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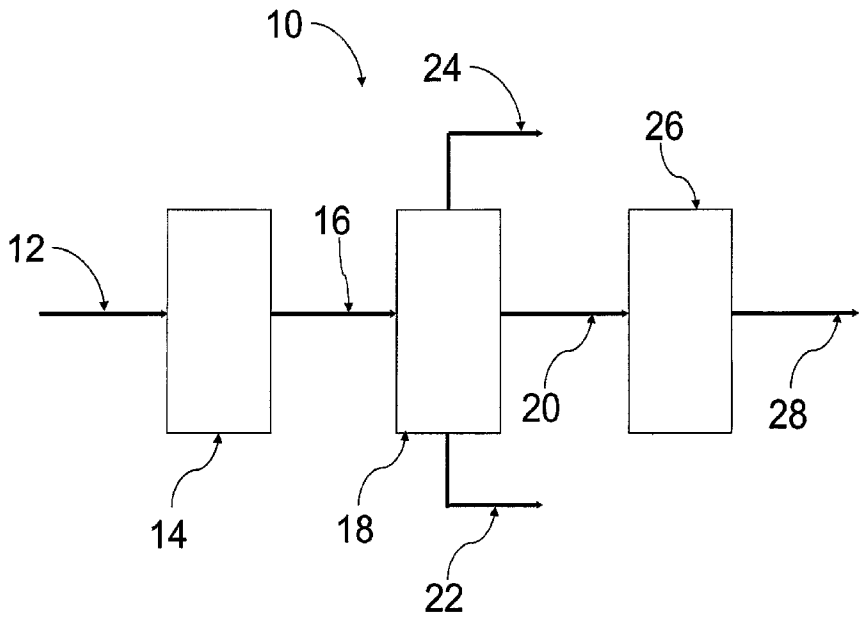
(54) Title: PROCESS FOR MAKING BUTENES FROM AQUEOUS 1-BUTANOL



(57) Abstract: The present invention relates to a catalytic process for making butenes using a reactant comprising 1 -butanol and water. The butenes so produced may be converted to isoalkanes, alkyl-substituted aromatics, isooctanes, isooctanols and ethers, which are useful as transportation fuels.

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TITLE

Process for making butenes from aqueous 1-butanol

Cross-Reference to Related Application

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Serial No. 60/814,158 (filed June 16, 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 butenes using aqueous 1-butanol as a reactant.

BACKGROUND

Butenes are useful intermediates for the production of linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), as well as for the production of transportation fuels and fuel additives. The production of butenes from butanol is known, however the dehydration of butanol to butenes results in the formation of water, and thus these reactions have historically been carried out in the absence of water.

Efforts directed at improving air quality and increasing energy production from renewable resources have resulted in renewed interest in 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 fermentation of renewable resources for the production of butenes, without first performing steps to completely remove, or substantially remove, the butanol from the aqueous stream.

Ruwet, M., *et al* (Bull. Soc. Chim. Belg. (1987) 96:281-292) disclose the production of olefins from pure 1-butanol and from a simulated acetone:butanol:ethanol (ABE) fermentation mixture containing water in the presence of basic catalysts. They report that the production of olefins was greatly diminished in the ABE/water mixture relative to that of pure butanol.

U.S. Patent No. 4,873,392 discloses a process for converting diluted ethanol to ethylene in the presence of a ZSM-5 zeolite catalyst having a Si/Al ratio from 5 to 50 and impregnated with 0.5 to 7 wt. % of triflic acid; similar experiments were performed with trifluoromethanesulfonic acid bound to ZSM-5 (Le Van Mao, R., *et al* (Applied Catalysis (1989) 48:265-277)).

SUMMARY

The present invention relates to a process for making at least one butene comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene, and recovering said at least one butene from said reaction product to obtain at least one recovered butene. In one embodiment, the reactant is obtained from fermentation broth.

The at least one recovered butene is useful as an intermediate for the production of transportation fuels and fuel additives. In particular, the at least one recovered butene can be converted to isoalkanes, C_{10} to C_{13} alkyl substituted aromatic compounds, and butyl alkyl ethers. In addition, the at least one recovered butene can be converted to isooctenes, which can further be converted to additional useful fuel additives, such as isooctanes, isooctanols or isooctyl alkyl ethers.

In alternative embodiments, the reaction product produced by contacting aqueous 1-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 butene from the reaction product. For example, the reaction product is useful for the production of C_{10} to C_{13} alkyl substituted aromatic compounds and butyl alkyl ethers.

BRIEF DESCRIPTION OF THE DRAWING

The Drawing consists of eight figures.

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

Figure 2 illustrates a method for producing a 1-butanol/water stream using distillation wherein fermentation broth comprising 1-butanol, but being substantially free of acetone and ethanol, is used as the feed stream.

Figure 3 illustrates a method for producing a 1-butanol/water stream using distillation wherein fermentation broth comprising 1-butanol, ethanol and acetone is used as the feed stream.

Figure 4 illustrates a method for producing a 1-butanol/water stream using gas stripping wherein fermentation broth comprising 1-butanol and water is used as the feed stream.

Figure 5 illustrates a method for producing a 1-butanol/water stream using liquid-liquid extraction wherein fermentation broth comprising 1-butanol and water is used as the feed stream.

Figure 6 illustrates a method for producing a 1-butanol/water stream using adsorption wherein fermentation broth comprising 1-butanol and water is used as the feed stream.

Figure 7 illustrates a method for producing a 1-butanol/water stream using pervaporation wherein fermentation broth comprising 1-butanol and water is used as the feed stream.

Figure 8 illustrates a method for producing a 1-butanol/water stream using distillation wherein fermentation broth comprising 1-butanol and ethanol, but being substantially free of acetone, is used as the feed stream.

DETAILED DESCRIPTION

The present invention relates to a process for making at least one butene from a reactant comprising water and 1-butanol. The at least one butene so produced is useful as an intermediate for the production of transportation fuels. 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 butenes produced by the process of the invention.

In its broadest embodiment, the process of the invention comprises contacting a reactant comprising 1-butanol and water with at least one acid catalyst to produce a reaction product comprising at least one butene, and recovering said at least one butene from said reaction product to obtain at least one recovered butene. The term "butene" includes 1-butene, isobutene, and/or cis and trans 2-butene.

Although the reactant could comprise less than about 5% water by weight relative to the weight of the water plus 1-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 1-butanol.

In one preferred embodiment, the reactant is derived from fermentation broth, and comprises at least about 50% 1-butanol (by weight relative to the weight of the butanol plus water) (sometimes referred to herein as "aqueous 1-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 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 1-butanol at levels currently seen with wild-type microorganisms, or with genetically modified microorganisms from which enhanced production of 1-butanol is obtained.

The most well-known method for the microbial production of 1-butanol is the acetone-butanol-ethanol (ABE) fermentation carried out by solventogenic clostridia, such as *Clostridium beijerinickii* or *C. acetobutylicum*. Substrates useful for clostridial fermentation include glucose, maltodextrin, starch and sugars, which may be obtained from

biomass, such as corn waste, sugar cane, sugar beets, wheat, hay or straw. A discussion of anaerobiosis and detailed procedures for the preparation of growth media and the growth and storage of anaerobic bacteria (including the sporeforming clostridial species) can be found in Section II of Methods for General and Molecular Bacteriology (Gerhardt, P. et al. (ed.), (1994) American Society for Microbiology, Washington, D.C.). U.S. Patent Nos. 6,358,717 (Column 3, line 48 through Column 15, line 21) and 5,192,673 (Columns 2, line 43 through Column 6, line 57) describe in detail the growth of, and production of butanol by, mutant strains of *C. beijerinckii* and *C. acetobutylicum*, respectively.

An alternative method for the production of 1-butanol by fermentation is a continuous, two-stage process as described in U.S. Patent No. 5,753,474 (Column 2, line 55 through Column 10, line 67) in which 1-butanol is the major product. In the first stage of the process, a clostridial species, such as *C. tyrobutyricum* or *C. thermobutyricum*, is used to convert a carbohydrate substrate predominantly to butyric acid. In a minor, parallel process, a second clostridial species, such as *C. acetobutylicum* or *C. beijerinkii*, is grown on a carbohydrate substrate under conditions that promote acidogenesis. The butyric acid produced in the first stage is transferred to a second fermentor, along with the second clostridial species, and in the second, solventogenesis stage of the process, the butyric acid is converted by the second clostridial species to 1-butanol.

1-Butanol can also be fermentatively produced by recombinant microorganisms as described in copending and commonly owned U.S. Patent Application No. 60/721677, page 3, line 22 through page 48, line 23, including the sequence listing. The biosynthetic pathway enables recombinant organisms to produce a fermentation product comprising 1-butanol from a substrate such as glucose; in addition to 1-butanol, ethanol is formed. The biosynthetic pathway to 1-butanol comprises the following substrate to product conversions:

a) acetyl-CoA to acetoacetyl-CoA, as catalyzed for example by acetyl-CoA acetyltransferase encoded by the genes given as SEQ ID NO:1 or 3;

b) acetoacetyl-CoA to 3-hydroxybutyryl-CoA, as catalyzed for example by 3-hydroxybutyryl-CoA dehydrogenase encoded by the gene given as SEQ ID NO:5;

c) 3-hydroxybutyryl-CoA to crotonyl-CoA, as catalyzed for example by crotonase encoded by the gene given as SEQ ID NO:7;

d) crotonyl-CoA to butyryl-CoA, as catalyzed for example by butyryl-CoA dehydrogenase encoded by the gene given as SEQ ID NO:9;

e) butyryl-CoA to butyraldehyde, as catalyzed for example by butyraldehyde dehydrogenase encoded by the gene given as SEQ ID NO:11; and

f) butyraldehyde to 1-butanol, as catalyzed for example by butanol dehydrogenase encoded by the genes given as SEQ ID NO:13 or 15.

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 60/721677.

The biological production of butanol by microorganisms is believed to be limited by butanol toxicity to the host organism. Copending and commonly owned application docket number CL-3423, page 5, line 1 through page 36, Table 5, and including the sequence listing (filed 4 May 2006) enables a method for selecting for microorganisms having enhanced tolerance to butanol, wherein "butanol" refers to 1-butanol, 2-butanol, isobutanol or combinations thereof. A method is provided for the isolation of a butanol tolerant microorganism comprising:

a) providing a microbial sample comprising a microbial consortium;

b) contacting the microbial consortium in a growth medium comprising a fermentable carbon source until the members of the microbial consortium are growing;

c) contacting the growing microbial consortium of step (b) with butanol; and

d) isolating the viable members of step (c) wherein a butanol tolerant microorganism is isolated.

The method of application docket number CL-3423 can be used to isolate microorganisms tolerant to 1-butanol at levels greater than 1% weight per volume.

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 1-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 1-butanol. By "refining process" is meant a process comprising one unit operation or a series of unit operations that allows for the purification of an impure aqueous stream comprising 1-butanol to yield an aqueous stream comprising substantially pure 1-butanol. For example, in one embodiment, the refining process yields a stream that comprises at least about 5% water and 1-butanol, but is substantially free of ethanol and/or acetone that may have been present in the fermentation broth.

Typically, refining processes will utilize one or more distillation steps as a means for producing an aqueous 1-butanol stream. It is well known, however, that fermentative processes typically produce 1-butanol at very low concentrations. This can lead to large capital and energy expenditures to recover the aqueous 1-butanol by distillation alone. As

such, other techniques can be used either alone or in combination with distillation as a means of recovering the aqueous 1-butanol. In such processes where separation techniques are integrated with the fermentation step, cells are often removed from the stream to be refined by centrifugation or membrane separation techniques, yielding a clarified fermentation broth. The removed cells are then returned to the fermentor to improve the productivity of the 1-butanol fermentation process. The clarified fermentation broth is then subjected to such techniques as pervaporation, gas stripping, liquid-liquid extraction, perstraction, adsorption, distillation or combinations thereof. Depending on product mix, these techniques can provide a stream comprising water and 1-butanol suitable for use in the process of the invention. If further purification is necessary, the stream can be treated further by distillation to yield an aqueous 1-butanol stream.

Distillation

In the ABE fermentation, acetone and ethanol are produced in addition to 1-butanol. The recovery of a butanol stream from an ABE fermentation is well known, and is described, for example, by D.T. Jones (in Clostridia, John Wiley & Sons, New York, 2001, page 125) or by Lenz, T.G. and Moreira, A.R. (Ind. Eng. Chem. Prod. Res. Dev. (1980) 19:478-483). Fermentation broth is first fed to a beer still. A vapor stream comprising a mixture of 1-butanol, acetone, ethanol and water is recovered from the top of the column, while a mixture comprising water and cell biomass is removed from the bottom of the column. The vapor stream is subjected to one distillation step or a series of distillation steps, by which acetone and ethanol are separated from the vapor stream, and a stream comprising 1-butanol and water is obtained. The 1-butanol/water stream comprises at least about 42% water (by weight relative to the weight of water plus 1-butanol) and can be used directly as the reactant for the process of the present invention, or can be fed to a condenser. One skilled in the art will know that solubility is a function of temperature, and that the actual concentration of water in the aqueous 1-butanol stream

will vary with temperature. Upon cooling in the condenser, a butanol-rich phase (comprising at least about 18% water (by weight relative to the weight of water plus 1-butanol)) will separate from a water-rich phase. The butanol-rich phase can be decanted and used for the process of the invention, and the water-rich phase preferably is returned to the distillation column.

For fermentation processes in which 1-butanol is the predominant alcohol of the fermentation broth (see U.S. Patent No. 5,753,474 as described above), aqueous 1-butanol can be recovered by azeotropic distillation, as described generally in Ramey, D. and Yang, S.-T. (Production of butyric acid and butanol from biomass, Final Report of work performed under U. S. Department of Energy DE-F-G02-00ER86106, pages 57-58) for the production of 1-butanol. An aqueous butanol stream from the fermentation broth is fed to a distillation column, from which a butanol-water azeotrope is removed as a vapor phase. The vapor phase from the distillation column (comprising at least about 42% water (by weight relative to the weight of water plus 1-butanol)) can then be used directly as the reactant for the process of the present invention, or can be fed to a condenser. Upon cooling, a butanol-rich phase (comprising at least about 18% water (relative to the weight of water plus 1-butanol)) will separate from a water-rich phase in the condenser. One skilled in the art will know that solubility is a function of temperature, and that the actual concentration of water in the aqueous 1-butanol stream will vary with temperature. The butanol-rich phase can be decanted and used for the process of the invention, and the water-rich phase preferably is returned to the distillation column.

For fermentation processes in which an aqueous stream comprising 1-butanol and ethanol are produced, without significant quantities of acetone, the aqueous 1-butanol/ethanol stream is fed to a distillation column, from which a ternary 1-butanol/ethanol/water azeotrope is removed. The azeotrope of 1-butanol, ethanol and water is fed to a second distillation column from which an ethanol/water azeotrope is

removed as an overhead stream. A stream comprising 1-butanol, water and some ethanol is then cooled and fed to a decanter to form a butanol-rich phase and a water-rich phase. The butanol-rich phase is fed to a third distillation column to separate a 1-butanol/water stream from an ethanol/water stream. The 1-butanol/water stream can be used for the process of the invention.

Pervaporation

Generally, there are two steps involved in the removal of volatile components by pervaporation. One is the sorption of the volatile component into a 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. A stream comprising 1-butanol and water will be recovered from this process, 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 1-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 from an ABE fermentation 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. An enriched stripping gas comprising 1-butanol and water will be recovered from this process, 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 1-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. An aqueous stream comprising desorbed 1-butanol can be recovered from this process, 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 1-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 processes are believed to produce an aqueous 1-butanol stream that can be used directly as the reactant of the present invention, or can be further treated by distillation to produce an aqueous 1-butanol that can be used as the reactant of the present invention.

Aqueous streams comprising 1-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 butene 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 42% water. The vapor phase is directly used as 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 butenes may be produced when 1-butanol is contacted with an acid catalyst. Additional products comprise dibutyl ethers (such as di-1-butyl ether) and isooctenes. Standard experimentation, performed as described in the Examples herein, can be used to optimize the yield of butenes 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 butene 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 butene 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 1-butanol can be recovered following separation of the at least one butene 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 butenes from aqueous 1-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 1-butanol and water. A stream 16 of the fermentation broth is introduced into refining apparatus 18 in order to make a stream of aqueous 1-butanol. The aqueous 1-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 1-butanol stream 20 is introduced into reaction vessel 26 containing an acid catalyst (not shown) capable of converting the 1-butanol into a reaction product comprising at least one butene. 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 1-butanol stream, when the fermentation broth comprises 1-butanol and water, and

is substantially free of acetone and ethanol. 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 1-butanol from water such that a 1-butanol/water azeotrope can be removed as a vaporous 1-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 butanol/water azeotrope overhead stream 110 is roughly 57% by weight butanol of the total butanol and water stream. This is the first opportunity by which a concentrated and partially purified butanol and water stream could be obtained; this partially purified butanol and water stream can be used as the feed stream to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene. Vaporous butanol/water azeotrope stream 110 can be fed to a condenser 116, which lowers the stream temperature causing the vaporous butanol/water azeotrope overhead stream 110 to condense into a biphasic liquid stream 118, which is introduced into decanter 120. Decanter 120 will contain a lower phase 122 that is approximately 92% by weight water and approximately 8% by weight 1-butanol and an upper phase 124 that is around 82% by weight 1-butanol and 18% by weight water. A reflux stream 126 of lower phase 122 is introduced near the top of beer column 108. A stream 128 of upper phase 124 can then be used as the feed stream to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene.

Referring now to Figure 3, there is shown a block diagram for refining apparatus 200, suitable for an aqueous 1-butanol stream, when the fermentation broth comprises 1-butanol, ethanol, acetone, and water.

A stream 202 of fermentation broth is introduced into a feed preheater 204 to raise the broth to a temperature of 95°C to produce a heated feed stream 206 which is introduced into a beer column 208. Beer column 208 is equipped with reboiler 210 necessary to supply heat to the column. The beer column 208 needs to have a sufficient number of theoretical stages to cause separation of acetone from a mixture of 1-butanol, ethanol, acetone and water. Leaving the top of beer column 208 is a vaporous acetone stream 212. Vaporous acetone stream 212 is then fed to condenser 214 where it is fully condensed from a vapor phase to a liquid phase. Leaving condenser 214 is liquid acetone stream 216. Liquid acetone stream 216 is then split into two fractions. A first fraction of liquid acetone stream 216 is returned to the top of beer column 208 as acetone reflux stream 218. Liquid acetone product stream 220 is obtained as a second fraction of liquid acetone stream 216. Leaving the bottom of beer column 208 is hot water bottoms stream 222. Hot water bottoms stream 222 is used to supply heat to feed preheater 204 and leaves as lower temperature bottoms stream 224. Also leaving beer column 208 is vaporous side draw stream 226. Vaporous side draw stream 226 contains a mixture of ethanol, butanol, and water. Vaporous side draw stream 226 is then fed to ethanol rectification column 228 in such a manner as to supply both vapor feed stream to the column and a substantial fraction of the necessary heat to drive the separation of butanol from ethanol. In addition, ethanol rectification column 228 also contains a reboiler 229 necessary to supply the remaining heat necessary to drive the separation of ethanol and butanol. Ethanol rectification column 228 contains a sufficient number of theoretical stages to effect the separation of ethanol as vaporous ethanol overhead stream 230 from biphasic butanol bottoms stream 240 comprising butanol and water. Vaporous overhead ethanol stream 230 is then fed to condenser 232 where it is fully condensed from a vapor phase to a liquid phase. Leaving condenser 232 is aqueous liquid ethanol stream 234. Liquid ethanol stream 234 is then split into two fractions. A first fraction of liquid ethanol stream 234 is returned to the top

of ethanol rectification column 228 as ethanol reflux stream 236. Liquid ethanol product stream 238 is obtained as a second fraction of liquid ethanol stream 234. Biphasic butanol bottoms stream 240 comprising roughly 57% by weight butanol of the total butanol and water stream is the first opportunity where an appropriate aqueous 1-butanol stream could be used as a feed stream to a reaction vessel (not shown) for catalytically converting 1-butanol to a reaction product comprising at least one butene. Optionally, biphasic butanol bottoms stream 240 could be fed to cooler 242 where the temperature is lowered to ensure complete phase separation of butanol-rich and water-rich phases. Leaving cooler 242 is cooled bottoms stream 244 which is then introduced into decanter 246 where the butanol rich phase 248 is allowed to phase separate from water rich phase 250. The water rich phase stream 252 leaving decanter 246 is returned to beer column 208 below side draw stream 226. The butanol rich stream 254 comprising roughly 82% by weight butanol can then be used as the feed stream to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene.

Referring now to Figure 4, there is shown a block diagram for refining apparatus 300, suitable for producing an aqueous 1-butanol stream when the fermentation broth comprises 1-butanol and water, and may additionally comprise acetone and/or ethanol. Fermentor 302 contains a fermentation broth comprising liquid 1-butanol and water and a gas phase comprising CO_2 and to a lesser extent some vaporous butanol and water. Both phases may additionally comprise acetone and/or ethanol. 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 as a clarified fermentation broth stream 318 from cell separator 317 and

heated 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 which 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 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 butanol depleted clarified fermentation broth stream 322 that is recirculated to fermentor 302. A butanol enriched gas stream 324 leaving gas stripping column 314 is then fed to compressor 326 where it is compressed to approximately 157 kPa (7 psig). Following compression, a compressed gas stream comprising butanol 328 is then fed to condenser 330 where the 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 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 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 butanol phase in condenser 330 leaves as aqueous 1-butanol stream 342 and can be used as the feed to a distillation apparatus that is capable of separating aqueous 1-butanol from acetone and/or ethanol, or can be used directly as a feed to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene.

Referring now to Figure 5, there is shown a block diagram for refining apparatus 400, suitable for producing an aqueous 1-butanol stream, when the fermentation broth comprises 1-butanol and water, and may additionally comprise acetone and/or ethanol. Fermentor 402 contains a fermentation broth comprising 1-butanol and water and a gas

phase comprising CO_2 and to a lesser extent some vaporous butanol and water. Both phases may additionally comprise acetone and ethanol. 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 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 contains solvent, 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 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 contains an azeotropic mixture of butanol and water with trace amounts of solvent. This represents the first substantially concentrated and partially purified butanol/water stream that could fed to a reaction vessel (not shown) for catalytically converting the 1-butanol to a reaction product that comprises at least one butene. Optionally, solvent overhead stream 434 could be fed into condenser 436 where the vaporous solvent overhead stream is caused to condense into a biphasic liquid stream 438 and introduced into decanter 440. Decanter 440 will contain a lower phase 442 that is approximately 94% by weight water and approximately 6% by weight 1-butanol and an upper phase 444 that is around 80% by weight 1-butanol and 9% by weight water and a small amount of solvent. The lower phase

442 of decanter 440 leaves decanter 440 as water rich stream 446. Water rich stream 446 is then split into two fractions. A first fraction of water rich stream 446 is returned as water rich reflux stream 448 to solvent column 426. A second fraction of water rich stream 446, water rich product stream 450, is sent on to be mixed with butanol rich stream 456. A stream 452 of upper phase 444 is split into two streams. Stream 454 is fed to solvent column 426 to be used as reflux. Stream 456 is combined with stream 450 to produce product stream 458. Product stream 458 can be introduced as the feed to a distillation apparatus that is capable of separating aqueous 1-butanol from acetone and/or ethanol or can be used directly as a feed to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene.

Referring now to Figure 6, there is shown a block diagram for refining apparatus 500, suitable for concentrating 1-butanol, when the fermentation broth comprises 1-butanol and water, and may additionally comprise acetone and/or ethanol. Fermentor 502 contains a fermentation broth comprising 1-butanol and water and a gas phase comprising CO_2 and to a lesser extent some vaporous butanol and water. Both phases may additionally comprise acetone and ethanol. A 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 butanol is preferentially removed from the liquid stream and adsorbed on the solid phase adsorbent (not shown). Diagramatically, this is shown in Figure 6 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 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 butanol concentration of the 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 butanol is adsorbed onto the adsorbent (not shown). Leaving the top of second adsorption column 518 is a butanol depleted stream which is essentially the same as butanol depleted stream 516. Switching valves 520 and 524 perform the function to divert flow of depleted 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 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 butanol and water. The CO_2 stream 526 leaving fermentor 502 is first mixed with makeup gas stream 528 to produced 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 butanol and water from the solid adsorbent. Leaving either adsorption column is butanol/water rich gas stream 546. Butanol/water rich gas stream 546 then enters gas chiller 548 which causes the vaporous butanol and water in 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 butanol/water phase is separated from the gas stream. Leaving decanter 534 is an aqueous 1-butanol stream 552 which is then fed to a distillation apparatus that is capable of separating aqueous 1-butanol from acetone and/or ethanol, or used directly as a feed to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene. Also leaving decanter 534 is cooled gas stream 532.

Referring now to Figure 7, there is shown a block diagram for refining apparatus 600, suitable for producing an aqueous 1-butanol stream, when the fermentation broth comprises 1-butanol and water, and may additionally comprise acetone and/or ethanol. Fermentor 602 contains a fermentation broth comprising 1-butanol and water and a gas phase comprising CO_2 and to a lesser extent some vaporous butanol and water. Both phases may additionally comprise acetone and/or ethanol. A butanol-containing fermentation broth stream 604 leaving fermentor 602 is introduced into cell separator 606. 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 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. Diagramatically, two pervaporation units are shown in Figure 7, although any number of units can be used. In first pervaporation module 616 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 butanol stream 618 exiting first pervaporation module 616 then enters second pervaporation module 620. Second 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 butanol/water stream 624. Low pressure butanol stream/water 624 is then fed into cooler 626 where the butanol and water in low pressure butanol/water stream 624 is caused to condense. Leaving cooler 626 is condensed low pressure butanol/water stream 628. Condensed low pressure butanol/water stream 628 is then fed to receiver vessel 630 where the condensed 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 1-butanol stream 632 is then fed to a distillation apparatus that is capable of separating aqueous 1-butanol from acetone and/or ethanol, or is used directly as a feed to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene.

Referring now to Figure 8, there is shown a block diagram for refining apparatus 700, suitable for producing an aqueous 1-butanol stream, when the fermentation broth comprises 1-butanol, ethanol, and water, but is substantially free of acetone. A stream 702 of fermentation broth is introduced into a feed preheater 704 to raise the broth temperature to produce a heated feed stream 706 which is introduced into a beer column 708. The beer column 708 needs to have a sufficient

number of theoretical stages to cause separation of a ternary azeotrope of 1-butanol, ethanol, and water to be removed as an overhead product stream 710 and a hot water bottoms stream 712. Hot water bottoms stream 712, is used to supply heat to feed preheater 704 and leaves as lower temperature bottoms stream 714. Reboiler 716 is used to supply heat to beer column 708. Overhead stream 710 is a ternary azeotrope of butanol, ethanol and water and is fed to ethanol column 718. Ethanol column 718 contains a sufficient number of theoretical stages to effect the separation of an ethanol water azeotrope as overhead stream 720 and biphasic bottoms stream 721 comprising butanol, ethanol and water. Biphasic bottoms stream 721 is then fed to cooler 722 where the temperature is lowered to ensure complete phase separation. Leaving cooler 722 is cooled bottoms stream 723 which is then introduced into decanter 724 where a butanol rich phase 726 is allowed to phase separate from a water rich phase 728. Both phases still contain some amount of ethanol. A water rich phase stream 730 comprising a small amount of ethanol and butanol is returned to beer column 708. A butanol rich stream 732 comprising a small amount of water and ethanol is fed to butanol column 734. Butanol column 734 is equipped with reboiler 736 necessary to supply heat to the column. Butanol column 734 is equipped with a sufficient amount of theoretical stages to produce a butanol/water bottoms stream 738 and an ethanol/water azeotropic stream 740 that is returned to ethanol column 718. Butanol/water bottoms stream 738 (i.e., aqueous 1-butanol stream) can then be used as a feed to a reaction vessel (not shown) in which the aqueous 1-butanol is catalytically converted to a reaction product that comprises at least one butene.

The at least one recovered butene is useful as an intermediate for the production of linear, low density polyethylene (LLDPE) or high density polyethylene (HDPE), as well as for the production of transportation fuels and fuel additives. For example, butenes can be used to produce alkylate, a mixture of highly branched alkanes, mainly isooctane, having octane numbers between 92 and 96 RON (research octane number) (Kumar, P.,

et al (Energy & Fuels (2006) 20:481-487). In some refineries, isobutene is converted to methyl t-butyl ether (MTBE). In addition, butenes are useful for the production of alkyl aromatic compounds. Butenes can also be dimerized to isooctenes and further converted to isooctanes, isooctanols and isooctyl alkyl ethers that can be used as fuel additives to enhance the octane number of the fuel.

In one embodiment of the invention, the at least one recovered butene is contacted with at least one straight-chain, branched or cyclic C_3 to C_5 alkane in the presence of at least one acid catalyst to produce a reaction product comprising at least one isoalkane. Methods for the alkylation of olefins are well known in the art and process descriptions can be found in Kumar, P., *et al* (*supra*) for the alkylation of isobutane and raffinate II (a mixture comprising primarily butanes and butenes); and U. S. 6,600,081 (Column 3, lines 42 through 63) for the reaction of isobutane and isobutylene to produce trimethylpentanes (TMPs). Generally, the acid catalysts useful for these reactions have been homogeneous catalysts, such as sulfuric acid or hydrogen fluoride, or heterogeneous catalysts, such as zeolites, heteropolyacids, metal halides, Bronsted and Lewis acids on various supports, and supported or unsupported organic resins. The reaction conditions and product selectivity are dependent on the catalyst. Generally, the reactions are carried out at a temperature between about -20 degrees C and about 300 degrees C, and at a pressure of about 0.1 MPa to about 10 MPa.

The at least one isoalkane produced by the reaction can be recovered by distillation (see Seader, J.D., *supra*) and added to a transportation fuel. Unreacted butenes or alkanes can be recycled and used in subsequent reactions to produce isoalkanes.

In another embodiment, the at least one recovered butene is contacted with benzene, a C_1 to C_3 alkyl-substituted benzene, or combination thereof, in the presence of at least one acid catalyst or at least one basic catalyst to produce a reaction product comprising at least

one C_{10} to C_{13} substituted aromatic compound. C_1 to C_3 alkyl-substituted benzenes include toluene, xylenes, ethylbenzene and trimethyl benzene.

Methods for the alkylation of aromatic compounds are well known in the art; discussions of such reactions can be found in Handbook of Heterogeneous Catalysis, Volume 5, Chapter 4 (Ertl, G., Knözinger, H., and Weitkamp, J. (eds), 1997, VCH Verlagsgesellschaft mbH, Weinheim, Germany) and Vora, B.V., *et al* (Alkylation, in Kirk-Othmer Encyclopedia of Chemical Technology, Volume 2, pages 169-203, John Wiley & Sons, Inc., New York).

In the alkylation of aromatic compounds, acid catalysts promote the addition of butenes to the aromatic ring itself. Typical acid catalysts are homogenous catalysts, such as sulfuric acid, hydrogen fluoride, phosphoric acid, $AlCl_3$ and boron fluoride, or heterogeneous catalysts, such as alumino-silicates, clays, ion-exchange resins, mixed oxides, and supported acids. Examples of heterogeneous catalysts include ZSM-5, Amberlyst® (Rohm and Haas, Philadelphia, PA) and Nafion®-silica (DuPont, Wilmington, DE).

In base-catalyzed reactions, the butenes are added to the alkyl group of an aromatic compound. Typical basic catalysts are basic oxides, alkali-loaded zeolites, organometallic compounds such as alkyl sodium, and metallic sodium or potassium. Examples include alkali-cation-exchanged X- and Y-type zeolites, magnesium oxide, titanium oxide, and mixtures of either magnesium oxide or calcium oxide with titanium dioxide.

The at least one C_{10} to C_{13} substituted aromatic compound produced by the reaction can be recovered by distillation (see Seader, J.D., *supra*) and added to a transportation fuel. Unreacted butenes, benzene or alkyl-substituted benzene can be recycled and used in subsequent reactions to produce substituted aromatic compounds.

In yet another embodiment, the at least one recovered butene is contacted with methanol, ethanol, a C_3 to C_{15} straight-chain, branched or cyclic alcohol, or a combination thereof, in the presence of at least one acid catalyst, to produce a reaction product comprising at least one butyl

alkyl ether. The "butyl" group can be 1-butyl, 2-butyl or isobutyl, and the "alkyl" group can be straight-chain, branched or cyclic. The reaction of alcohols with butenes is well known and is described in detail by Stűwe, A. *et al* (Handbook of Heterogeneous Catalysis, Volume 4, Section 3.11, pages 1986-1998 (Ertl, G., Knözinger, H., and Weitkamp, J. (eds), 1997, VCH Verlagsgesellschaft mbH, Weinheim, Germany)) for the production of methyl-t-butyl ether (MTBE) and methyl-t-amyl ether (TAME). In general, butenes are reacted with alcohols in the presence of an acid catalyst, such as an ion exchange resin. The etherification reaction can be carried out at pressures of about 0.1 to about 20.7 MPa, and at temperatures from about 50 degrees Centigrade to about 200 degrees Centigrade.

The at least one butyl alkyl ether produced by the reaction can be recovered by distillation (see Seader, J.D., *supra*) and added to a transportation fuel. Unreacted butenes or alcohols can be recycled and used in subsequent reactions to produce butyl alkyl ether.

In another embodiment, the at least one recovered butene can be dimerized to isooctenes, and further converted to isooctanes, isooctanols or isooctyl alkyl ethers, which are useful fuel additives. The terms isooctenes, isooctanes and isooctanols are all 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.

The dimerization reaction can be carried out as described in U. S. 6,600,081 (Column 3, lines 42 through 63) for the reaction of isobutane and isobutylene to produce trimethylpentanes (TMPs). The at least one recovered butene is contacted with at least one dimerization catalyst (for example, silica-alumina) at moderate temperatures and pressures and high throughputs to produce a reaction product comprising at least one isooctene. Typical operations for a silica-alumina catalyst involve temperatures of about 150 degrees Centigrade to about 200 degrees Centigrade, pressures of about 2200 kPa to about 5600 kPa, and liquid

hourly space velocities of about 3 to 10. Other known dimerization processes use either hydrogen fluoride or sulfuric acid catalysts. With the use of the latter two catalysts, reaction temperatures are kept low (generally from about 15 degrees Centigrade to about 50 degrees Centigrade with hydrogen fluoride and from about 5 degrees Centigrade to about 15 degrees Centigrade with sulfuric acid) to ensure high levels of conversion. Following the reaction, the at least one isooctene can be separated from a solid dimerization catalyst, such as silica-alumina, by any suitable method, including decantation. The at least one isooctene can be recovered from the reaction product by distillation (see Seader, J.D., *supra*) to produce at least one recovered isooctene. Unreacted butenes can be recycled and used in subsequent reactions to produce isooctenes.

The at least one recovered isooctene produced by the dimerization reaction can then be 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 recovered isooctene produced by the dimerization reaction 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*), 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 recovered isooctene produced by the dimerization reaction 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 Stűwe, 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. Alternatively, the reaction product itself can be 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, butenes produced by the reaction of aqueous 1-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 embodiments, the reaction product comprising butenes can also be used in subsequent reactions without first recovering said butenes.

Thus, one alternative embodiment of the invention is a process for making at least one C_{10} to C_{13} substituted aromatic compound comprising:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene;

(b) contacting said first reaction product with benzene, a C_1 to C_3 alkyl-substituted benzene, or a combination thereof, in the presence of at least one acid catalyst or at least one basic catalyst at a temperature of about 100 degrees C to about 450 degrees C, and at a pressure of about 0.1 MPa to about 10 MPa to produce a second reaction product comprising at least one C_{10} to C_{13} substituted aromatic compound; and

(c) recovering the at least one C_{10} to C_{13} substituted aromatic compound from the second reaction product to obtain at least one recovered C_{10} to C_{13} substituted aromatic compound.

The at least one recovered C_{10} to C_{13} substituted aromatic compound can then be added to a transportation fuel.

Another embodiment of the invention is a process for making at least one butyl alkyl ether comprising:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene;

(b) contacting said first reaction product with methanol, ethanol, a C_3 to C_{15} straight-chain, branched or cyclic alcohol, or a combination thereof, in the presence of at least one acid catalyst at a temperature of about 50 degrees C to about 200 degrees C, and at a pressure of about 0.1 MPa to about 20.7 MPa to produce a second reaction product comprising at least one butyl alkyl ether; and

(c) recovering the at least one butyl alkyl ether from the second reaction product to obtain at least one recovered butyl alkyl ether.

The at least one recovered butyl alkyl ether can be added to a transportation fuel.

An alternative process for making at least one butyl alkyl ether comprises:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene and at least some unreacted 1-butanol;

(b) contacting said first reaction product with at least one acid catalyst, and optionally with methanol, ethanol, a C_3 to C_{15} straight-chain, branched or cyclic alcohol, or a combination thereof, at a temperature of about 50 degrees C to about 200 degrees C, and at a pressure of about 0.1 MPa to about 20.7 MPa to produce a second reaction product comprising at least one butyl alkyl ether; and

(c) recovering the at least one butyl alkyl ether from the second reaction product to obtain a recovered butyl alkyl ether.

The at least one recovered butyl alkyl ether can then also be added to a transportation fuel.

Another embodiment of the invention is a process for making a reaction product comprising at least one isooctane comprising:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene;

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

(c) contacting said at least one recovered butene with at least one acid catalyst to produce a second reaction product comprising at least one isooctene;

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

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

The third reaction product or the at least one recovered isooctane can then also 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, 1-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). Gamma alumina was obtained from Strem Chemical, Inc. (Newburyport, MA).

General Procedure for the Conversion of 1-Butanol to Butenes

Catalyst was added to a mixture (1 ml) of 1-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.

EXAMPLE 1 (Comparative Example)

Reaction of 1-butanol with the basic catalyst gamma alumina to produce butenes

The feedstock was 80% 1-butanol/20% water (by weight). The reaction was carried out for 2 hours at 200 C under 6.9 MPa of N_2. The conversion of 1-butanol was 0.1%, and the selectivity for butenes was 69%. See Examples 2-8 for experiments performed under similar conditions with acid catalysts.

EXAMPLES 2-8

Reaction of 1-butanol (1-BuOH) with an acid catalyst to produce butenes

The reactions were carried out for 2 hours at 6.9 MPa of N_2. The feedstock was 80% 1-butanol/20% water (by weight).

Example Number	Catalyst (50 mg)	Temp (C)	1-BuOH % Conversion	Butenes % Selectivity
2	H_2SO_4	200	69.6	54.2
3	Amberlyst® 15	200	26.0	31.6
4	13% Nafion®/SiO_2	200	8.2	33.0
5	CBV-3020E	200	41.8	46.5
6	H-Mordenite	200	28.0	43.0
7	Tungstic Acid	200	3.1	72.6
8	Sulfated Zirconia	200	2.5	86.0

EXAMPLES 9-15

Reaction of 1-butanol (1-BuOH) with an acid catalyst to produce butenes

Reactions were performed under the conditions described for Examples 2-8, but at a reduced temperature.

Example Number	Catalyst (50 mg)	Temp (C)	1-BuOH % Conversion	Butenes % Selectivity
9	H_2SO_4	120	4.3	87.1
10	Amberlyst® 15	120	0.2	100.0
11	13% Nafion®/SiO_2	120	0.2	100.0
12	CBV-3020E	120	0.3	72.9
13	H-Mordenite	120	0.5	94.0
14	Tungstic Acid	120	0.4	100.0
15	Sulfated Zirconia	120	0.4	100.0

CLAIMS

1. A process for making at least one butene comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene, and recovering said at least one butene from said reaction product to obtain at least one recovered butene.

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, and distillation.

4. The process of Claim 3, wherein said distillation produces a vapor phase having a water concentration of at least about 42% (by weight relative to the weight of the water plus 1-butanol), and wherein the vapor phase is used as the reactant.

5. 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.

6. The process of Claim 3, wherein said distillation produces a vapor phase, wherein the vapor phase is condensed to produce a butanol-rich liquid phase having a water concentration of at least about 18% (by weight

relative to the weight of the water plus 1-butanol) and a water-rich liquid phase, wherein the butanol-rich liquid phase is separated from the water-rich phase, and wherein the butanol-rich liquid phase is used as the reactant.

7. A process for making a reaction product comprising at least one isoalkane, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said first reaction product to obtain at least one recovered butene, and contacting said at least one recovered butene with a straight-chain, branched or cyclic C_3 to C_5 alkane in the presence of at least one acid catalyst, to produce said reaction product comprising at least one isoalkane.

8. The process of Claim 7, wherein the reaction is performed at a temperature between about -20 degrees C and about 300 degrees C, and at a pressure of about 0.1 MPa to about 10 MPa.

9. The process of Claim 9, further comprising adding the at least one recovered isoalkane to a transportation fuel.

10. A process for making a reaction product comprising at least one C_{10} to C_{13} substituted aromatic compound, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said first reaction product to obtain at least one recovered butene, and contacting the at least one recovered butene with benzene, a C_1 to C_3 alkyl-substituted benzene, or a combination thereof, in the presence of at least one acid catalyst or at least one basic catalyst at a temperature of about 100 degrees C to about 450 degrees C, and at a pressure of about 0.1 MPa to about 10 MPa to produce said reaction product comprising at least one C_{10} to C_{13} substituted aromatic compound.

11. The process of Claim 10, further comprising isolating the at least one C_{10} to C_{13} substituted aromatic compound from the reaction product to produce at least one recovered C_{10} to C_{13} substituted aromatic compound.

12. A process for making a reaction product comprising at least one butyl alkyl ether, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said first reaction product to obtain at least one recovered butene, and contacting the at least one recovered butene with methanol, ethanol, a C_3 to C_{15} straight-chain, branched or cyclic alcohol, or a combination thereof, in the presence of at least one acid catalyst at a temperature of about 50 degrees C to about 200 degrees C, and at a pressure of about 0.1 MPa to about 20.7 MPa to produce said reaction product comprising at least one butyl alkyl ether.

13. The process of Claim 12, further comprising isolating the at least one butyl alkyl ether from the reaction product to produce at least one recovered butyl alkyl ether.

14. A process for making a reaction product comprising at least one isooctene, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said first reaction product to obtain at least one recovered butene, and contacting the at least one recovered butene with at least one acid catalyst to produce said reaction product comprising at least one isooctene.

15. The process of Claim 14, further comprising isolating the at least one isooctene from the reaction product to produce at least one recovered isooctene.

16. A process for making a reaction product comprising at least one isooctane, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said first reaction product to obtain at least one recovered butene, contacting the at least one recovered butene with at least one acid catalyst to produce a second reaction product comprising at least one isooctene, isolating the at least one isooctene from the second reaction product to produce at least one recovered isooctene, and

(a) 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

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

17. A process for making a reaction product comprising at least one isooctanol, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said first reaction product to obtain at least one recovered butene, contacting the at least one recovered butene with at least one acid catalyst to produce a second reaction product comprising at least one isooctene, isolating the at least one isooctene from the second reaction product to produce at least one recovered isooctene, and

(a) 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

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

18. A process for making a reaction product comprising at least one isooctyl alkyl ether, comprising contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol), wherein said reactant is obtained from a fermentation broth, 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 butene, recovering said at least one butene from said reaction product to obtain at least one recovered butene, contacting the at least one recovered butene with at least one acid catalyst to produce a second reaction product comprising at least one isooctene, isolating the at least

one isooctene from the second reaction product to produce at least one recovered isooctene, and

(a) 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

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

19. A process for making at least one C_{10} to C_{13} substituted aromatic compound comprising:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene;

(b) contacting said first reaction product with benzene, a C_1 to C_3 alkyl-substituted benzene, or a combination thereof, in the presence of at least one acid catalyst or at least one basic catalyst at a temperature of about 100 degrees C to about 450 degrees C, and at a pressure of about 0.1 MPa to about 10 MPa to produce a second reaction product comprising at least one C_{10} to C_{13} substituted aromatic; and

(c) recovering the at least one C_{10} to C_{13} substituted aromatic compound from the second reaction product to obtain at least one recovered C_{10} to C_{13} substituted aromatic compound.

20. A process for making at least one butyl alkyl ether comprising:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene;

(b) contacting said first reaction product with methanol, ethanol, a C_3 to C_{15} straight-chain, branched or cyclic alcohol, or a combination thereof, in the presence of at least one acid catalyst at a temperature of about 50 degrees C to about 200 degrees C, and at a pressure of about 0.1 MPa to about 20.7 MPa to produce a second reaction product comprising at least one butyl alkyl ether; and

(c) recovering the at least one butyl alkyl ether from the second reaction product to obtain a recovered butyl alkyl ether.

21. A process for making at least one butyl alkyl ether comprising:

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-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 butene and at least some unreacted 1-butanol;

(b) contacting said first reaction product with at least one acid catalyst, and optionally with methanol, ethanol, a C_3 to C_{15} straight-chain, branched or cyclic alcohol, or a combination thereof, at a temperature of about 50 degrees C to about 200 degrees C, and at a pressure of about 0.1 MPa to about 20.7 MPa to produce a second reaction product comprising at least one butyl alkyl ether; and

(c) recovering the at least one butyl alkyl ether from the second reaction product to obtain a recovered butyl alkyl ether.

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

(a) contacting a reactant comprising 1-butanol and at least about 5% water (by weight relative to the weight of the water plus 1-butanol) with at least one acid catalyst at a temperature of about 50

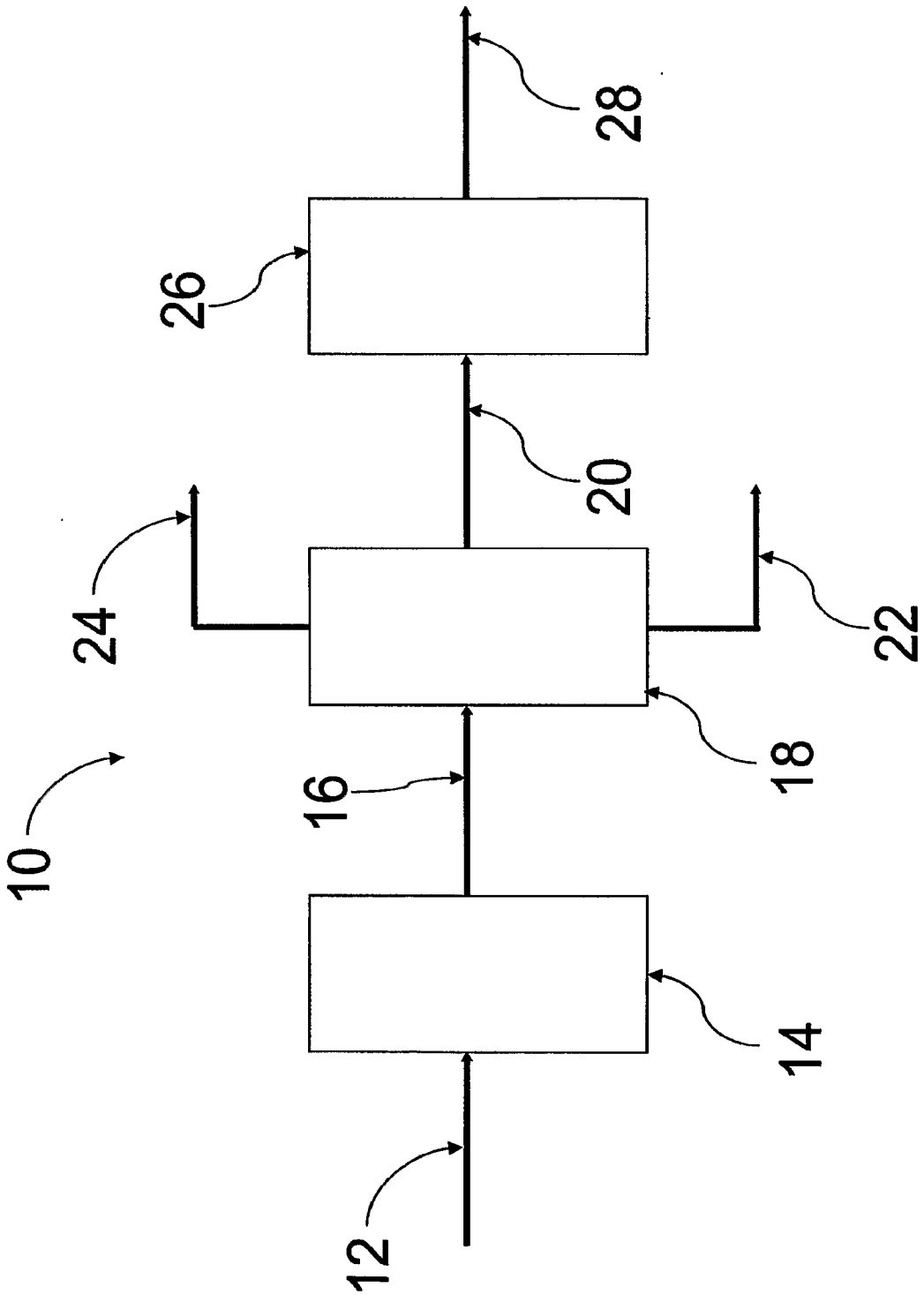
degrees C to about 450 degrees C and a pressure from about 0.1 MPa to about 20.7 MPa to produce a first reaction product comprising at least one butene;

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

(c) contacting said at least one recovered butene with at least one acid catalyst to produce a second reaction product comprising at least one isooctene;

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

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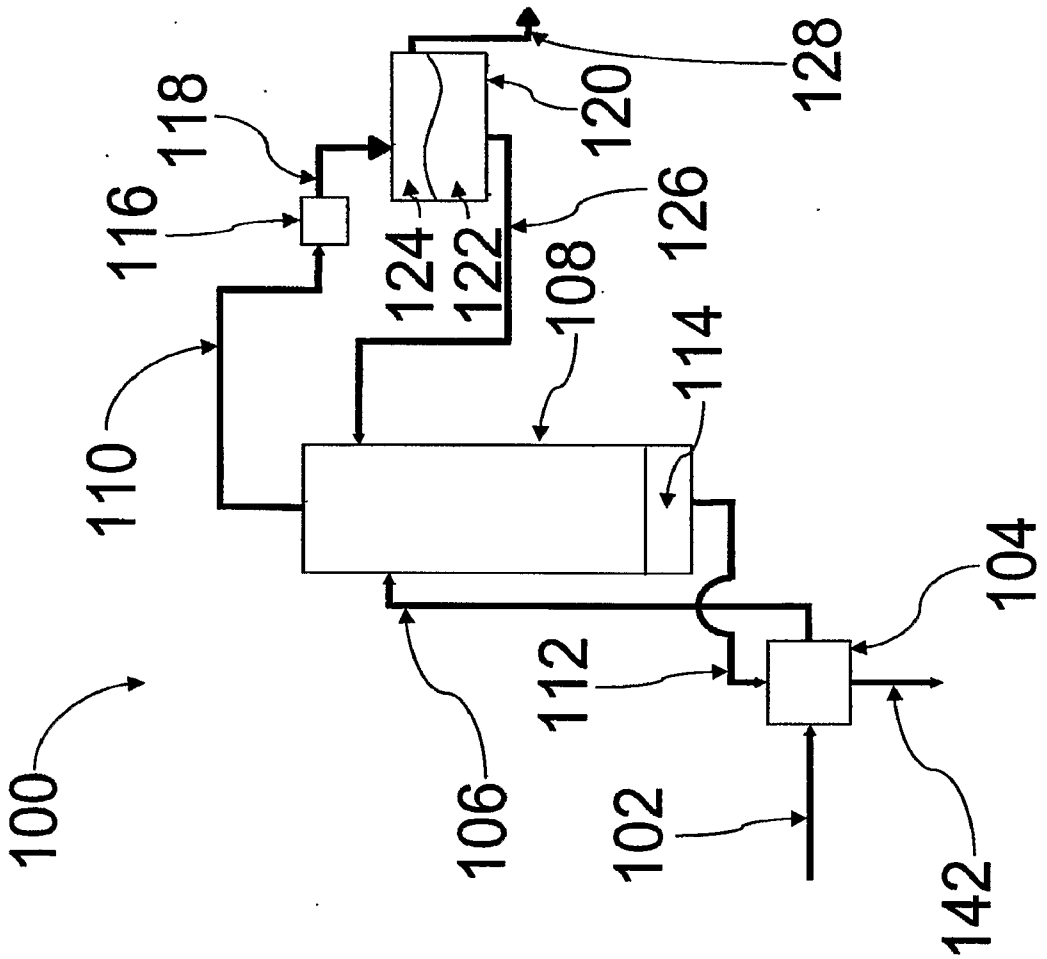
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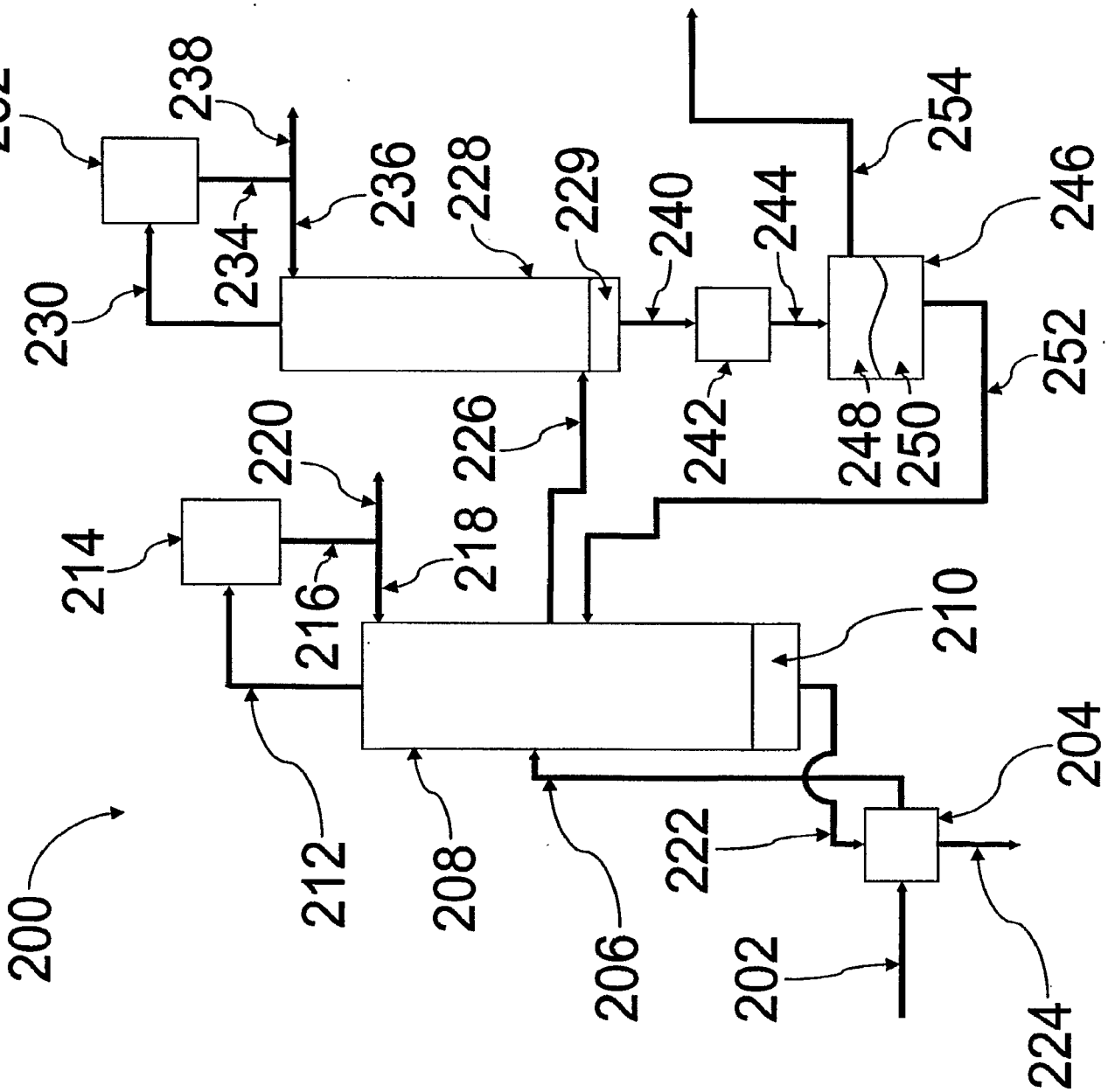
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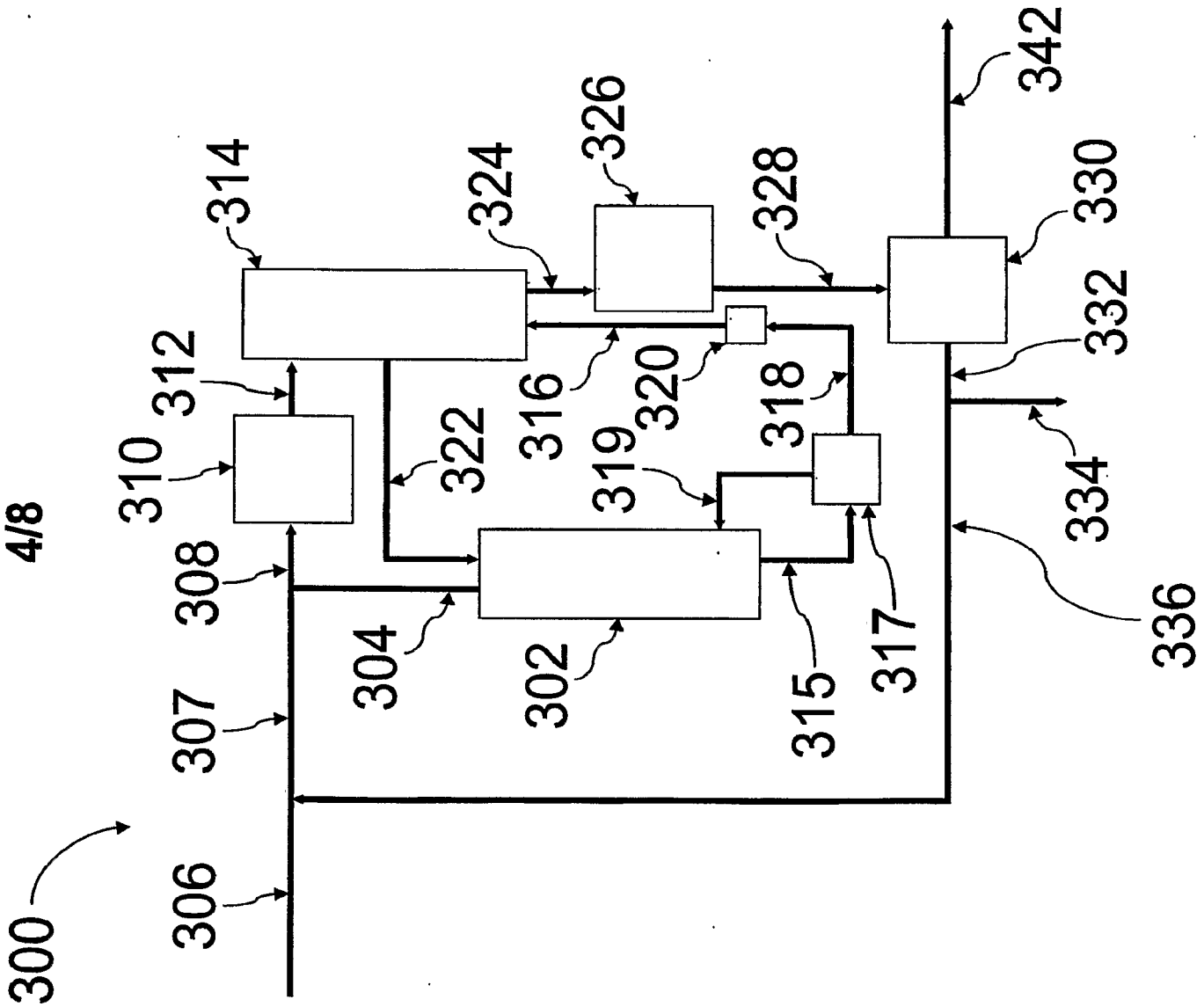
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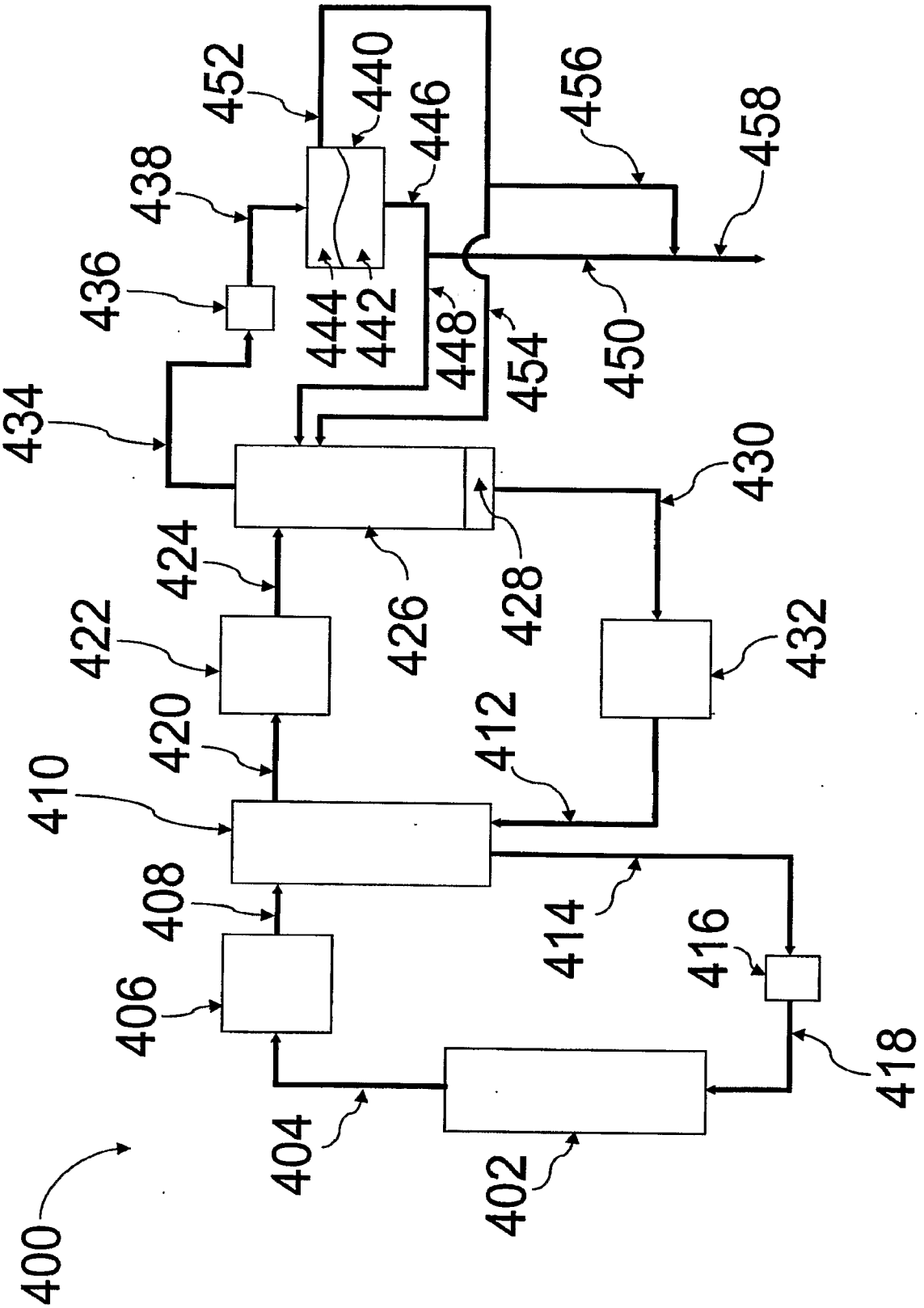
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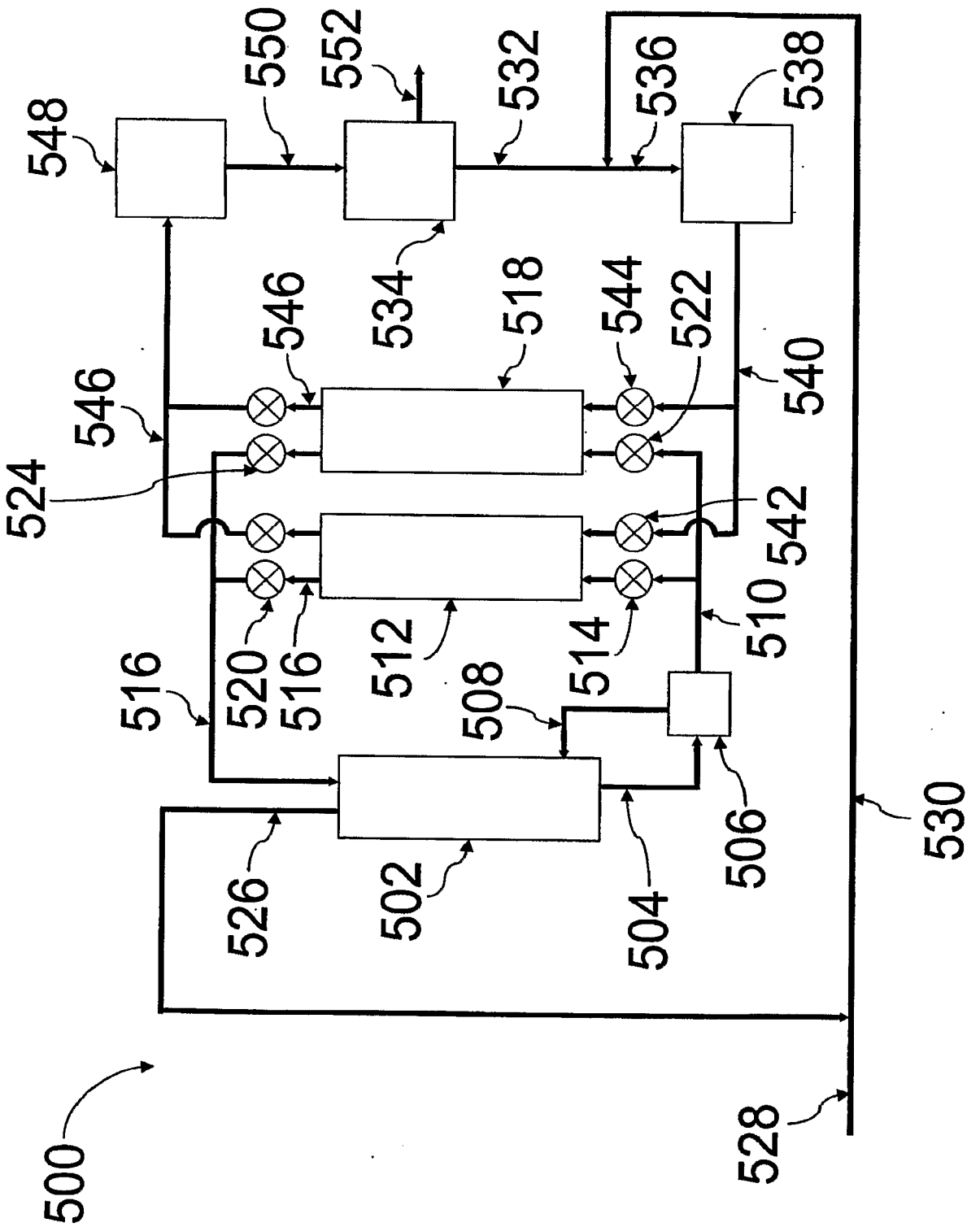
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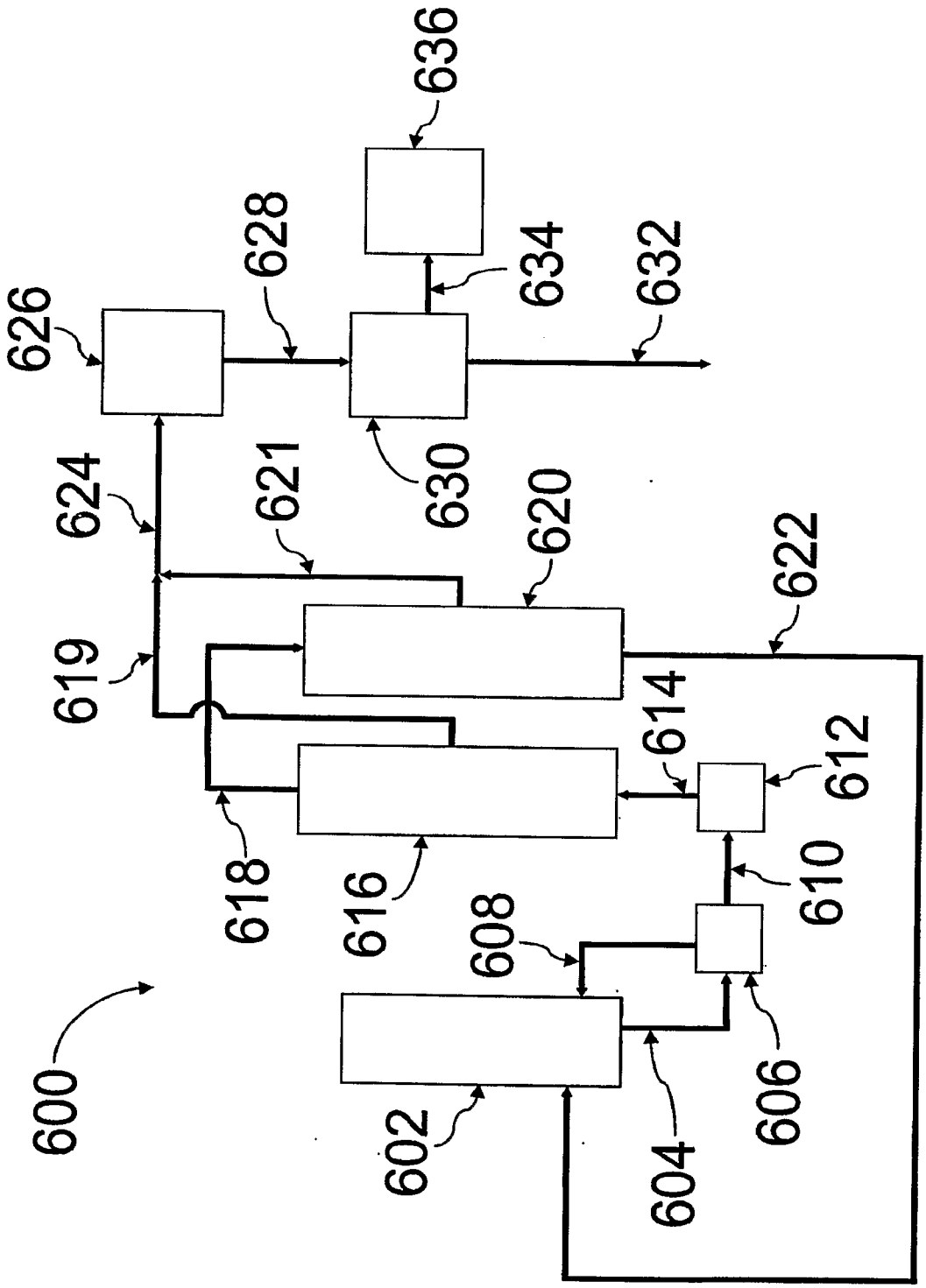
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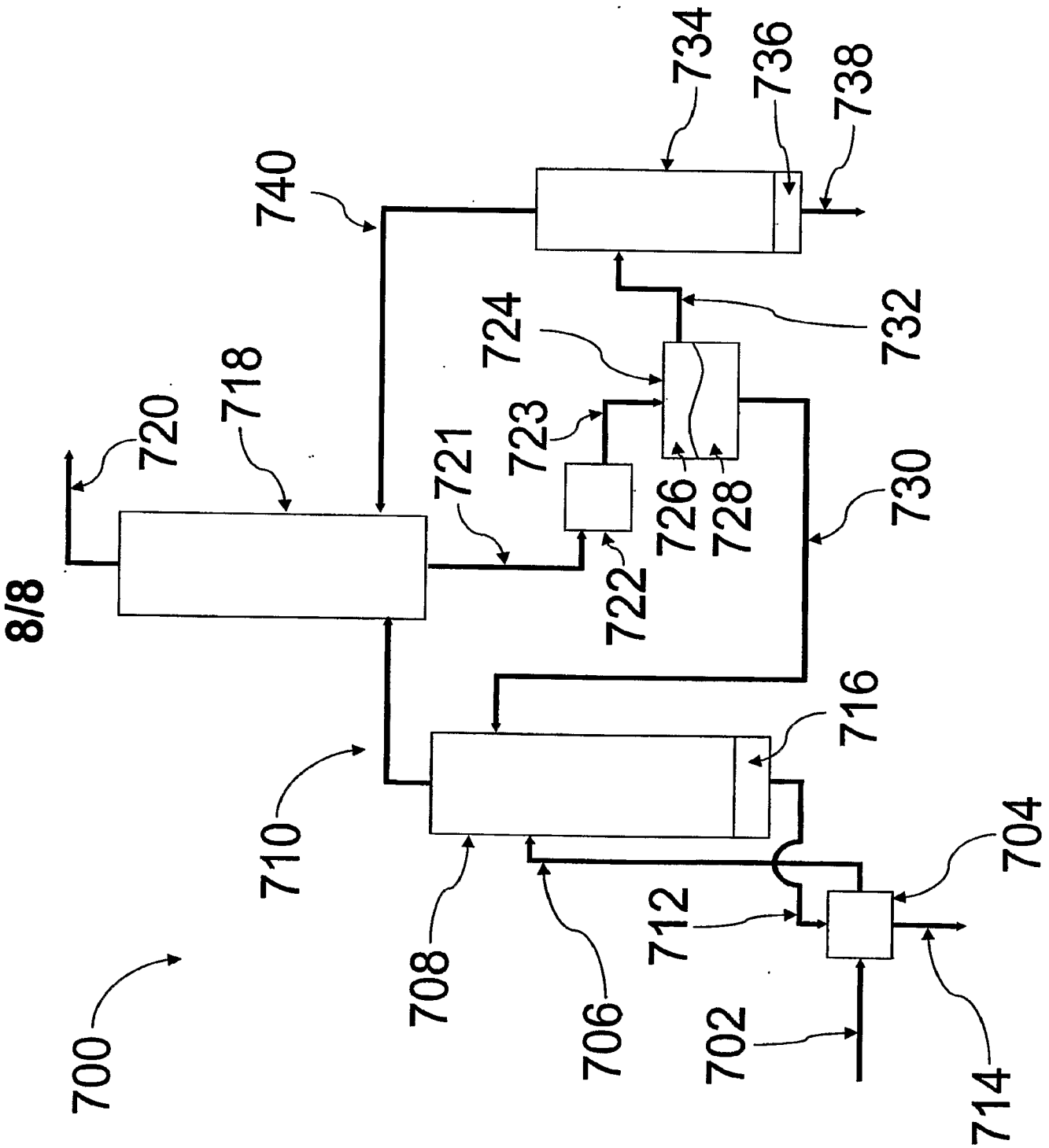
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