ethyl Acetate	< 3	0.001 to 2	0.001 to 0.5
Acetic Acid	< 0.5	0.001 to 0.3	0.001 to 0.2

[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. 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 column with water as an extraction agent as the second column 108, the weight ratio of ethyl acetate in the second residue to second distillate is essentially zero or is zero.

[0080] As shown, the second residue from the bottom of second column 108, which comprises ethanol and water, is fed via line 118 to third column 109, also referred to as the “product column.” More preferably, the second residue in line 118 is introduced in the lower part of third column 109, e.g., lower half or lower third. Third column 109 recovers ethanol, which preferably is substantially pure other than the azeotropic water content, as the distillate in line 119. The distillate of third column 109 preferably is refluxed as shown in FIG. 1, for example, at a reflux ratio of from 1:10 to 10:1, e.g., from 1:3 to 3:1 or from 1:2 to 2:1. The third residue in line 121, which preferably comprises primarily water, preferably is removed from the system 100 or may be partially returned to any portion of the system 100. In one embodiment, at least a portion of the water in the third residue is recycled to the second column 108 as indicated by line 121’. Third column 109 is preferably a tray column as described above and preferably operates at atmospheric pressure. The temperature of the third distillate exiting in line 119 from third column 109 preferably is from 60°C to 110°C, e.g., from 70°C to 100°C

or from 75°C to 95°C. The temperature of the third residue exiting from third column 109 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 105°C, when the column is operated at atmospheric pressure. Exemplary components of the distillate and residue compositions for third column 109 are provided in Table 5 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 5
THIRD COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	75 to 96	80 to 96	85 to 96
Water	< 12	1 to 9	3 to 8
Acetic Acid	< 1	0.001 to 0.1	0.005 to 0.01
Ethyl Acetate	< 5	0.001 to 4	0.01 to 3
<u>Residue</u>			
Water	75 to 100	80 to 100	90 to 100
Ethanol	< 0.8	0.001 to 0.5	0.005 to 0.05
Ethyl Acetate	< 1	0.001 to 0.5	0.005 to 0.2
Acetic Acid	< 2	0.001 to 0.5	0.005 to 0.2

[0081] Any of the compounds that are carried through the distillation process from the feed or crude reaction product generally remain in the third distillate in amounts of less 0.1 wt.%, based on the total weight of the third distillate composition, e.g., less than 0.05 wt.% or less than 0.02 wt.%. In one embodiment, one or more side streams may remove impurities from any of the columns 107, 108 and/or 109 in the system 100. Preferably at least one side stream is used to remove impurities from the third column 109. The impurities may be purged and/or retained within the system 100.

[0082] The third distillate in line 119 may be further purified to form an anhydrous ethanol product stream, i.e., “finished anhydrous ethanol,” using one or more additional separation systems, such as, for example, distillation columns (e.g., a finishing column) or mole sieves.

[0083] Returning to second column 108, the second distillate preferably is refluxed as shown in FIG. 1, for example, at a reflux ratio of from 1:10 to 10:1, e.g., from 1:5 to 5:1 or from 1:3 to 3:1. In one embodiment, the ethyl acetate solvent comprises the all or a portion of the second distillate in line 120.

[0084] In another embodiment, as shown in FIG. 2, the second distillate is fed via line 120 to fourth column 123, also referred to as the “acetaldehyde removal column.” In fourth column 123 the second distillate is separated into a fourth distillate, which comprises acetaldehyde, in line 124. 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 110, or added directly to the reactor 103. As shown, the fourth distillate is co-fed with the acetic acid in feed line 105 to vaporizer 110. Without being bound by theory, since acetaldehyde may be hydrogenated to form ethanol, the recycling of a stream that contains acetaldehyde to the reaction zone increases the yield of ethanol and decreases byproduct and waste generation. In another embodiment (not shown in the figure), 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.

[0085] The fourth residue of fourth column 123 in line 125 primarily comprises ethyl acetate and ethanol and is highly suitable for use as an ethyl acetate solvent. In one preferred embodiment, the acetaldehyde is removed from the second distillate in fourth column 123 such that no detectable amount of acetaldehyde is present in the residue of column 123.

[0086] Fourth column 123 is preferably a tray column as described above and preferably operates above atmospheric pressure. In one embodiment, the pressure is from 120 KPa to 5,000 KPa, e.g., from 200 KPa to 4,500 KPa, or from 400 KPa to 3,000 KPa. In a preferred embodiment the fourth column 123 may operate at a pressure that is higher than the pressure of the other columns.

[0087] The temperature of the fourth distillate exiting in line 124 from fourth column 123 preferably is from 60°C to 110°C, e.g., from 70°C to 100°C or from 75°C to 95°C. The temperature of the residue exiting from fourth column 125 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 110°C. Exemplary components of the distillate and residue compositions for fourth column 109 are provided in Table 6 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 6
FOURTH COLUMN

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

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

TABLE 7
FINISHED ETHANOL COMPOSITIONS

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	75 to 96	80 to 96	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	< 0.01	< 0.005	< 0.05
Acetone	< 0.01	< 0.005	< 0.05
Isopropanol	< 0.5	< 0.1	< 0.05
n-propanol	< 0.5	< 0.1	< 0.05

[0088] 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.

[0089] 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 aircrafts. 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.

[0090] The finished ethanol composition may also be used a chemical feedstock to make other chemicals such as vinegar, ethyl acrylate, ethyl acetate, ethylene, glycol ethers, ethylamines, aldehydes, and higher alcohols, especially butanol. In the production of ethyl acetate, the finished ethanol composition may be esterified with acetic acid or reacted with polyvinyl acetate. The finished ethanol composition may be dehydrated to produce ethylene. Any of known dehydration catalysts can be employed in to dehydrate ethanol, such as those described in U.S. Pub. Nos. 2010/0030001 and 2010/0030002, 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 by reference.

[0091] Turning now to FIGS. 3, 4, and 5, an ethyl acetate solvent is prepared from the hydrogenation of acetic acid in hydrogenation system 200. Similar to the processes described above in FIGS. 1 and 2, the hydrogenation of acetic acid occurs in reaction zone 201 and the resulting crude product is processed in distillation zone 202. Hydrogen and acetic acid are fed to a vaporizer 210 via lines 204 and 205, respectively, to create a vapor feed stream in line 211 that is directed to reactor 203. A crude product stream is withdrawn, preferably continuously, from reactor 203 via line 212. The crude product stream may be condensed and fed to flasher 206, which, in turn, provides a vapor stream and a liquid stream. The vapor stream exiting the flasher may comprise hydrogen and hydrocarbons, which may be purged and/or returned to reaction zone 201 via line 213 through compressor 214 and is combined with the hydrogen feed and co-fed to vaporizer 210. The liquid from flasher 206 is withdrawn and pumped via line

215 to the distillation zone 202. The liquid in line 215 may have the composition of the crude product in Table 1 or the feed stream of Table 2.

[0092] In FIG. 3, liquid feed in line 215 is introduced in fifth distillation column 240. Fifth column 240 operates in a similar manner as the fourth column described above in FIG. 2, with a different feed. Fifth column 240 removes acetaldehyde in line 241 as the fifth distillate and recycles a portion of the fifth distillate in line 241 to the reaction zone 201. The fifth residue of distillation column 240 is withdrawn in line 242 and is preferably an ethyl acetate solvent. The fifth residue preferably has a higher acid content than the fourth residue withdrawn in FIG. 2. Exemplary components of the distillate and residue compositions for fifth column 240 are provided in Table 8 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 8
FIFTH COLUMN

	Conc. (wt%)	Conc. (wt%)	Conc. (wt%)
<u>Distillate</u>			
Acetaldehyde	2 to 80	2 to 50	5 to 40
Ethyl Acetate	< 90	30 to 80	40 to 75
Ethanol	< 30	0.001 to 25	0.01 to 20
Water	< 25	0.001 to 20	0.01 to 15
Acetic Acid	0 to 10	0 to 5	0 to 1
<u>Residue</u>			
Ethanol	5 to 70	10 to 60	15 to 50
Acetic Acid	< 90	5 to 80	15 to 70
Water	5 to 35	5 to 30	10 to 30
Ethyl Acetate	< 20	0.001 to 15	1 to 12
Acetaldehyde	< 1	< 0.5	< 0.25
Acetal	< 1	< 0.5	< 0.25
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

[0093] In FIG. 4, liquid feed in line 215 is introduced to sixth distillation column 243. Sixth column 243 operates in a similar manner as the first column 107 described above in FIGS. 1 and 2 and removes acid from the liquid feed in line 215. The acid withdrawn as the sixth residue preferably is returned to the reaction zone 201 as shown by line 248. The sixth

distillate is condensed from the sixth column 243 in line 244 and fed to an overhead decanter 245. In one embodiment characterized by an ethanol concentration in 244 of about 25 wt.% or less, two phases will form in the overhead decanter 245. A light phase is withdrawn in line 246 from the decanter and is preferably an ethyl acetate solvent. The light phase comprises mainly ethyl acetate, for example more than about 75 wt.% or preferably more than 80 wt.%. A heavy phase is withdrawn from the decanter in line 247 and is refluxed to the sixth column 243. The heavy phase comprises mainly water, for example more than about 70 wt.% or preferably more than 75 wt.%.

[0094] In another embodiment, characterized by an ethanol concentration in 244 is more than 25 wt.%, a single phase exists in overhead decanter 245 and a portion of the material in 245 is refluxed to column 243 in line 247 and the remaining material is an ethyl acetate solvent in line 246. Exemplary components of the sixth distillate compositions, for the single phase, and sixth residue are provided in Table 9 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 9
SIXTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate (single phase)</u>			
Ethanol	20 to 75	30 to 70	40 to 65
Water	10 to 40	15 to 35	20 to 35
Acetic Acid	< 2	0.001 to 0.5	0.01 to 0.2
Ethyl Acetate	< 60	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

[0095] In FIG. 5, liquid feed in line 215 is introduced into a distillation zone that comprises seventh distillation column 250 and eighth distillation column 253. Seventh column 250 operates in a similar manner as the first column 107, as described above in FIGS. 1 and 2 and exemplary compositions of the seventh distillate and seventh residue are described above in

Table 3 (with reference to the first column). The seventh residue of column 250 comprises acetic acid and preferably is withdrawn in line 252 and returned to reaction zone 201.

[0096] The seventh distillate, e.g., overhead stream, of seventh column 250 optionally is condensed and refluxed as shown in FIG. 5, preferably, at a reflux ratio of from 5:1 to 10:1. The distillate in line 251 preferably comprises ethanol, ethyl acetate, and water, along with other impurities. The seventh distillate in line 251 is introduced to the eighth column 253, preferably in the lower part of column 253. The seventh distillate may comprise an azeotrope of ethyl acetate, ethanol and water. To facilitate separation of this azeotrope, in one embodiment, the eighth column 253 may be an azeotropic distillation column. Eighth column preferably operates to remove water as the residue in line 255 from the seventh distillate. The eighth distillate from eighth column 253 is withdrawn in line 254, optionally condensed and refluxed, and may be an ethyl acetate solvent.

[0097] Eighth column 253 may be a tray or packed column. In one embodiment, eighth column 253 is a tray column having from 5 to 50 trays, e.g., from 15 to 31 trays or from 25 to 27 trays. Although the temperature and pressure of eighth column 253 may vary, when at atmospheric pressure, the temperature of the eighth residue exiting in line 255 from eighth column 253 preferably is from 80°C to 110°C, e.g., from 90°C to 110°C or from 95°C to 105°C. The temperature of the eighth distillate exiting in line 254 from eighth column 253 preferably is from 50°C to 90°C, e.g., from 60°C to 85°C or from 65°C to 80°C. In other embodiments, the pressure of eighth column 253 may be from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa. Exemplary components of the eighth distillate and residue compositions for eighth column 253 are provided in Table 10 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

TABLE 10
EIGHTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	20 to 75	30 to 70	40 to 65
Acetic Acid	< 2	0.001 to 0.5	0.01 to 0.2
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>			
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

[0098] The following examples describe the various distillation processes of the present invention.

Examples

Example 1

[0099] An ethyl acetate solvent was obtained from a crude product comprising ethanol, acetic acid, water and ethyl acetate was produced by reacting a vaporized feed comprising 95.2 wt.% acetic acid and 4.6 wt.% water with hydrogen in the presence of a catalyst comprising 1.6 wt.% platinum and 1 wt.% tin supported on 1/8 inch calcium silicate modified silica extrudates at an average temperature of 291°C, an outlet pressure of 2,063 KPa. Unreacted hydrogen was recycled back to the inlet of the reactor such that the total H₂/acetic acid molar ratio was 5.8 at a GHSV of 3,893 hr⁻¹. Under these conditions, 42.8% of the acetic acid was converted, and the selectivity to ethanol was 87.1%, selectivity to ethyl acetate was 8.4%, and selectivity to acetaldehyde was 3.5%. The crude product was purified using a separation scheme having distillation columns as shown in FIG. 1.

[0100] The crude product was fed to the first column at a feed rate of 20 g/min. The composition of the liquid feed is provided in Table 11. The first column is a 2 inch diameter Oldershaw with 50 trays. The column was operated at a temperature of 115°C at atmospheric pressure. Unless otherwise indicated, a column operating temperature is the temperature of the liquid in the reboiler and the pressure at the top of the column is ambient (approximately one

atmosphere). The column differential pressure between the trays in the first column was 7.4 KPa. The first residue was withdrawn at a flow rate of 12.4 g/min and returned to the hydrogenation reactor.

[0101] The first distillate was condensed and refluxed at a 1:1 ratio at the top of the first column, and a portion of the distillate was introduced to the second column at a feed rate of 7.6 g/min. The second column is a 2 inch diameter Oldershaw design equipped with 25 trays. The second column was operated at a temperature of 82°C at atmospheric pressure. The column differential pressure between the trays in the second column was 2.6 KPa. The second residue was withdrawn at a flow rate of 5.8 g/min and directed to the third column. The second distillate was refluxed at a ratio of 4.5:0.5 and the remaining distillate was collected as the ethyl acetate solvent for analysis.

TABLE 11

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

Example 2

[0102] The ethyl acetate solvent of Example 1 was further purified using a separation scheme having distillation columns as shown in FIG. 2. The fourth column is a 1 inch diameter Oldershaw column containing 25 trays and designed to operate at elevated pressures. The fourth column was operated at a pressure of 25 psig, and the differential pressure between the trays in the fourth column was 2.2 KPa. The fourth column was fed with the second distillate. The fourth distillate was refluxed at a ratio of 28:1 and returned to the hydrogenation reactor. The residue of the fourth column was withdrawn at a flow rate of 1.6 g/min and collected as the ethyl acetate solvent for analysis. The compositions of the feed, distillates, and residues are provided in Table 12.

TABLE 12

Component	Second Distillate Feed (wt.%)	Fourth Column	
		Distillate (wt.%)	Residue (wt.%)
Water	5.1	2.1	4.7
Acetaldehyde	8.3	61.5	nd
Acetic Acid	0.03	0.02	0.03
Ethanol	12.4	5.4	14.3
Ethyl Acetate	76.0	39.8	80.5
Acetal	0.006	0.001	0.017
Acetone	0.03	0.08	0.01

Example 3

[0103] Ethanol was co-produced with the ethyl acetate solvent obtained in Examples 1 or 2. A feed stream having a similar composition as residue from the second column from Example 1 was collected from several runs and introduced above the 25 tray to the third column, a 2 inch Oldershaw containing 60 trays, at a rate of 10 g/min. The third column was operated at a temperature of 103°C at standard pressure. The column differential pressure between the trays in the third column was 6.2 KPa. The third residue was withdrawn at a flow rate of 2.7 g/min. The third distillate was condensed and refluxed at a 3:1 ratio at the top of the third column, and recovered an ethanol composition as shown in Table 13. The ethanol composition also contained 10 ppm of n-butyl acetate.

TABLE 13

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

Example 4

[0104] An ethyl acetate solvent was obtained from a crude product comprising ethanol, acetic acid, water and ethyl acetate was produced by reacting a vaporized feed comprising 96.3 wt.% acetic acid and 4.3 wt.% water with hydrogen in the presence of a catalyst comprising 1.6 wt.% platinum and 1% tin supported on 1/8 inch calcium silicate modified silica extrudates at an average temperature of 290 °C, an outlet pressure of 2,049 kPa. Unreacted hydrogen was recycled back to the inlet of the reactor such that the total H₂/acetic acid molar ratio was 10.2 at a GHSV of 1,997 hr⁻¹. Under these conditions, 74.5% of the acetic acid was converted, and the selectivity to ethanol was 87.9%, selectivity to ethyl acetate was 9.5%, and selectivity to acetaldehyde was 1.8%. The crude product was purified using a separation scheme having distillation columns as shown in FIG. 1.

[0105] The crude product was fed to the first column at a feed rate of 20 g/min. The composition of the liquid feed is provided in Table 14. The first column is a 2 inch diameter Oldershaw with 50 trays. The column was operated at a temperature of 116 °C at atmospheric pressure. The column differential pressure between the trays in the first column was 8.1 KPa. The first residue was withdrawn at a flow rate of 10.7 g/min and returned to the hydrogenation reactor.

[0106] The first distillate was condensed and refluxed at a 1:1 ratio at the top of the first column, and a portion of the distillate was introduced to the second column at a feed rate of 9.2 g/min. The second column is a 2 inch diameter Oldershaw design equipped with 25 trays. The second column was operated at a temperature of 82°C at atmospheric pressure. The column differential pressure between the trays in the second column was 2.4 KPa. The second residue was withdrawn at a flow rate of 7.1 g/min and directed to the third column. The second distillate was refluxed at a ratio of 4.5:0.5 and the remaining distillate was collected as the ethyl acetate solvent for analysis.

TABLE 14

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

Example 5

[0107] The ethyl acetate solvent of Example 4 was further purified using a separation scheme having distillation columns as shown in FIG. 2. The fourth column is a 1 inch diameter Oldershaw column containing 25 trays and designed to operate at elevated pressures. The fourth column was operated at a pressure of 25 psig, and the differential pressure between the trays in the fourth column was 1.2 KPa. The fourth column was fed with the second distillate. The fourth distillate was refluxed and returned to the hydrogenation reactor. The residue of the fourth column was withdrawn at a flow rate of 1.4 g/min and collected as the ethyl acetate solvent for analysis. The compositions of the feed, distillates, and residues are provided in Table 15.

TABLE 15

Component	Second Distillate Feed (wt.%)	Fourth Column	
		Distillate (wt.%)	Residue (wt.%)
Water	3.0	0.5	7.4
Acetaldehyde	10.3	>40.00	nd
Acetic Acid	0.04	0.05	0.04
Ethanol	13.3	1.9	16.4
Ethyl Acetate	75.7	8.3	79.9
Acetal	0.01	0.01	0.03
Acetone	0.03	0.02	0.03

Example 6

[0108] Ethanol was co-produced with the ethyl acetate solvent obtained in Examples 4 or 5. A feed stream having a similar composition as residue from the second column from Example 4 was collected from several runs and introduced above the 25 tray to the third column, a 2 inch Oldershaw containing 60 trays, at a rate of 10 g/min. The third column was operated at a temperature of 103°C at standard pressure. The column differential pressure between the trays in the third column was 6.5 KPa. The third residue was withdrawn at a flow rate of 2.8 g/min. The third distillate was condensed and refluxed at a 3:1 ratio at the top of the third column, and recovered an ethanol composition as shown in Table 16. The ethanol composition also contained 86 ppm of isopropanol and 2.3 ppm of n-propyl acetate.

TABLE 16

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

[0109] While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference. In addition, it should be understood that aspects of the invention and portions of various embodiments and various features recited below and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one of skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

We claim:

1. A process for recovering an ethyl acetate solvent, comprising the steps of:
hydrogenating acetic acid in a reactor in the presence of a catalyst to form a crude product;
separating at least a portion of the crude product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, wherein the first residue comprises substantially all of the acetic acid from the at least a portion of the crude product; and
separating at least a portion of the first distillate to form the ethyl acetate solvent comprising ethyl acetate and ethanol.
2. The process of claim 1, wherein the catalyst comprises a combination metals selected from the group consisting of platinum/tin, platinum/ruthenium, platinum/rhenium, palladium/ruthenium, palladium/rhenium, cobalt/palladium, cobalt/platinum, cobalt/chromium, cobalt/ruthenium, silver/palladium, copper/palladium, nickel/palladium, gold/palladium, ruthenium/rhenium, and ruthenium/iron.
3. A process for recovering an ethyl acetate solvent, comprising the steps of:
providing a crude product comprising ethanol, ethyl acetate, water, and acetic acid;
separating at least a portion of the crude product in a first column into a first distillate comprising ethanol, water and ethyl acetate, and a first residue comprising acetic acid, wherein the first residue comprises substantially all of the acetic acid from the at least a portion of the crude product; and
separating at least a portion of the first distillate to form the ethyl acetate solvent comprising ethyl acetate and ethanol.
4. The process as in one of claims 1-3, further comprising the steps of:
separating the at least a portion of the first distillate in a second column into a second distillate comprising the ethyl acetate solvent and a second residue comprising water.

5. The process as in one of claims 1-4, wherein the second residue comprises water in an amount from 90 wt.% to 100 wt.%.
6. The process as in one of claims 1-5, wherein the second residue comprises water and ethanol.
7. The process as in one of claims 1-6, further comprising the steps of:
separating at least a portion of the second residue in a third column into a third distillate comprising ethanol and a third residue comprising water.
8. The process as in one of claims 1-7, further comprising the steps of:
separating at least a portion of the second distillate in a fourth column into a fourth distillate comprising acetaldehyde and a fourth residue comprising the ethyl acetate solvent.
9. The process as in one of claims 1-8, wherein when the first distillate comprises ethanol in an amount of 25 wt.% or less and further comprising condensing the distillate and biphasically separating the condensed distillate to form a heavy phase comprising water and a light phase comprising the ethyl acetate solvent.
10. The process as in one of claims 1-9, wherein the at least a portion of the crude product comprises acetic acid.
11. The process as in one of claims 1-10, further comprising returning at least a portion of the first residue to a reactor for the hydrogenation of acetic acid.
12. A process for recovering an ethyl acetate solvent, comprising the steps of:
hydrogenating acetic acid in a reactor in the presence of a catalyst to form a crude product; and
separating at least a portion of the crude product in a distillation column into a distillate comprising acetaldehyde and a residue comprising the ethyl acetate solvent, wherein the ethyl acetate solvent comprises ethyl acetate, acetic acid, water and ethanol.

13. The process of claim 12, wherein the catalyst comprises a combination metals selected from the group consisting of platinum/tin, platinum/ruthenium, platinum/rhenium, palladium/ruthenium, palladium/rhenium, cobalt/palladium, cobalt/platinum, cobalt/chromium, cobalt/ruthenium, silver/palladium, copper/palladium, nickel/palladium, gold/palladium, ruthenium/rhenium, and ruthenium/iron.

14. A process for recovering an ethyl acetate solvent, comprising the steps of:
providing a crude product comprising ethanol, ethyl acetate, water, acetaldehyde, and acetic acid; and
separating at least a portion of the crude product in a distillation column into a distillate comprising acetaldehyde and a residue comprising the ethyl acetate solvent, wherein the ethyl acetate solvent comprises ethyl acetate, acetic acid, water and ethanol.

15. The process as in one of claims 12-14, wherein at least a portion of the distillate is returned to the reactor.

16. The process as in one of claims 12-15, wherein the distillate comprises 2 to 80 wt.% of acetaldehyde.