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## ETHANOL COMPOSITIONS

### PRIORITY 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. 12/852,290, filed on August 6, 2010, the entire contents and disclosures of which are incorporated herein by reference.

### FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for producing and/or purifying ethanol and, in particular, to ethanol compositions obtained from these processes.

### BACKGROUND OF THE INVENTION

[0003] Ethanol for industrial use is conventionally produced from petrochemical feed stocks, such as oil, natural gas, or coal, from feed stock intermediates, such as syngas, or from starchy materials or cellulose materials, such as corn or sugar cane. Conventional methods for producing ethanol from petrochemical feed stocks, as well as from cellulose materials, include the acid-catalyzed hydration of ethylene, methanol homologation, direct alcohol synthesis, and Fischer-Tropsch synthesis. Instability in petrochemical feed stock prices contributes to fluctuations in the cost of conventionally produced ethanol, making the need for alternative sources of ethanol production all the greater when feed stock prices rise. 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.

[0004] Conventional ethanol compositions are formed as a result of the above-identified processes that contain impurities which must be removed.

[0005] For example, U.S. Pat. No. 5,488,185 utilizes a petrochemical feed stock and relates to an ethene stream which contains ethane as an impurity or a propene stream which contains

propane as an impurity that is hydrated with water vapor in the presence of a hydration catalyst to produce ethanol or isopropanol, respectively. After removal of the alcohol the gaseous product stream is subjected to adsorption, thereby producing an ethene-enriched stream or a propene-enriched stream. The ethene-enriched stream or the propene-enriched stream is recycled to the hydration reactor.

[0006] U.S. Pat. Nos. 5,185,481 and 5,284,983 relate to conventional fermentation methods for producing ethanol. The produced ethanol compositions comprise impurities such as methanol, acetaldehyde, n-propanol, n-butanol, ethyl acetate, 3-methylbutanol, diethyl ether, acetone, secondary butanol, and crotonaldehyde. These references also disclose separation methods for treating the crude ethanol aqueous solution with an extracting solvent comprising carbon dioxide in a liquid state or carbon dioxide in a super-critical state.

[0007] U.S. Pat. Nos. 5,445,716; 5,800,681; and 5,415,741 relate to separation methods for mixtures of ethanol and isopropanol. Ethanol is difficult to separate from isopropanol by conventional distillation or rectification because of the proximity of their boiling points. Ethanol can be readily separated from isopropanol by extractive distillation. Effective extractive agents are dipentene, anisole, and ethyl benzene. The mixtures in these references, comprise a significant amount of isopropanol, e.g., at least 21.5 wt.% isopropanol.

[0008] Also, U.S. Pat No. 5,858,031 relates to a method for enhancing the visibility of a flame produced during free-burning of an aqueous alcohol-based fuel composition in air. The fuel includes between approximately 10% and 30% by volume of water, and between approximately 70% and 90% by volume of a mixture of alcohols including ethanol and isopropanol, the ethanol constituting between approximately 24% and 83% by volume of the fuel composition. The method includes providing an amount of isopropanol ranging between approximately 7% and 60% by volume of the fuel composition, in which the volume ratio of isopropanol to ethanol in the fuel does not exceed 2:1.

[0009] Although conventional processes may produce and/or purify ethanol compositions, these processes rely on petrochemical feed stocks or fermentation techniques to yield the ethanol compositions. Further, in the resultant ethanol compositions that do comprise isopropanol, the isopropanol is present in large amounts.

[0010] Therefore, the need exists for an ethanol production process that does not rely on petrochemical feed stocks, and does not utilize fermentation techniques.

## SUMMARY OF THE INVENTION

**[0011]** In one embodiment, the invention is to an ethanol composition. The ethanol composition comprises ethanol and isopropanol. Preferably, the ethanol composition comprises at least 92 wt.% ethanol; and from 95 wppm to 1,000 wppm isopropanol. The ethanol composition has a high degree of purity and may further comprise less than 1 wt.% of one or more organic impurities. These organic impurities may include, for example, acetaldehyde, acetic acid, diethyl acetal, ethyl acetate, n-propanol, butanol, 2-butanol, isobutanol, and mixtures thereof. For example, the ethanol composition may comprise less than 10 wppm acetaldehyde; less than 10 wppm of diethyl acetal; and/or less than 300 wppm C<sub>4</sub> to C<sub>5</sub> alcohols. In other embodiments, the ethanol composition is substantially free of benzene, methanol, and/or C<sub>5</sub> alcohols.

**[0012]** In another embodiment, the invention is to an ethanol composition comprising at least 95 wt. % ethanol and at least 95 wppm isopropanol. In another embodiment, the isopropanol is present in an amount less than 1000 wppm. Preferably, the ethanol composition further comprises acetaldehyde, and the amount of acetaldehyde in the ethanol composition is less than the amount of isopropanol. As one example, the acetaldehyde may be present in an amount less than 10 wppm. In another embodiment, the ethanol composition further comprises n-propanol. Preferably, the weight ratio of isopropanol to n-propanol ranges from 1:1 to 1:2. The isopropanol may be present in an amount of less than 1000 wppm and/or the n-propanol may be present in an amount of less than 270 wppm.

**[0013]** In another embodiment, the invention is to an ethanol composition comprising at least 92 wt.% ethanol; and at least two other alcohols, which are, optionally, present in an amount less than 1 wt.%. The at least two other alcohols may be selected from the group consisting of n-propanol, isopropanol, butanol, 2-butanol, and isobutanol. In another embodiment, one of the at least two other alcohols is isopropanol and the ethanol composition comprises at least 95 wppm isopropanol. The ethanol composition may comprise isopropanol in an amount less than 1000 wppm. Preferably, the ethanol composition is substantially methanol free.

## BRIEF DESCRIPTION OF DRAWINGS

[0014] The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts.

[0015] FIG. 1 is a schematic diagram of a hydrogenation system in accordance with one embodiment of the present invention.

[0016] FIG. 2 is a schematic diagram of the reaction zone in accordance with one embodiment of the present invention.

[0017] FIG. 3 is a graph displaying isopropanol contents for several conventional ethanol compositions.

## DETAILED DESCRIPTION OF THE INVENTION

[0018] The present invention relates to processes for recovering a finished ethanol composition produced by a hydrogenation process. The hydrogenation process comprises hydrogenating acetic acid in the presence of a catalyst. The hydrogenation process produces a crude ethanol product that is different from the crude ethanol composition produced by other ethanol production processes. For example, fermentation processes produce crude ethanol compositions having low ethanol content. Crude ethanol compositions produced from petrochemical feed stocks produces crude ethanol compositions comprising other alcohols, especially methanol, n-propanol and higher alcohols. The crude ethanol product produced hydrogenation of acetic acid preferable is separated to remove impurities and recover a finished ethanol composition.

[0019] The inventive ethanol composition, in one embodiment, comprises a major portion of ethanol and a minor portion of isopropanol. The ethanol composition is primarily ethanol and contains from 92 wt.% to 96 wt.% ethanol, e.g., from 93 wt.% to 96 wt.%, or from 95 wt.% to 96 wt.%. Preferably, the ethanol composition comprises at least 92 wt.% ethanol, e.g., at least 93 wt.%, or at least 95 wt.%. Higher amounts of ethanol, for example anhydrous ethanol, may be possible by further removing the water of the ethanol composition. The isopropanol may be present in amounts ranging from 95 wppm to 1,000 wppm, e.g., from 110 wppm to 800 wppm, or from 110 wppm to 400 wppm. In terms of lower limits, in one embodiment, the ethanol composition comprises at least 95 wppm isopropanol, e.g., at least 110 wppm or at least 150 wppm. In terms of upper limits, in one embodiment, the ethanol composition comprises less

than 1,000 wppm isopropanol, e.g., less than 800 wppm or less than 400 wppm. In contrast, FIG. 3 displays isopropanol levels of 176 conventional ethanol compositions. These ethanol compositions were derived from various conventional sources and techniques such as sugarcane fermentation, molasses fermentation, and Fischer-Tropsch synthesis. As shown in FIG. 3, each of these conventional ethanol compositions has a very low isopropanol concentration, and none comprise isopropanol in an amount greater than 94 wppm.

[0020] In one embodiment, the ethanol composition further comprises water, for example, in an amount less than 8 wt.% water, less than 5 wt.% or less than 2 wt.%. In another embodiment, the weight ratio of isopropanol to water in the ethanol composition ranges from 1:80 to 1:800, e.g. from 1:100 to 1:500. In one embodiment, the ethanol composition comprises essentially no other detectable compounds, such as methanol, benzene, and/or higher alcohols, e.g., C<sub>4+</sub> alcohols. In some embodiments, the ethanol composition may comprise minor amounts of other impurities, such as those described below in Table 7.

[0021] In another embodiment, the invention is to an ethanol composition comprising ethanol and at least two other alcohols. The at least two other alcohols may be selected from the group consisting of n-propanol, isopropanol, butanol, 2-butanol, and isobutanol. Preferably, one of the at least two other alcohols is isopropanol. In these embodiments, the isopropanol is present in an amount of at least 95 wppm isopropanol, e.g., at least 110 wppm or at least 150 wppm. In preferred embodiments, when the weight percentages of the at least two other alcohols are added together, the at least two other alcohols, collectively, are present in an amount of less than 1 wt.%.

[0022] Without being bound by theory, it is believed that isopropanol is formed during the hydrogenation of acetic acid. For example, the isopropanol may be formed via the hydrogenation of acetone. The acetone may be generated via an acetic acid ketonization reaction. The n-propanol, if present in the ethanol composition, is believed to be formed from impurities in the acetic acid feed. The ethanol compositions of the present invention preferably comprise n-propanol in an amount less than 0.5 wt.% n-propanol, e.g., less than 0.1 wt.% or less than 0.05 wt.%. Optionally, ethanol compositions of the present invention may preferably have less n-propanol than isopropanol. The ethanol compositions formed by the inventive processes comprise a higher amount of *in situ*-formed isopropanol than conventional ethanol compositions. Preferably, in the inventive ethanol compositions, the amount of n-propanol is

less than the amount of isopropanol, e.g., less than 10% the amount of isopropanol or less than 50% the amount of isopropanol. Further, in one embodiment, the weight ratio of isopropanol to n-propanol in the inventive ethanol composition may range from 0.1:1 to 10:1, e.g., from 0.5:1 to 10:1, from 1:1 to 5:1, or from 1:1 to 2:1. In terms of limits, the weight ratio of isopropanol to n-propanol may be at least 0.5:1, e.g., at least 1:1, at least 1.5:1, at least 2:1, at least 5:1 or at least 10:1. In conventional ethanol production processes, isopropanol is typically not present in the amounts discussed above. Thus, the weight ratio of isopropanol or n-propanol favors more n-propanol, e.g., greater than 10:1.

**[0023]** In one embodiment of the present invention, isopropanol preferably is not added to the finished ethanol composition after the separation and recovery of ethanol. The isopropanol formed during the hydrogenation of acetic acid may be carried with the ethanol through the separation process.

**[0024]** In addition, conventional hydrogenation reactions often form higher amounts of acetaldehyde, as compared to isopropanol. The inventive ethanol compositions comprise low amounts of acetaldehyde, as well as other acetal compounds. Preferably, in the inventive ethanol compositions, the amount of acetaldehyde is less than the amount of isopropanol. For example, the amount of acetaldehyde may be less than 50% of the amount of isopropanol, e.g., less than 10% of the amount of isopropanol or less than 5% of the amount of isopropanol. Further the weight ratio of isopropanol to acetaldehyde in the inventive ethanol composition may range from 1:100 to 1:1000, e.g., from 1:100 to 1:500.

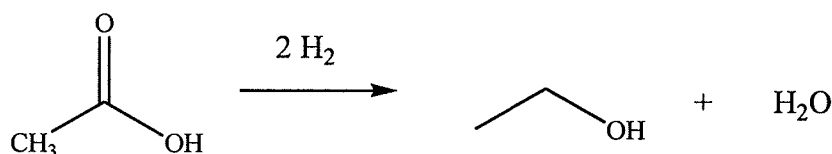
**[0025]** In one embodiment, the ethanol composition of the present invention comprises minor amounts of organic impurities. These organic impurities may include acetaldehyde, acetic acid, diethyl acetal, ethyl acetate, n-propanol, methanol, butanol, 2-butanol, isobutanol, isoamyl alcohol, amyl alcohol, benzene and/or mixtures thereof. Beneficially, in one embodiment, the ethanol composition comprises less than 1 wt.% organic impurities, e.g., less than 0.75 wt.% or less than 0.5 wt.%. Depending on the amount of these organic impurities, the impurities may have detrimental effects on the ethanol composition. For example, other alcohols in the crude ethanol composition may esterify with the acetic acid to form other esters. Also, it has been found that isobutanol, iso-amyl alcohol, and 2-methyl-1-butanol ("active amyl alcohol") contribute to residual odor in ethanol and ethyl acetate compositions.



[0026] In preferred embodiments, the ethanol composition is substantially methanol-free and may comprise less than 10 wppm methanol, e.g., less than 1 wppm. In addition, in preferred embodiments, the ethanol composition is substantially free of C<sub>5</sub> alcohols and may comprises less than 10 wppm of C<sub>5</sub> alcohols , e.g., less than 1 wppm.

[0027] Benzene, dioxanes, and cyanides are known to present toxicity issues in ethanol compositions. Typically, cyanides result from fermentation methods that utilize cassava as a feed stock. The inventive ethanol compositions comprise low amounts of these components. Preferably, the ethanol composition contains no detectable amount of benzene, dioxanes, and cyanides.

[0028] Turning to the production of the crude ethanol composition, generally, the hydrogenation of acetic acid forms ethanol and water as shown by the following reaction:



[0029] In addition to water and ethanol, other compounds may be formed during the hydrogenation of the acetic, as discussed below in Table 1.

[0030] 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.

[0031] 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.

**[0032]** 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.

**[0033]** 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.

**[0034]** 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.

**[0035]** 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.%.

**[0036]** 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.

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

**[0038]** 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 ( $\text{CaSiO}_3$ ). If the support modifier comprises calcium metasilicate, it is preferred that at least a portion of the calcium metasilicate is in crystalline form.

**[0039]** 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  $250 \text{ m}^2/\text{g}$ ; a median pore diameter of about 12 nm; an average pore volume of about  $1.0 \text{ cm}^3/\text{g}$  as measured by mercury intrusion porosimetry and a packing density of about  $0.352 \text{ g}/\text{cm}^3$  ( $22 \text{ lb}/\text{ft}^3$ ).

**[0040]** 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  $0.562 \text{ g}/\text{ml}$ , in absorptivity of

about 0.583 g H<sub>2</sub>O/g support, a surface area of about 160 to 175 m<sup>2</sup>/g, and a pore volume of about 0.68 ml/g.

**[0041]** 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.

**[0042]** 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.

**[0043]** 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.

**[0044]** 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.

**[0045]** 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.

**[0046]** 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<sup>-1</sup>, e.g., greater than 1000 hr<sup>-1</sup>, greater than 2500 hr<sup>-1</sup> or even greater than 5000 hr<sup>-1</sup>. In terms of ranges the GHSV may range from 50 hr<sup>-1</sup> to 50,000 hr<sup>-1</sup>, e.g., from 500 hr<sup>-1</sup> to 30,000 hr<sup>-1</sup>, from 1000 hr<sup>-1</sup> to 10,000 hr<sup>-1</sup>, or from 1000 hr<sup>-1</sup> to 6500 hr<sup>-1</sup>.

[0047] 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<sup>-1</sup> or 6,500 hr<sup>-1</sup>.

[0048] 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.

[0049] 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.

[0050] 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. U.S. Pat. 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.

**[0051]** 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.

**[0052]** 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 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. Pat. No. 5,821,111, which discloses a process for converting waste biomass through gasification into synthesis gas as well as U.S. Pat. No. 6,685,754, the disclosures of which are incorporated herein by reference.

**[0053]** 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. 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, 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.

**[0054]** Alternatively, acetic acid in vapor form may be taken directly as crude product from the flash vessel of a methanol carbonylation unit of the class described in U.S. Pat. No. 6,657,078, the entirety of which is incorporated herein by reference. The crude vapor product, for example, may be fed directly to the ethanol synthesis reaction zones of the present invention

without the need for condensing the acetic acid and light ends or removing water, saving overall processing costs.

[0055] 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.

[0056] 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.

[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 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.

[0058] The term “productivity,” as used herein, refers to the grams of 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.

[0059] In various embodiments, the crude ethanol product produced by the hydrogenation process, before any subsequent processing, such as purification and separation, will typically comprise unreacted acetic acid, ethanol and water. As used herein, the term “crude ethanol product” refers to any composition comprising from 5 to 70 wt.% ethanol and from 5 to 35 wt.% water. In some exemplary embodiments, the crude ethanol 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 ethanol product. Preferably, the crude ethanol product contains at least 10 wt.% ethanol, at least 15 wt.% ethanol or at least 20 wt.% ethanol. The crude ethanol 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 ethanol 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 ETHANOL 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	--

[0060] FIG. 1 shows a hydrogenation system 100 suitable for the hydrogenation of acetic acid and separating ethanol from the crude reaction mixture according to one embodiment of the invention. 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, third column 109, and fourth column 123. Hydrogen and acetic acid are fed to a vaporizer 110 via lines 104 and 105, respectively, to create a vapor feed stream in line 111 that is directed to 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 in FIG. 2.

[0061] Reactor 103 contains the catalyst that is used in the hydrogenation of the carboxylic acid, preferably acetic acid. In one embodiment, one or more guard beds (not shown) may be used to protect the catalyst from poisons or undesirable impurities contained in the feed or return/recycle streams. Such guard beds may be employed in the vapor or liquid streams. Suitable guard bed materials are known in the art and include, for example, carbon, silica, alumina, ceramic, or resins. In one aspect, the guard bed media is functionalized to trap particular species such as sulfur or halogens. During the hydrogenation process, a crude ethanol product is withdrawn, preferably continuously, from reactor 103 via line 112. The crude ethanol product may be condensed and fed to flasher 106, which, in turn, provides a vapor stream and a liquid stream. The flasher 106 in one embodiment preferably operates at a temperature of from 50°C to 500°C, e.g., from 70°C to 400°C or from 100°C to 350°C. In one embodiment, the pressure of flasher 106 preferably is from 50 KPa to 2000 KPa, e.g., from 75 KPa to 1500 KPa or from 100 to 1000 KPa. In one preferred embodiment the temperature and pressure of the flasher is similar to the temperature and pressure of the reactor 103.

[0062] 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.

[0063] The liquid from flasher 106 is withdrawn and pumped as a feed composition via line 115 to the side of first column 107, also referred to as the acid separation column. The contents of line 115 typically will be substantially similar to the product obtained directly from the reactor, and may, in fact, also be characterized as a crude ethanol product. However, the feed composition in line 115 preferably has substantially no hydrogen, carbon dioxide, methane or ethane, which are removed by flasher 106. Exemplary components of liquid in line 115 are provided in Table 2. It should be understood that liquid line 115 may contain other components, not listed, such as components in the feed.

**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

**[0064]** 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.%.

**[0065]** 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.

**[0066]** 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.

**[0067]** In the embodiment shown in FIG. 1, line 115 is introduced in the lower part of first column 107, e.g., lower half or lower third. In first column 107, unreacted acetic acid, a portion of the water, and other heavy components, if present, are removed from the composition in line 115 and are withdrawn, preferably continuously, as residue. Some or all of

the residue may be returned and/or recycled back to reaction zone 101 via line 116. First column 107 also forms an overhead distillate, which is withdrawn in line 117, and which may be condensed and refluxed, for example, at a ratio of from 10:1 to 1:10, e.g., from 3:1 to 1:3 or from 1:2 to 2:1.

**[0068]** Any of columns 107, 108, 109, or 123 may comprise any distillation column capable of separation and/or purification. The columns preferably comprise tray columns having from 1 to 150 trays, e.g., from 10 to 100 trays, from 20 to 95 trays or from 30 to 75 trays. The trays may be sieve trays, fixed valve trays, movable valve trays, or any other suitable design known in the art. In other embodiments, a packed column may be used. For packed columns, structured packing or random packing may be employed. The trays or packing may be arranged in one continuous column or they may be arranged in two or more columns such that the vapor from the first section enters the second section while the liquid from the second section enters the first section, etc.

**[0069]** The associated condensers and liquid separation vessels that may be employed with each of the distillation columns may be of any conventional design and are simplified in FIG. 1. As shown in FIG. 1, heat may be supplied to the base of each column or to a circulating bottom stream through a heat exchanger or reboiler. Other types of reboilers, such as internal reboilers, may also be used in some embodiments. The heat that is provided to reboilers may be derived from any heat generated during the process that is integrated with the reboilers or from an external source such as another heat generating chemical process or a boiler. Although one reactor and one flasher are shown in FIG. 1, additional reactors, flashers, condensers, heating elements, and other components may be used in embodiments of the present invention. As will be recognized by those skilled in the art, various condensers, pumps, compressors, reboilers, drums, valves, connectors, separation vessels, etc., normally employed in carrying out chemical processes may also be combined and employed in the processes of the present invention.

**[0070]** 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.

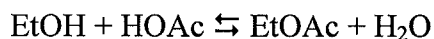
[0071] When column 107 is operated under standard atmospheric pressure, the temperature of the residue exiting in line 116 from column 107 preferably is from 95°C to 120°C, e.g., from 105°C to 117°C or from 110°C to 115°C. The temperature of the distillate exiting in line 117 from column 107 preferably is from 70°C to 110°C, e.g., from 75°C to 95°C or from 80°C to 90°C. In other embodiments, the pressure of first column 107 may range from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa. Exemplary components of the distillate and residue compositions for first column 107 are provided in Table 3 below. It should also be understood that the distillate and residue may also contain other components, not listed, such as components in the feed. For convenience, the distillate and residue of the first column may also be referred to as the “first distillate” or “first residue.” The distillates or residues of the other columns may also be referred to with similar numeric modifiers (second, third, etc.) in order to distinguish them from one another, but such modifiers should not be construed as requiring any particular separation order.

**TABLE 3**  
**FIRST COLUMN**

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	20 to 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

[0072] As shown in Table 3, without being bound by theory, it has surprisingly and unexpectedly been discovered that when any amount of acetal is detected in the feed that is introduced to the acid separation column (first column 107), the acetal appears to decompose in the column such that less or even no detectable amounts are present in the distillate and/or residue.

[0073] Depending on the reaction conditions, the crude ethanol product exiting reactor 103 in line 112 may comprise ethanol, acetic acid (unconverted), ethyl acetate, and water. After exiting reactor 103, a non-catalyzed equilibrium reaction may occur between the components contained in the crude ethanol product until it is added to flasher 106 and/or first column 107. This equilibrium reaction tends to drive the crude ethanol product to an equilibrium between ethanol/acetic acid and ethyl acetate/water, as shown below.



[0074] In the event the crude ethanol product is temporarily stored, e.g., in a holding tank, prior to being directed to distillation zone 102, extended residence times may be encountered. Generally, the longer the residence time between reaction zone 101 and distillation zone 102, the greater the formation of ethyl acetate. For example, when the residence time between reaction zone 101 and distillation zone 102 is greater than 5 days, significantly more ethyl acetate may form at the expense of ethanol. Thus, shorter residence times between reaction zone 101 and distillation zone 102 are generally preferred in order to maximize the amount of ethanol formed. In one embodiment, a holding tank (not shown), is included between the reaction zone 101 and distillation zone 102 for temporarily storing the liquid component from line 115 for up to 5 days, e.g., up to 1 day, or up to 1 hour. In a preferred embodiment no tank is included and the condensed liquids are fed directly to the first distillation column 107. In addition, the rate at which the non-catalyzed reaction occurs may increase as the temperature of the crude ethanol product, e.g., in line 115, increases. These reaction rates may be particularly problematic at temperatures exceeding 30°C, e.g., exceeding 40°C or exceeding 50°C. Thus, in one embodiment, the temperature of liquid components in line 115 or in the optional holding tank is maintained at a temperature less than 40°C, e.g., less than 30°C or less than 20°C. One or more cooling devices may be used to reduce the temperature of the liquid in line 115.

[0075] As discussed above, a holding tank (not shown) may be included between the reaction zone 101 and distillation zone 102 for temporarily storing the liquid component from line 115, for example from 1 to 24 hours, optionally at a temperature of about 21°C, and corresponding to an ethyl acetate formation of from 0.01 wt.% to 1.0 wt.% respectively. In addition, the rate at which the non-catalyzed reaction occurs may increase as the temperature of the crude ethanol product is increased. For example, as the temperature of the crude ethanol product in line 115 increases from 4°C to 21°C, the rate of ethyl acetate formation may increase from about 0.01 wt.% per hour to about 0.005 wt.% per hour. Thus, in one embodiment, the temperature of liquid components in line 115 or in the optional holding tank is maintained at a temperature less than 21°C, e.g., less than 4°C or less than -10°C.

[0076] 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.

[0077] The distillate, e.g., overhead stream, of column 107 optionally is condensed and refluxed as shown in FIG. 1, preferably, at a reflux ratio of 1:5 to 10:1. The distillate in line 117 preferably comprises ethanol, ethyl acetate, and water, along with other impurities, which may be difficult to separate due to the formation of binary and tertiary azeotropes.

[0078] 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.

[0079] 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.

[0080] Although the temperature and pressure of second column 108 may vary, when at atmospheric pressure the temperature of the second residue exiting in line 118 from second column 108 preferably is from 60°C to 90°C, e.g., from 70°C to 90°C or from 80°C to 90°C. The temperature of the second distillate exiting in line 120 from second column 108 preferably

is from 50°C to 90°C, e.g., from 60°C to 80°C or from 60°C to 70°C. Column 108 may operate at atmospheric pressure. In other embodiments, the pressure of second column 108 may range from 0.1 KPa to 510 KPa, e.g., from 1 KPa to 475 KPa or from 1 KPa to 375 KPa. Exemplary components for the distillate and residue compositions for second column 108 are provided in Table 4 below. It should be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

**TABLE 4**  
**SECOND COLUMN**

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethyl Acetate	10 to 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

**[0081]** The weight ratio of ethanol in the second residue to ethanol in the second distillate preferably is at least 3:1, e.g., at least 6:1, at least 8:1, at least 10:1 or at least 15:1. The weight ratio of ethyl acetate in the second residue to ethyl acetate in the second distillate preferably is less than 0.4:1, e.g., less than 0.2:1 or less than 0.1:1. In embodiments that use an extractive column with water as an extraction agent as the second column 108, the weight ratio of ethyl acetate in the second residue to ethyl acetate in the second distillate approaches zero.

**[0082]** As shown, the second residue from the bottom of second column 108, which comprises ethanol and water, is fed via line 118 to third column 109, also referred to as the “product column.” More preferably, the second residue in line 118 is introduced in the lower part of third column 109, e.g., lower half or lower third. Third column 109 recovers ethanol, which preferably is substantially pure other than the azeotropic water content, as the distillate in line 119. The distillate of third column 109 preferably is refluxed as shown in FIG. 1, for example, at a reflux ratio of from 1:10 to 10:1, e.g., from 1:3 to 3:1 or from 1:2 to 2:1. The



third residue in line 121, which preferably comprises primarily water, preferably is removed from the system 100 or may be partially returned to any portion of the system 100. Third column 109 is preferably a tray column as described above and preferably operates at atmospheric pressure. The temperature of the third distillate exiting in line 119 from third column 109 preferably is from 60°C to 110°C, e.g., from 70°C to 100°C or from 75°C to 95°C. The temperature of the third residue exiting from third column 109 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 105°C, when the column is operated at atmospheric pressure. Exemplary components of the distillate and residue compositions for third column 109 are provided in Table 5 below. It should be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

**TABLE 5**  
**THIRD COLUMN**

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Distillate</u>			
Ethanol	75 to 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

**[0083]** The ethanol composition may comprise the impurities discussed above. The ethanol composition, in some embodiments, may further comprise other compounds that result from the reaction or separation processes. These other compounds may be carried through the distillation process from the feed or crude reaction product may generally remain in the third distillate in small amounts. For example, the other compounds may be present in amounts less than 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.

[0084] The third distillate in line 119 may be further purified to form an anhydrous ethanol product stream, i.e., “finished anhydrous ethanol,” using one or more additional separation systems, such as, for example, distillation columns (e.g., a finishing column) or molecular sieves.

[0085] Returning to second column 108, the second distillate preferably is refluxed as shown in FIG. 1, for example, at a reflux ratio of from 1:10 to 10:1, e.g., from 1:5 to 5:1 or from 1:3 to 3:1. The second distillate may be fed via line 120 to fourth column 123, also referred to as the “acetaldehyde removal column.” In fourth column 123 the second distillate is separated into a fourth distillate, which comprises acetaldehyde, in line 124 and a fourth residue, which comprises ethyl acetate, in line 125. The fourth distillate preferably is refluxed at a reflux ratio of from 1:20 to 20:1, e.g., from 1:15 to 15:1 or from 1:10 to 10:1, and a portion of the fourth distillate is returned to the reaction zone 101 as shown by line 124. 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.

[0086] The fourth residue of fourth column 123 may be purged via line 125. The fourth residue primarily comprises ethyl acetate and ethanol, which may be suitable for use as a solvent mixture or in the production of esters. In one preferred embodiment, the acetaldehyde is removed from the second distillate in fourth column 123 such that no detectable amount of acetaldehyde is present in the residue of column 123.

[0087] 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.

[0088] The temperature of the fourth distillate exiting in line 124 from fourth column 123 preferably is from 60°C to 110°C, e.g., from 70°C to 100°C or from 75°C to 95°C. The temperature of the residue exiting from fourth column 125 preferably is from 70°C to 115°C, e.g., from 80°C to 110°C or from 85°C to 110°C. Exemplary components of the distillate and residue compositions for fourth column 123 are provided in Table 6 below. It should be understood that the distillate and residue may also contain other components, not listed, such as components in the feed.

**TABLE 6**  
**FOURTH COLUMN**

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

[0089] Although one reactor and one flasher are shown in FIG. 1, additional reactors and/or components may be included in various optional embodiments of the present invention. FIG. 2 represents a hydrogenation system 100' that comprises dual reactors 103, 103', dual flashers 106, 106', heat exchanger 130, and pre-heater 131. In this embodiment, acetic acid in line 105, along with the recycled acetic acid in line 116 and recycled acetaldehyde from line 124, are heated in a heat exchanger 130 and sent to vaporizer 110 via line 132. The temperature of the contents of line 132 preferably is from 30°C to 150°C, e.g., from 50°C to 130°C or from 75°C to 120°C. Hydrogen is fed via line 104 to vaporizer 110, which forms vaporized stream 111. Vaporized stream 111 passes through pre-heater 131, which further heats stream 111 to a temperature of preferably from 200°C to 300°C, e.g., from 210°C to 275°C or from 220°C to 260°C. The heated stream is then fed to first reactor 103. In order to control the reaction exotherm, the crude reaction mixture is removed from first reactor 103 via line 133 and cooled

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

**[0090]** The remaining liquid in flasher 106 is withdrawn via line 134 and fed to a second flasher 106' to remove any residual vapor that is dissolved in the liquid. Second flasher 106' may operate at a lower temperature and/or pressure than the first flasher 106. In one embodiment, the temperature of second flasher 106' preferably is from 20°C to 100°C, e.g., from 30°C to 85°C or from 40°C to 70°C. In one embodiment, the temperature of second flasher 106' preferably is at least 50°C lower than first flasher 106, e.g., at least 75°C lower or at least 100°C lower. The pressure of second flasher 106' preferably is from 0.1 KPa to 1000 KPa, e.g., from 0.1 KPa to 500 KPa or from 0.1 KPa to 100 KPa. In one embodiment, the pressure of second flasher 106' preferably is at least 50 KPa lower than first flasher 106, e.g., at least 100 KPa lower or at least 200 KPa lower. The vapor stream 135 exiting the second

flasher may comprise hydrogen and hydrocarbons, which may be purged and/or returned to the reaction zone in a manner similar to that of the first flasher 106. The remaining liquid in flasher 106' is withdrawn and pumped via line 115 to the side of the first column (not shown in FIG. 2) and is further purified to form an ethanol product stream, i.e., "finished ethanol," as described, for example, in connection with FIG. 1.

**[0091]** The finished ethanol compositions obtained by the processes of the present invention preferably comprises ethanol, water and minor amounts of isopropanol. As indicated above, preferably, the ethanol composition is primarily ethanol and contains from 92 wt.% to 96 wt.% ethanol, e.g., from 93 wt.% to 96 wt.%, or from 95 wt.% to 96 wt.%. In addition, the amount of isopropanol in the ethanol composition ranges from 95 wppm to 1,000 wppm, e.g., from 110 wppm to 800 wppm, or from 110 wppm to 400 wppm.

**[0092]** In another embodiment, the ethanol composition comprises less than 270 wppm n-propanol, e.g., less than 200 wppm. In terms of ranges, the ethanol composition comprises from 95 wppm to 270 wppm n-propanol, e.g., from 100 wppm to 250 wppm, or from 120 wppm to 200 wppm. In preferred embodiments, the ethanol compositions the total amount of isopropanol and n-propanol is less than 1,000 wppm, generally, e.g., less than 400 wppm or less than 200 wppm.

**[0093]** In addition, the ethanol compositions may comprise small amounts of various organic impurities. Examples of these impurities include acetaldehyde, acetic acid, diethyl acetal, ethyl acetate, n-propanol, methanol, butanol, 2-butanol, isobutanol, isoamyl alcohol, amyl alcohol, benzene and mixtures thereof. In a preferred embodiment, the inventive ethanol composition comprises low amounts of the organic impurities, e.g., less than 1 wt.% of organic impurities, less than 0.75 wt.%, or less than 0.5 wt.%. In another embodiment, the inventive ethanol composition comprises low amounts, if any, C<sub>5</sub> alcohols. For example, the ethanol composition may comprise less than 0.005 wt.% C<sub>5</sub> alcohols, e.g., less than 0.001 wt.% or less than 0.0005 wt.%. Exemplary weight percentages for individual components are provided in Table 7.

**TABLE 7**  
**FINISHED ETHANOL COMPOSITIONS**

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Ethanol	92 to 96	93 to 96	95 to 96
Water	< 8	< 5	< 2
Acetic Acid	< 1	< 0.1	< 0.01
Ethyl Acetate	< 2	< 0.5	< 0.05
Acetone	< 0.05	< 0.01	< 0.005
Isopropanol	0.0095 to 0.1	0.01 to 0.08	0.011 to 0.04
n-propanol	< 0.5	< 0.1	< 0.05
C <sub>4</sub> alcohols	< 0.01	< 0.005	< 0.003
C <sub>5</sub> alcohols	< 0.003	< 0.0015	< 0.0005
C <sub>2+</sub> alcohols	< 0.75	< 0.5	< 0.1
Acetaldehyde	< 0.001	< 0.0005	< 0.0002
Diethyl acetal	< 0.001	< 0.0005	< 0.0002
Methanol	< 0.005	< 0.004	0
Butanol	< 0.002	< 0.0001	0
2-Butanol	< 0.008	< 0.0008	0
Isobutanol	< 0.02	< 0.003	0
Isoamyl alcohol	< 0.02	< 0.0009	0
Amyl alcohol	< 0.02	< 0.0004	0

**[0094]** 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.

**[0095]** 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.

[0096] In order that the invention disclosed herein may be more efficiently understood, a non-limiting example is provided below. The following examples describe various embodiments of the inventive ethanol composition.

### Examples

#### Example 1

[0097] Several ethanol compositions were prepared using the hydrogenation process described above as well as the separation process. Crude ethanol products comprising ethanol, acetic acid, water and ethyl acetate were 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 H<sub>2</sub>/acetic acid molar ratio was 5.8 at a GHSV of 3,893 hr<sup>-1</sup>. The crude ethanol products were purified using a separation scheme having distillation columns as shown in FIG. 1.

[0098] Table 8 shows compositional data for these ethanol compositions. The term “C<sub>2+</sub> alcohols” as used herein relates to alcohols having more than two carbon atoms.

**TABLE 8**  
**FINISHED ETHANOL COMPOSITION RANGES**

Component	Avg.
Ethanol	92.7 wt.%
Water	7.4 wt.%
Acetic Acid	14 wppm
Ethyl Acetate	70 wppm
Isopropanol	110 wppm
n-propanol	160 wppm
C <sub>4</sub> alcohols	21 wppm
C <sub>5</sub> alcohols	0
C <sub>2+</sub> alcohols	291 wppm
Acetaldehyde	5 wppm
Diethyl acetal	1 wppm
Methanol	not detectable

**Comparative Example A**

[0099] Table 9 shows data for a comparative ethanol compositions prepared via fermentation of sugarcane.

**TABLE 9**  
**COMPARATIVE ETHANOL**  
**COMPOSITION RANGES**

Component	Avg.
Ethanol	93.4 wt.%
Water	6.6 wt.%
Acetic Acid	11 wppm
Ethyl Acetate	51 wppm
Isopropanol	2 wppm
n-propanol	238 wppm
C <sub>4</sub> alcohols	35 wppm
C <sub>5</sub> alcohols	12 wppm
C <sub>2+</sub> alcohols	288 wppm
Acetaldehyde	29 wppm
Diethyl acetal	59 wppm
Methanol	51 wppm

**Comparative Example B**

[0100] Table 10 shows data for a comparative ethanol compositions prepared via fermentation of molasses.



**TABLE 10**  
**COMPARATIVE ETHANOL**  
**COMPOSITION RANGES**

Component	Avg.
Ethanol	93.4 wt. %
Water	6.5 wt. %
Acetic Acid	10 wppm
Ethyl Acetate	--
Isopropanol	17 wppm
n-propanol	109 wppm
C <sub>4</sub> alcohols	20 wppm
C <sub>5</sub> alcohols	11 wppm
C <sub>2+</sub> alcohols	156 wppm
Acetaldehyde	18 wppm
Diethyl acetal	55 wppm
Methanol	42 wppm

**Comparative Example C**

**[0101]** Table 11 shows data for a comparative ethanol compositions prepared via Fischer-Tropsch synthesis.

**TABLE 11**  
**COMPARATIVE ETHANOL**  
**COMPOSITION RANGES**

Component	Avg.
Ethanol	93.1 wt. %
Water	6.9 wt. %
Acetic Acid	8 wppm
Ethyl Acetate	--
C <sub>4</sub> alcohols	17 wppm
C <sub>5</sub> alcohols	5 wppm
C <sub>2+</sub> alcohols	261 wppm
Isopropanol	10 wppm
n-propanol	121 wppm
Higher alcohols	131 wppm
Acetaldehyde	4 wppm
Diethyl acetal	10 wppm
Methanol	46 wppm

[0102] Surprisingly and unexpectedly, the amount of isopropanol in Example 1 is higher than in Comparative Examples A-C. Also, the amount of methanol in Example 1 is, advantageously, not detectable. In contrast, the amount of methanol in Comparative Examples A-C is significantly higher, e.g., 42 wppm to 51 wppm.

[0103] 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. An ethanol composition comprising:  
at least 92 wt.% ethanol; and  
from 95 wppm to 1,000 wppm isopropanol.
2. The composition of claim 1, further comprising less than 8 wt.% water.
3. The composition of claim 2, wherein the weight ratio of isopropanol to water in the ethanol composition ranges from 1:80 to 1:1000.
4. The composition as in one of claims 1-3, further comprising one or more organic impurities selected from the group consisting of acetaldehyde, acetic acid, diethyl acetal, ethyl acetate, n-propanol, butanol, 2-butanol, isobutanol, and mixtures thereof.
5. The composition of claim 4, wherein the ethanol composition comprises less than 1 wt.% of the one or more organic impurities.
6. The composition as in one of claims 1-5, further comprising less than 10 wppm acetaldehyde.
7. The composition as in one of claims 1-6, further comprising less than 10 wppm of diethyl acetal.
8. The composition as in one of claims 1-7, further comprising less than 300 wppm C<sub>4</sub> to C<sub>5</sub> alcohols.
9. The composition as in one of claims 1-8, further comprising n-propanol, wherein the weight ratio of isopropanol to n-propanol is at least 0.5:1.

10. The composition as in one of claims 1-9, further comprising from 95 wppm to 270 wppm of n-propanol.
11. The composition as in one of claims 1-10, wherein the composition is substantially benzene free.
12. The composition as in one of claims 1-11, wherein the composition is substantially methanol free.
13. The composition as in one of claims 1-12, wherein the composition is substantially free of C<sub>5</sub> alcohols.
14. An ethanol composition comprising:
  - at least 95 wt. % ethanol;
  - at least 95 wppm isopropanol; and
  - acetaldehyde, wherein the amount of acetaldehyde is less than the amount of isopropanol.
15. The composition of claim 14, wherein the isopropanol is in an amount of less than 1000 wppm.
16. The composition as in any one of claims 14 and 15, wherein the acetaldehyde is in an amount of less than 10 wppm.
17. The composition as in one of claims 14-16, further comprising less than 5 wt.% water.
18. An ethanol composition comprising:
  - at least 92 wt.% ethanol; and
  - at least two other alcohols selected from the group consisting of n-propanol, isopropanol, butanol, 2-butanol, and isobutanol, provided that one of the at least two other alcohols is isopropanol and there is at least 95 wppm isopropanol,

wherein the ethanol composition is substantially methanol free.

19. The composition of claim 18, wherein the at least two other alcohols are present in an amount of less than 1 wt. %.
20. The composition as in any one of claims 18 and 19, wherein the isopropanol is in an amount of less than 1000 wppm.
21. The composition as in one of claims 18-20, further comprising less than 8 wt. % water.
22. An ethanol composition comprising:  
at least 95 wt. % ethanol;  
at least 95 wppm isopropanol; and  
n-propanol, wherein the weight ratio of isopropanol to n-propanol is at least 0.5:1.
23. The composition of claim 22, wherein the weight ratio of isopropanol to n-propanol is at least 1:1.
24. The composition as in any one of claims 22 and 23, wherein the isopropanol is in an amount of less than 1000 wppm.
25. The composition as in one of claims 22-24, wherein the n-propanol is in an amount of less than 270 wppm.
26. The composition as in one of claims 22-25, further comprising less than 5 wt. % water.

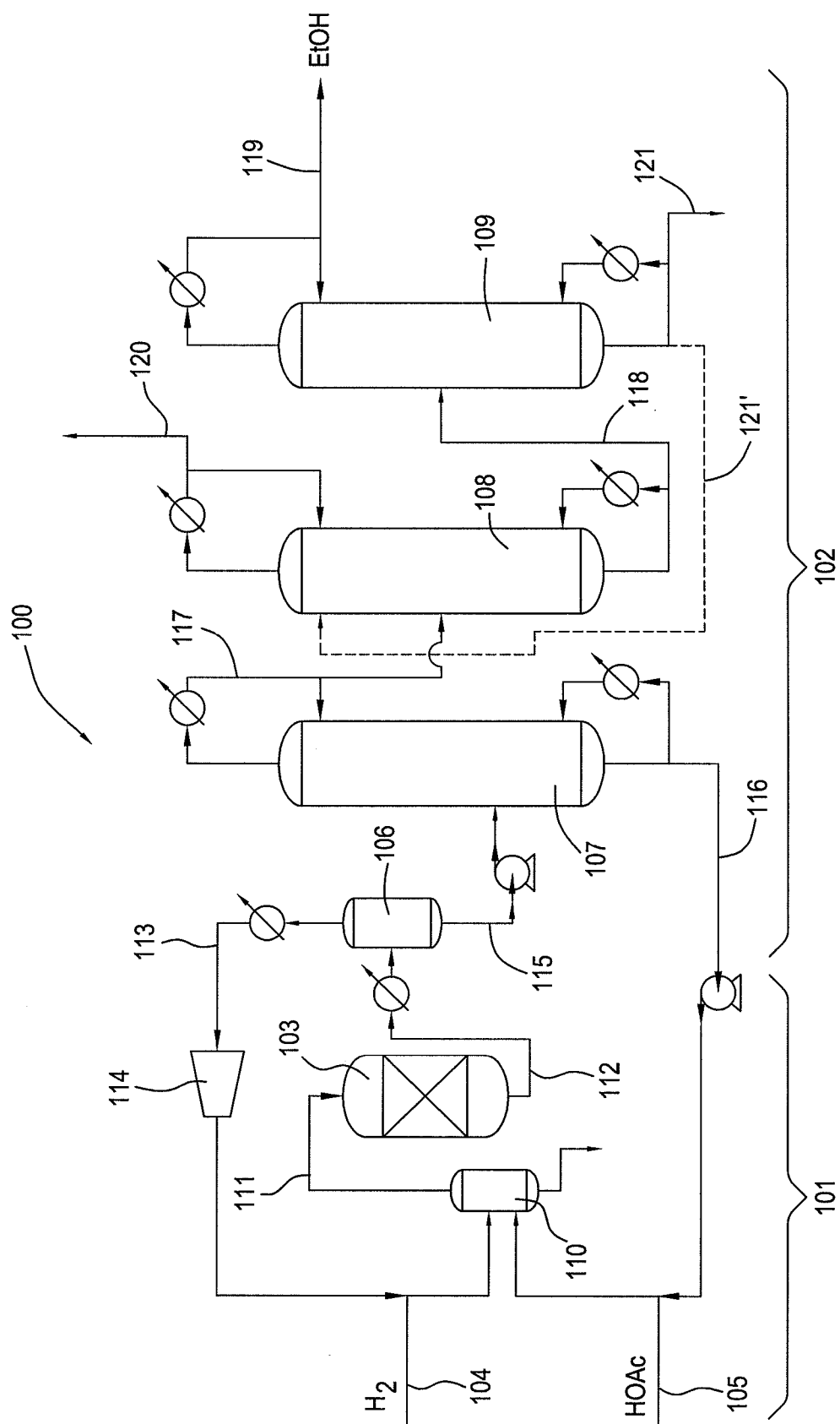


FIG. 1

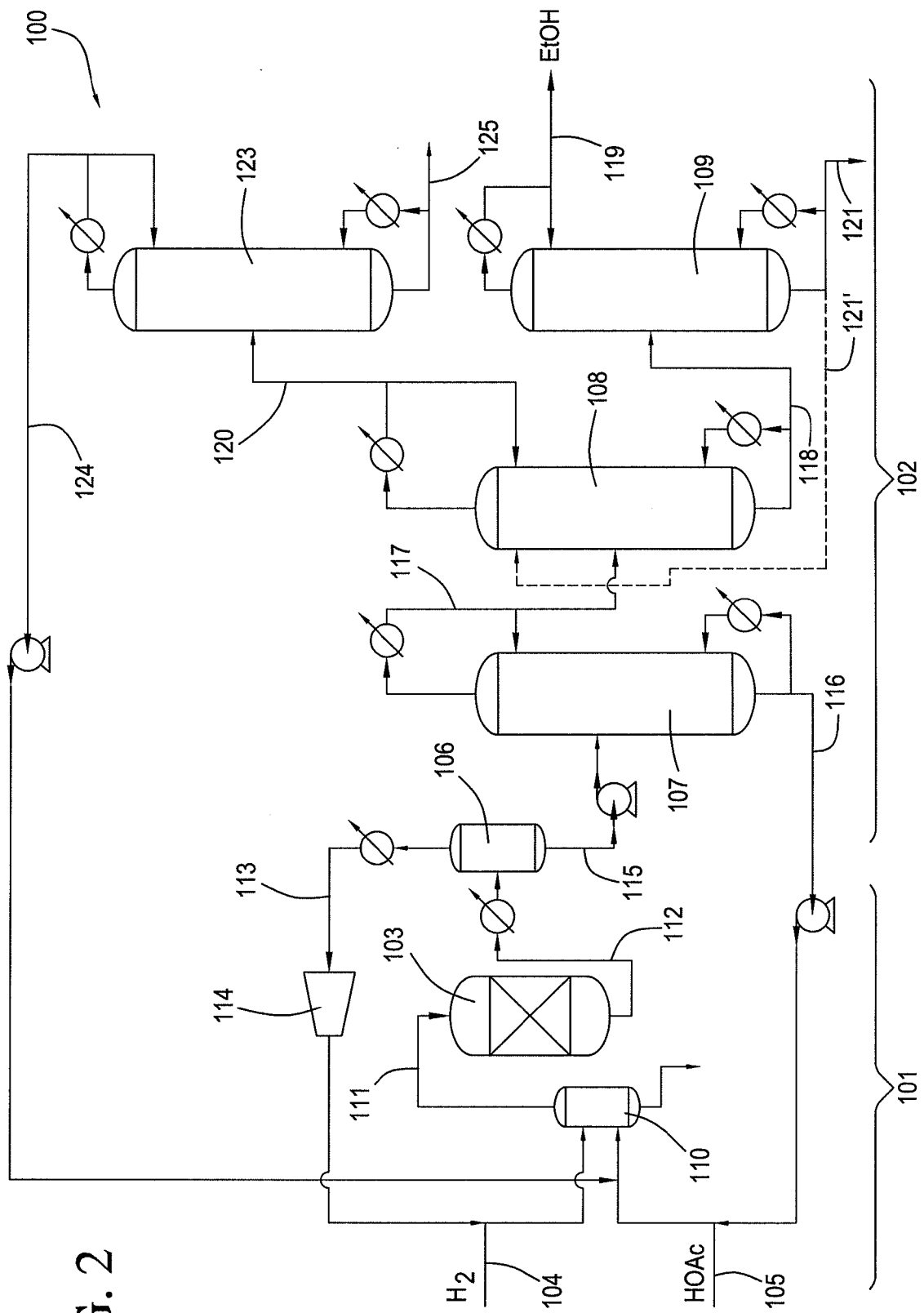
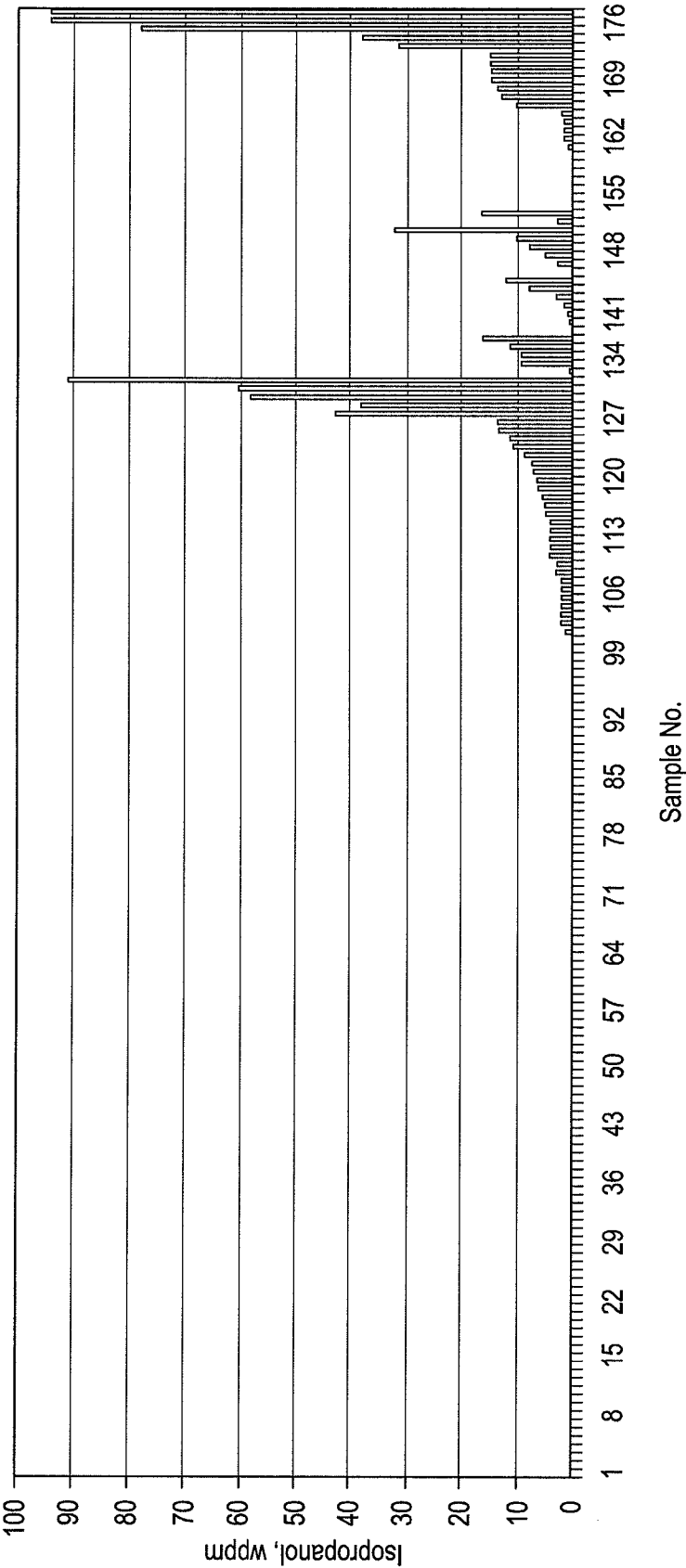


FIG. 2

3/3

FIG. 3





## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2011/023278

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C29/149 C07C31/08 C07C31/10 B01J23/62  
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 B01J

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

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

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 992 484 A1 (KVAERNER PROCESS TECH LTD [GB]) 12 April 2000 (2000-04-12) abstract example 13 table 6 claim 1  -----	1-13



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 document but published on or after the international filing date

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

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

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

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

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

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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

2 May 2011

Date of mailing of the international search report

18/07/2011

Name and mailing address of the ISA/

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Fischbach, Malaika

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2011/023278

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

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

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

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

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

see additional sheet

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

see additional sheet

### Remark on Protest

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

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13

An ethanol composition comprising at least 92 wt.% ethanol and from 95 wppm to 1,000 wppm isopropanol.

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2. claims: 14-17

An ethanol composition comprising at least 95 wt. % ethanol at least 95 wppm isopropanol and acetaldehyde, wherein the amount of acetaldehyde is less than the amount of isopropanol.

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3. claims: 18-21

An ethanol composition comprising at least 92 wt.% ethanol and at least two other alcohols selected from the group consisting of n-propanol, isopropanol, butanol, 2-butanol, and isobutanol, provided that one of the at least two other alcohols is isopropanol and there is at least 95 wppm isopropanol, wherein the ethanol composition is substantially methanol free.

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4. claims: 22-26

An ethanol composition comprising at least 95 wt. % ethanol at least 95 wppm isopropanol and n-propanol, wherein the weight ratio of isopropanol to n-propanol is at least 0.5:1.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/023278

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