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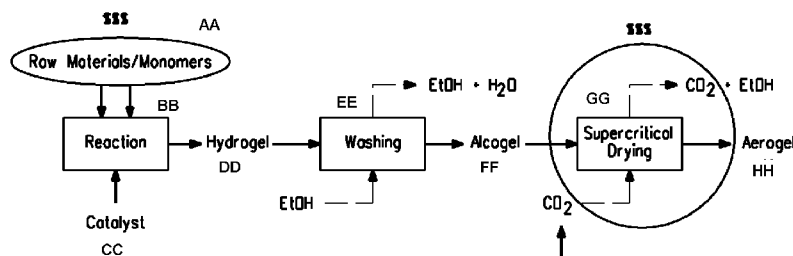


FIG. 1

(57) Abstract: There is disclosed herein an integrated manufacturing process, wherein a fermentation process is integrated with an extraction process that uses a supercritical fluid. The process ferments a carbohydrate to produce a fermentation product and gaseous CO₂, then compresses the gaseous CO₂ to form a supercritical CO₂ using the supercritical CO₂ as an extractant to separate one component from a mixture.

TITLE

ENERGY EFFICIENT FERMENTATION PROCESS INTEGRATED WITH AN EXTRACTION PROCESS USING A SUPERCRITICAL FLUID

5

Field of the Invention

This invention relates to an energy efficient fermentation process integrated with an extraction process that uses a supercritical fluid.

10 Background

Conventional fermenters frequently run at a carbohydrate concentration that is no more than about 10 wt%. Higher feed concentrations are often not possible because the bacteria cells used for fermentation exhibit reduced activity at carbohydrate concentrations higher than about 10 wt%. In addition, undesirable bacteria cells become more active at higher carbohydrate concentrations, catalyze undesirable reactions in the fermenter, and thereby compromise selectivity of the reaction to the product of interest.

One approach to controlling the concentration of carbohydrates in a fermentation reaction is to dilute the reaction mixture with water. This not only uses large volumes of water, but makes recovery of the fermentation product more difficult in view of the need to separate the product from the water. Use of large volumes of water also increases the amount of stillage and other waste material left behind after completion of the fermentation reaction, and disposal of such waste material in a cost-effective, environmentally benign manner is difficult. In addition, when the source of water to be added to the fermentation reaction is a fresh water source such as a river, the water must typically be treated with a biocide to limit the growth of undesirable bacteria in the fermenter.

30 Problems such as described above can be mitigated if a fermenter can be cooled to operate at a temperature less than about 30°C. When the reaction is run at cooler temperatures, there is less need for dilution of the

reaction mixture, and less water will in such case be added to the reaction mixture. This ameliorates the recovery and disposal problems caused by the use of large volumes of water. In addition, the growth of undesirable bacteria is inherently reduced at a lower reaction temperature.

5 Despite the benefits of running a fermentation reaction at lower temperatures, many fermenters in hot, humid climates currently operate above about 32° C. The cooling of a fermenter would require chillers with very large energy loads. For most fermentation processes, the capital and operating costs of adding such cooling capacity would make the
10 fermentation process uneconomical. A need thus remains for a fermentation process that can be run on a more energy efficient basis, particularly a process where the fermentation reaction can be cooled at a reasonable cost.

 One by-product of fermentation reactions is CO₂. One use to which
15 the CO₂ can be utilized is in the manufacture of aerogels. Aerogels are nanoporous materials that have the lowest known thermal conductivity and the highest insulation value. Even though aerogel insulation could significantly reduce energy losses in buildings, appliances, vehicles and other parts of the cold chain, the high cost of manufacturing aerogels has
20 previously reduced their attractiveness because the payback time for investment in their use is quite long. The high cost of the aerogel is due primarily to the high cost of raw materials needed to make the sol (the precursor to the gel), and the high cost associated with the supercritical drying of the alcogel, which relies on the presence of CO₂ to displace the
25 solvent contained in the alcogel. Supercritical drying with CO₂ is usually required to prevent the pore structure of an aerogel from collapsing due to capillary forces.

 Similar materials could indeed be cheaper to manufacture than aerogels that require supercritical drying, but the thermal performance is
30 not as good as aerogels obtained from supercritical drying. Manufacturing aerogels by the use of supercritical drying with CO₂ will thus continue to be the process of choice for the foreseeable future.

Aerogels have been known for over 70 years but they have not made a significant commercial impact primarily because of the high cost of manufacturing. Thus, even though aerogel insulation could significantly reduce energy losses in buildings, appliances, transportation and the cold chain, aerogels are not prevalently used because the payback time for investment is too long.

Therefore, if the two processes – fermentation and aerogel manufacturing – can be synergistically combined, there is the potential for producing cost effective aerogel product.

Summary

There is disclosed herein an integrated manufacturing process, comprising a fermentation process integrated with an extraction process that uses a supercritical fluid.

In another embodiment, the process further comprises the steps:

- a) fermenting a carbohydrate to produce a fermentation product and gaseous CO₂;
- b) compressing the gaseous CO₂ to form a supercritical CO₂; and
- c) using the supercritical CO₂ as an extractant to separate a component from a mixture.

Brief Description of the Drawings

Figure 1 illustrates an aerogel process.

Figures 2, 4A and 4B illustrate a conceptual schematic of certain embodiments of the methods hereof.

Figure 3 illustrates a schematic of the integration fermentation process in concert with the manufacturing of aerogels.

Figure 5 illustrates a flow sheet of a fermentation process that converts sugar must to ethanol.

Figure 6 illustrates the entering and leaving streams to and from the heat exchanger employed in a typical sugar mill to control the temperature of the fermenter.

Figure 7 illustrates the flow diagram for a chiller and the heat exchanger used to cool the fermenter.

Figure 8 illustrates the energy, raw materials and equipment requirements in an organic aerogel manufacturing process that is set up as a standalone unit without the advantage of energy and material integration with a fermentation based manufacturing process.

Figure 9 illustrates a flow sheet for the gelation process used for this example.

Figure 10 illustrates a distillation column used to separate the water and concentrate the ethanol stream.

Figures 11A, 11B, and 12 illustrate a process flow sheet for heating and compressing the liquid CO₂.

Figure 13 illustrates a simplified process diagram highlighting the pertinent process streams involved in cooling the fermentation vessel in the ethanol plant.

Detailed Description

Disclosed herein are methods related to the operation of a fermentation process on a more energy efficient basis. In certain particular embodiments, the methods hereof take advantage of the fact that, although CO₂ is a byproduct of the fermentation process, it is nevertheless a chemical compound that itself has several valuable uses. Therefore, the fermentation process combined with an extraction process utilizes the CO₂ to produce a low cost aerogel.

As seen in Figure 1, a typical aerogel process requires large amounts of a solvent such as ethanol in the washing step, and large amounts of CO₂ and energy in the supercritical drying step. The supercritical drying step in an aerogel process requires the use of a large compressor to compress the CO₂ to be used to obtain effective drying of the alcogel.

One embodiment of the methods hereof, thus, involves the operation of a fermentation process in concert with the manufacturing process of aerogels. A schematic of the integration can be seen in Figures 2 and 3. A solvent such as ethanol, CO₂ and excess energy (steam and electricity) can be obtained from a fermenter such as a sugar mill/bio-fuel plant. Fermentation processes suitable for such purpose can use switch grass, corn products such as corn stover or corn cobs, or other cellulosic materials as the carbohydrate feedstock. Such carbohydrates can be fermented by the action of bacteria such as *Saccharomyces* or *Lactobacillus*. Other aspects of such a fermentation process are described in USP 2010/0139154, which is by this reference incorporated in its entirety as a part hereof for all purposes.

A compressor as used for the compression of CO₂ to form a supercritical CO₂ stream for use in the supercritical drying of the alcogel can be used to treat some or all of the outflow stream coming from the fermenter. The compression process will be able to separate a fermentation product such as ethanol and water from the CO₂ stream, cycle the original stream less CO₂ back to the fermenter, and route the clean CO₂ stream for use in the supercritical cycle of the aerogel plant. The CO₂ that is not used in the aerogel plant can also be used or sold for other applications. The decompression step in the supercritical CO₂ cycle is similar to a refrigeration cycle with sufficient energy load to cool the fermenter to a preferred temperature.

A schematic of a manufacturing plant where a solvent such as bio-ethanol and aerogels are produced by methods that achieve energy integration is shown in Figures 2, 4A and 4B.

The benefits to the aerogel plant include:

- Existing Infrastructure
- Process integration
- Excess electricity and steam
- Access to on-site CO₂

Connect into ethanol stream

The benefits to the biorefinery include:

- Higher efficiency of fermenters
- 5 Savings in energy
- Reduced stillage and disposal cost
- Lower water & biocide usage
- Opportunity to sell CO₂

10 Various embodiments of the methods hereof are as set forth below.
Any of these embodiments can be combined with any one or more of the
other embodiments, *viz*:

A method of preparing supercritical CO₂, comprising (a) fermenting a
15 carbohydrate to prepare a fermentation product, CO₂ and a waste material,
(b) separating the waste material from the fermentation product, (c) burning
the waste material to yield thermal energy, and (d) applying the thermal
energy to compress the CO₂. Step (d) can comprise burning the waste
material to generate electricity, and powering a compressor with the
20 electricity.

A method of separating a fermentation product from water,
comprising (a) fermenting a carbohydrate to prepare a fermentation product
in a mixture with water, (b) providing a supercritical CO₂, (c) cooling the
supercritical CO₂ to reduce the temperature thereof and extract thermal
25 energy therefrom, and (d) applying the extracted thermal energy to heat the
mixture of the fermentation product and water to separate the components
of the mixture. The method can also comprise preparing CO₂ in the
fermentation process and compressing the CO₂ produced in the
fermentation process to provide the supercritical CO₂.

30 A method of cooling a fermentation process, comprising (a)
fermenting a carbohydrate to prepare a fermentation product, (b) providing
a supercritical CO₂, (c) cooling the supercritical CO₂ to reduce the

temperature thereof and extract thermal energy therefrom, and (d) applying the extracted thermal energy to cool the fermentation process. Step (d) can also comprise heating, with the extracted thermal energy, a mixture of a refrigerant and an absorbent in an absorption chiller to separate refrigerant, in vapor form, from the absorbent, and increase the pressure of the refrigerant vapor. The method can also comprise preparing gaseous CO₂ in the fermentation process and compressing the CO₂ produced in the fermentation process to provide the supercritical CO₂.

A method of cooling a fermentation process that liberates thermal energy, comprising (a) providing a supercritical CO₂, and (b) releasing the pressure on the supercritical CO₂ to absorb the thermal energy as liberated by the fermentation process. The fermentation process can be conducted in a fermenter, and step (b) can comprise releasing pressure on the supercritical CO₂ proximate to a thermal energy transfer medium that is proximate also to the fermenter or a feed thereto.

A method of preparing an alcogel, comprising (a) fermenting a carbohydrate to prepare a fermentation product, and (b) contacting a hydrogel with the fermentation product to expel water from the hydrogel and give an alcogel. The fermentation product can comprise an alcohol.

A method of displacing a volatile chemical from a substrate, comprising (a) fermenting a carbohydrate to produce a fermentation product and gaseous CO₂, (b) separating the gaseous CO₂ from the fermentation product, and (c) contacting the substrate with the gaseous CO₂ as produced from fermentation to expel the volatile chemical from the substrate. The method can further comprise compressing the gaseous CO₂ before contact with the substrate. The substrate can comprise an alcogel, and a solvent can be expelled from an alcogel to give an aerogel.

A method of displacing a volatile chemical from a substrate, comprising (a) compressing CO₂ to form a supercritical CO₂, (b) exposing the supercritical CO₂ to a thermal energy transfer medium to provide a cooled CO₂, (c) further compressing the cooled CO₂, (d) contacting the substrate with the further compressed CO₂ to expel the volatile chemical

from the substrate, and (e) releasing the pressure on the CO₂ in proximity to the thermal energy transfer medium to absorb thermal energy therefrom.

A method of providing a purified CO₂, comprising (a) fermenting a carbohydrate to produce a fermentation product in a mixture with water and gaseous CO₂, and (b) compressing the mixture to separate water and/or the fermentation product from the CO₂.

A method of providing a supercritical CO₂, comprising (a) fermenting a carbohydrate to produce a fermentation product in a mixture with water and CO₂, (b) separating the CO₂ from the mixture, and (c) compressing the CO₂ forming supercritical CO₂.

An integrated manufacturing process, comprising a fermentation process integrated with an extraction process that uses a supercritical fluid.

For purposes of this application, a supercritical fluid is defined as a fluid that is near or above both its critical pressure and critical temperature. The preparation and properties of supercritical fluids are well known in the art; see for example "Supercritical Fluids", Kirk-Othmer Encyclopedia of Chemical Technology, Tomasko and Guo, 14 APR 2006, John Wiley & Sons, Inc. A particularly suitable fluid is CO₂. For purposes of this application, supercritical CO₂ is defined as being above about 800° C and 20 PSI (0.59 MPa).

Examples of extraction processes include but are not limited to the separation of azeotropic mixtures, such as ethanol and water, extracting materials such as flavors and fragrances from food and natural plant materials, removal of caffeine from products such as coffee and tea, purification of pharmaceuticals, polymers, or environmental materials, and removal of long chain alcohols from sugar cane crude wax (a byproduct of sugar cane production).

Also described is an integrated manufacturing process comprising:

- a) fermenting a carbohydrate to produce a fermentation product and gaseous CO₂,
- b) compressing the gaseous CO₂ to form a supercritical CO₂;

- c) using the supercritical CO₂ as an extractant to separate one component from a mixture.

5 The mixture can be a gel, and the component can be a continuous phase. In one embodiment, an aerogel is formed after the separation of the component from the mixture. In another embodiment the fermentation product and the component is ethanol. In yet another embodiment the process further comprises after step b: contacting a hydrogel with the ethanol to remove water from the hydrogel to form the gel.

10

A gel is typically an interconnected colloidal state in which a dispersed phase has combined with a continuous phase to produce a viscous product. The gel can be an alcogel (in which the continuous phase is an alcohol) or a hydrogel (in which the continuous phase is water).

15

Also described is an integrated manufacturing process comprising:

- a) fermenting a carbohydrate to produce a fermentation product, gaseous CO₂ and thermal energy;
- 20 b) forming a supercritical CO₂ from the gaseous CO₂ and the thermal energy;
- c) using the supercritical CO₂ as an extractant to separate a component from a mixture; and
- d) separating the component from the supercritical CO₂ by reducing the pressure to form a liquid phase CO₂.

25

In one embodiment the process further comprises:

- e) recycling the liquid phase CO₂ by mixing the liquid phase CO₂ with the gaseous CO₂ in step b).

30 In one embodiment, an aerogel is formed after the separation of the component from the mixture.

Also described is an integrated manufacturing process comprising:

- 5 a) fermenting a carbohydrate to produce a fermentation product, gaseous CO₂, and thermal energy wherein the thermal energy is transferred to a cooled water stream forming a heated water stream;
- b) compressing the gaseous CO₂ to form a liquid CO₂;
- c) forming a supercritical CO₂ from the liquid CO₂ and the thermal energy from the heated water stream to form a cooled water stream;
- 10 d) using the supercritical CO₂ as an extractant to separate a component from a mixture;
- e) separating the component from the supercritical CO₂ by reducing the pressure, to form a liquid phase CO₂.

15 In one embodiment the process further comprises recycling the cooled water stream in step c) to step a).

In one embodiment the process further comprises recycling the liquid phase CO₂ formed in step e to step b).

20 In one embodiment, an aerogel is formed after the separation of the component from the mixture.

Although various embodiments of the methods hereof have been described and illustrated with specific reference to the production of ethanol as a fermentation product, the methods hereof are not limited to ethanol as
25 a fermentation product, or to the production of an alcohol as the fermentation reaction.

Where a range of numerical values is recited or established herein, the range includes the endpoints thereof and all the individual integers and fractions within the range, and also includes each of the narrower ranges
30 therein formed by all the various possible combinations of those endpoints and internal integers and fractions to form subgroups of the larger group of values within the stated range to the same extent as if each of those

narrower ranges was explicitly recited. Where a range of numerical values is stated herein as being greater than a stated value, the range is nevertheless finite and is bounded on its upper end by a value that is operable within the context of the invention as described herein. Where a
5 range of numerical values is stated herein as being less than a stated value, the range is nevertheless bounded on its lower end by a non-zero value.

In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage, where an embodiment of the subject
10 matter hereof is stated or described as comprising, including, containing, having, being composed of or being constituted by or of certain features or elements, one or more features or elements in addition to those explicitly stated or described may be present in the embodiment. An alternative
15 embodiment of the subject matter hereof, however, may be stated or described as consisting essentially of certain features or elements, in which embodiment features or elements that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of the subject matter
20 hereof may be stated or described as consisting of certain features or elements, in which embodiment, or in insubstantial variations thereof, only the features or elements specifically stated or described are present.

In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage, amounts, sizes, ranges, formulations, parameters, and other quantities and characteristics recited herein,
25 particularly when modified by the term "about", may but need not be exact, and may also be approximate and/or larger or smaller (as desired) than stated, reflecting tolerances, conversion factors, rounding off, measurement error and the like, as well as the inclusion within a stated value of those values outside it that have, within the context of this invention, functional
30 and/or operable equivalence to the stated value.

EXAMPLES

Example 1

5 This example shows the performance of a typical fermenter in a sugar mill ethanol plant and the cooling loop employed to control the temperature in the fermenter.

Figure 5 shows a flow sheet of a fermentation process that converts sugar must to ethanol. The size of fermentation plant can vary over a wide range but all calculations presented to demonstrate the present invention
10 are based on a fermentation plant that produces 90,000 m³ of ethanol per year. Those skilled in the art of producing ethanol from sugar will know that the chosen plant size is typical in the ethanol industry.

Table 1 shows the size, composition and temperature of the major process streams in the sugar to ethanol fermentation plant. Sugar must,
15 water and yeast are added to the fermentation vessel. Since aerobic fermentation process is exothermic, the temperature in the fermenter can rise to undesirable levels. In order to control the temperature in the fermenter, part of the wine from the fermenter is sent to a plate heat exchanger where it is cooled with help of process water from the cooling
20 towers. The rest of the wine exiting the fermenter is sent to a centrifuge where the yeast is separated from the wine and is recycled back to the fermenter. The ethanol water solution is sent to the beer well and then to the distillation column where ethanol is separated from water. The ethanol rich stream from the distillation condenser is sent to a molecular sieve
25 column, where it is further purified to yield almost anhydrous ethanol. The waste or stillage from the distillation column is collected and disposed.

Table 1

	Must	Water Dilution	Wine (recirculation)	Cooling Water (from cooling tower)	Cooling Water (to cooling tower)
Temperature (°C)	32	25	36	30	34
Pressure (bar)	3,46	2,97	3,46	2,97	2,97
Vapor Frac	0	0	0	0	0
Mole Flow (kmol/hr)	14272,01	349,70	39208,81	39910,56	39910,56
Mass Flow (kg/hr)	273000	6300	750000	719000	719000
Volume Flow (cum/hr)	281,01	6,34	775,21	726,91	729,78
Enthalpy (MMBtu/hr)	-3879,74	-94,69	-10647,82	-10793,59	-10782,95
Mole Flow (kmol/hr)					
WATER	13789,96	349,70	37884,51	39910,56	39910,56
SUCRO-01	7,98		21,91		
ETHAN-01	474,07		1302,39		
CARBO-01	0,00				

	Must	Water Dilution	Wine (recirculation)	Cooling Water (from cooling tower)	Cooling Water (to cooling tower)
Temperature (°C)	32	25	36	30	34
Pressure (bar)	3,46	2,97	3,46	2,97	2,97
Vapor Frac	0	0	0	0	0
Mole Flow (kmol/hr)	14272,01	349,70	39208,81	39910,56	39910,56
Mass Flow (kg/hr)	273000	6300	750000	719000	719000
Volume Flow (cum/hr)	281,01	6,34	775,21	726,91	729,78
Enthalpy (MMBtu/hr)	-3879,74	-94,69	-10647,82	-10793,59	-10782,95
Mole Flow (kmol/hr)					
WATER	13789,96	349,70	37884,51	39910,56	39910,56
SUCRO-01	7,98		21,91		
ETHAN-01	474,07		1302,39		
CARBO-01	0,00				

Sugar cane is predominantly produced in temperate and tropical regions of the world where, during the sugar cane season, the ambient wet bulb temperatures can be high. For example, typical wet bulb temperature in Brazil during the sugar and ethanol production season may be around 30° C.

5 As a result, the cooling water from the cooling towers can be 30° C or higher.

Figure 6 shows the entering and leaving streams to and from the heat exchanger employed in a typical sugar mill to control the temperature of the fermenter. Table 2 shows the size, temperature and enthalpy of the streams entering and leaving the heat exchanger. The net energy exchanged in the
10 heat exchanger for this example is 10,640 MM Btu/hr. It can also be seen that the temperature of the fermenter can be no lower than 32° C.

Table 2

Ethanol Mill Cooling Fermentation					
Stream ID		1 (Wine from fermenter)	2 (Wine to Fermenter)	4 (cooling water from cooling tower)	5 (water to Cooling tower)
Temperatura	C	36,0	32,1	30,0	34,0
Pressure	bar	3,46	3,46	2,97	2,97
Vapor Frac.		0,000	0,000	0,000	0,000
Mole Flow	Kmol/hr	39208811	39208811	39919565	39910565
Mass Flow	kg/hr	750000,000	750000,000	719000,000	719000,000
Volume Flow	cum/hr	775,208	772,056	726,908	729,777
Enthalpy	MMBtu/hr	-10647,819	-10658,460	-10793,591	-10782,951
Mole Flow	Kmol/hr				
Water		37884,507	37884,507	39910,565	39910,565
Sucro-01		21,911	21,911		
Ethan-01		1302,393	1302,393		
Carbo -01					

Example 2

This example shows the energy used in separating ethanol from water in the distillation train of a typical sugar mill ethanol plant.

- 5 According to Table 1 the energy and water needed to separate the water from ethanol at the distillation column are:

Energy: 151.2 MMBtu/hr;

Water: 1500000 kg/h.

10 Example 3

This example shows the improvement in ethanol yield possible if the fermenter can be cooled to 30° C.

- Dedini S/A, Sao Paulo, Brazil evaluated the advantages of cooling the ethanol fermentation process to temperatures below 32° C. The study
15 was carried out on a semi industrial scale fermentation process comprising a 100 m³ fed batch fermenter, a lithium bromide absorption chiller and 315 m³/hr evaporative cooling tower. Results from the study were published by Oliverio et. al., in the Proceedings of the International Society of Sugar Cane Technology (Vol. 27, 2010). In this study the fermentation unit was
20 run at different temperatures at and below 32° C and its effect was evaluated by measuring a number of dependent variables including the concentration of ethanol in the fermentation broth and the total yield of ethanol from the plant.

- Table 3 shows that ethanol yields in the plant were improved from
25 85.05% to 86.79% when the temperature of the fermenter was reduced from 32° C to 30° C.

Table 3

Temperature	Fermentation yields (%)
28	84.02
30	86.79
32	85.05

Example 4

This example shows the size of a chiller and the additional heat exchange needed to cool the fermenters in order to improve ethanol yield of the plant that produces 90,000 m³ of ethanol per year.

As was previously presented in this invention, reducing the temperature in the fermenter to 30° C or lower can have a significant impact on the ethanol yields, quantity of stillage generated and the energy used for ethanol water separation. In Example 1, it was shown that by using water from cooling towers, the temperature of the sugar must being recycled back to the fermenter can only be cooled to 32° C.

In order for the same stream to be cooled to 30° C, a chiller will need to be installed at the ethanol plant. Figure 7 shows the flow diagram for a chiller and the heat exchanger used to cool the fermenter. Table 4 shows the size, temperature and enthalpy of the streams when a chiller is installed and the heat load required for the chiller.

Table 4

	Wine 1	Wine 2	Chilled 1	Chilled 2
Temperature (°C)	36	30,00	20	25
Pressure (bar)	3,4649125	3,46	2,97	2,97
Vapor Frac	0	0	0	0
Mole Flow (kmol/hr)	39208,8106	39208,81	49402,51	49402,51
Mass Flow (kg/hr)	750000	750000	890000	890000
Volume Flow (cum/hr)	775,207694	770,42	891,10	895,41
Enthalpy (MMBtu/hr)	-10647,819	-10664,02	-13393,17	-13376,97
Mole Flow (kmol/hr)				
WATER	37884,5069	37884,51	49402,51	49402,51
SUCRO-01	21,9105996	21,91		
ETHAN-01	1302,3931	1302,39		
CARBO-01				

20

Example 5.

Example 3 showed the increase in ethanol yield if the fermentation process could be run at 30° C. This example shows additional savings in

energy and reduction in waste stillage if the fermentation process can be cooled to 30° C.

It has been shown (Oliverio et al, Proc. Int. Soc. Sugar Cane Technol., Vol. 27, 2010) that if a chiller can be installed in a sugar mill ethanol plant so as to allow the fermentation process to run at temperature at or below 30° C, the sugar concentration in the fermenter can be increased allowing for a) higher ethanol concentration in the fermenter , b) lower water usage in the ethanol plant, c) lower energy usage in the ethanol water distillation process and d) lower energy usage for the distillation process. Table 5 shows the effect of increasing the ethanol concentration in the fermenter from 8% to 15%. If the fermenter can be run at ethanol concentration of 11.98 % (12%), Table 5.1 shows that stillage production can be reduced by 34% by volume and stream required for the distillation step can be reduced by 23% by weight.

15

Table 5

Indicators	Data				
% Ethanol in the wine			0	1	5
Volume of stillage generated (L/L EtOH)	0.6	.1			
Water circulated in the fermentation (L/L EtOH)	9.9	00	00	01	7.2
Steam consumption for distillation (kg/ L EtOH)	.6	.36	.16	.99	.5
Fermentation time (hours)	.1	.06	0.6	1	5
Ethanol production per batch (1000 kg)	9.8	6	2.8	9.4	6.3
Specific steam consumption (kg/1000 kg of EtOH)	54	33	16	02	39
Energy available for Co-generation (kWh/tc)	8.2	9.7	1	2.2	9.5

Examples 6 and Figure 8 are presented to demonstrate the energy, raw materials and equipment requirements in an organic aerogel manufacturing process that is set up as a standalone unit without the advantage of energy and material integration with a fermentation based manufacturing process. Aerogels of both inorganic and organic compositions are well known. See, for example, the Aerogel Handbook (Editors Leventis and Koebel, 2011, Springer) and Aerogels (Hüsing and Schubert, Ullman's Encyclopedia of Industrial Chemistry, 15 Dec 2006 DOI: 10.1002/14356007.c01_c01.pub2). All aerogel processes requiring supercritical extraction will benefit from integration with a fermentation process. But in order to demonstrate the advantages of an integrated process all of the examples presented hereafter assume an aerogel manufacturing plant that produces an organic aerogel formed by the reaction between phenol and formaldehyde. The size of the aerogel manufacturing plant is assumed to be such that it produces 90,000 m³ of aerogel/year.

A flow sheet for a typical phenol formaldehyde aerogel process is shown Figure 8. Phenol and formaldehyde are reacted in an aqueous solution, in the presence of a base catalyst to form a low molecular weight phenol formaldehyde resin precursor. The precursor in dilute form is further reacted in the presence of an acid catalyst to form a hydrogel. The water in the hydrogel is removed by washing with the help of another solvent such as ethanol. The resulting phenol formaldehyde gel rich in ethanol is transferred to a super critical extraction unit where the ethanol is removed from the gel thus producing a phenol formaldehyde aerogel.

Example 6

This example shows the energy used to convert an organic phenol formaldehyde solution to a hydrogel in a phenol formaldehyde aerogel manufacturing process.

As has been discussed previously, the formation of a gel is an important precursor in the manufacture of aerogel. Figure 8 and Figure 9

show a flow sheet for the gelation process used for this example. Phenol and dilute formaldehyde solution are reacted in the presence of acid catalyst to form a crosslinked hydrogel. A particle formation process may be integrated with the gelation process in order to convert the hydrogel
5 being formed into discrete gel beads. In order to facilitate the gelation process, energy needs to be supplied to the gelation process. Depending on the chemistry used and the rate of the gelation reactions, gelation may be carried out over a wide range of temperature. However, for this example gelation is assumed to be carried out at 65° C. Thus 4550 kg/hr of
10 condensate steam at 85° C is supplied to heat the gelation vessel.

Example 7

This example demonstrates the distillation process and the energy needed to concentrate and recycle the ethanol stream back to the washing
15 unit.

After the water washing step, the water ethanol stream exiting the washing unit needs to be separated so that concentrated ethanol can be recycled back to the water washing step. Figure 10 shows a distillation column used to separate the water and concentrate the ethanol stream.
20 Table 6 shows the composition and enthalpy of the different streams entering and leaving the distillation column. Aspen model based calculations show that distillation column comprising 12 plates and running at a reflux ratio of 2.5 is required to achieve the desired separation of ethanol from water. In order to accomplish this separation 32.3 MMBtu/hr of
25 energy is required to cool the condenser and 32.4 MMBtu/hr of energy is needed in for the reboiler. The net result of the separation is 1230 kg/hr of stillage from distillation column bottom.

Table 6

	ETOH96	ETOH99	STILLAGE
Temperature C	30,00	79,25	103,26
Pressure bar	1,50	1,05	1,70
Vapor Frac	0,00	0,00	0,00
Mole Flow kmol/hr	293,38	249,40	43,98
Mass Flow kg/hr	12775,00	11475,34	1299,66
Volume Flow cum/hr	15,98	15,67	1,69
Enthalpy MMBtu/hr	-77,20	-63,84	-11,43
Mass Flow kg/hr			
WATER	475,68	9,24	466,44
ETHAN-01	12299,32	11466,09	833,23
Mass Frac			
WATER	0,04	0,00	0,36
ETHAN-01	0,96	1,00	0,64
Mole Flow kmol/hr			
WATER	26,40	0,51	25,89
ETHAN-01	266,98	248,89	18,09

Example 8

5 This example shows the energy required to prepare the liquid CO₂ needed for supercritical extraction in the aerogel manufacturing process.

For a 90,000 m³ aerogel plant about 10,267 Kg/hr of supercritical carbon dioxide would be needed for the supercritical extraction of ethanol. In a standalone aerogel plant, liquid CO₂ will need to be shipped from an external source. Liquid CO₂ is usually stored and shipped at 24 atm and -13° C in special high pressure vessels.

At the aerogel plant liquid CO₂ will be compressed and heated to 85 atm and 30° C to reach supercritical conditions for CO₂. The process flow sheet for heating and compressing the liquid CO₂ is shown in Figures 11A, 11B, and 12, and the enthalpy associated with each stream is presented in Table 7 (with the assumption of entropy across the compressor).

Based on thermodynamic calculations, the total energy required to heat up the liquid carbon dioxide from -13 °C to 30 °C would be around 3 MMBtu/hr.

In the process of purchasing liquid CO₂ a cooling system is needed to keep the temperature at -13° C during transportation and storage. Liquid transportation and storage in the integrated process is not required.

- During the supercritical liquid extraction a 1200 kg/hr of
- 5 decompression to atmosphere is required but in the integrated process this decompression can be routed for the first stage of the compressor and only a small amount of CO₂ is required to compensate the process losses.

Table 7

	CO ₂ make-up	CO ₂ (drying)	CO ₂ (1)	CO ₂ (2)	CO ₂ (3)	Liquid	CO ₂ (4)	CO ₂ (5)
Temperature (°C)	35	35,00	80,60	35,00	35,00	35,00	5,00	6,22
Pressure (bar)	1,11	25,00	50,00	50,00	49,00	56,91	49,00	69,66
Vapor Frac	1,00	1,00	1,00	1,00	1,00	0,74	0,00	0,00
Mole Flow (kmol/hr)	2,80	2,80	238,51	238,51	238,51	2,80	238,51	238,51
Mass Flow (kg/hr)	120	120,00	10496,55	10496,55	10496,55	119,77	10496,55	10496,55
Volume Flow (cum/hr)	64,59	64,59	140,30	122,21	124,71	0,97	11,69	11,80
Enthalpy (MMBtu/hr)	-0,26	-0,26	-22,29	-22,40	-22,40	-0,26	-23,00	-22,99
Mole Flow (kmol/hr)		0,00						
CARBON DIOXIDE	114	114,00	10496,47	10496,47	10496,47	113,77	10496,47	10496,47
WATER	2,4	2,40	0,03	0,03	0,03	2,40	0,03	0,03
ETHANOL	3,6	3,60	0,04	0,04	0,04	3,60	0,04	0,04
ETHANOL								

	CO ₂ (6)	Cooling Water (1)	Cooling Water (2)	Chilled Water (1)	Chilled Water (2)
Temperature (°C)	23,00	30,00	30,00	-0,045	-10,00
Pressure (bar)	69,66	3,00	3,00	2,975	2,97
Vapor Frac	0,00			0,000	0,00
Mole Flow (kmol/hr)	238,51	715,52	1192,53	2170,655	2170,66
Mass Flow (kg/hr)	10496,55	31489,64	52482,73	100000,000	100000,00
Volume Flow (cum/hr)	14,05	32205,16	53675,26	120,952	119,38
Enthalpy (MMBtu/hr)	-22,76	-68,74	-114,48	-145,457	-146,06
Mole Flow (kmol/hr)					
CARBON DIOXIDE	10496,47			0,000	0,00
WATER	0,03	0,09	0,15	0,000	0,00
ETHANOL	0,04			100000,000	100000,00
ETHANOL					

Example 9

As of 2011, without the deployment of new merchant CO₂ plants, there are about 36 standing CO₂ plants which are only fed by ethanol by-product raw gas. This represents about 32% of the total number of fermentation plants serving the merchant sector. The total number of merchant CO₂ plants is around 111 in the United States. Further, numerous additional CO₂ plants are under consideration, or slated to be built alongside future of existing ethanol ventures. (see reference at site: <http://www.biofuelsdigest.com/bdigest/2011/11/23/carbon-dioxide-applications-%E2%80%93-a-key-to-ethanol-project-developments/>)

A 90,000 m³ ethanol plant will generate about 85,000 ton of CO₂ that can be liquefied and sold in the market with minor investments and operational costs.

15

The examples that follow show the advantages of lower energy and material usage and reduced investment in process equipment when an ethanol fermentation process is integrated with an aerogel manufacturing process. For the examples that follow, an integrated ethanol aerogel process is assumed to produce 90,000 m³ of ethanol per year and 90,000 m³ of aerogel per year. Thus the integrated process is assumed to produce the same amount of ethanol and aerogel as was assumed above for ethanol and aerogel plants running separately without the advantage of energy, material and process equipment integration.

25

Example 10

In Example 3 the advantage of cooling the fermentation process in a standalone sugar mill ethanol plant was presented. In order to accomplish the desired cooling of the fermentation process, Example 4 showed the size of a separate refrigeration unit required and the energy used to operate the refrigeration unit. This example shows that the same desired cooling of the fermentation process can be achieved by energy and

30

material integration of process streams in the ethanol and aerogel process without the operation of a separate refrigeration unit with considerable savings in energy cost.

Figure 13 shows a simplified process diagram highlighting the pertinent process streams involved in cooling the fermentation vessel in the ethanol plant. In this example the use part of the water from the cooling tower (streams 17 and 18) exchanging heat (through the heat exchanger HEX3) with the liquid carbon dioxide (streams 9, 16 and 19) that is pumped to be used in the supercritical extraction is shown. The temperature for pumping the liquid carbon dioxide is 5 °C and the temperature required for the supercritical extraction is 30 °C so this temperature difference can be used to cool down the cooling water. This water will be used to complement the fermentation cooling.

Table 8

	LIQCO2-1	LIQCO2-2	LIQCO2-3	WATER1	WATER2
Temperature C	-5	-3,2464858	29	30	25,0003864
Pressure bar	55	84,369775	84,369775	2,00E-05	2,00E-05
Vapor Frac	0	0	0	1	1
Mole Flow kmol/hr	336,74318	336,74318	336,74318	16652,5305	16652,5305
Mass Flow kg/hr	14820	14820	14820	300000	300000
Volume Flow cum/hr	15,5085239	15,6643155	22,885954	2,10E+10	2,06E+10
Enthalpy MMkcal/hr	-32,607566	-32,585099	-31,917163	-961,13407	-961,80201
Mass Flow kg/hr					
CARBO-01	14820	14820	14820	0	0
WATER	0	0	0	300000	300000
Mass Frac					
CARBO-01	1	1	1	0	0
WATER	0	0	0	1	1
Mole Flow kmol/hr					
CARBO-01	336,74318	336,74318	336,74318	0	0
WATER	0	0	0	16652,5305	16652,5305

According to Oliverio et al (op cit.) with this integration the following savings can be obtained:

Ethanol mill savings:

34% of dilution water (for 90,000 m³ of ethanol 324,000 m³ of water);

34% of stillage (for 90,000 m³ of ethanol 324,000 m³ of stillage);
23% of steam (for 90,000 m³ of ethanol 54,000 ton of steam).

Aerogel process savings:

- 5 Cost and logistics for liquid carbon dioxide (carbon dioxide is available at ethanol plant)
450 kg/h of saturated steam (heating can be done using condensate instead of steam)
Ethanol supply (ethanol will be used as a catalyst and can be all recovered)
- 10 3 MMBtu/h Energy required to heat CO₂.

Claims

What is claimed is:

- 5 1. An integrated manufacturing process comprising a fermentation process integrated with an extraction process that uses a supercritical fluid.
- 10 2. A integrated manufacturing process comprising:
 - a) fermenting a carbohydrate to produce a fermentation product and gaseous CO₂;
 - b) compressing the gaseous CO₂ to form a supercritical CO₂; and
 - c) using the supercritical CO₂ as an extractant to separate a component from a mixture.
- 15 3. The process of Claim 2 wherein the mixture is a gel.
4. The process of Claim 2 wherein the component is a continuous phase.
- 20 5. The process of Claim 2 wherein separating the component from the mixture forms an aerogel.
6. The process of Claim 2 wherein the fermentation product and the component is ethanol.
- 25 7. The process of Claim 6 further comprising after step b: contacting a hydrogel with the ethanol to remove water from the hydrogel to form the gel.
- 30 8. An integrated manufacturing process comprising:

- 5 a) fermenting a carbohydrate to produce a fermentation product,
 gaseous CO₂ and thermal energy;
 b) forming a supercritical CO₂ from the gaseous CO₂ and the
 thermal energy;
 c) using the supercritical CO₂ as an extractant to separate a
 component from a mixture; and
 d) separating the component from the supercritical CO₂ by
 reducing the pressure to form a liquid phase CO₂.
- 10 9. The process of claim 8 further comprising:
 e) recycling the liquid phase CO₂ by mixing the liquid phase CO₂
 with the gaseous CO₂ in step b).
- 15 10. An integrated manufacturing process comprising:
 a) fermenting a carbohydrate to produce a fermentation product,
 gaseous CO₂, and thermal energy wherein the thermal energy is
 transferred to a cooled water stream forming a heated water
 stream;
 b) compressing the gaseous CO₂ to form a liquid CO₂;
20 c) forming a supercritical CO₂ from the liquid CO₂ and the thermal
 energy from the heated water stream to form a cooled water
 stream;
 d) using the supercritical CO₂ as an extractant to separate a
 component from a mixture;
25 e) separating the component from the supercritical CO₂ by reducing
 the pressure to form a liquid phase CO₂.
- 30 11. The process of claim 10 further comprising recycling the cooled
 water stream from step c) to step a).
12. The process of claim 10 further comprising recycling the liquid
 phase CO₂ from step e) to step b).

13. The process of Claim 8 wherein separating the component from the mixture forms an aerogel.
- 5 14. The process of Claim 10 wherein separating the component from the mixture forms an aerogel.

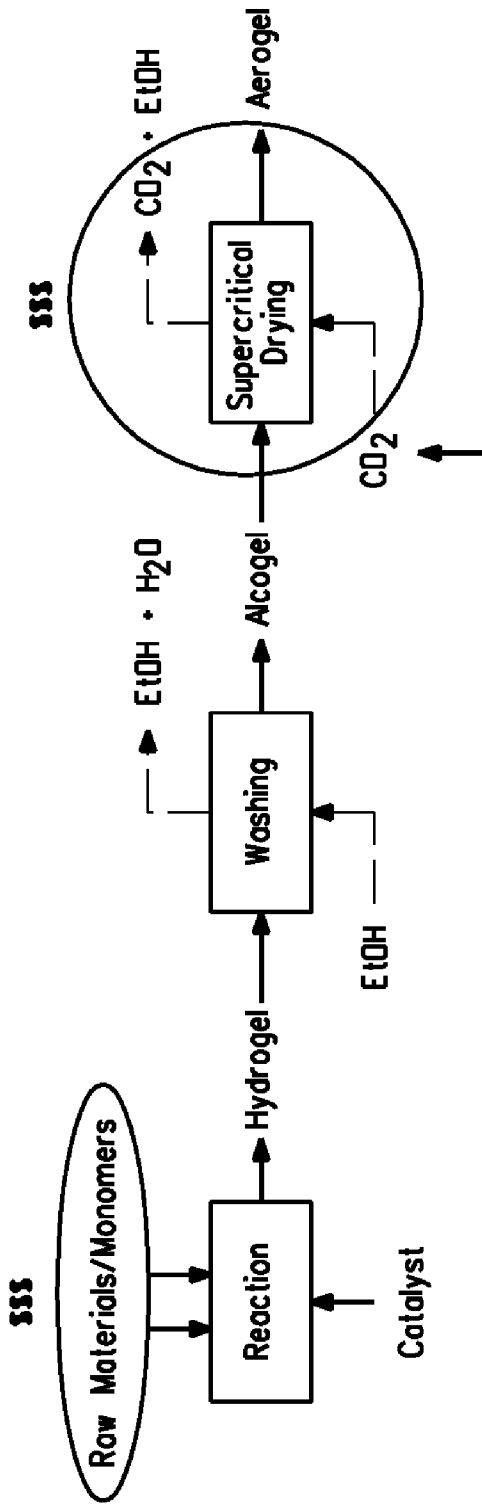


FIG. 1

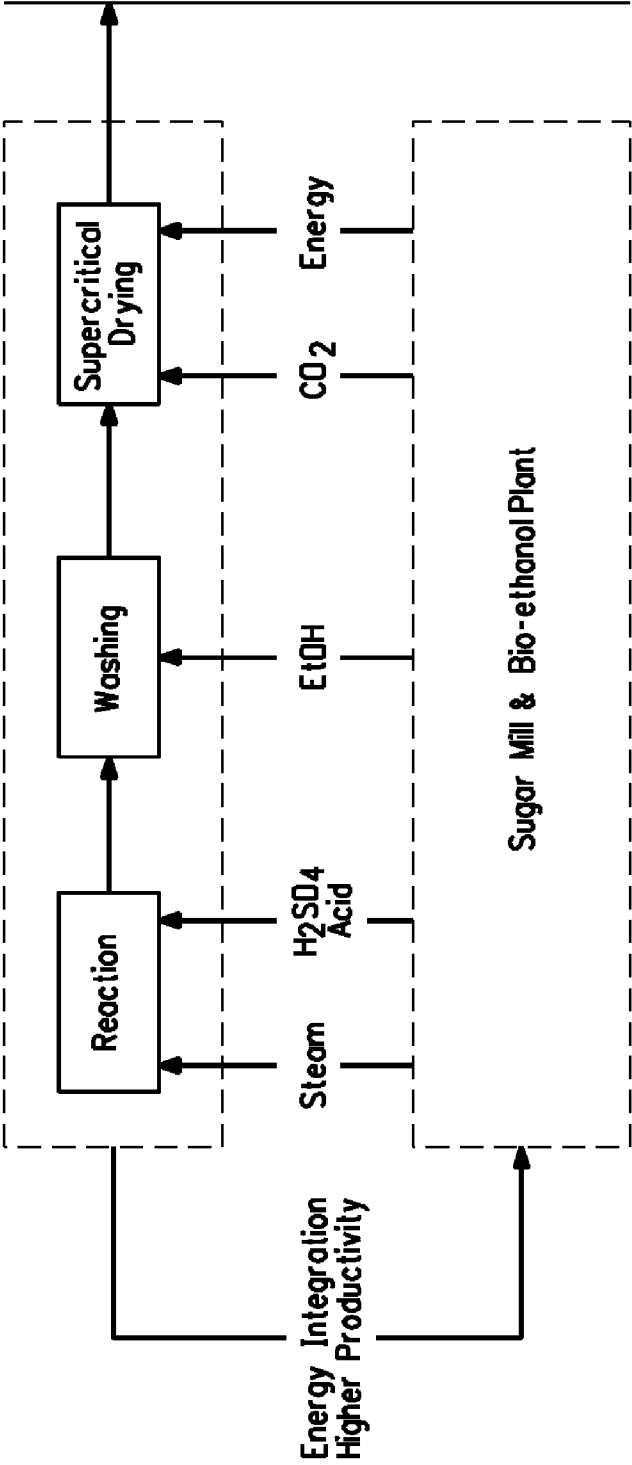


FIG. 2

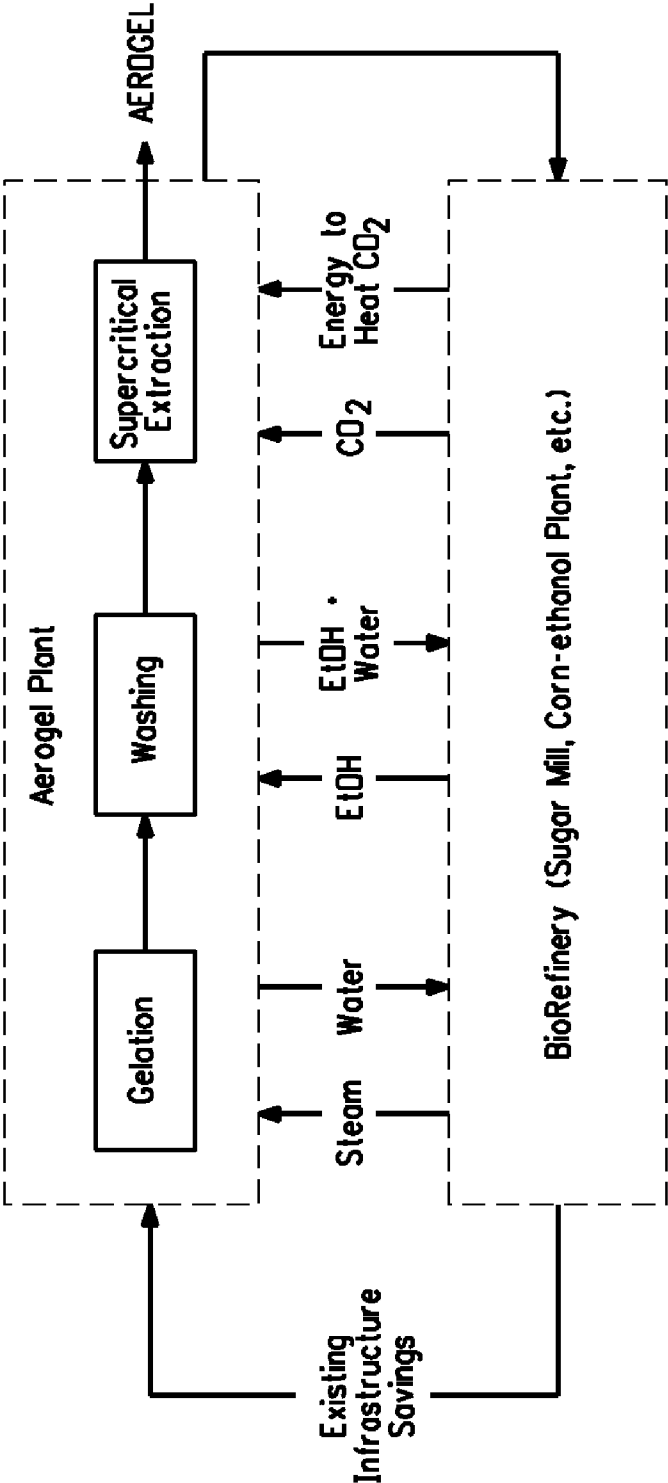


FIG. 3

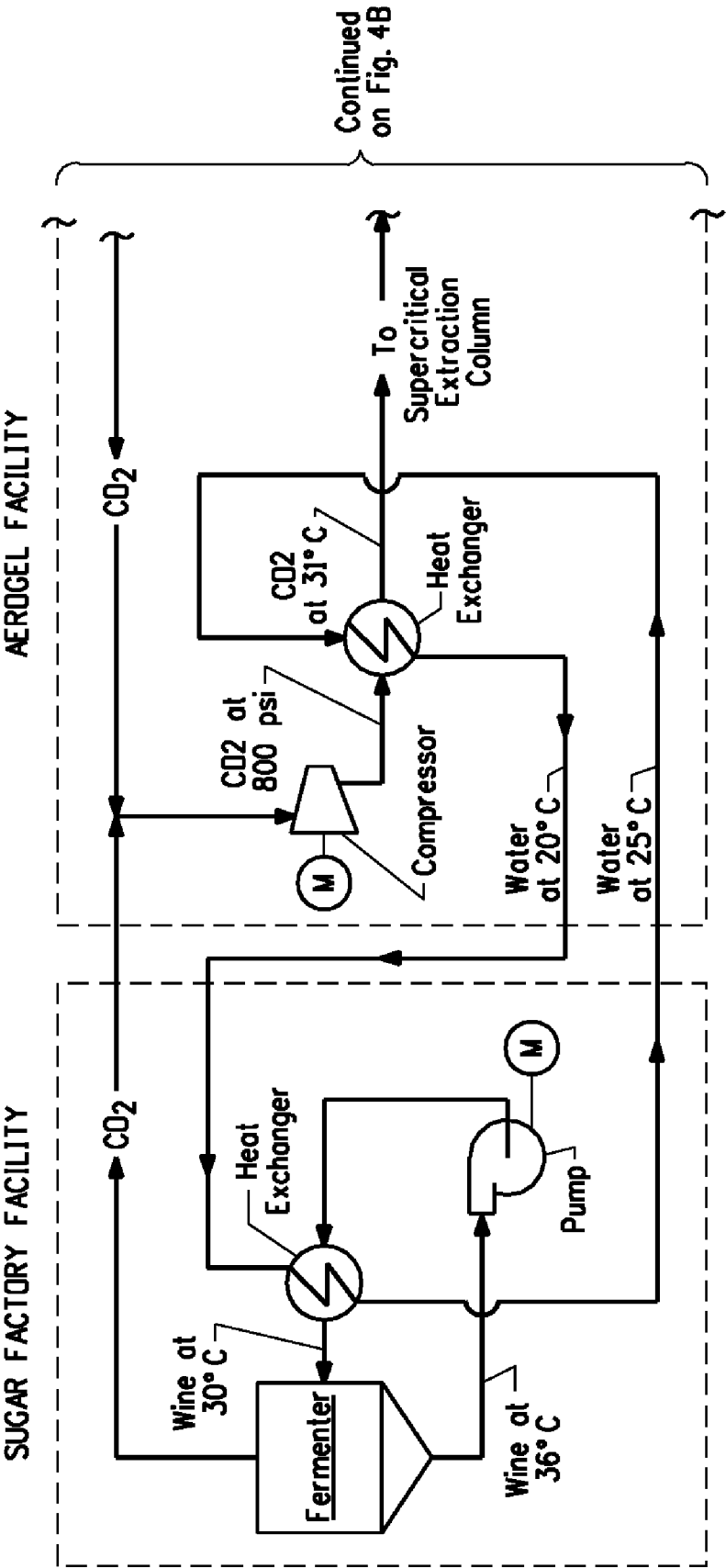


FIG. 4A

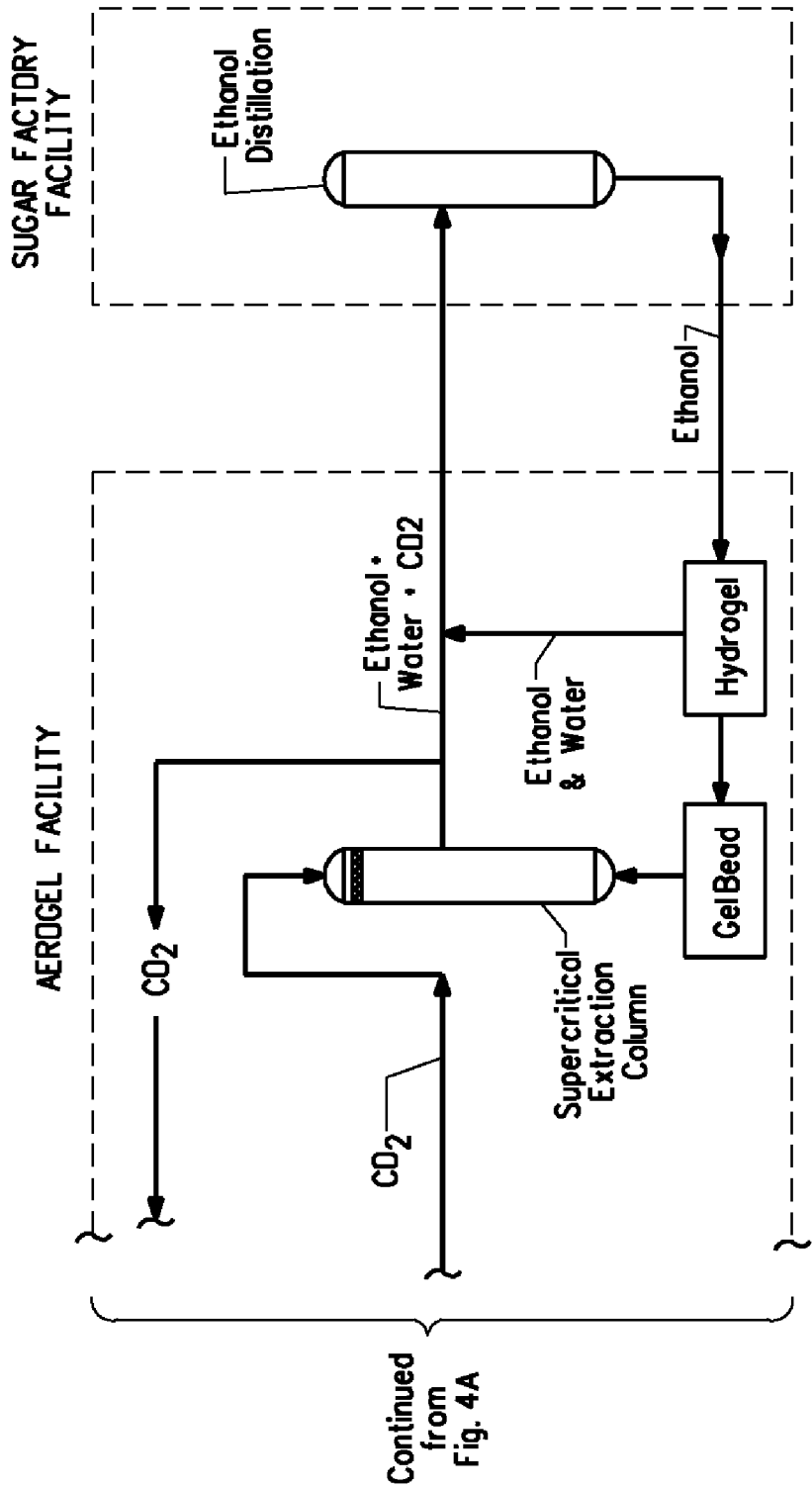


FIG. 4B

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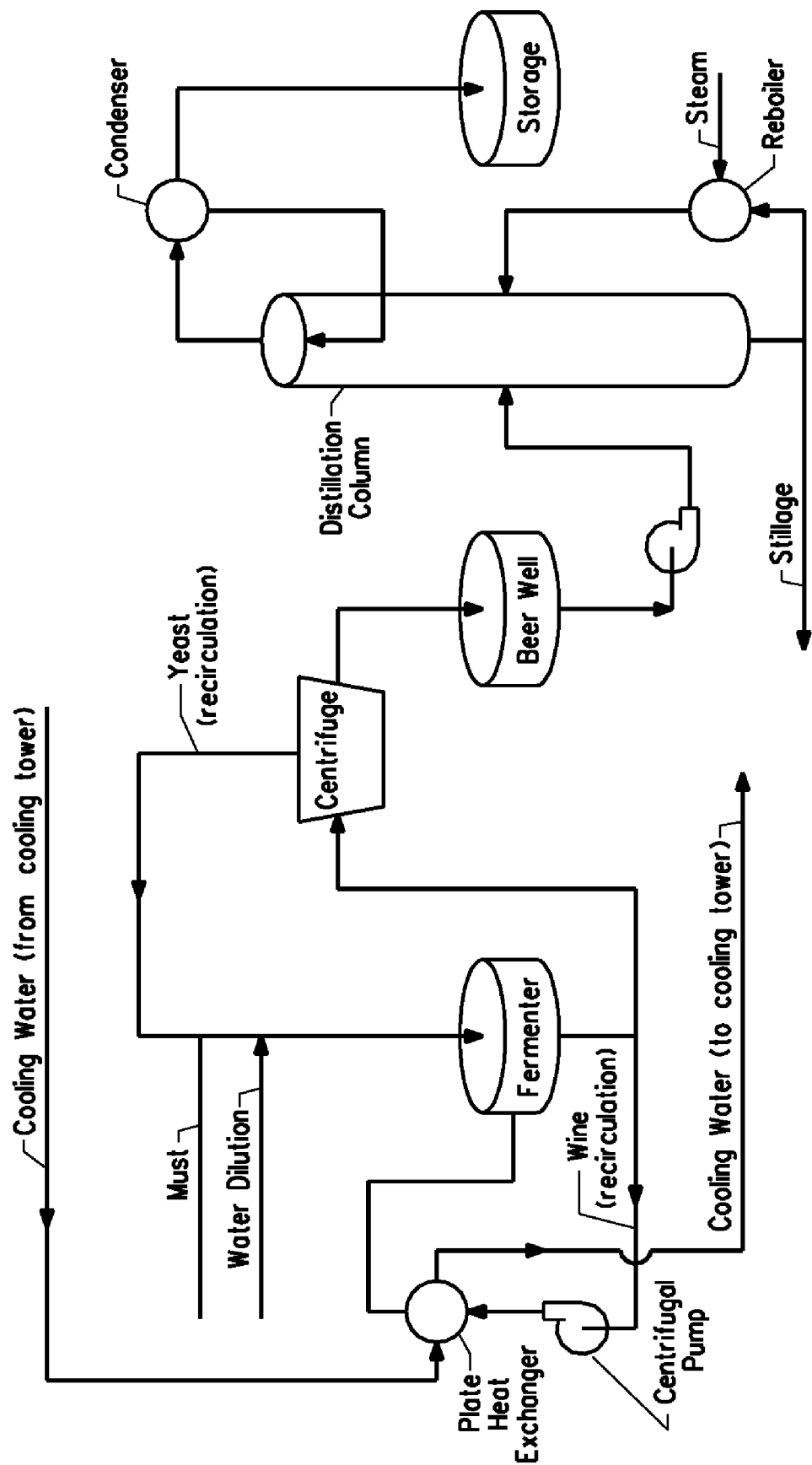


FIG. 5

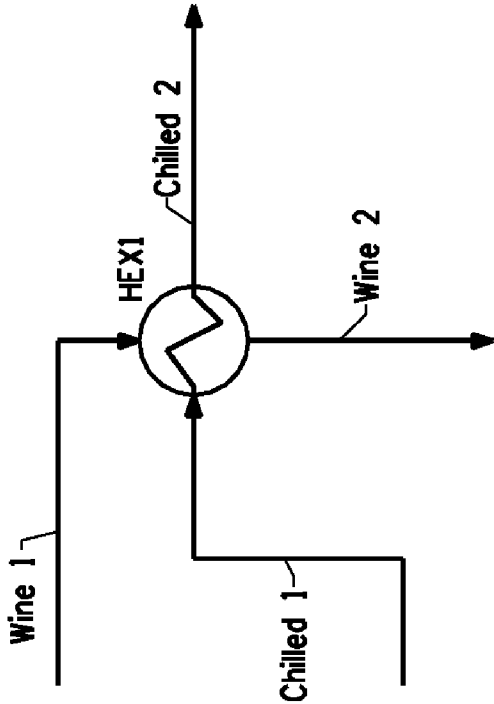


FIG. 7

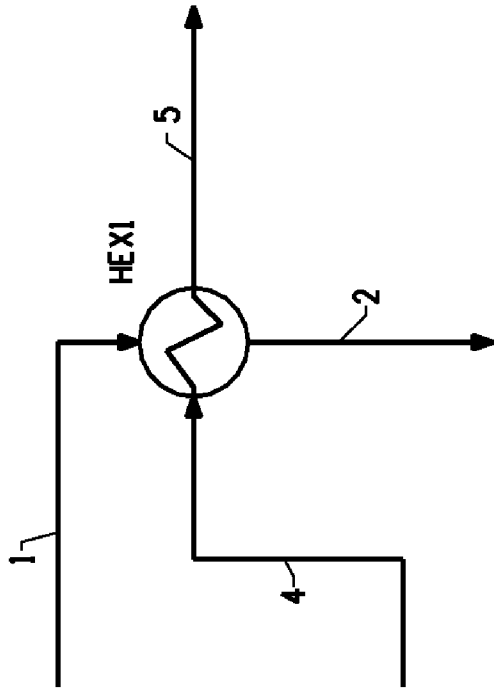
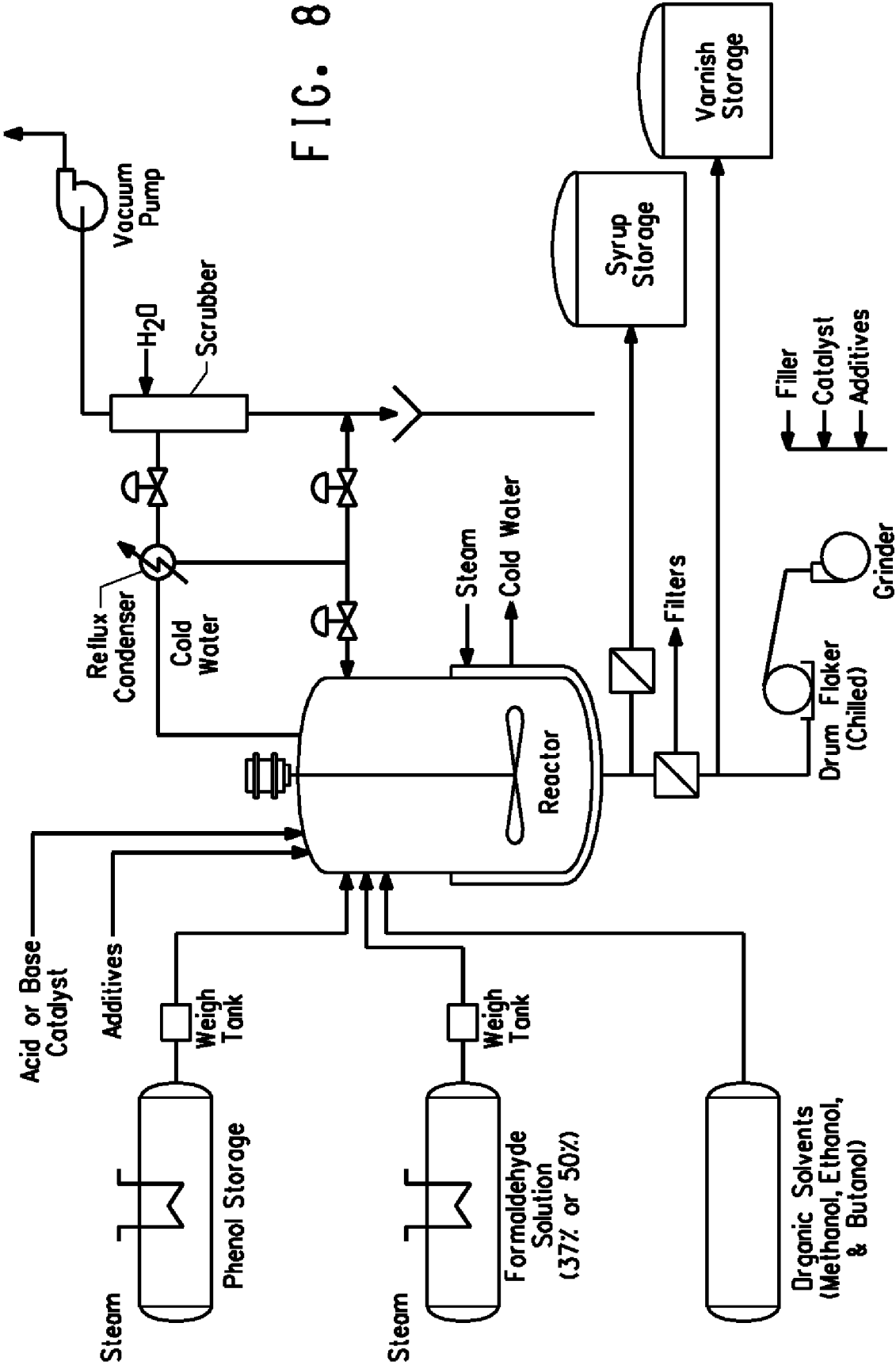


FIG. 6

FIG. 8



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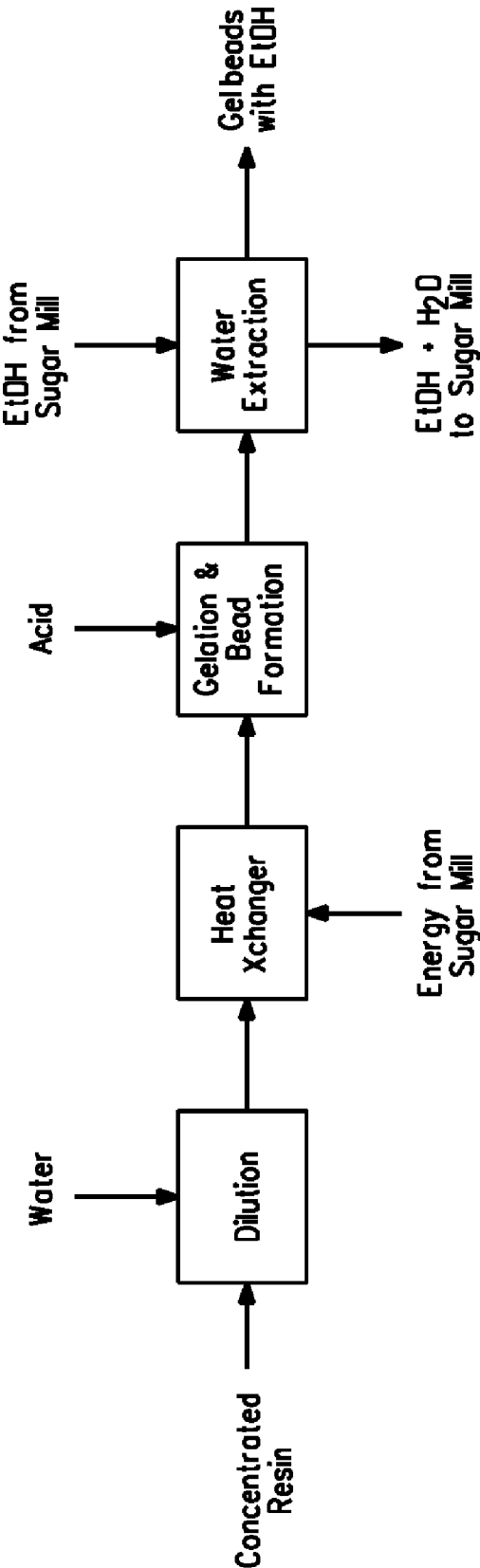


FIG. 9

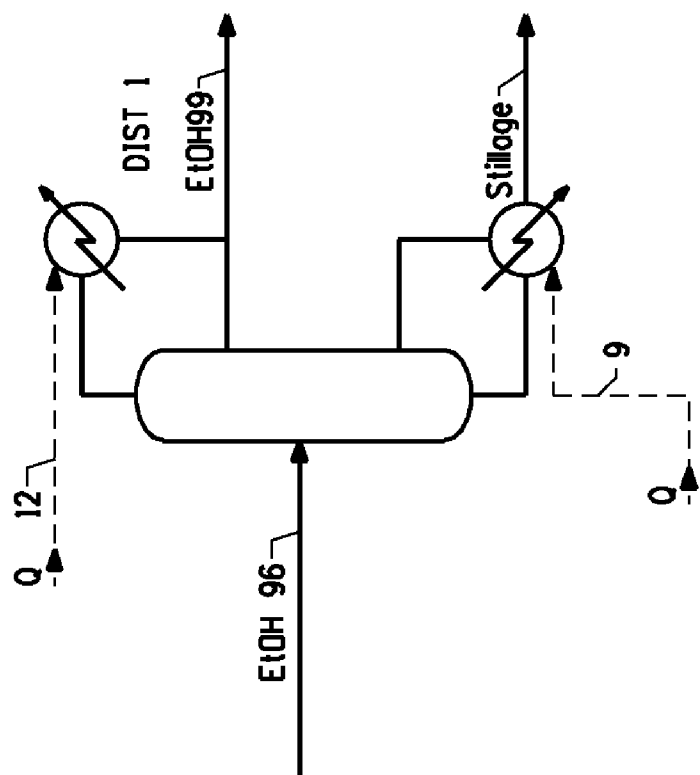
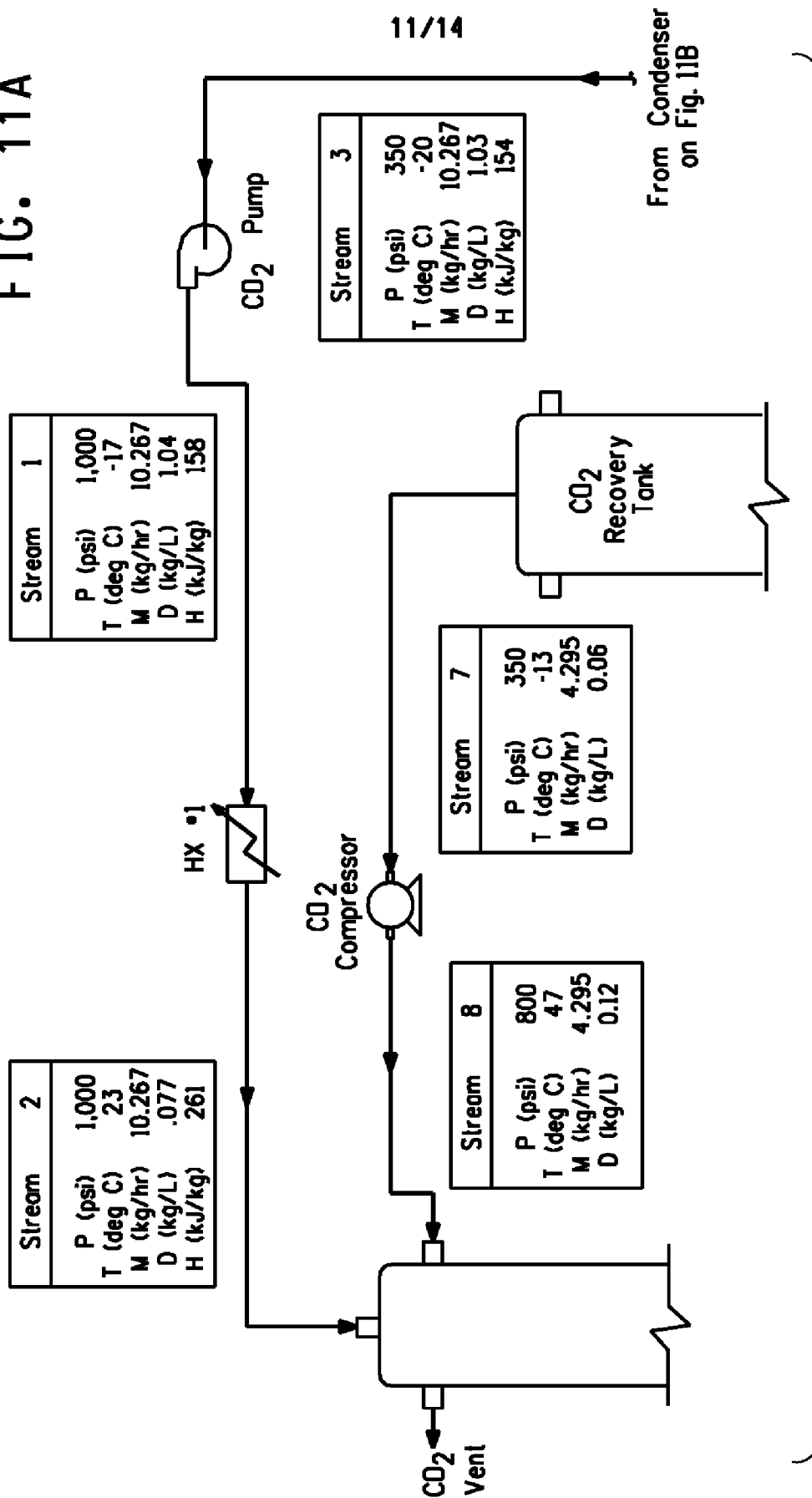


FIG. 10

FIG. 11A



Continued on Fig. 11B

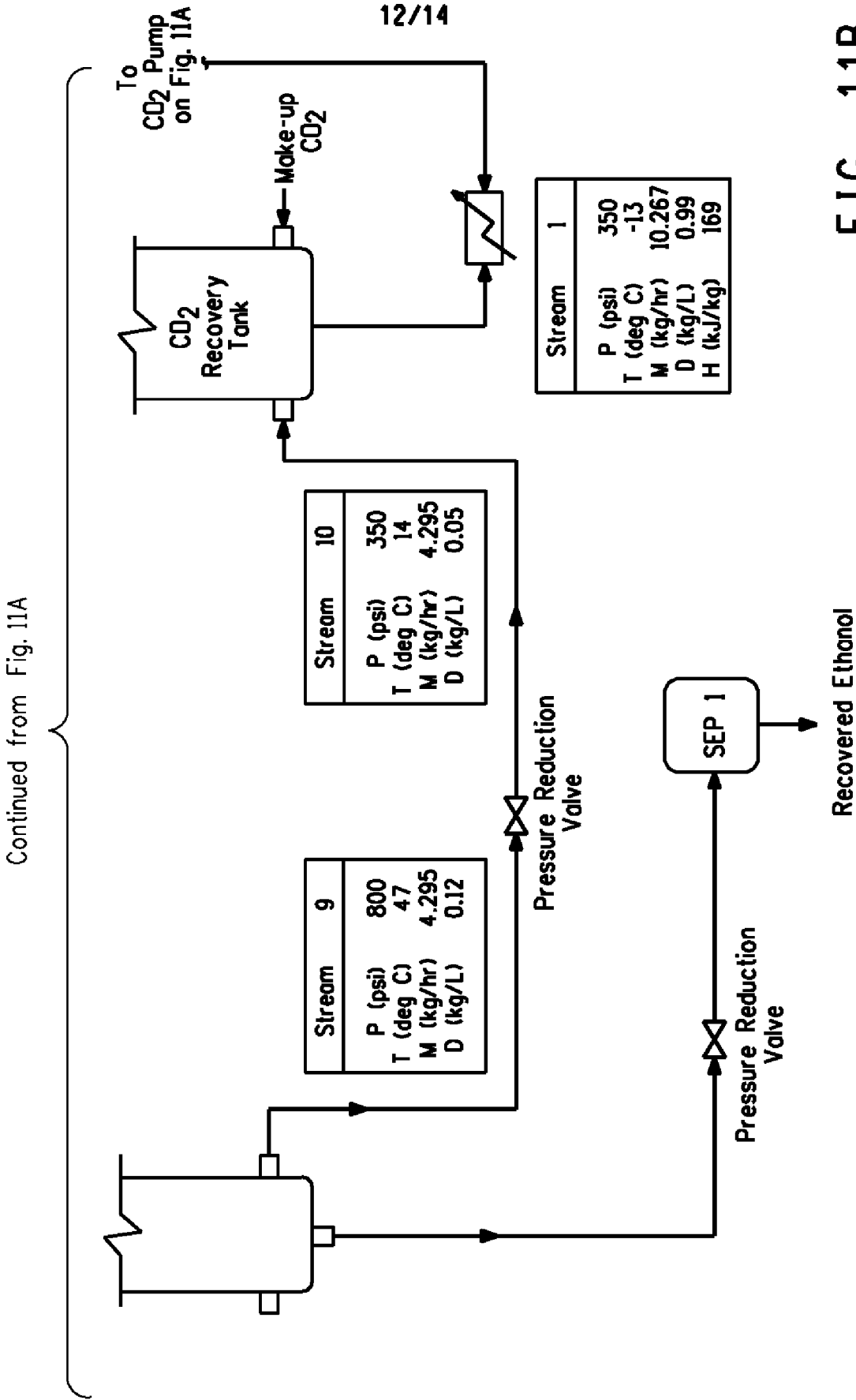


FIG. 11B

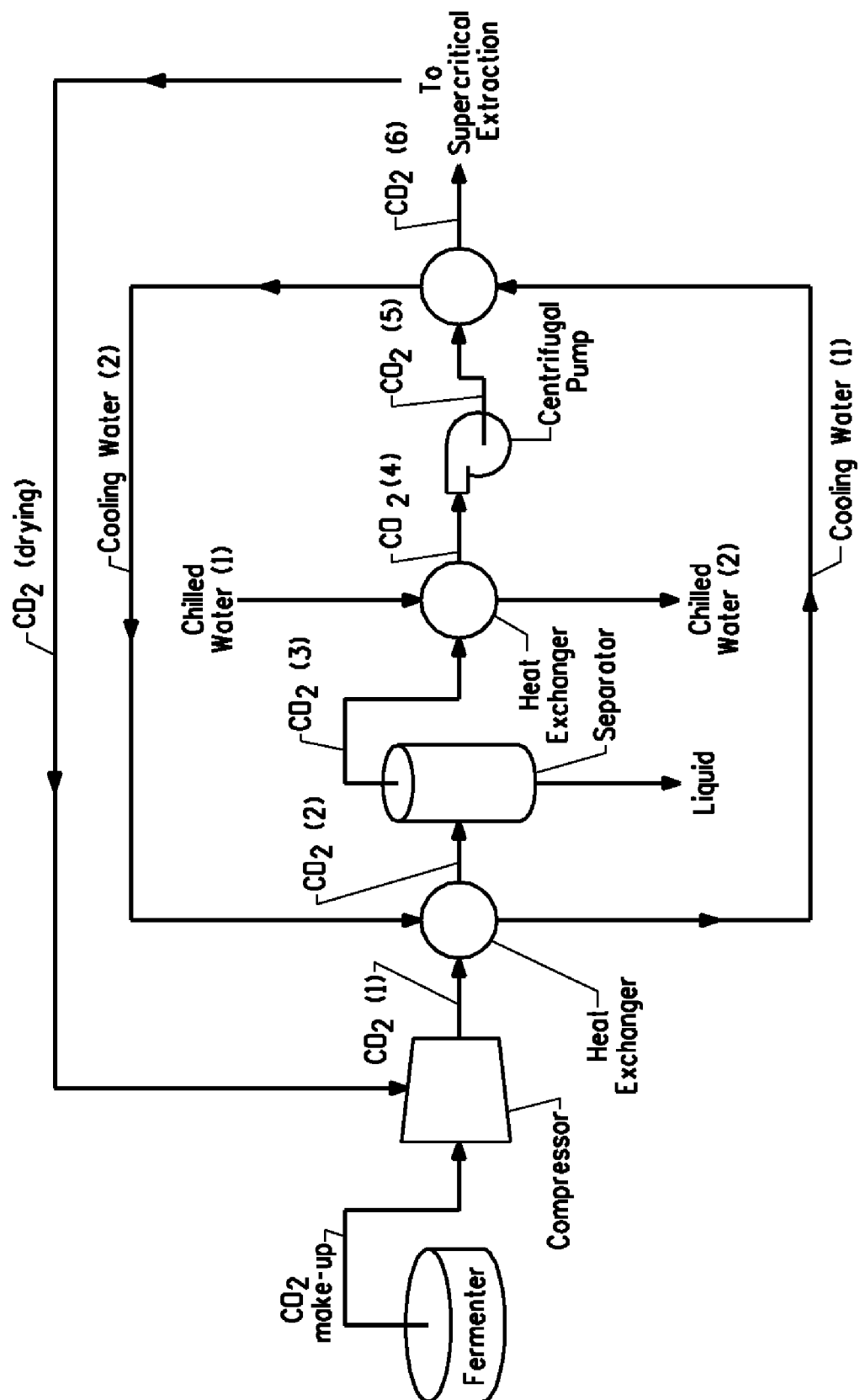


FIG. 12

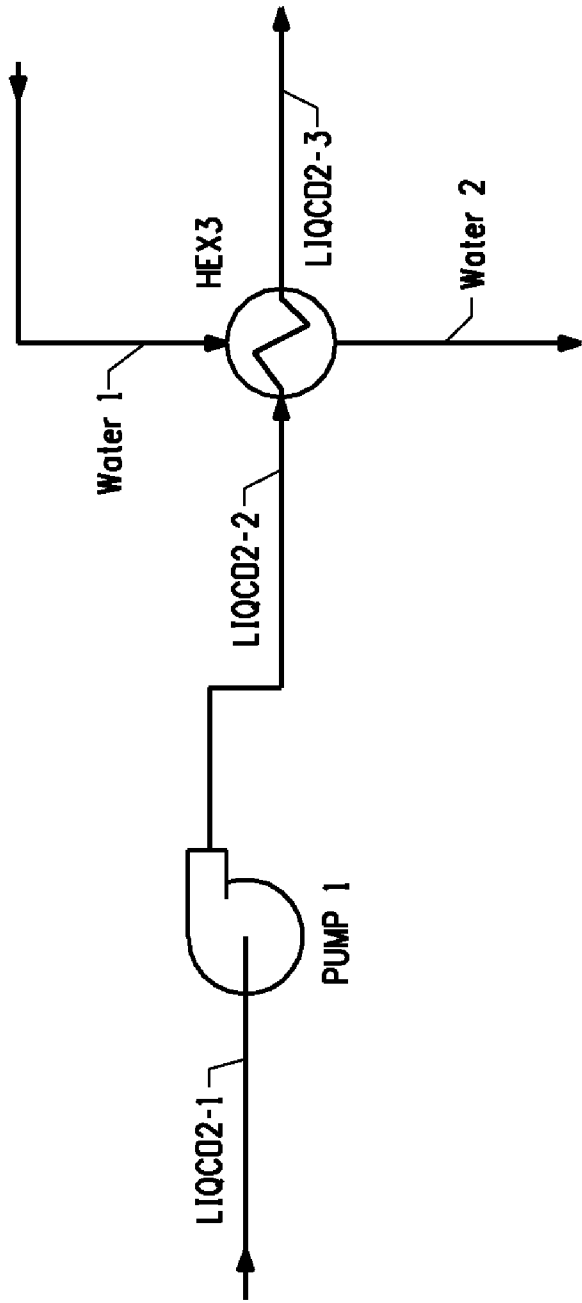


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/056644

A. CLASSIFICATION OF SUBJECT MATTER

INV. C12P7/06 B01J13/00 C12F3/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C12P C12F B01J

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

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

EPO-Internal, WPI Data, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 361 741 A1 (PROCTER & GAMBLE [US]) 31 August 2011 (2011-08-31) [0043]	1,2
X	----- KHOSRAVI-DARANI K; VASHEGHANI-FARAHANI E: "Application of supercritical fluid extraction in biotechnology", CRITICAL REVIEWS IN BIOTECHNOLOGY, vol. 25, 2005, pages 231-242, XP008158772, page 236, column 1, paragraph 5 - page 238, column 1, paragraph 1	1
A	----- WO 2011/021856 A2 (KIM YOUNG-IL [KR]) 24 February 2011 (2011-02-24) the whole document ----- -/-	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

14 December 2012

Date of mailing of the international search report

21/12/2012

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Authorized officer

Schönwasser, D

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/056644

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	SOLEIMANI DORCHEH ET AL: "Silica aerogel; synthesis, properties and characterization", JOURNAL OF MATERIALS PROCESSING TECHNOLOGY, ELSEVIER, NL, vol. 199, no. 1-3, 1 November 2007 (2007-11-01), pages 10-26, XP022409626, ISSN: 0924-0136 the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/056644

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