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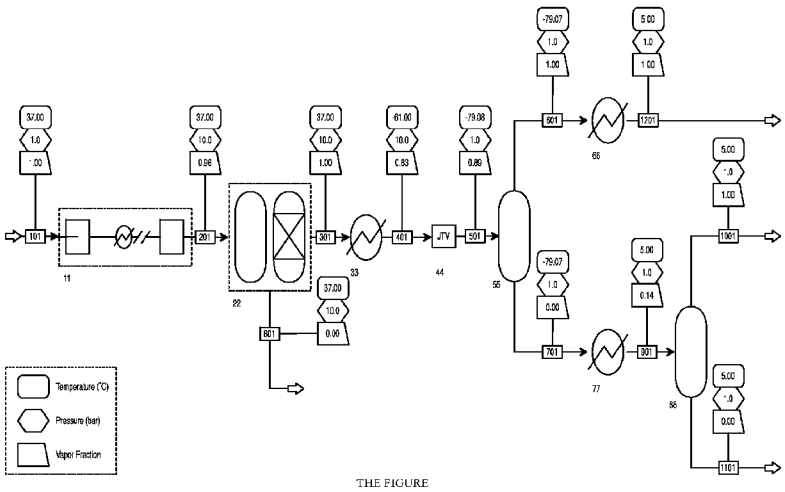


THE FIGURE

(57) Abstract: The present invention discloses methods of recovering isoprene from a feed stream consisting of isoprene, water, ethanol, and lower boiling compounds. The isoprene- containing feed stream is compressed in a manner to avoid excessive heat while condensing a portion of the water contained in the feed stream, the vapor stream is further dried, and isoprene is condensed there form thus separating the isoprene from a substantial portion of the lower boiling compounds, and collecting the isoprene.

WO 2015/127435 A1

RECOVERY OF ISOPRENE FROM FERMENTATION PROCESSES USING MECHANICAL COMPRESSION AND CONDENSATION

RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 61/943,702, filed February 24, 2014. The entire teachings of the above application are incorporated herein by reference.

FIELD OF THE INVENTION

The present invention generally relates to processes for the recovery of isoprene produced via fermentation processes. More specifically, the present disclosure relates to the recovery of isoprene produced via a fermentation process, from the gas streams exiting the fermentor using a combination of mechanical compression and condensation to convert the isoprene from the gaseous phase to the liquid phase.

BACKGROUND OF THE INVENTION

Currently, many high-value chemicals or fuels are manufactured by thermochemical processes from hydrocarbons, including petroleum oil and natural gas. Also, high-value chemicals may be produced as by-products during the processing of crude oil into usable fractions.

Isoprene (CAS Number 78-79-5) is a 5-carbon hydrocarbon useful as a starting material for synthesizing a wide variety of chemicals. In particular, isoprene may be used as a monomer or co-monomer for the production of higher value polymers. Examples of chemicals that can be produced using isoprene include polyisoprene, as a copolymer in polybutylene, styrene-isoprene-styrene block co-polymers, and others. An example of an industry that uses isoprene is the synthetic rubber industry. The majority of isoprene is produced as a "by-product" during the processing of crude oil into usable fractions. For example, isoprene has typically been produced during the catalytic cracking of crude oil fractions. However, recently the use of catalytic crackers has diminished due to the availability of inexpensive natural gas, resulting in a reduced supply of the four and five carbon chain molecules that are found in crude oil, but not natural gas.

Given the increasing demand, decreasing supply and the many uses of isoprene, a new method of isoprene production is desired. Also, as the concerns of energy security, increasing oil and natural gas prices, and global warming escalate, the chemical production industry is seeking ways to replace chemicals made from non-renewable feedstocks with chemicals produced from renewable feedstocks using environmentally friendly practices.

The biological production of isoprene has been studied since the 1950s (Sharkey, T.D. 2009. The Future of Isoprene Research. *Bull. Georg. Natl. Acad. Sci.* **3**: 106-113). Although microbes that naturally produce isoprene are known in the art (Kuzma, J., Nemecek-Marshall, M., Pollock, W.H., and R. Fall. 1995. Bacteria produce the volatile hydrocarbon isoprene. *Curr. Microbiol.* **30**: 97-103; Wagner, W.P., Nemecek-Marshall, M., and R. Fall. 1999. Three distinct phases of isoprene formation during growth and sporulation of Bacillus subtilis. J. Bact. 181: 4700-4703; Fall, R. and S.D. Copley. 2000. Bacterial sources and sinks of isoprene, a reactive atmospheric hydrocarbon. *Env. Microbiol.* **2**: 123-130; Xue, J., and B.K. Ahring. 2011. Enhancing isoprene production by the genetic modification of the 1-deoxy-D-xylulose-5-phosphate pathway in Bacillus subtilis. *Appl. Env. Microbiol.* **77**: 2399-2405), the mechanism of isoprene production is unknown and the levels of isoprene production are relatively low. Several non-naturally occurring microorganisms have been engineered to produce isoprene, *e.g.*, U.S. Patent Application Ser. No. 12/335,071. An example of a fermentation process for producing isopreme is also found in Patent Application Ser. No. 12/335,071.

Isoprene boils at 34°C under atmospheric pressure and is hardly soluble in water. When using a fermentation-based process to produce isoprene, substantially all of the isoprene exits the fermentor in the vapor phase. Thus, the advent of fermentation-based isoprene production has required the concomitant development of technologies and processes for recovering isoprene from the gases exiting the fermentor. While some recovery processes for bio-based isoprene have been proposed, *e.g.*, U.S. Patents 8,324,442, 8,492,605 and 8,569,562, these recovery processes have limitations that affect their utility. U.S. Patents 8,324,442, and 8,492,605 teach the removal of water from the fermentation gases using cold condensation at temperatures as low as -10°C. This leaves residual water in the process gases that may freeze on surfaces as the process gases are further cooled to -35°C and below. The accumulated ice may block process gas lines, reducing operability and potentially creating a dangerous failure of the isoprene recovery system. U.S. Patent 8,569,562 teaches using a gas-

liquid absorber to separate isoprene from non-condensable gases by absorbing the isoprene into a solvent. The isoprene is then recovered from the solvent using significant heat. Heat accelerates the formation of isoprene dimers and oligomers that may accumulate in the solvent or foul equipment surfaces.

Thus, there is a need for a new recovery process for bio-based isoprene that avoids these potential problems.

SUMMARY OF THE INVENTION

The present invention provides processes for the recovery of bio-based isoprene from vapor streams produced using a fermentation process. Preferably, isoprene is recovered from the initial vapor stream produced by the fermentation process in three or more steps by compressing the initial vapor stream to condense a portion of the water contained therein to produce a second vapor stream with lower water content and a water condensate stream; drying the second vapor stream to remove substantially all of the water thereby producing a third vapor stream from which substantially all of the water has been removed; and condensing the isoprene present in the third vapor stream by one or more of lowering the temperature of the third vapor stream or adiabatically decompressing (also referred to herein as "adiabatic expansion") the third vapor stream to form an isoprene condensate stream and a fourth vapor stream from which substantially all the isoprene has been removed. The process further optionally comprises recovering the isoprene from the isoprene condensate stream and optionally purifying the isoprene recovered therefrom.

Preferably, isoprene is recovered from the initial vapor stream by compressing the initial vapor stream in one or more stages, each stage consisting of a compressor and an intercooler or heat exchanger, followed by a vapor-liquid separator to produce a second compressed vapor stream and a water condensate stream; drying the second compressed vapor stream with either a molecular sieve or a membrane-based gas dryer to produce a compressed, third vapor stream from which substantially all of the water has been removed; and condensing the isoprene in the third vapor stream preferably using one or more heat exchangers to produce an isoprene condensate and a fourth compressed vapor stream from which substantially all of the isoprene has been removed; and optionally recovering and optionally further purifying the isoprene in the condensate stream.

Preferably, isoprene is recovered from the initial vapor stream by compressing the vapor stream in one or more stages with isothermal compressors followed by a vapor-liquid separator to produce a compressed, second vapor stream and a water condensate stream; drying the compressed, second vapor stream with either a molecular sieve or a membrane-based gas dryer to produce a compressed third vapor stream from which substantially all of the water has been removed; and condensing the isoprene in the third compressed vapor stream using, for example, one or more heat exchangers to produce an isoprene condensate stream and a fourth compressed vapor stream from which substantially all of the isoprene has been removed; and optionally, recovering and optionally further purifying the isoprene in the isoprene condensate stream.

Preferably, isoprene is recovered from the initial vapor stream by compressing the vapor stream in one or more stages, each stage consisting of a compressor and an intercooler or heat exchanger, followed by a vapor-liquid separator to produce a second compressed vapor stream and a water condensate stream; drying the second compressed vapor stream with either a molecular sieve or a membrane-based gas dryer to produce a third compressed vapor stream from which substantially all of the water has been removed; and condensing the isoprene in the third compressed vapor stream using, for example, one or more heat exchangers followed by adiabatic expansion to produce an isoprene condensate and a fourth vapor stream from which substantially all of the isoprene has been removed; and optionally, recovering and optionally further purifying the isoprene from the isoprene condensate stream.

Preferably, isoprene is recovered from the initial vapor stream by compressing the initial vapor stream in one or more stages with isothermal compressors followed by a vapor-liquid separator to produce a compressed, second vapor stream and a water condensate stream; drying the second vapor stream with either a molecular sieve or a membrane-based gas dryer to produce a compressed, third vapor stream from which substantially all of the water has been removed; and condensing the third vapor stream using, for example, one or more heat exchangers to lower the temperature of the third vapor stream optionally followed by adiabatic expansion to produce an isoprene condensate stream and a fourth vapor stream from which substantially all of the isoprene has been removed; and optionally, recovering and further purifying the isoprene from the isoprene condensate stream.

BRIEF DESCRIPTION OF THE DRAWING

The Figure is a process flow diagram showing one process for the recovery of isoprene from fermentor gases in accordance with the invention.

DETAILED DESCRIPTION

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only, and are not restrictive of the invention, as claimed. In this application, the use of the singular includes the plural, the word "a" or "an" means "at least one", and the use of "or" means "and/or", unless specifically stated otherwise. Furthermore, the use of the term "including", as well as other forms, such as "includes" and "included", is not limiting. Also, terms such as "element" or "component" encompass both elements or components comprising one unit and elements or components that comprise more than one unit unless specifically stated otherwise. All numbers disclosed herein are approximate values, regardless whether the word "about" or "approximate" is used in connection therewith. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number falling within the range is specifically disclosed as well.

The section headings used herein are for organizational purposes only and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, are hereby expressly incorporated herein by reference in their entirety for any purpose. In the event that one or more of the incorporated literature and similar materials defines a term in a manner that contradicts the definition of that term in this application, this application controls.

The present invention provides a method of recovering isoprene with high efficiency and purity from a vapor stream containing water, ethanol, and lower boiling components. An example of such a vapor stream is the vapor stream of bio-based isoprene production using non-naturally occurring microorganisms engineered to produce isoprene from various carbon sources such as glucose, sucrose and other sugars; glycerol; fatty acids, monoglycerides, diglycerides or triglycerides; carbon dioxide or carbon monoxide; methanol; ethanol; or acetate. Lower boiling components (with boiling points lower than that of isoprene under similar conditions) that may be present include acetaldehyde, hydrogen (H_2), nitrogen, (N_2), oxygen (O_2), and carbon dioxide (CO_2). Other higher boiling components (with boiling

points higher than that of isoprene under similar conditions) that may be present include acetone, ethyl acetate, 3-methyl-3-buten-1-ol, 3-methyl-2-buten-1-ol, 2-methyl-3-buten-2-ol, prenyl acetate and prenal. The feed stream may contain additional components, including one or more sulfur-containing compounds such as methanethiol, dimethyl disulfide, or 3-methyl thiophene. An initial vapor stream resulting from a fermentation process may comprise about 0.1% to 20% by volume isoprene. Water may be present in an amount that is greater than about 70% of its saturation point. For an initial vapor stream at atmospheric pressure and approximately 37 °C, this is approximately 30 to 50 grams of water per kilogram of vapor stream.

The present invention provides for at least three steps in the recovery of isoprene from a vapor feed stream. In the first step, the initial vapor feed stream resulting directly from fermentation is compressed isothermally or compressed with intercooling thereby forming a compressed, second vapor stream. By limiting the change in temperature of the initial vapor feed stream during the compression process, a portion of the water contained in the initial vapor feed stream is condensed, and the water condensate is separated from the compressed second vapor stream. Preferably, the temperature of the vapor stream at the start of the compression process is about 20 °C to about 50 °C and the final temperature is about 20 °C to about 150 °C.

In a second step, the compressed, second vapor stream is dried to remove substantially all of the water present thereby forming a compressed third vapor stream from which substantially all of the water has been removed. Preferably, substantially all of the water remaining in the third vapor stream means that water has been reduced to 0.01 gram of water per kilogram of vapor stream.

The first compression step and the second drying step may occur in any order. That is, as an alternate to the order described above, the initial vapor feed stream may be dried to remove substantially all of the water from the initial vapor feed stream prior to compression.

In a third step, the compressed third vapor stream is condensed such that substantially all of the isoprene present in the third vapor stream is condensed to form isoprene condensate. Preferably, substantially all of the isoprene present in the third vapor stream is at least about 90% by volume, preferably at least about 95% by volume and preferably at least about 99% by volume of the isoprene present in the third vapor stream.

Optionally, the isoprene condensate is separated and recovered from the compressed fourth vapor stream which is substantially free of isoprene. Preferably, the fourth vapor stream is substantially free of isoprene if less than about 10% by volume, less than about 5% by volume and preferably less than about 1% by volume of isoprene remains in the fourth vapor stream.

The condensation of the isoprene in the vapor stream may occur in one or more stages. The condensation may be achieved through the use of, for example, chillers, heat exchangers, rapid expansion of the compressed vapor stream (the Joule-Thomson effect, for example), or through a combination of technologies.

The first compression of the initial vapor stream step may occur in one or more stages. That is a single compressor may be used to compress the initial vapor feed stream to the desired final pressure, or two or more compressors may be used to compress the vapor feed stream to the desired final pressure. The compressor may be of any type suitable for vapor compression, including but not limited to, rotary compressors such as sliding vane, scroll, liquid ring, screw or lobe compressors; reciprocating compressors such as double-acting, diaphragm or piston compressors; centrifugal compressors; or axial compressors. Preferably, the one or more compressors are isothermal compressors. Examples of isothermal compressors include liquid ring seal compressors or screw compressors with coolant injection. The injected coolant may be liquid water or another fluid to absorb the heat. Condensate from the compressors may be separated from the compressed vapor stream using a vapor-liquid separator.

Preferably, the one or more compressors may be compressors with intercoolers. In such an arrangement, the compressor unit consists of a compressor, an intercooler, and a vapor-liquid separator. Typically, multiple compressor units are used in series to achieve the desired level of compression while limiting the temperature increase of the vapor stream as it is compressed to avoid unwanted chemical reactions of isoprene at the high temperatures normally caused by compression. The intercooler may be a heat exchanger, for example, a double pipe heat exchanger, a shell and tube heat exchanger, a plate heat exchanger, a plate and shell heat exchanger, a plate fin heat exchanger, a pillow plate heat exchanger, an adiabatic wheel heat exchanger, or a phase-change heat exchanger.

Preferably, where compression of the initial vapor feed stream occurs prior to drying, the initial vapor feed stream, typically with a moisture content of between 20 g water per kg of vapor feed stream and 500 g water per kg of vapor feed stream, an initial pressure between 0 and 2.5 bar(g), and an initial temperature of about 20°C to about 50°C, is compressed to form a second vapor streaming having a final moisture content between 0.01 g water per kg of vapor feed stream and 250 g water per kg of vapor feed stream, a final pressure between 5 and 50 bar(g) and a final temperature of 20°C and 150°C. Preferably, the final moisture content is between 0.01 g water per kg of vapor feed stream and 50 g water per kg of vapor feed stream, the final pressure is between 5 and 15 bar(g) and the final temperature is between 20°C and 100°C.

The drying step of the second vapor stream may be achieved using a variety of different technologies. Molecular sieves, for example zeolite molecular sieves or activated alumina, may be used to dry the compressed vapor stream. A membrane system employing a membrane that selectively permits the separation of the water vapor from the isoprene vapor may be used to dry the compressed vapor stream. Solid desiccants or deliquescent solids, for example magnesium sulfate or calcium sulfate, may be used to dry the compressed vapor stream. Liquid desiccants, for example, glycol desiccants or concentrated sulfuric acid, may be used to dry the compressed vapor stream. Water may be condensed from the second vapor stream to achieve drying followed by separation of the second vapor stream from the water condensate stream.

Preferably, the compressed second vapor stream, with a moisture content between 0.01 and 250 g water per kg of compressed vapor feed stream, a pressure of between 5 and 50 bar(g), and a temperature of about 20°C to about 150°C is dried using molecular sieves, for example, a 3Å or 4Å zeolite molecular sieve or activated alumina desiccant, in a simple passage or a pressure swing adsorption configuration thereby forming a third vapor stream from which substantially all of the water has been removed. Preferably, the compressed second vapor stream is dried using a membrane gas dryer thereby forming a third vapor stream from which substantially all of the water has been removed. The drying step reduces the moisture content of the compressed third vapor stream to 0.01 g water per kg of compressed vapor feed stream or less, preferably below 0.001 g water per kg of compressed third vapor stream or less, and more preferably, below 0.0001 g water per kg of compressed vapor stream. The drying step reduces the water content to a level that is below the dew

point or frost point for water at the temperature and pressure used to condense the isoprene in the condensing step.

The isoprene-condensing step may be achieved, for example, by decreasing the temperature of the compressed vapor stream in one stage, for example, from 20°C to -60°C or in two or more stages, for example, cooling from 20°C to 0°C followed by cooling from 0°C to -60°C. Isoprene from the compressed third vapor stream condenses to form an isoprene condensate and a second compressed vapor phase with reduced isoprene content. Preferably, more than 80%, 85%, 90%, 95%, 98% or 99% of the isoprene present in the compressed second vapor stream is condensed to form the isoprene condensate. More preferably, substantially all of the isoprene is condensed from the compressed second vapor stream to form the isoprene condensate.

Isoprene condensation can be achieved, for example, by using one or more heat exchangers. Examples of such heat exchangers include a double pipe heat exchanger, a shell and tube heat exchanger, a plate heat exchanger, a plate and frame heat exchanger, a plate and shell heat exchanger, a plate fin heat exchanger, a pillow plate heat exchanger, an adiabatic wheel heat exchanger, or a phase-change heat exchanger. Cooling for the heat exchangers may be supplied by one or more refrigeration systems, for example an ammonia cycle refrigeration system or a propane cycle refrigeration system, or a mixed refrigerant system. Preferably, the second compressed vapor phase with reduced isoprene content is recycled to a heat exchanger to provide at least a portion of the cooling requirements. Preferably, the second compressed vapor phase with reduced isoprene content that is recycled to a heat exchanger to assist with cooling is optionally at a temperature ranging from about -60 °C to about -90 °C. Optionally, solid carbon dioxide (also known as “dry ice”) that may be formed during any of the process steps described herein, particularly where temperatures are below -81 °C may be removed using known techniques for withdrawing solid carbon dioxide from the process.

Alternatively, condensation can be achieved through, for example, the adiabatic expansion of the compressed vapor stream. The compressed vapor stream is passed through an appropriate valve or porous plug, *e.g.*, a Joule-Thomson valve, into a zone of lower pressure. The rapid expansion of the compressed vapor stream produces a second vapor stream of lower temperature and pressure, causing a portion of the isoprene to condense into an isoprene condensate. Examples of devices that may be used for adiabatic expansion of the

compressed vapor stream include Joule-Thomson valves, globe valves, stop-check valves, and other throttling equipment.

Preferably, the temperature of the compressed vapor stream is lowered to facilitate isoprene condensation using a combination of heat exchangers and adiabatic expansion using Joule-Thomson valves to achieve a temperature at which isoprene forms a condensate. The temperature of the compressed vapor stream is typically in the range of -30°C to -80°C, preferably in the range of -40°C to -60°C, while the pressure is typically in the range of 5 bar(g) to 50 bar(g), preferably between 5 bar(g) and 15 bar(g). After passage of the compressed vapor stream through the valve, the pressure is reduced to 0 to 20 bar(g), preferably between 0 and 2 bar(g), and the temperature is reduced to -45°C to -90°C. Preferably after passage of the compressed vapor stream through the valve, the pressure is reduced to 0 to 20 bar(g), preferably between 0 and 4 bar(g), and the temperature is reduced to -45°C to -120 °C.

As discussed above, preferably solid carbon dioxide (also known as "dry ice") that may be formed during any of the process steps described herein, particularly where temperatures are below -81 °C may be removed using known techniques for withdrawing solid carbon dioxide from the process. Preferably the process can be operated by also removing and isolating the carbon dioxide in the process gas at every stage in the process (e.g. stream 101 through stream 701 et seq).

This can be done in a number of ways from absorption methods to adsorption onto mole sieves at elevated pressure and release at diminished pressure to membrane separation that will selectively hold back certain component of the feed stream and allow others to pass through. With an initial compression step, adsorption and membrane techniques are particular suited in this effort. The step 22 where water removal is achieved can be used to remove carbon dioxide in the same or an additional unit operation using the known principles to separate carbon dioxide from a gas stream. The concentration of the carbon dioxide in the stream 301 is preferably in the range of 0 to 2% preferably between 0 and 0.1% and more preferably between 0 and 0.01% of carbon dioxide by volume.

The removal of carbon dioxide leads to a smaller amount of residual dissolved gasses in the liquefied isoprene stream. Once the carbon dioxide is removed, the lower temperature for the condensation step Step 44 with stream 501 is no longer limited by the potential condensation of carbon dioxide in solid form (i.e. dry ice). Consequently, the temperature can be reduced further to eliminate isoprene from the gas stream more completely and thus improve the yield of the process. This will lead to removal efficiency for isoprene of 99.9 % at -110 °C.

The elevation of the final condensation pressure in step 44, stream 501 has a similar effect. A doubling of the pressure from 1 atm to 2 atm will reduce the remaining isoprene in the gas stream by 50%. A combination of elevated pressure and lowered temperatures can be used to provide degree of elimination of the isoprene from the gas stream that result in an off-gas that can be released to the environment without further treatment.

The table below shows the Temperature-Pressure combinations for a certain vapor pressure of isoprene that would correspond to a release of less than 10 ppm (30 mg/m3) isoprene in the off-gas stream 601 and consecutive.

Table 3: Residual Isoprene in Gas Stream after condensation at different Temperatures and Pressures.

Temperature °C	p isoprene kPa	p total kPa	Cisoprene ppm
-70	0.294	101.3	2,907
-80	0.111	101.3	1,100
-90	0.037	101.3	364
-100	0.010	101.3	103
-110	0.002	101.3	24
-120	0.000	101.3	4
-130	0.000	101.3	1
-70	0.294	202.6	1,453
-80	0.111	202.6	550
-90	0.037	202.6	182
-100	0.010	202.6	51
-110	0.002	202.6	12
-120	0.000	202.6	2
-130	0.000	202.6	0
-70	0.294	405.2	727
-80	0.111	405.2	275
-90	0.037	405.2	91
-100	0.010	405.2	26
-110	0.002	405.2	6
-120	0.000	405.2	1

EXAMPLE 1

Referring to The Figure, non-naturally occurring microorganisms are used to convert fatty acids to isoprene in a fermentation-based process that results in an isoprene-rich vapor feed stream, stream **101**. The major components of stream **101** are presented in Table 1 and Table 2. Isoprene is recovered from this vapor feed stream, stream **101**, in high yield using the process of the present invention.

TABLE 1: STREAM 101 COMPOSITION	
Mole Fraction	
ISOPRENE	0.094
N2	0.722
CO2	0.095
O2	0.040
WATER	0.049
Total	1.000

In this example, feed stream **101** at a vapor fraction of 1, 37°C and 0 bar(g) is compressed in compressor train **11**, which comprises two compressor stages, to a vapor fraction of 0.96 (part of the water present in stream **101** is condensed to the liquid fraction), 37°C and 10 bar(g) to produce a second vapor/liquid stream **201**.

The vapor/liquid stream **201** is then passed to a vapor/liquid separator and molecular sieve **22** to yield a vapor stream **301** that is substantially free of water and a liquid stream **801**.

The vapor stream **301** comprises mostly isoprene and lower boiling, non-condensable gases such as N_2, CO_2, and O_2, while the liquid stream **801** comprises mostly water and some residual, higher boiling, polar components such as traces of acetone, ethanol, ethyl acetate, *etc*. The vapor stream **301** is sufficiently dry that any traces of water present in vapor stream **301** will not freeze out onto piping and equipment surfaces, thereby reducing the risk of blocking the gas flow with ice.

The vapor stream **301** is passed through a heat exchanger **33**, which may comprise one or more heat exchangers in series or in parallel, to yield stream **401** at -61°C and 10 bar(g).

Stream **401** is then decompressed by adiabatic expansion using a Joule-Thomson valve **44** resulting in stream **501** with a reduced temperature of -79°C and a reduced pressure of 0 bar(g). Isoprene present in stream **501** condenses to the liquid phase, while non-condensable gases such as N_2, CO_2, and O_2 remain in the vapor phase.

Stream **501** is passed to vapor/liquid separator **55** to produce a vapor stream **601** comprised primarily of non-condensable gases such as N_2, CO_2, and O_2 and a liquid stream **701** comprised primarily of the majority of the isoprene and a small amount of dissolved CO_2.

Stream **601** is passed through a heat exchanger **66** to produce stream **1201**, increasing the temperature of the vapor phase to 5°C.

Stream **701** is then passed through heat exchanger **77** to produce stream **901**, increasing the temperature of the liquid isoprene to 5°C and lowering the solubility of CO_2 dissolved in the isoprene.

To conserve energy and lower the operational costs of the process, streams **601** and **701** may be used to supply a portion of the cooling required to cool stream **301** by integrating heat exchangers **66** and **77** into heat exchanger **33**, thereby lowering the energy requirements and operational costs of the process.

Stream **901** is then routed to vapor-liquid separator **88** to remove residual CO_2 in the vapor phase (stream **1001**), while the liquid isoprene (stream **1101**) is recovered and stored for further use. Residual isoprene present in stream **1001** may be recovered by combining stream **1001** with stream **101**, thereby improving the yield of isoprene recovered by the process.

TABLE 2: ISOPRENE RECOVERY PROCESS

	101	201	301	401	501	601	701	801	901	1001	1101	1201
Composition (Mass Flow, kg/hr)												
ISOPRENE	492.9	492.9	492.9	492.9	492.9	5.1	487.8	0.0	487.8	25.4	462.4	5.1
N2	1552.4	1552.4	1552.4	1552.4	1552.4	1545.0	7.5	0.0	7.5	7.2	0.3	1545.0
CO2	319.9	319.9	319.9	319.9	319.9	292.3	27.6	0.0	27.6	21.4	6.2	292.3
O2	98.5	98.5	98.5	98.5	98.5	98.0	0.5	0.0	0.48	0.43	0.04	98.02
WATER	67.1	67.1	0.0	0.0	0.0	0.0	0.0	67.1	6.71E-05	2.18E-06	6.49E-05	4.11E-08
Total Flow kg/hr	2530.9	2530.9	2463.8	2463.8	2463.8	1940.4	523.4	67.1	523.4	54.5	468.9	1940.4
Temperature (°C)	37	37	37	-61	-79.1	-79.1	-79.1	37	5	5	5	5
Pressure (bar)	1	10	10	10	1	1	1	10	1	1	1	1
Vapor Fraction	1	0.96	1	0.83	0.89	1	0	0	0.14	1	0	1
Liquid Fraction	0	0.04	0	0.17	0.11	0	1	1	0.86	0	1	0

EXAMPLE 2

Example 2 describes an embodiment, which further increases the recovery rate of isoprene from the product gas mix and reduces the isoprene load of the off-gas.

Referring to The Figure, non-naturally occurring microorganisms are used to convert fatty acids to isoprene in a fermentation-based process that results in an isoprene-rich vapor feed stream, stream **101**. The major components of stream **101** are presented in Table 1 and Table 2 above. Isoprene is recovered from this vapor feed stream, stream **101**, in high yield using the process of the present invention.

In this example, feed stream **101** at a vapor fraction of 1, 37°C and 0 bar(g) is compressed in compressor train **11**, which comprises two compressor stages, to a vapor fraction of 0.96 (part of the water present in stream **101** is condensed to the liquid fraction), 37°C and 10 bar(g) to produce a second vapor/liquid stream **201**.

The vapor/liquid stream **201** is then passed to separator **22** suitable to remove carbon dioxide from the gas mixture to yield a vapor stream **301** that is substantially free of carbon dioxide and a carbon dioxide containing stream **801**.

The vapor stream **301** comprises mostly isoprene and lower boiling, non-condensable gases such as N_2, and O_2, while the liquid stream **801** comprises mostly carbon dioxide, some water and some residual, higher boiling, polar components such as traces of acetone, ethanol, ethyl acetate, *etc*. The vapor stream **301** is sufficiently dry that any traces of water present in vapor stream **301** will not freeze out onto piping and equipment surfaces, thereby reducing the risk of blocking the gas flow with ice.

The vapor stream **301** is treated similar to example 1 in that it is passed through a heat exchanger **33**, which may comprise one or more heat exchangers in series or in parallel, to yield stream **401** at sufficiently cooled to below -70°C and 10 bar(g).

Stream **401** is then decompressed by adiabatic expansion using a Joule-Thomson valve **44** resulting in stream **501** with a reduced temperature of below -80°C and a reduced pressure of 0 bar(g) or higher, e.g. 1 bar(g) or 2 bar(g), or 4 bar(g). Isoprene present in stream **501** condenses to the liquid phase, while non-condensable gases such as N_2, and O_2 remain in the vapor phase.

Stream **501** is passed to vapor/liquid separator **55** to produce a vapor stream **601** comprised primarily of non-condensable gases such as N_2, and O_2 and a liquid stream **701** comprised primarily of the majority of the isoprene and a only traces of dissolved gases like nitrogen. The off-gas stream **601** is now much lower in residual isoprene concentration depending on the final temperature and pressure in the gas liquid separator.

Stream **601** is passed through a heat exchanger **66** to produce stream **1201**, increasing the temperature of the vapor phase to 5°C.

Stream **701** is then passed through heat exchanger **77** to produce stream **901**, increasing the temperature of the liquid isoprene to 5°C and lowering the solubility of CO_2 dissolved in the isoprene.

The patent and scientific literature referred to herein establishes the knowledge that is available to those with skill in the art. All United States patents and published or unpublished United States patent applications cited herein are incorporated by reference. All published foreign patents and patent applications cited herein are hereby incorporated by reference. All other published references, documents, manuscripts and scientific literature cited herein are hereby incorporated by reference.

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims. It should also be understood that the embodiments described herein are not mutually exclusive and that features from the various embodiments may be combined in whole or in part in accordance with the invention.

CLAIMS

What is claimed is:

1. A method for the recovery of bio-based isoprene from an initial vapor stream produced during fermentation wherein the initial vapor stream comprises at least isoprene and water produced during the fermentation process, comprising the steps of:

   a. compressing the initial vapor stream to condense at least a portion of the water contained in the initial vapor stream to produce a compressed, second vapor stream having a lower water content than the initial vapor stream and a water condensate stream;

   b. drying the compressed, second vapor stream to remove substantially all of the water, thus producing a compressed, third vapor stream from which substantially all of the water has been removed; and

   c. condensing isoprene from the compressed, third vapor stream to produce an isoprene condensate stream and a compressed, fourth vapor stream from which substantially all of the isoprene has been removed and optionally recovering the isoprene from the isoprene condensate stream and optionally further purifying the isoprene recovered from the isoprene condensate stream.

2. The method of claim 1, wherein the compressed, second vapor stream of step (b) is dried using a molecular sieve or a membrane-based gas dryer.

3. The method of claim 1, wherein the initial vapor stream of step (a) is compressed in one or more stages to produce a compressed, second vapor stream and a water condensate stream.

4. The method of claim 3, wherein each of the one or more stages comprises the use of a compressor and an intercooler or heat exchanger followed by a vapor-liquid separator to produce the compressed, second vapor stream and a water condensate stream.

5. The method of claim 3, wherein each of the one or more stages comprises the use of isothermal compressors followed by a vapor liquid separator to produce a compressed second vapor stream and water condensate stream.

6. The method of claim 1, wherein step the condensation of step (c), comprises lowering the temperature of the compressed, third vapor stream optionally followed by adiabatic expansion of the compressed, third vapor stream.

7. The method of claim 6, wherein the temperature of the compressed, third vapor stream is lowered by using a heat exchanger or a chiller.

8. The method of claim 1, wherein the compressed, second vapor stream of step (a) has a final temperature of about 20 °C to about 150 °C.

9. The method of claim 1, wherein the compressed, third vapor stream of step (b) has a moisture content of about 0.01 g or less water per kg of compressed vapor stream.

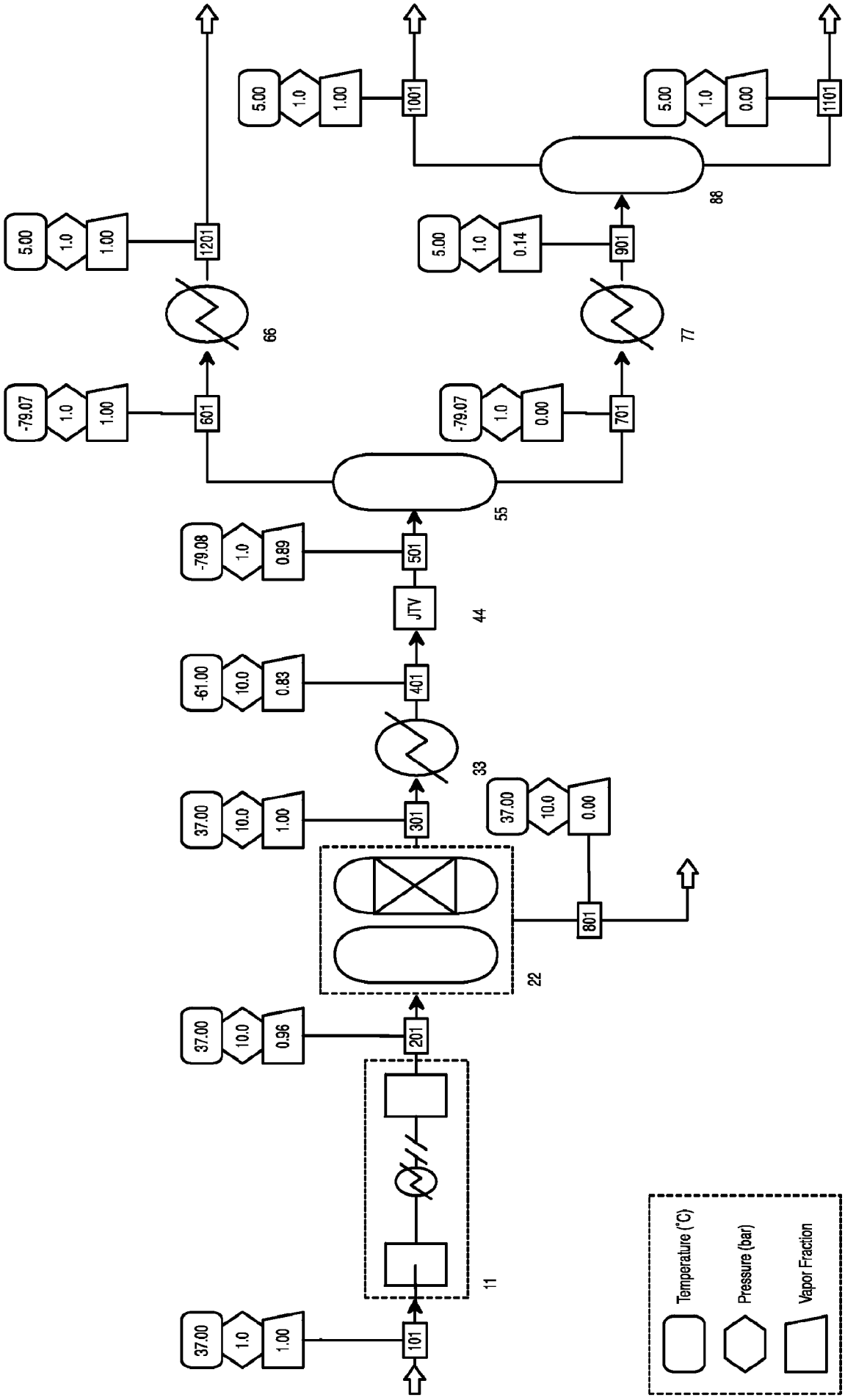
10. The method of claim 1, wherein the condensation of step (c) is carried out in one or more stages.

11. The method of claim 10, wherein the first stage of condensation lowers the temperature of the third vapor stream to 20 °C to 0 °C.

12. The method of claim 11, wherein a second stage of condensation lowers the temperature of the third vapor stream to 0 °C to -60 °C.

13. The method of claim 1, wherein the condensing step of step (c) comprises adiabatic expansion wherein the resulting isoprene condensate stream after adiabatic expansion has a pressure of around 0 to 20 bar(g) and a temperature of about -45 °C to about -90 °C.

14. The method of claim 1, wherein the condensing step of step (c) comprises adiabatic expansion wherein the resulting isoprene condensate stream after adiabatic expansion has a pressure of around 0 to 20 bar(g) and a temperature of about -45 °C to about -120 °C.


37.00
1.0
1.00
101
11
37.00
10.0
0.96
201
22
37.00
10.0
1.00
301
33
-61.00
10.0
0.83
401
44
-79.08
1.0
0.89
501
JTV
55
-79.07
1.0
1.00
601
66
5.00
1.0
1.00
1201
-79.07
1.0
0.00
701
77
5.00
1.0
0.14
901
88
5.00
1.0
1.00
1001
5.00
1.0
0.00
1101
37.00
10.0
0.00
801
Temperature (°C)
Pressure (bar)
Vapor Fraction

THE FIGURE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 15/17285

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07C 7/09; C07C 11/18 (2015.01)
CPC - C07C 11/18; C07C 7/09
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)
IPC(8): C07C 7/09; C07C 11/18 (2015.01)
CPC; C07C 11/18; C07C 7/09

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 585/601; 585/810

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase; FreePatentsOnline; GoogleScholar. Search Terms: isoprene, recovery/isolation/purification, condensation, water removal, drying, isothermal compressors

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO 2011/075534 A2 (Feher et al.) 23 June 2011 (23.06.2011) para [0009], [0010], [0063], [0066-0068], [0105], [0106], [0124], [0125], [0166]	1-12 --- 13 and 14
Y	US 4,885,063 A (Andre) 05 December 1989 (05.12.1989) Abstract; col 3, ln 42-44l col 4, ln 38-41; col 6, ln 51-52	13 and 14
A	US 8,470,561 B2 (Chotani et al.) 25 June 2013 (25.06.2013) Entire Document	1-14
A	US 2011/0040058 A1 (McAuliffe et al.) 17 February 2011 (17.02.2011) Entire Document	1-14

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 April 2015 (13.04.2015)	20 MAY 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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