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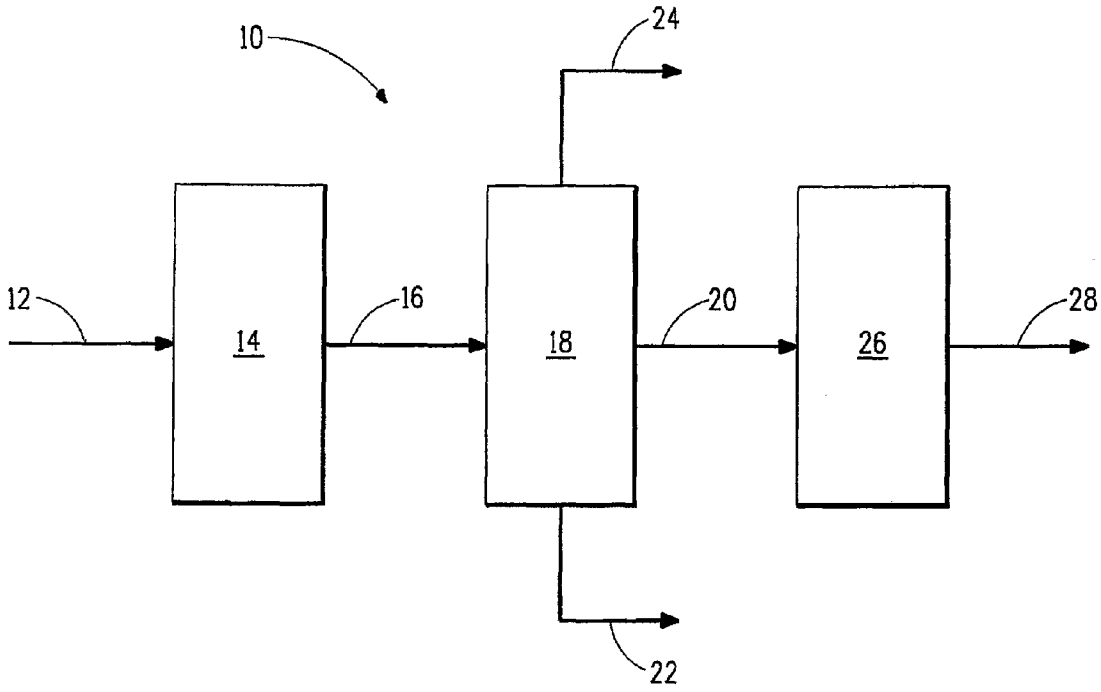
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(54) Title: PROCESS FOR MAKING ISOOCTENES FROM AQUEOUS 2-BUTANOL



(57) Abstract: The present invention relates to a catalytic process for making isooctenes using a reactant comprising 2-butanol and water. The isooctenes so produced are useful for the production of fuel additives.

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TITLE

Process for making isooctenes from aqueous 2-butanol

Cross-Reference to Related Application

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Serial No. 60/872,392 (filed December 1, 2006), the disclosure of which is incorporated by reference herein for all purposes as if fully set forth.

FIELD OF INVENTION

The present invention relates to a process for making isooctenes using aqueous 2-butanol as a reactant.

BACKGROUND

Isooctenes are useful intermediates for the production of fuel additives. Isooctenes are typically produced from the reaction of isobutene or isobutene-containing hydrocarbon mixtures with an acid catalyst. U.S. Patent Application No. 2004/0054246, for example, describes the production of diisobutene from isobutene or mixtures comprising isobutenes using a solid acidic ion-exchange resin. U.S. Patent Application No. 2002/0045786 describes the preparation of diisobutylene from an isobutanol-containing raffinate using an acidic catalyst.

The present invention involves the preparation of isooctenes using at least one acid catalyst and aqueous 2-butanol as a feedstock. There is currently renewed interest in the production of alternative fuels, such as ethanol and butanol, that might replace gasoline and diesel fuel. It would be desirable to be able to utilize aqueous butanol streams produced by the fermentation of renewable resources for the production of isooctenes, without first performing steps to completely remove, or substantially remove, the butanol from the aqueous stream. The isooctenes so produced could be used for the production of fuel additives.

SUMMARY

The present invention relates to a process for making at least one isooctene comprising contacting a reactant comprising 2-butanol and at

least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a reaction product comprising said at least one isooctene, and recovering said at least one isooctene from said reaction product to obtain at least one recovered isooctene. In one embodiment, the reactant is obtained from fermentation broth.

The at least one recovered isooctene is useful as an intermediate for the production of transportation fuels and fuel additives. In particular, the at least one recovered isooctene can be converted to isooctanes, isooctanols or isooctyl alkyl ethers.

In an alternative embodiment, the reaction product produced by contacting aqueous 2-butanol with at least one acid catalyst can be used in subsequent reactions to produce compounds useful in transportation fuels without first recovering the at least one isooctene from the reaction product. The reaction product can be used to produce at least one isooctane by contacting the reaction product with at least one hydrogenation catalyst.

BRIEF DESCRIPTION OF THE DRAWING

The Drawing consists of six figures.

Figure 1 illustrates an overall process useful for carrying out the present invention.

Figure 2 illustrates a method for producing a 2-butanol/water stream using distillation wherein fermentation broth comprising 2-butanol and water is used as the feed stream.

Figure 3 illustrates a method for producing a 2-butanol/water stream using gas stripping wherein fermentation broth comprising 2-butanol and water is used as the feed stream.

Figure 4 illustrates a method for producing a 2-butanol/water stream using liquid-liquid extraction wherein fermentation broth comprising 2-butanol and water is used as the feed stream.

Figure 5 illustrates a method for producing a 2-butanol/water stream using adsorption wherein fermentation broth comprising 2-butanol and water is used as the feed stream.

Figure 6 illustrates a method for producing a 2-butanol/water stream using pervaporation wherein fermentation broth comprising 2-butanol and water is used as the feed stream.

DETAILED DESCRIPTION

The present invention relates to a process for making at least one isooctene from a reactant comprising water and 2-butanol. The at least one isooctene so produced is useful as an intermediate for the production of transportation fuels, wherein transportation fuels include, but are not limited to, gasoline, diesel fuel and jet fuel. The present invention further relates to the production of transportation fuel additives using isooctenes produced by the process of the invention.

In its broadest embodiment, the process of the invention comprises contacting a reactant comprising 2-butanol and water with at least one acid catalyst to produce a reaction product comprising at least one isooctene, and recovering said at least one isooctene from said reaction product to obtain at least one recovered isooctene. By isooctene is meant any olefin having eight carbons, wherein at least one of the carbons is a secondary or tertiary carbon.

Although the reactant could comprise less than about 5% water by weight relative to the weight of the water plus 2-butanol, it is preferred that the reactant comprise at least about 5% water. In a more specific embodiment, the reactant comprises from about 5% to about 80% water by weight relative to the weight of the water plus 2-butanol.

In one preferred embodiment, the reactant is derived from fermentation broth, and comprises at least about 50% 2-butanol (by weight relative to the weight of the butanol plus water) (sometimes referred to herein as "aqueous 2-butanol"). One advantage to the microbial (fermentative) production of butanol is the ability to utilize feedstocks derived from renewable sources, such as corn stalks, corn grain, corn cobs, sugar cane, sugar beets or wheat, for the fermentation process.

Efforts are currently underway to engineer (through recombinant means) or select for organisms that produce butanol with greater efficiency than is obtained with current microorganisms. Such efforts are expected to be successful, and the process of the present invention will be applicable to any fermentation process that produces 2-butanol at levels currently seen with wild-type microorganisms, or with genetically modified microorganisms from which enhanced production of 2-butanol is obtained.

2-Butanol can be produced by fermentatively producing 2,3-butanediol, followed by converting the 2,3-butanediol chemically to 2-butanol as described in co-filed and commonly owned Patent Application Docket Number CL-3082. According to CL-3082, 2,3-butanediol is converted to 2-butanol by a process comprising contacting a reactant comprising dry or wet 2,3-butanediol, optionally in the presence of at least one inert solvent, with hydrogen in the presence of a catalyst system that can function both as an acid catalyst and as a hydrogenation catalyst at a temperature between about 75 and about 300 degrees Centigrade and a hydrogen pressure between about 345 kPa and about 20.7 MPa, to produce a reaction product comprising 2-butanol; and recovering 2-butanol from the reaction product.

Suitable inert solvents for the conversion of 2,3-butanediol to 2-butanol as described in CL-3082 include liquid hydrocarbons, liquid aromatic compounds, liquid ethers, 2-butanol, and combinations thereof. Preferred solvents include C_5 to C_{20} straight-chain, branched or cyclic liquid hydrocarbons, C_6 to C_{20} liquid aromatic compounds, and liquid dialkyl ethers wherein the individual alkyl groups of the dialkyl ether are straight-chain or branched, and wherein the total number of carbons of the dialkyl ether is from 4 to 16.

The 2,3-butanediol (BDO) can be obtained by fermentation; microbial fermentation for the production of BDO has been reviewed in detail by Syu, M.-J. (Appl. Microbiol. Biotechnol (2001) 55:10-18). Strains of bacteria useful for producing BDO include *Klebsiella pneumoniae* and *Bacillus polymyxa*, as well as recombinant strains of *Escherichia coli*. Carbon and energy sources, culture media, and growth conditions (such

as pH, temperature, aeration and inoculum) are dependent on the microbial strain used, and are described by Ledingham, G.A. and Neish, A.C. (Fermentative production of 2,3-butanediol, in Underkofler, L.A. and Hickey, R.J., Industrial Fermentations, Volume II, Chemical Publishing Co., Inc., New York, 1954, pages 27-93), Garg, S.K. and Jain, A. (Bioresource Technology (1995) 51:103-109), and Syu (*supra*). These references also describe the use of biomass as the carbon (i.e., sugar) source, as well as the bioreactors and additional fermentation equipment and conditions required for fermentation. One example wherein *K. pneumoniae* was utilized to produce BDO was provided by Grover, B.S., et al (World J. Microbiol. and Biotech. (1990) 6:328-332). Grover, B.S., et al described the production of BDO using *K. pneumoniae* NRRL B-199 grown on the reducing sugars in wood hydrolysate. Optimal conditions for a 48 hour fermentation were pH 6.0, a temperature of 30 degrees Centigrade, and 50 grams of reducing sugars per liter of medium.

BDO can be recovered from fermentation broth by a number of techniques well known to those skilled in the art, including distillation, vacuum membrane distillation using a microporous polytetrafluoroethylene membrane and solvent extraction using solvents such as ethyl acetate, diethyl ether, and *n*-butanol as reviewed by Syu (*supra*).

The heterogeneous catalyst system useful for the conversion of 2,3-butanediol to 2-butanol is a catalyst system that can function both as an acid catalyst and as a hydrogenation catalyst. The heterogeneous catalyst system can comprise independent catalysts, i.e., at least one solid acid catalyst plus at least one solid hydrogenation catalyst. Alternatively, the heterogeneous catalyst system can comprise a dual function catalyst. A dual function catalyst is defined in CL-3082 as a catalyst wherein at least one solid acid catalyst and at least one solid hydrogenation catalyst are combined into one catalytic material.

Suitable acid catalysts are heterogeneous (or solid) acid catalysts. The at least one solid acid catalyst may be supported on at least one catalyst support (herein referred to as a supported acid catalyst). Solid acid catalysts include, but are not limited to, (1) heterogeneous

heteropolyacids (HPAs) and their salts, (2) natural clay minerals, such as those containing alumina or silica (including zeolites), (3) cation exchange resins, (4) metal oxides, (5) mixed metal oxides, (6) metal salts such as metal sulfides, metal sulfates, metal sulfonates, metal nitrates, metal phosphates, metal phosphonates, metal molybdates, metal tungstates, metal borates, and (7) combinations of groups 1 to 6. When present, the metal components of groups 4 to 6 may be selected from elements from Groups I, IIa, IIIa, VIIa, VIIIa, Ib and IIb of the Periodic Table of the Elements, as well as aluminum, chromium, tin, titanium and zirconium.

Preferred solid acid catalysts include cation exchange resins, such as Amberlyst® 15 (Rohm and Haas, Philadelphia, PA), Amberlite® 120 (Rohm and Haas), Nafion®, and natural clay materials, including zeolites such as mordenite.

The heterogeneous catalyst system useful for converting 2,3-butanediol to 2-butanol must also comprise at least one solid hydrogenation catalyst. The at least one solid hydrogenation catalyst may be supported on at least one catalyst support (herein referred to as a supported hydrogenation catalyst).

The hydrogenation catalyst may be a metal selected from the group consisting of nickel, copper, chromium, cobalt, rhodium, ruthenium, rhenium, osmium, iridium, platinum, palladium, at least one Raney® metal, platinum black; compounds thereof; and combinations thereof. A promoter such as, without limitation, tin, zinc, copper, gold, silver and combinations thereof may be used to affect the reaction, for example, by increasing activity and catalyst lifetime.

Preferred hydrogenation catalysts include ruthenium, iridium, palladium; compounds thereof; and combinations thereof.

A suitable dual function catalyst can be, but is not limited to, a hydrogenation catalyst comprising a metal selected from the group consisting of nickel, copper, chromium, cobalt, rhodium, ruthenium, rhenium, osmium, iridium, platinum, and palladium; compounds thereof; and combinations thereof; deposited by any means described above on an acid catalyst selected from the group consisting of (1) heterogeneous

heteropolyacids (HPAs) and their salts, (2) natural clay minerals, such as those containing alumina or silica (including zeolites), (3) cation exchange resins, (4) metal oxides, (5) mixed metal oxides, (6) metal salts such as metal sulfides, metal sulfates, metal sulfonates, metal nitrates, metal phosphates, metal phosphonates, metal molybdates, metal tungstates, metal borates, and (7) combinations of groups 1 to 6.

Preferred dual function catalysts comprise a hydrogenation catalyst comprising a metal selected from the group consisting of nickel, copper, chromium, cobalt, rhodium, ruthenium, rhenium, osmium, iridium, platinum, and palladium; compounds thereof; and combinations thereof deposited by any means described above on an acid catalyst selected from the group consisting of (1) natural clay minerals, such as those containing alumina or silica (including zeolites), (2) cation exchange resins, (3) Nafion®, (4) metal salts such as metal sulfides, metal sulfates, metal sulfonates, metal nitrates, metal phosphates, metal phosphonates, metal molybdates, metal tungstates, metal borates, and (5) combinations of groups 1 to 4.

The reaction product comprises 2-butanol, as well as water, and may comprise unreacted BDO and/or methyl ethyl ketone. 2-Butanol can be recovered as described below.

2-Butanol can also be fermentatively produced by recombinant microorganisms as described in copending and commonly owned U.S. Patent Application No. 60/796816, page 4, line 7 through page 42, line 26, including the sequence listing. In one embodiment, the invention described in 60/796816 provides a recombinant microbial host cell comprising at least one DNA molecule encoding a polypeptide that catalyzes a substrate to product conversion selected from the group consisting of:

i) pyruvate to alpha-acetolactate

ii) alpha-acetolactate to acetoin

iii) acetoin to 2,3-butanediol

iv) 2,3-butanediol to 2-butanone

v) 2-butanone to 2-butanol

wherein the at least one DNA molecule is heterologous to said microbial host cell and wherein said microbial host cell produces 2-butanol. Methods for generating recombinant microorganisms, including isolating genes, constructing vectors, transforming hosts, and analyzing expression of genes of the biosynthetic pathway are described in detail by Donaldson, *et al.* in 60/796816.

Fermentation methodology is well known in the art, and can be carried out in a batch-wise, continuous or semi-continuous manner. As is well known to those skilled in the art, the concentration of 2-butanol in the fermentation broth produced by any process will depend on the microbial strain and the conditions, such as temperature, growth medium, mixing and substrate, under which the microorganism is grown.

Following fermentation, the fermentation broth from the fermentor can be used for the process of the invention. In one preferred embodiment the fermentation broth is subjected to a refining process to produce an aqueous stream comprising an enriched concentration of 2-butanol. By "refining process" is meant a process comprising one or more unit operations that allows for the purification of an aqueous stream comprising 2-butanol and other materials in the fermentation broth to yield an aqueous stream in which 2-butanol and water are the predominant components. For example, in one embodiment, the refining process yields a stream that contains at least about 5% water and 2-butanol.

Refining processes utilize one or more unit operations, and typically employ at least one distillation step as a means for recovering a fermentation product. It is expected, however, that fermentative processes will produce 2-butanol at very low concentrations relative to the concentration of water in the fermentation broth. This can lead to large capital and energy expenditures to recover the 2-butanol by distillation alone. As such, other techniques can be used either alone or in combination with distillation, or alternatively with molecular sieves, as a means of concentrating the dilute 2-butanol product. In such processes where separation techniques are integrated with the fermentation step,

cells can optionally be removed from the stream to be refined by centrifugation or membrane separation techniques, yielding a clarified fermentation broth. These cells are then returned to the fermentor to improve the productivity of the 2-butanol fermentation process. The clarified fermentation broth is then subjected to such techniques as pervaporation, gas stripping, liquid-liquid extraction, perstraction, adsorption, distillation, molecular sieves, or combinations thereof to provide a stream comprising water and 2-butanol suitable for use in the process of the invention.

Separation of 2-butanol from water

1-Butanol and 2-butanol have many common features that allow the separation schemes devised for the separation of 1-butanol and water to be applicable to the 2-butanol and water system. For instance both 1-butanol and 2-butanol are hydrophobic molecules possessing log Kow coefficients of 0.88 and 0.61, respectively. Kow is defined as the partition coefficient of a species at equilibrium in an octanol-water system. Since both 1-butanol and 2-butanol are hydrophobic molecules (Kow = 7.6 and 4.1, respectively), one would expect both molecules to favorably partition into a separate non-aqueous phase such as decanol or adsorb onto various hydrophobic solid phases such as silicone or silicalite. In this regard liquid-liquid extraction and adsorption are viable separation options for 2-butanol from water.

In addition, both 1-butanol and 2-butanol are relatively volatile molecules at dilute concentration and have favorable K values, or vapor-liquid partition coefficients, relative to ethanol, when in solution with water. Another useful thermodynamic term is α, or relative volatility, which is the ratio of partition coefficients, K values, for a given binary system. For a given concentration and temperature less than 100°C, the values for K and α are greater for 2-butanol vs. 1-butanol in their respective butanol-water systems, i.e. 5.3 vs. 4.6, and 43 vs. 37, respectively. This indicates that in evaporative separation schemes such as gas stripping, pervaporation, and distillation, 2-butanol should separate more efficiently from water than 1-

butanol from water at a given temperature. At 100°C the K and α values are very similar between 2-butanol and 1-butanol, 31 vs. 30, and 31 vs. 30, respectively, indicating that separation processes based on evaporative means and designed for operation in this temperature range should perform with equal efficiency.

The separation of 1-butanol from water, and the separation of 1-butanol from a mixture of acetone, ethanol, 1-butanol and water as part of the ABE fermentation process by distillation have been described. In particular, in a 1-butanol and water system, 1-butanol forms a low boiling heterogeneous azeotrope in equilibrium with 2 liquid phases comprised of 1-butanol and water. This azeotrope is formed at a vapor phase composition of approximately 58% by weight 1-butanol (relative to the weight of water plus 1-butanol) when the system is at atmospheric pressure (as described by Doherty, M.F. and Malone, M.F. in Conceptual Design of Distillation Systems (2001), Chapter 8, pages 365-366, McGraw-Hill, New York). The liquid phases are roughly 6% by weight 1-butanol (relative to the weight of water plus 1-butanol) and 80% by weight 1-butanol (relative to the weight of water plus 1-butanol), respectively.

Unlike 1-butanol, 2-butanol forms a minimum boiling homogeneous azeotrope with water. In this regard 2-butanol behaves more like ethanol than 1-butanol. In the 2-butanol-water azeotrope the vapor phase is in equilibrium with a single liquid phase of the same composition. The azeotrope is formed at a vapor phase composition of 73% by weight 2-butanol (relative to the weight of water plus 2-butanol) (as described by Doherty, M.F. and Malone, M.F. in Conceptual Design of Distillation Systems (2001), Chapter 8, pages 365-366, McGraw-Hill, New York). Although the high relative volatility of 2-butanol over water makes distillation an attractive separations option, the homogeneous azeotrope provides a boundary to further increasing the purity of the butanol product stream by simple distillation. In systems where homogeneous azeotropes are present, a separate component can be added to modify the separation characteristics of the material to be separated from the bulk medium. The added component is typically called an entrainer and the process of

distillation using the entrainer referred to as extractive distillation. Such systems have been described for separating 2-butanol from water. For example, the commercial process for making 2-butanol from n-butylenes uses azeotropic distillation to remove impurities, including water. The separation scheme underpinning the commercial 2-butanol process has been described by Takaoka, S., *Acetone, Methyl Ethyl Ketone, and Methyl Isobutyl Ketone*, Report No. 77, Process Economics Program, Stanford Research Institute, Menlo Park, CA, May 1972; Kovach III, J.W. and W. D. Seider, "Heterogeneous Azeotropic Distillation: Experimental and Simulation Results," *AIChE J.*, 33(8), 1300-1314, 1987; Kovach III, J.W. and W. D. Seider, "Vapor-Liquid and Liquid-Liquid Equilibria for the System sec-Butyl Alcohol-Di-sec-Butyl Ether-Water," *J. Chem. Eng. Data*, 33, 16-20, 1988; and Baumann, G. P., "Secondary Butanol Purification Process", US Patent No. 3,203,872. In the latter example, the entrainer used is a reaction byproduct (di-sec-butyl ether) already in the feed to the column.

Distillation

An aqueous 2-butanol stream from the fermentation broth is fed to a distillation column, from which a 2-butanol-water azeotrope is removed as a vapor phase. Since the feed to the reaction is to be comprised of 2-butanol and water, no entrainers are needed to allow for separation to proceed beyond the azeotrope. Thus, the vapor phase from the distillation column (comprising at least about 27% water (by weight relative to the weight of water plus 2-butanol)) can then be used directly as the reactant for the process of the present invention, or can be fed to a condenser and condensed into a liquid phase of similar composition. One skilled in the art will know that solubility is a function of temperature, and that the actual concentration of water in the aqueous 2-butanol stream will vary with temperature.

Pervaporation

Generally, there are two steps involved in the removal of volatile components by pervaporation. One is the sorption of the volatile component into the membrane, and the other is the diffusion of the volatile

component through the membrane due to a concentration gradient. The concentration gradient is created either by a vacuum applied to the opposite side of the membrane or through the use of a sweep gas, such as air or carbon dioxide, also applied along the backside of the membrane. Pervaporation for the separation of 1-butanol from a fermentation broth has been described by Meagher, M.M., *et al* in U.S. Patent No. 5,755,967 (Column 5, line 20 through Column 20, line 59) and by Liu, F., *et al* (Separation and Purification Technology (2005) 42:273-282). According to U.S. 5,755,967, acetone and/or 1-butanol were selectively removed from an ABE fermentation broth using a pervaporation membrane comprising silicalite particles embedded in a polymer matrix. Examples of polymers include polydimethylsiloxane and cellulose acetate, and vacuum was used as the means to create the concentration gradient. The method of U.S. 5,755,967 can similarly be used to recover a stream comprising 2-butanol and water from fermentation broth, and this stream can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous 2-butanol stream that can be used as the reactant of the present invention.

Gas stripping

In general, gas stripping refers to the removal of volatile compounds, such as butanol, from fermentation broth by passing a flow of stripping gas, such as carbon dioxide, helium, hydrogen, nitrogen, or mixtures thereof, through the fermentor culture or through an external stripping column to form an enriched stripping gas. Gas stripping to remove 1-butanol during the ABE fermentation process has been exemplified by Ezeji, T., *et al* (U.S. Patent Application No. 2005/0089979, paragraphs 16 through 84). According to U.S. 2005/0089979, a stripping gas (carbon dioxide and hydrogen) was fed into a fermentor via a sparger. The flow rate of the stripping gas through the fermentor was controlled to give the desired level of solvent removal. The flow rate of the stripping gas is dependent on such factors as configuration of the system, cell concentration and solvent concentration in the fermentor. This process can also be used to produce an enriched stripping gas comprising 2-

butanol and water, and this stream can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous 2-butanol stream that can be used as the reactant of the present invention.

Adsorption

Using adsorption, organic compounds of interest are removed from dilute aqueous solutions by selective sorption of the organic compound by a sorbant, such as a resin. Feldman, J. in U. S. Patent No. 4,450,294 (Column 3, line 45 through Column 9, line 40 (Example 6)) describes the recovery of an oxygenated organic compound from a dilute aqueous solution with a cross-linked polyvinylpyridine resin or nuclear substituted derivative thereof. Suitable oxygenated organic compounds included ethanol, acetone, acetic acid, butyric acid, n-propanol and n-butanol. The adsorbed compound was desorbed using a hot inert gas such as carbon dioxide. This process can also be used to recover an aqueous stream comprising desorbed 2-butanol, and this stream can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous 2-butanol stream that can be used as the reactant of the present invention.

Liquid-liquid extraction

Liquid-liquid extraction is a mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly immiscible liquid (solvent) that exhibits preferential affinity or selectivity towards one or more of the components in the feed, allowing selective separation of said one or more components from the feed. The solvent comprising the one or more feed components can then be separated, if necessary, from the components by standard techniques, such as distillation or evaporation. One example of the use of liquid-liquid extraction for the separation of butyric acid and butanol from microbial fermentation broth has been described by Cenedella, R.J. in U.S. Patent No. 4,628,116 (Column 2, line 28 through Column 8, line 57). According to U.S. 4,628,116, fermentation broth containing butyric acid and/or butanol was acidified to a pH from about 4 to about 3.5, and the acidified fermentation

broth was then introduced into the bottom of a series of extraction columns containing vinyl bromide as the solvent. The aqueous fermentation broth, being less dense than the vinyl bromide, floated to the top of the column and was drawn off. Any butyric acid and/or butanol present in the fermentation broth was extracted into the vinyl bromide in the column. The column was then drawn down, the vinyl bromide was evaporated, resulting in purified butyric acid and/or butanol.

Other solvent systems for liquid-liquid extraction, such as decanol, have been described by Roffler, S.R., *et al.* (Bioprocess Eng. (1987) 1:1-12) and Taya, M., *et al* (J. Ferment. Technol. (1985) 63:181). In these systems, two phases were formed after the extraction: an upper less dense phase comprising decanol, 1-butanol and water, and a more dense phase comprising mainly decanol and water. Aqueous 1-butanol was recovered from the less dense phase by distillation.

These extractive processes can also be used to obtain an aqueous stream comprising 2-butanol that can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous 2-butanol stream that can be used as the reactant of the present invention.

Aqueous streams comprising 2-butanol, as obtained by any of the methods above, can be the reactant for the process of the present invention. The reaction to form at least one isooctene is performed at a temperature of from about 50 degrees Centigrade to about 450 degrees Centigrade. In a more specific embodiment, the temperature is from about 100 degrees Centigrade to about 250 degrees Centigrade.

The reaction can be carried out under an inert atmosphere at a pressure of from about atmospheric pressure (about 0.1 MPa) to about 20.7 MPa. In a more specific embodiment, the pressure is from about 0.1 MPa to about 3.45 MPa. Suitable inert gases include nitrogen, argon and helium.

The reaction can be carried out in liquid or vapor phase and can be run in either batch or continuous mode as described, for example, in H.

Scott Fogler, (Elements of Chemical Reaction Engineering, 2nd Edition, (1992) Prentice-Hall Inc, CA).

The at least one acid catalyst can be a homogeneous or heterogeneous catalyst. Homogeneous catalysis is catalysis in which all reactants and the catalyst are molecularly dispersed in one phase. Homogeneous acid catalysts include, but are not limited to inorganic acids, organic sulfonic acids, heteropolyacids, fluoroalkyl sulfonic acids, metal sulfonates, metal trifluoroacetates, compounds thereof and combinations thereof. Examples of homogeneous acid catalysts include sulfuric acid, fluorosulfonic acid, phosphoric acid, *p*-toluenesulfonic acid, benzenesulfonic acid, hydrogen fluoride, phosphotungstic acid, phosphomolybdic acid, and trifluoromethanesulfonic acid.

Heterogeneous catalysis refers to catalysis in which the catalyst constitutes a separate phase from the reactants and products. Heterogeneous acid catalysts include, but are not limited to 1) heterogeneous heteropolyacids (HPAs), 2) natural clay minerals, such as those containing alumina or silica, 3) cation exchange resins, 4) metal oxides, 5) mixed metal oxides, 6) metal salts such as metal sulfides, metal sulfates, metal sulfonates, metal nitrates, metal phosphates, metal phosphonates, metal molybdates, metal tungstates, metal borates, 7) zeolites, and 8) combinations of groups 1 – 7. See, for example, Solid Acid and Base Catalysts, pages 231-273 (Tanabe, K., in Catalysis: Science and Technology, Anderson, J. and Boudart, M (eds.) 1981 Springer-Verlag, New York) for a description of solid catalysts.

The heterogeneous acid catalyst may also be supported on a catalyst support. A support is a material on which the acid catalyst is dispersed. Catalyst supports are well known in the art and are described, for example, in Satterfield, C. N. (Heterogeneous Catalysis in Industrial Practice, 2nd Edition, Chapter 4 (1991) McGraw-Hill, New York).

In one embodiment of the invention, the reaction is carried out using a heterogeneous catalyst, and the temperature and pressure are chosen so as to maintain the reactant and reaction product in the vapor phase. In a more specific embodiment, the reactant is obtained from a

fermentation broth that is subjected to distillation to produce a vapor phase having at least about 27% water. The vapor phase is directly used a reactant in a vapor phase reaction in which the acid catalyst is a heterogeneous catalyst, and the temperature and pressure are chosen so as to maintain the reactant and reaction product in the vapor phase. It is believed that this vapor phase reaction would be economically desirable because the vapor phase is not first cooled to a liquid prior to performing the reaction.

One skilled in the art will know that conditions, such as temperature, catalytic metal, support, reactor configuration and time can affect the reaction kinetics, product yield and product selectivity. Depending on the reaction conditions, such as the particular catalyst used, products other than isooctenes may be produced when 2-butanol is contacted with an acid catalyst. Additional products comprise dibutyl ethers (such as di-1-butyl ether) and butenes. Standard experimentation, performed as described in the Examples herein, can be used to optimize the yield of isooctenes from the reaction.

Following the reaction, if necessary, the catalyst can be separated from the reaction product by any suitable technique known to those skilled in the art, such as decantation, filtration, extraction or membrane separation (see Perry, R.H. and Green, D.W. (eds), Perry's Chemical Engineer's Handbook, 7th Edition, Section 13, 1997, McGraw-Hill, New York, Sections 18 and 22).

The at least one isooctene can be recovered from the reaction product by distillation as described in Seader, J.D., *et al* (Distillation, in Perry, R.H. and Green, D.W. (eds), Perry's Chemical Engineer's Handbook, 7th Edition, Section 13, 1997, McGraw-Hill, New York). Alternatively, the at least one isooctene can be recovered by phase separation, or extraction with a suitable solvent, such as trimethylpentane or octane, as is well known in the art. Unreacted 2-butanol can be recovered following separation of the at least one isooctene and used in subsequent reactions.

The present process and certain embodiments for accomplishing it are shown in greater detail in the Drawing figures.

Referring now to Figure 1, there is shown a block diagram illustrating in a very general way apparatus 10 for deriving isooctenes from aqueous 2-butanol produced by fermentation. An aqueous stream 12 of biomass-derived carbohydrates is introduced into a fermentor 14. The fermentor 14 contains at least one microorganism (not shown) capable of fermenting the carbohydrates to produce a fermentation broth that comprises 2-butanol and water. A stream 16 of the fermentation broth is introduced into refining apparatus 18 in order to make a stream of aqueous 2-butanol. The aqueous 2-butanol is removed from the refining apparatus 18 as stream 20. Some water is removed from the refining apparatus 18 as stream 22. Other organic components present in the fermentation broth may be removed as stream 24. The aqueous 2-butanol stream 20 is introduced into reaction vessel 26 containing an acid catalyst (not shown) capable of converting the 2-butanol into a reaction product comprising at least one isooctene. The reaction product is removed as stream 28.

Referring now to Figure 2, there is shown a block diagram for refining apparatus 100, suitable for producing an aqueous 2-butanol stream, when the fermentation broth comprises 2-butanol and water. A stream 102 of fermentation broth is introduced into a feed preheater 104 to raise the broth to a temperature of approximately 95°C to produce a heated feed stream 106 which is introduced into a beer column 108. The design of the beer column 108 needs to have a sufficient number of theoretical stages to cause separation of 2-butanol from water such that a 2-butanol/water azeotrope can be removed as a vaporous 2-butanol/water azeotrope overhead stream 110 and hot water as a bottoms stream 112. Bottoms stream 112 is used to supply heat to feed preheater 104 and leaves feed preheater 104 as a lower temperature bottoms stream 142. Reboiler 114 is used to supply heat to beer column 108. Vaporous 2-butanol/water azeotrope overhead stream 110 is roughly 73% by weight relative to the total weight of the 2-butanol plus water in the stream. This

is the first opportunity by which a concentrated and partially purified 2-butanol and water stream could be obtained. This partially purified 2-butanol and water stream can be used as the feed stream to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene, or can be further dehydrated by the use of molecular sieves. Vaporous 2-butanol/water azeotrope stream 110 can also be fed to condenser 116, which lowers the stream temperature causing the vaporous 2-butanol/water azeotrope overhead stream 110 to condense into a liquid stream 118 of the same composition. Liquid stream 118 can then be used as the feed stream to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene, or can be further dehydrated by molecular sieves. The product of the molecular sieves can then be used as feed stream to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene. As is known to those skilled in the art, molecular sieves are adsorbent materials that have a stronger affinity for one type of atom or molecular in a stream than for other types in the stream. A common use of molecular sieves is the dehydration of ethanol as described, for example in R.L. B. Swain (Molecular sieve dehydrators, how they became the industry standard and how they work, in Jacques, K.A. et al (eds) in The Alcohol Textbook, 3rd Edition, Chapter 19, 1999, Nottingham University Press, U.K.).

Referring now to Figure 3, there is shown a block diagram for refining apparatus 300, suitable for producing an aqueous 2-butanol stream when the fermentation broth comprises 2-butanol and water. Fermentor 302 contains a fermentation broth comprising liquid 2-butanol and water and a gas phase comprising CO_2 and to a lesser extent some vaporous 2-butanol and water. A CO_2 stream 304 is then mixed with combined CO_2 stream 307 to give second combined CO_2 stream 308. Second combined CO_2 stream 308 is then fed to heater 310 and heated to 60°C to give heated CO_2 stream 312. Heated CO_2 stream is then fed to

gas stripping column 314 where it is brought into contact with heated clarified fermentation broth stream 316. Heated clarified fermentation broth stream 316 is obtained by heating clarified broth stream 318 to 50°C in heater 320. Clarified fermentation broth stream 318 is obtained following separation of cells in cell separator 317. Also leaving cell separator 317 is concentrated cell stream 319 that is recycled directly to fermentor 302. The feed stream 315 to cell separator 317 comprises the liquid phase of fermentor 302. Gas stripping column 314 contains a sufficient number of theoretical stages necessary to effect the transfer of 2-butanol from the liquid phase to the gas phase. The number of theoretical stages is dependent on the contents of both streams 312 and 316, as well as their flow rates and temperatures. Leaving gas stripping column 314 is a 2-butanol depleted clarified fermentation broth stream 322 that is recirculated to fermentor 302. A 2-butanol enriched gas stream 324 leaving gas stripping column 314 is then fed to compressor 326, where it is compressed. Following compression, a compressed gas stream 328 comprising 2-butanol is then fed to condenser 330 where the 2-butanol in the gas stream is condensed into a liquid phase that is separate from non-condensable components in the stream 328. Leaving the condenser 330 is 2-butanol depleted gas stream 332. A first portion of gas stream 332 is bled from the system as bleed gas stream 334, and the remaining second portion of 2-butanol depleted gas stream 332, stream 336, is then mixed with makeup CO_2 gas stream 306 to form combined CO_2 gas stream 307. The condensed 2-butanol phase in condenser 330 leaves as aqueous 2-butanol stream 342 and can be used as the feed to a distillation apparatus or to a bed of molecular sieves for further dehydration of the aqueous 2-butanol stream, or stream 342 can be used directly as a feed to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene.

Referring now to Figure 4, there is shown a block diagram for refining apparatus 400, suitable for producing an aqueous 2-butanol stream, when the fermentation broth comprises 2-butanol and water. Fermentor 402 contains a fermentation broth comprising 2-butanol and

water and a gas phase comprising CO_2 and to a lesser extent some vaporous 2-butanol and water. A stream 404 of fermentation broth is introduced into a feed preheater 406 to raise the broth temperature to produce a heated fermentation broth stream 408 which is introduced into solvent extractor 410. In solvent extractor 410, heated fermentation broth stream 408 is brought into contact with cooled solvent stream 412, the solvent used in this case being decanol. Leaving solvent extractor 410 is raffinate stream 414 that is depleted in 2-butanol. Raffinate stream 414 is introduced into raffinate cooler 416 where it is lowered in temperature and returned to fermentor 402 as cooled raffinate stream 418. Also leaving solvent extractor 410 is extract stream 420 that comprises solvent, 2-butanol and water. Extract stream 420 is introduced into solvent heater 422 where it is heated. Heated extract stream 424 is then introduced into solvent recovery distillation column 426, where the solvent is caused to separate from the 2-butanol and water. Solvent column 426 is equipped with reboiler 428 necessary to supply heat to solvent column 426. Leaving the bottom of solvent column 426 is solvent stream 430. Solvent stream 430 is then introduced into solvent cooler 432 where it is cooled to 50°C. Cooled solvent stream 412 leaves solvent cooler 432 and is returned to extractor 410. Leaving the top of solvent column 426 is solvent overhead stream 434 that comprises an azeotropic mixture of 2-butanol and water with trace amounts of solvent. This represents the first substantially concentrated and partially purified 2-butanol/water stream where a portion of the stream (azeotropic vapor stream 435) could be fed to a reaction vessel (not shown) for catalytically converting the 2-butanol to a reaction product that comprises at least one isooctene. The remaining portion of solvent overhead stream 434 (stream 437) is then fed into condenser 436 where the vaporous solvent overhead stream is caused to condense into a liquid stream 438 of similar composition. Stream 438 is then optionally split into 2 streams depending on if azeotropic vapor stream 435 is used as the feed stream for the process of the invention. Reflux stream 442 is sent back to solvent column 426 to provide rectification. If azeotropic vapor stream 435 is not used as a feed stream for the process of the

invention, optional intermediate product stream 444 can be introduced as the feed to a distillation apparatus or to a bed of molecular sieves that is capable of further dehydrating the aqueous 2-butanol stream, or stream 444 can be used directly as a feed to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene.

Referring now to Figure 5, there is shown a block diagram for refining apparatus 500, suitable for concentrating 2-butanol, when the fermentation broth comprises 2-butanol and water. Fermentor 502 contains a fermentation broth comprising 2-butanol and water and a gas phase comprising CO_2 and to a lesser extent some vaporous 2-butanol and water. A 2-butanol-containing fermentation broth stream 504 leaving fermentor 502 is introduced into cell separator 506. Cell separator 506 can be comprised of centrifuges or membrane units to accomplish the separation of cells from the fermentation broth. Leaving cell separator 506 is cell-containing stream 508 which is recycled back to fermentor 502. Also leaving cell separator 506 is clarified fermentation broth stream 510. Clarified fermentation broth stream 510 is then introduced into one or a series of adsorption columns 512 where the 2-butanol is preferentially removed from the liquid stream and adsorbed on the solid phase adsorbent (not shown). Diagrammatically, this is shown in Figure 5 as a two adsorption column system, although more or fewer columns could be used. The flow of clarified fermentation broth stream 510 is directed to the appropriate adsorption column 512 through the use of switching valve 514. Leaving the top of adsorption column 512 is 2-butanol depleted stream 516 which passes through switching valve 520 and is returned to fermentor 502. When adsorption column 512 reaches capacity, as evidenced by an increase in the 2-butanol concentration of the 2-butanol depleted stream 516, flow of clarified fermentation broth stream 510 is then directed through switching valve 522 by closing switching valve 514. This causes the flow of clarified fermentation broth stream 510 to enter second adsorption column 518 where the 2-butanol is adsorbed onto the adsorbent (not shown). Leaving the top of second adsorption column 518

is a 2-butanol depleted stream that is essentially the same as 2-butanol depleted stream 516. Switching valves 520 and 524 perform the function to divert flow of depleted 2-butanol stream 516 from returning to one of the other columns that is currently being desorbed. When either adsorption column 512 or second adsorption column 518 reaches capacity, the 2-butanol and water adsorbed into the pores of the adsorbent must be removed. This is accomplished using a heated gas stream to effect desorption of adsorbed 2-butanol and water. The CO_2 stream 526 leaving fermentor 502 is first mixed with makeup gas stream 528 to produce combined gas stream 530. Combined gas stream 530 is then mixed with the cooled gas stream 532 leaving decanter 534 to form second combined gas stream 536. Second combined gas stream 536 is then fed to heater 538. Leaving heater 538 is heated gas stream 540 which is diverted into one of the two adsorption columns through the control of switching valves 542 and 544. When passed through either adsorption column 512 or second adsorption column 518, heated gas stream 540 removes the 2-butanol and water from the solid adsorbent. Leaving either adsorption column is 2-butanol/water rich gas stream 546. 2-Butanol/water rich gas stream 546 then enters gas chiller 548 which causes the vaporous 2-butanol and water in 2-butanol/water rich gas stream 546 to condense into a liquid phase that is separate from the other noncondensable species in the stream. Leaving gas chiller 548 is a biphasic gas stream 550 which is fed into decanter 534. In decanter 534 the condensed 2-butanol/water phase is separated from the gas stream. Leaving decanter 534 is an aqueous 2-butanol stream 552 which is then fed to a distillation apparatus or to a bed of molecular sieves that is capable of further dehydrating the aqueous 2-butanol stream, or stream 552 can be used directly as a feed to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene. Also leaving decanter 534 is cooled gas stream 532.

Referring now to Figure 6, there is shown a block diagram for refining apparatus 600, suitable for producing an aqueous 2-butanol stream, when the fermentation broth comprises 2-butanol and water.

Fermentor 602 contains a fermentation broth comprising 2-butanol and water and a gas phase comprising CO_2 and to a lesser extent some vaporous 2-butanol and water. A 2-butanol-containing fermentation broth stream 604 leaving fermentor 602 is introduced into cell separator 606. 2-Butanol-containing stream 604 may contain some non-condensable gas species, such as carbon dioxide. Cell separator 606 can be comprised of centrifuges or membrane units to accomplish the separation of cells from the fermentation broth. Leaving cell separator 606 is concentrated cell stream 608 that is recycled back to fermentor 602. Also leaving cell separator 606 is clarified fermentation broth stream 610. Clarified fermentation broth stream 610 can then be introduced into optional heater 612 where it is optionally raised to a temperature of 40 to 80°C. Leaving optional heater 612 is optionally heated clarified broth stream 614. Optionally heated clarified broth stream 614 is then introduced to the liquid side of first pervaporation module 616. First pervaporation module 616 contains a liquid side that is separated from a low pressure or gas phase side by a membrane (not shown). The membrane serves to keep the phases separated and also exhibits a certain affinity for 2-butanol. In the process of pervaporation any number of pervaporation modules can used to effect the separation. The number is determined by the concentration of species to be removed and the size of the streams to be processed. Diagrammatically, two pervaporation units are shown in Figure 6, although any number of units can be used. In first pervaporation module 616, 2-butanol is selectively removed from the liquid phase through a concentration gradient caused when a vacuum is applied to the low pressure side of the membrane. Optionally a sweep gas can be applied to the non-liquid side of the membrane to accomplish a similar purpose. The first depleted 2-butanol stream 618 exiting first pervaporation module 616 then enters second pervaporation module 620. Second 2-butanol depleted stream 622 exiting second pervaporation module 620 is then recycled back to fermentor 602. The low pressure streams 619, 621 exiting first and second pervaporation modules 616 and 620, respectively, are combined to form low pressure 2-butanol/water stream 624. Low

pressure 2-butanol stream/water 624 is then fed into cooler 626 where the 2-butanol and water in low pressure 2-butanol/water stream 624 is caused to condense. Leaving cooler 626 is condensed low pressure 2-butanol/water stream 628. Condensed low pressure 2-butanol/water stream 628 is then fed to receiver vessel 630 where the condensed 2-butanol/water stream collects and is withdrawn as stream 632. Vacuum pump 636 is connected to the receiving vessel 630 by a connector 634, thereby supplying vacuum to apparatus 600. Non-condensable gas stream 634 exits decanter 630 and is fed to vacuum pump 636. Aqueous 2-butanol stream 632 is then fed to a distillation apparatus or to a bed of molecular sieves that is capable of further dehydrating the aqueous 2-butanol stream, or stream 632 can be used directly as a feed to a reaction vessel (not shown) in which the aqueous 2-butanol is catalytically converted to a reaction product that comprises at least one isooctene.

The at least one recovered isooctene can be further converted to isooctanes, isooctanols or isooctyl alkyl ethers, which are useful fuel additives. The terms isooctanes and isooctanols are meant to denote eight-carbon compounds having at least one secondary or tertiary carbon. The term isooctyl alkyl ether is meant to denote a compound, the isooctyl moiety of which contains eight carbons, at least one carbon of which is a secondary or tertiary carbon.

In one embodiment of the invention, the at least one isooctene is contacted with at least one hydrogenation catalyst in the presence of hydrogen to produce a reaction product comprising at least one isooctane. Suitable solvents, catalysts, apparatus, and procedures for hydrogenation in general can be found in Augustine, R.L. (Heterogeneous Catalysis for the Synthetic Chemist, Marcel Decker, New York, 1996, Section 3); the hydrogenation can be performed as exemplified in U.S. Patent Application No. 2005/0054861, paragraphs 17-36). In general, the reaction is performed at a temperature of from about 50 degrees Centigrade to about 300 degrees Centigrade, and at a pressure of from about 0.1 MPa to about 20 MPa. The principal component of the hydrogenation catalyst may be selected from metals from the group consisting of palladium,

ruthenium, rhenium, rhodium, iridium, platinum, nickel, cobalt, copper, iron, osmium; compounds thereof; and combinations thereof. The catalyst may be supported or unsupported. The at least one isooctane can be separated from the hydrogenation catalyst by any suitable method, including decantation. The at least one isooctane can then be recovered (for example, if the reaction does not go to completion or if a homogeneous catalyst is used) from the reaction product by distillation (see Seader, J.D., *supra*) to obtain a recovered isooctane, and added to a transportation fuel. Alternatively, the reaction product itself can be added to a transportation fuel. If present, unreacted isooctenes can be used in subsequent reactions to produce isooctanes.

In another embodiment, the at least one isooctene is contacted with water in the presence of at least one acidic catalyst to produce a reaction product comprising at least one isooctanol. The hydration of olefins is well known, and a method to carry out the hydration using a zeolite catalyst is described in U.S. Patent No. 5,288,924 (Column 3, line 48 to Column 7, line 66), wherein a temperature of from about 60 degrees Centigrade to about 450 degrees Centigrade and a pressure of from about 700 kPa to about 24,500 kPa are used. The water to olefin ratio is from about 0.05 to about 30. Where a solid acid catalyst is used, such as a zeolite, the at least one isooctanol can be separated from the at least one acid catalyst by any suitable method, including decantation. The at least one isooctanol can then be recovered from the reaction product by distillation (see Seader, J.D., *supra*) to obtain a recovered isooctanol, and added to a transportation fuel. Alternatively, the reaction product itself can be added to a transportation fuel. Unreacted isooctenes, if present, can be used in subsequent reactions to produce isooctanols.

In still another embodiment, the at least one isooctene is contacted with at least one acid catalyst in the presence of at least one straight-chain or branched C_1 to C_5 alcohol to produce a reaction product comprising at least one isooctyl alkyl ether. One skilled in the art will recognize that C_1 and C_2 alcohols cannot be branched. The etherification reaction is described by Stüwe, A., *et al* (Synthesis of MTBE and TAME and related

reactions, Section 3.11, in Handbook of Heterogeneous Catalysis, Volume 4, (Ertl, G., Knözinger, H., and Weitkamp, J. (eds), 1997, VCH Verlagsgesellschaft mbH, Weinheim, Germany)) for the production of methyl-t-butyl ether. The etherification reaction is generally carried out at temperature of from about 50 degrees Centigrade to about 200 degrees Centigrade at a pressure of from about 0.1 to about 20.7 MPa. Suitable acid catalysts include, but are not limited to, acidic ion exchange resins. Where a solid acid catalyst is used, such as an ion-exchange resin, the at least one isooctyl alkyl ether can be separated from the at least one acid catalyst by any suitable method, including decantation. The at least one isooctyl alkyl ether can then be recovered from the reaction product by distillation (see Seader, J.D., *supra*) to obtain a recovered isooctyl alkyl ether, and added to a transportation fuel. If present, unreacted isooctenes can be used in subsequent reactions to produce isooctyl alkyl ethers.

According to embodiments described above, isooctenes produced by the reaction of aqueous 2-butanol with at least one acid catalyst are first recovered from the reaction product prior to being converted to compounds useful in transportation fuels. However, as described in the following embodiment, the reaction product comprising isooctenes can also be used in subsequent reactions without first recovering said isooctenes.

Thus, one alternative embodiment of the invention is a process for making at least one isooctane comprising:

(a) contacting a reactant comprising 2-butanol and at least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

(b) contacting said first reaction product with hydrogen in the presence of at least one hydrogenation catalyst to produce a second reaction product comprising at least one isooctane; and

(c) recovering the at least one isooctane from the second reaction product to produce a recovered isooctane.

The at least one recovered isooctane can then be added to a transportation fuel.

GENERAL METHODS AND MATERIALS

In the following examples, "C" is degrees Centigrade, "mg" is milligram; "ml" is milliliter; "m" is meter, "mm" is millimeter, "min" is minute, "temp" is temperature; "MPa" is mega Pascal; "GC/MS" is gas chromatography/mass spectrometry.

Amberlyst® (manufactured by Rohm and Haas, Philadelphia, PA), tungstic acid, 2-butanol and H_2SO_4 were obtained from Alfa Aesar (Ward Hill, MA); CBV-3020E (HZSM-5) was obtained from PQ Corporation (Berwyn, PA); Sulfated Zirconia was obtained from Engelhard Corporation (Iselin, NJ); 13% Nafion®/SiO_2 (SAC-13) can be obtained from Engelhard; and H-Mordenite can be obtained from Zeolyst Intl. (Valley Forge, PA).

General Procedure for the Conversion of 2-Butanol to Isooctenes

Catalyst was added to a mixture (1 ml) of 2-butanol and water in a 2 ml vial equipped with a magnetic stir bar. The vial was sealed with a serum cap perforated with a needle to facilitate gas exchange. The vial was placed in a block heater enclosed in a pressure vessel. The vessel was purged with nitrogen and the pressure was set as indicated below. The block was brought to the indicated temperature and maintained at that temperature for the time indicated. After cooling and venting, the contents of the vial were analyzed by GC/MS using a capillary column (either (a) CP-Wax 58 [Varian; Palo Alto, CA], 25 m X 0.25 mm, 45 C/6 min, 10 C/min up to 200 C, 200 C/10 min, or (b) DB-1701 [J&W (available through Agilent; Palo Alto, CA)], 30 m X 0.2 5 mm, 50 C/10 min, 10 C/min up to 250 C, 250 C /2 min).

The examples below were performed according to this procedure under the conditions indicated for each example. "Selectivity" refers to the percent of a particular reaction product (not including the unreacted reactants). "Conversion" refers to the percent of a particular reactant that is converted to product.

EXAMPLES 1-8

Reaction of 2-butanol (2-BuOH) with an acid catalyst to produce isooctenes

The reactions were carried out under 6.9 MPa of N_2.

Abbreviations: Conv is conversion; Sel is selectivity.

Ex. No.	Catalyst (50 mg)	Hrs.	Temp (C)	Feedstock	2-BuOH % Conv	Isooctenes % Sel
1	13% Nafion/SiO_2	2	200	65 wt.% 2-BuOH/35 wt.% H_20	38.2	1.2
2	CBV-3020E	2	200	65 wt.% 2-BuOH/35 wt.% H_20	31.8	5.0
3	H-Mordenite	2	200	65 wt.% 2-BuOH/35 wt.% H_20	43.8	3.4
4	Tungstic Acid	2	200	65 wt.% 2-BuOH/35 wt.% H_20	36.5	1.9
5	Sulfated Zirconia	2	200	65 wt.% 2-BuOH/35 wt.% H_20	46.0	1.6
6	H-Mordenite	1	200	70 wt.% 2-BuOH/30 wt.% H_20	74.4	2.5
7	Sulfated Zirconia	1	200	70 wt.% 2-BuOH/30 wt.% H_20	11.1	0.2
8	H-Mordenite	1	175	70 wt.% 2-BuOH/30 wt.% H_20	90.2	0.7

As those skilled in the art of catalysis know, when working with any catalyst, the reaction conditions need to be optimized. Examples 1 to 5 show that the indicated catalysts were capable under the indicated conditions of producing the product isooctenes. Some of the catalysts shown in Examples 1 to 5 were ineffective when utilized under suboptimal conditions (data not shown).

CLAIMS

1. A process for making at least one isooctene comprising contacting a reactant comprising 2-butanol and at least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a reaction product comprising said at least one isooctene, and recovering said at least one isooctene from said reaction product to obtain at least one recovered isooctene.

2. The process of Claim 1, wherein the reactant is obtained from a fermentation broth.

3. The process of Claim 2, wherein the reactant is obtained by subjecting the fermentation broth to a refining process that comprises at least one step selected from the group consisting of pervaporation, gas-stripping, adsorption, liquid-liquid extraction, distillation and molecular sieves.

4. The process of Claim 3, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 2-butanol), and wherein the vapor phase is used as the reactant.

5. The process of Claim 3, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 2-butanol), wherein the vapor phase is condensed to produce a liquid phase, and wherein the liquid phase is used as the reactant.

6. The process of Claim 1 or Claim 4, wherein the at least one acid catalyst is a heterogeneous catalyst, and the temperature and the

pressure are chosen so as to maintain the reactant and the reaction product in the vapor phase.

7. A process for making a reaction product comprising at least one isooctane comprising:

(a) contacting a reactant comprising 2-butanol and at least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

(b) recovering said at least one isooctene from said first reaction product to obtain at least one recovered isooctene;

(c) contacting the at least one recovered isooctene with hydrogen in the presence of at least one hydrogenation catalyst to produce said reaction product comprising at least one isooctane; and

(d) optionally recovering at least one isooctane from the reaction product to obtain at least one recovered isooctane.

8. The process of Claim 7, wherein the reactant is obtained from a fermentation broth.

9. The process of Claim 8, wherein the reactant is obtained by subjecting the fermentation broth to a refining process that comprises at least one step selected from the group consisting of pervaporation, gas-stripping, adsorption, liquid-liquid extraction, distillation and molecular sieves.

10. The process of Claim 9, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), and wherein the vapor phase is used as the reactant.

11. The process of Claim 9, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), wherein the vapor phase is condensed to produce a liquid phase, and wherein the liquid phase is used as the reactant.

12. A process for making a reaction product comprising at least one isooctanol, comprising:

(a) contacting a reactant comprising 2-butanol and at least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

(b) recovering said at least one isooctene from said first reaction product to obtain at least one recovered isooctene;

(c) contacting the at least one recovered isooctene with water and at least one acid catalyst to produce said reaction product comprising at least one isooctanol; and

(d) optionally recovering at least one isooctanol from the reaction product to obtain at least one recovered isooctanol.

13. The process of Claim 12, wherein the reactant is obtained from a fermentation broth.

14. The process of Claim 13, wherein the reactant is obtained by subjecting the fermentation broth to a refining process that comprises at least one step selected from the group consisting of pervaporation, gas-stripping, adsorption, liquid-liquid extraction, distillation and molecular sieves.

15. The process of Claim 14, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight

relative to the weight of the water plus 1-butanol), and wherein the vapor phase is used as the reactant.

16. The process of Claim 14, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), wherein the vapor phase is condensed to produce a liquid phase, and wherein the liquid phase is used as the reactant.

17. A process for making a reaction product comprising at least one isooctyl alkyl ether comprising:

(a) contacting a reactant comprising 2-butanol and at least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

(b) recovering said at least one isooctene from said first reaction product to obtain at least one recovered isooctene;

(c) contacting the at least one recovered isooctene with at least one straight-chain or branched C_1 to C_5 alcohol and at least one acid catalyst to produce said reaction product comprising at least one isooctyl alkyl ether; and

(d) optionally recovering at least one isooctyl alkyl ether from the reaction product to obtain at least one recovered isooctyl alkyl ether.

18. The process of Claim 17, wherein the reactant is obtained from a fermentation broth.

19. The process of Claim 18, wherein the reactant is obtained by subjecting the fermentation broth to a refining process that comprises at least one step selected from the group consisting of pervaporation, gas-

stripping, adsorption, liquid-liquid extraction, distillation and molecular sieves.

20. The process of Claim 19, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), and wherein the vapor phase is used as the reactant.

21. The process of Claim 19, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), wherein the vapor phase is condensed to produce a liquid phase, and wherein the liquid phase is used as the reactant.

22. A process for making at least one isooctane comprising:

(a) contacting a reactant comprising 2-butanol and at least about 5% water (by weight relative to the weight of the water plus 2-butanol) with at least one acid catalyst at a temperature of about 50 degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one isooctene;

(b) contacting said first reaction product with hydrogen in the presence of at least one hydrogenation catalyst to produce a second reaction product comprising at least one isooctane; and

(c) recovering the at least one isooctane from the second reaction product.

23. The process of Claim 22, wherein the reactant is obtained from a fermentation broth.

24. The process of Claim 23, wherein the reactant is obtained by subjecting the fermentation broth to a refining process that comprises at least one step selected from the group consisting of pervaporation, gas-

stripping, adsorption, liquid-liquid extraction, distillation and molecular sieves.

25. The process of Claim 24, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), and wherein the vapor phase is used as the reactant.

26. The process of Claim 24, wherein said distillation produces a vapor phase having a water concentration of at least about 27% (by weight relative to the weight of the water plus 1-butanol), wherein the vapor phase is condensed to produce a liquid phase, and wherein the liquid phase is used as the reactant.

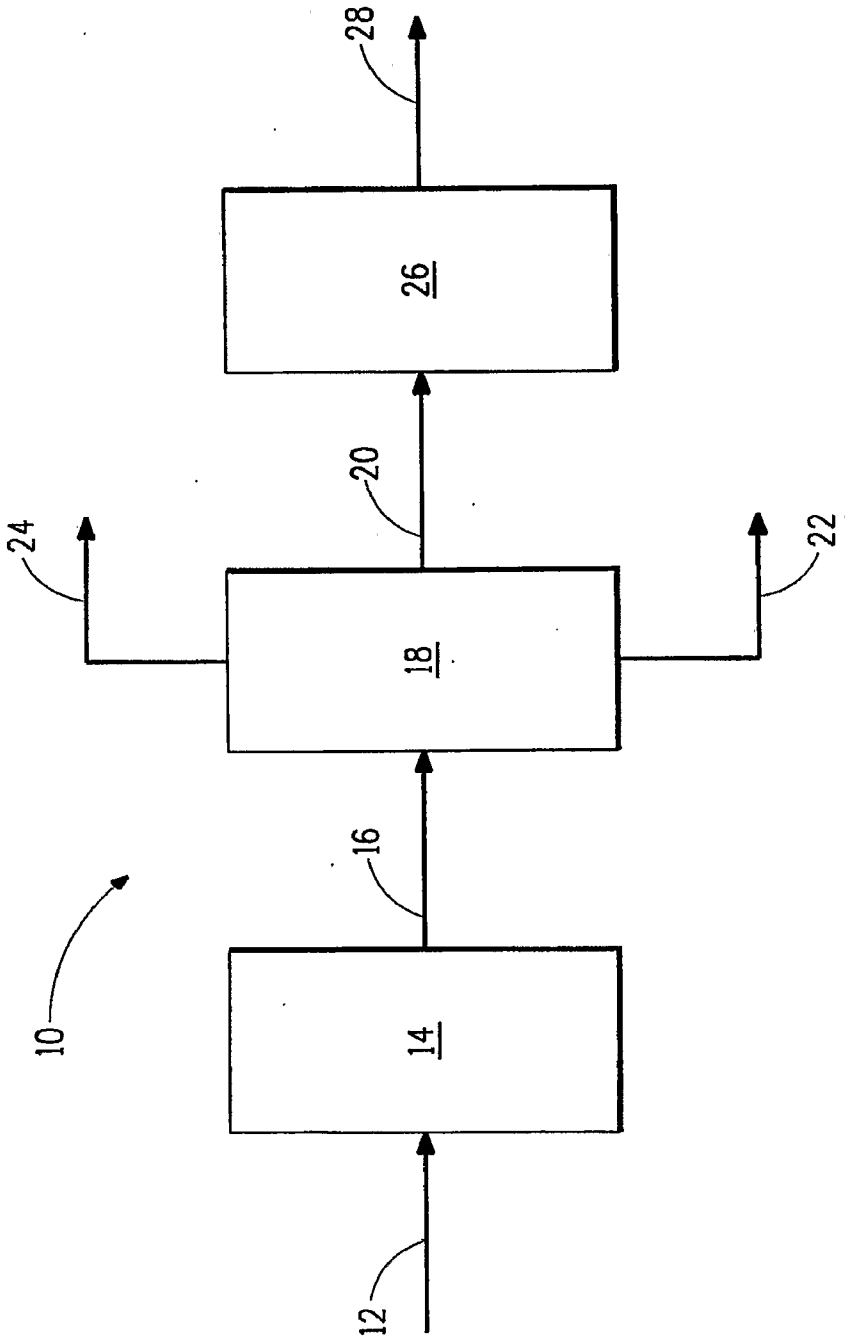


FIG. 1

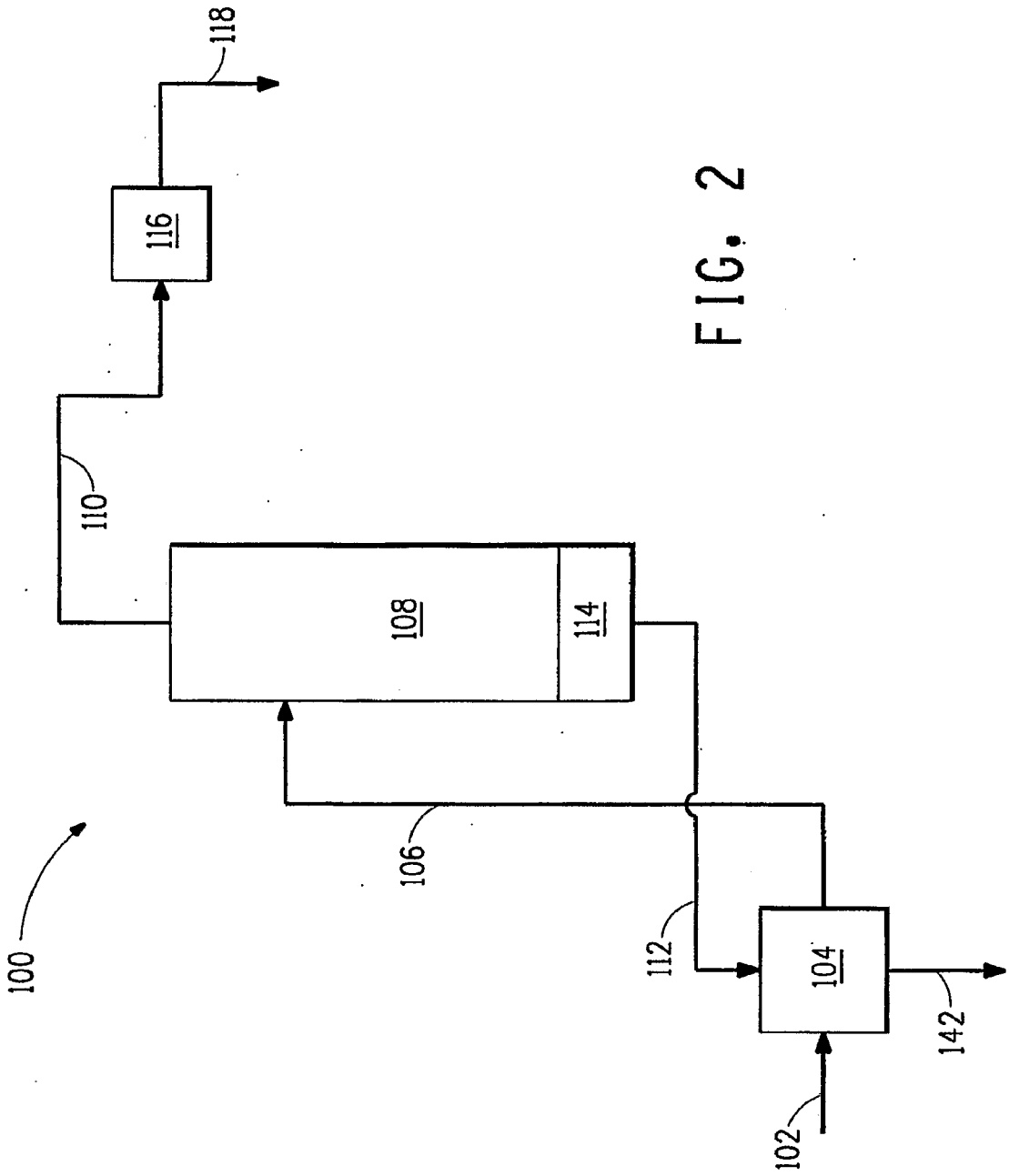


FIG. 2

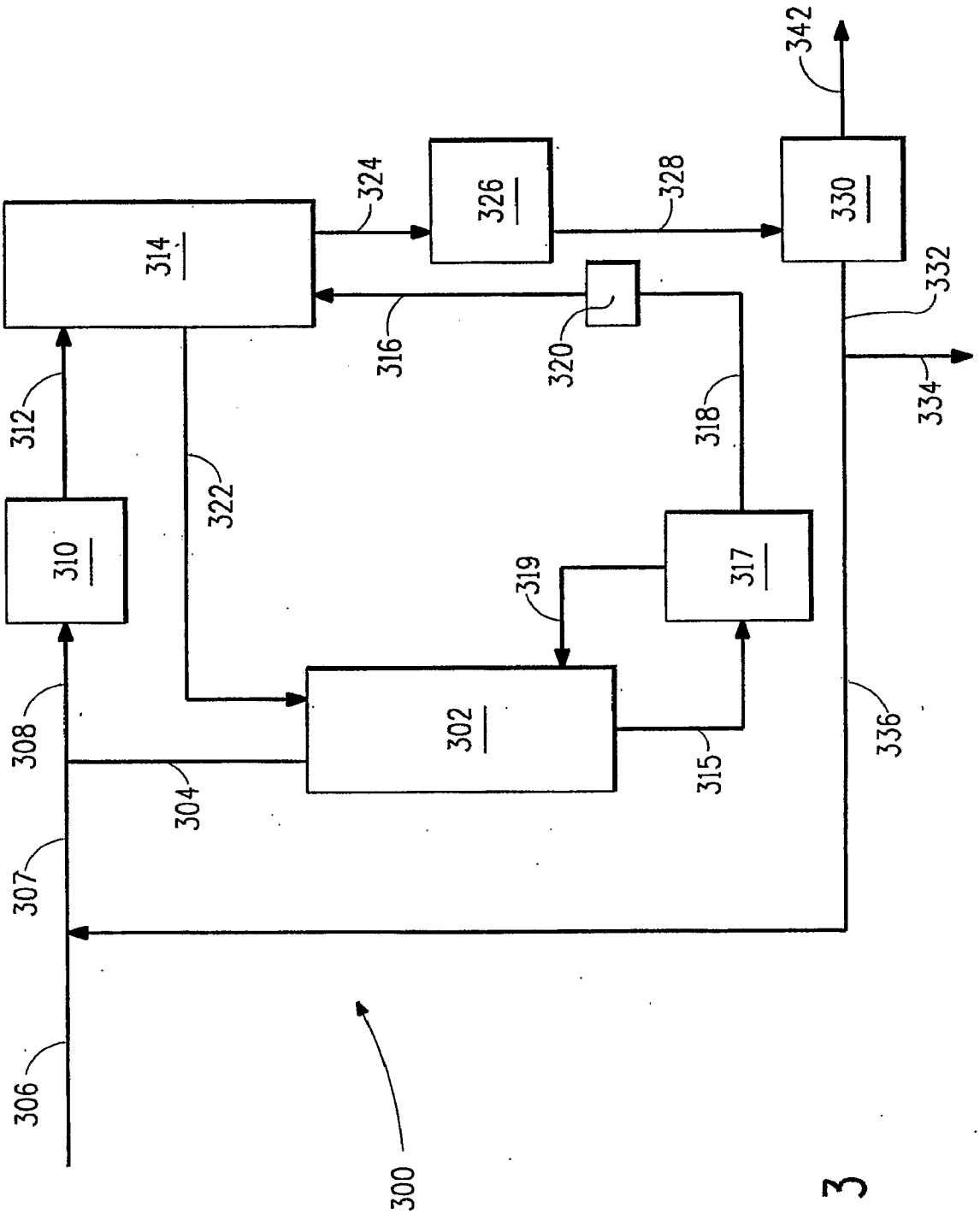

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FIG. 3

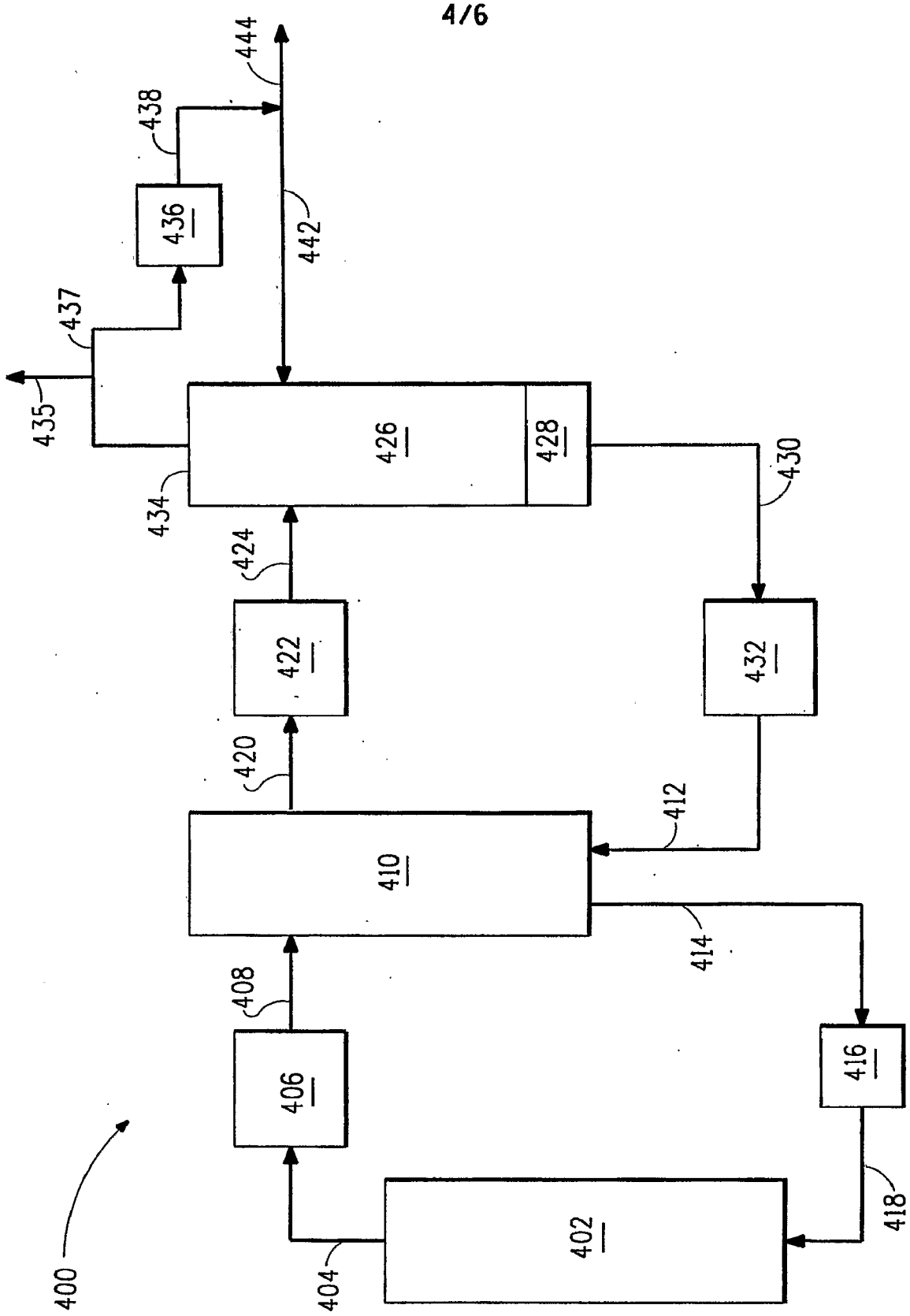

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FIG. 4

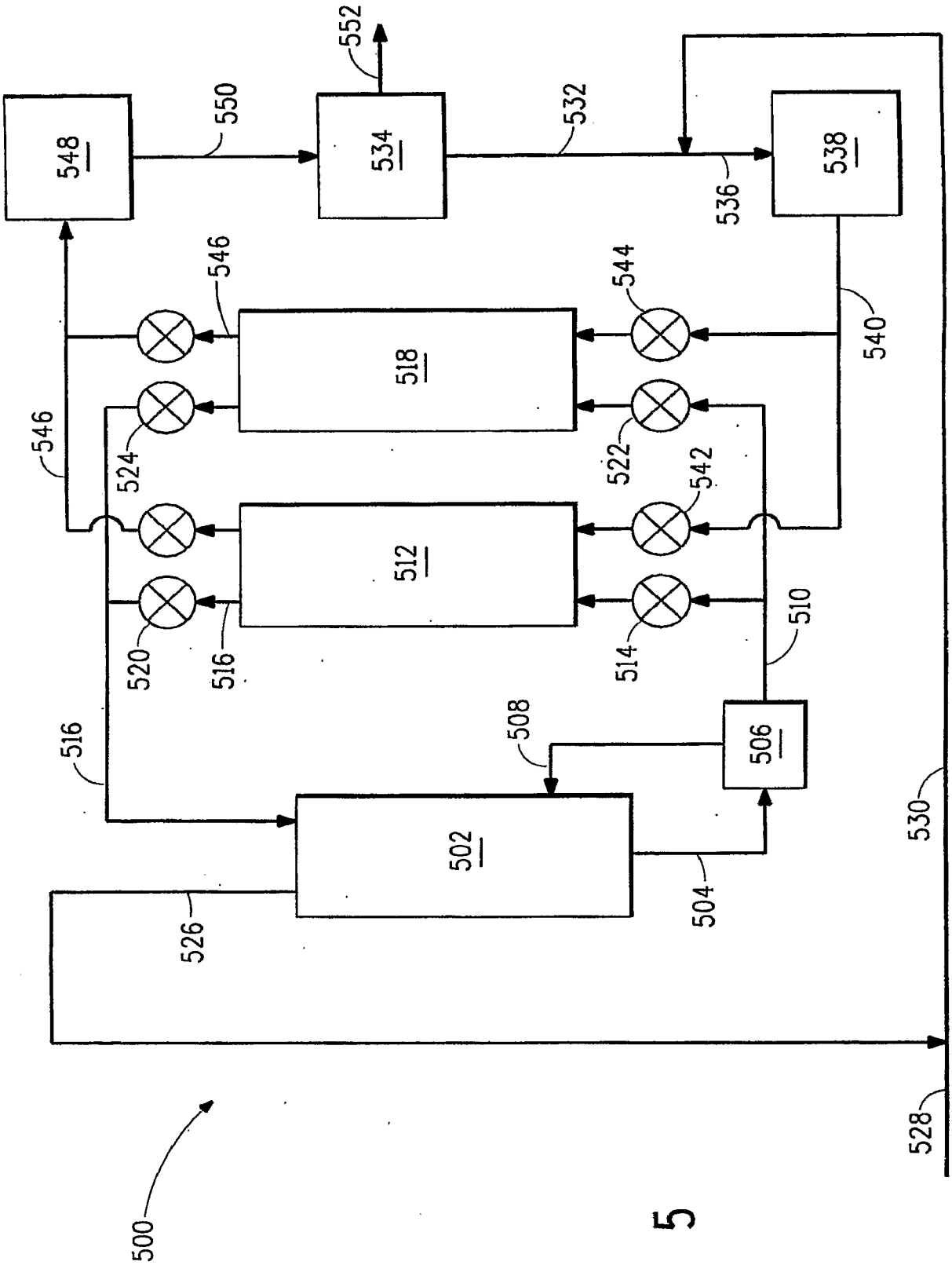

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FIG. 5

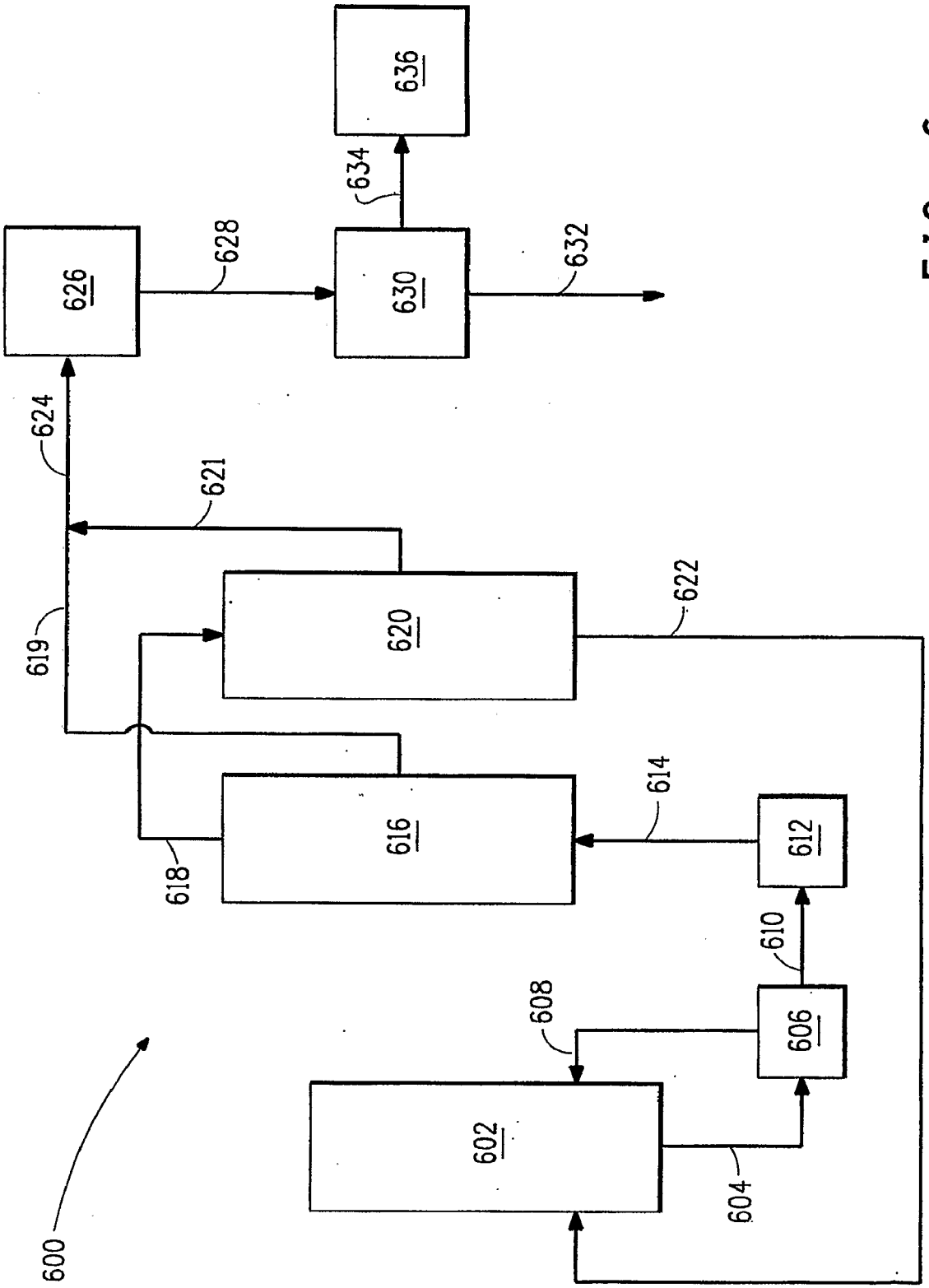

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FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/014164

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/00 C12P5/02

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 C12P

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, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DRAKE, VEITCH: "The action of sulfuric acid on butanol-2" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 57, 1935, pages 2623-2625, XP002459482	1
Y	the whole document	2-26
Y	WO 2005/056503 A (UNIV WATERLOO [CA]; NG FLORA TAK TAK [CA]; REMPEL GARRY LLEWELLYN [CA]) 23 June 2005 (2005-06-23) page 8, line 21 - line 25 page 9, line 1 - line 10 page 19, line 5 - line 23	7-11, 22-26

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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

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Date of the actual completion of the international search	Date of mailing of the international search report
7 December 2007	03/01/2008

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/014164

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	IPATIEFF, MONROE: "The dehydration of the lower aliphatic alcohols in the presence of dilute aqueous solutions of acids and salts" JOURNAL OF THE AMERICA CHEMICAL SOCIETY, vol. 66, 1944, pages 1627-1631, XP002458829 the whole document	2-26
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