US 20160003532A1

(19) **United States**
(12) **Patent Application Publication**
Young et al.
(10) **Pub. No.: US 2016/0003532 A1**
(43) **Pub. Date: Jan. 7, 2016**

(54) SYSTEMS AND METHODS FOR RECOVERING CARBON DIOXIDE FROM INDUSTRIALLY RELEVANT WASTE STREAMS, ESPECIALLY ETHANOL FERMENTATION PROCESSES, FOR APPLICATION IN FOOD AND BEVERAGE PRODUCTION

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(21) Appl. No.: **14/752,459**

(22) Filed: **Jun. 26, 2015**

Related U.S. Application Data

(60) Provisional application No. 62/020,883, filed on Jul. 3, 2014.

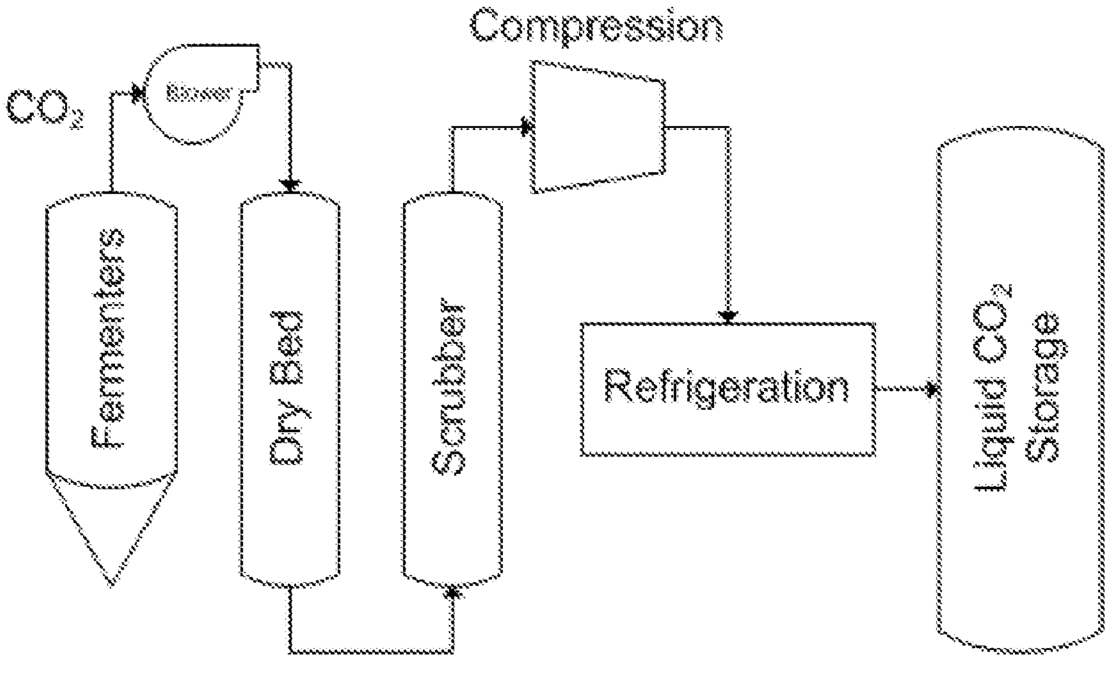
Publication Classification

(51) **Int. Cl.**
F25J 3/02 (2006.01)
F25J 3/08 (2006.01)

(52) **U.S. Cl.**
CPC . ***F25J 3/0266*** (2013.01); ***F25J 3/08*** (2013.01)

(57) ABSTRACT

A system for recovering CO2 via liquefaction and purification from a vented CO2 gas stream comprising a compressor; a dehydrator; a scrubber; a refrigerator having one or more stages; and a separation subsystem adapted to ensure non-condensable gas content in the final product meets industry standards. The liquid CO2 product is of sufficient purity to be used in applications requiring beverage-grade CO2. The system can be utilized as a single-brewery installation to reduce venting from ethanol fermenters to an absolute minimum, produce a high purity liquid CO2 product for use in-process or external sales, and offset the purchasing of expensive, industrial CO2 of inferior purity.



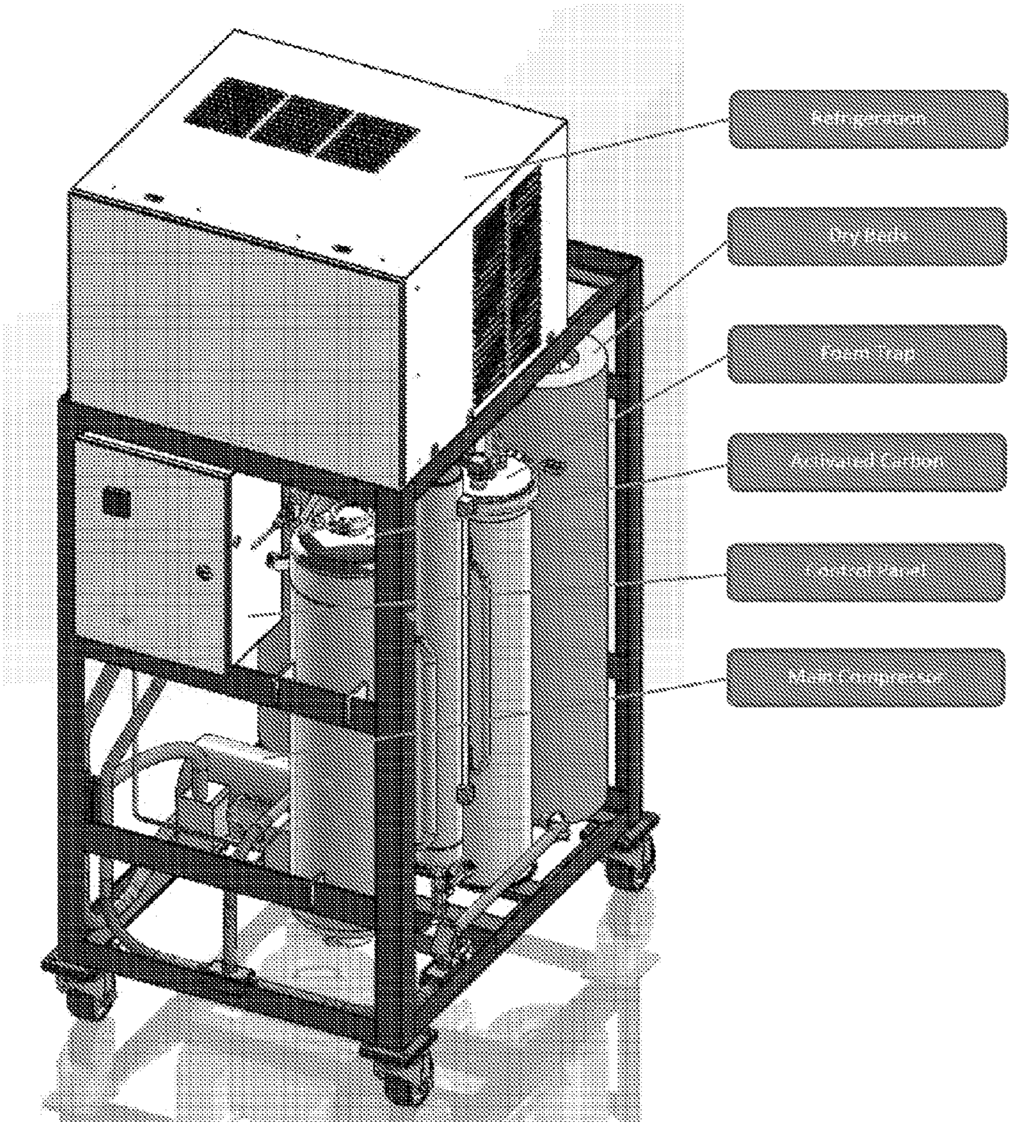

Refrigeration
Dry Beds
Foam Trap
Activated Carbon
Control Panel
Main Compressor

Fig. 1

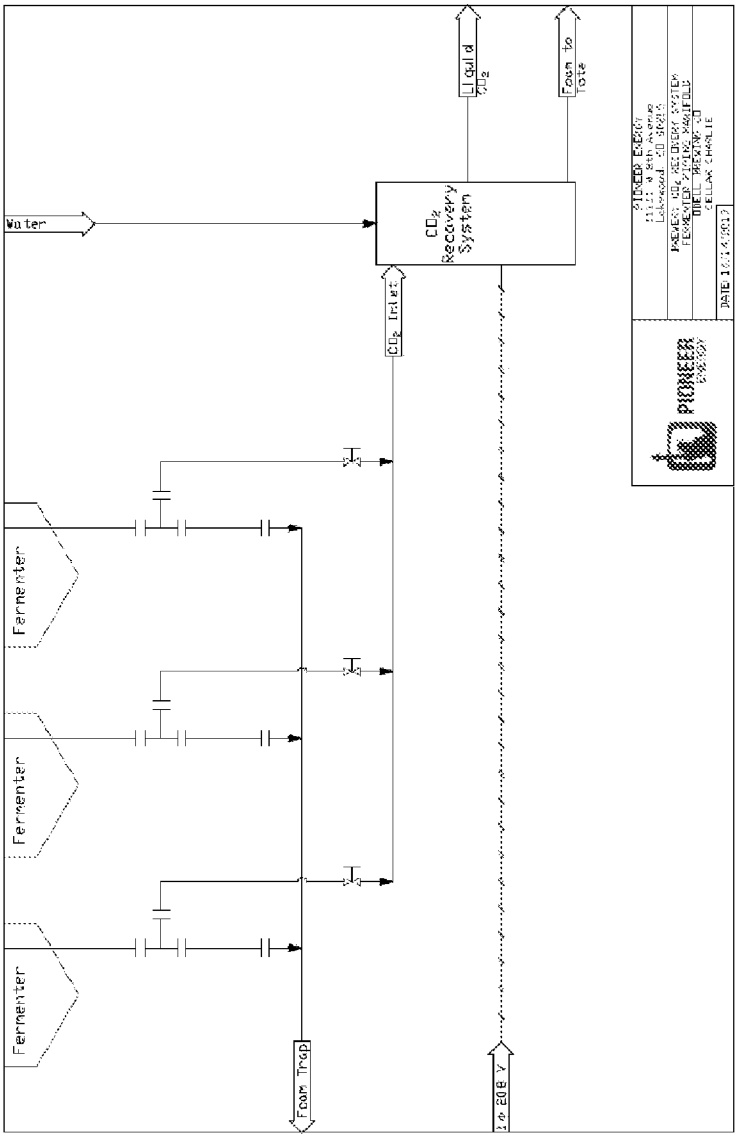

Fermenter
Fermenter
Fermenter
Foam Trap
Water
CO_2 Recovery System
CO_2 Inlet
Liquid CO_2
Foam to Tote
PIONEER ENERGY
Lakewood, CO
BREWERY CO_2 RECOVERY SYSTEM
FERMENTER PIPING MANIFOLD
ODELL BREWING CO
CELLAR CHARLIE
DATE
PIONEER ENERGY

Fig. 2

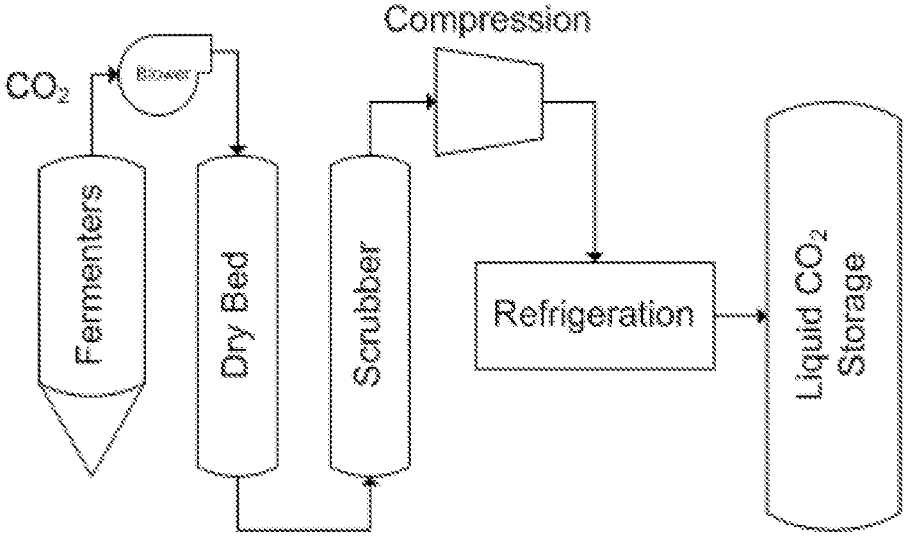

Compression
CO_2
Blower
Fermenters
Dry Bed
Scrubber
Refrigeration
Liquid CO_2 Storage

Fig. 3

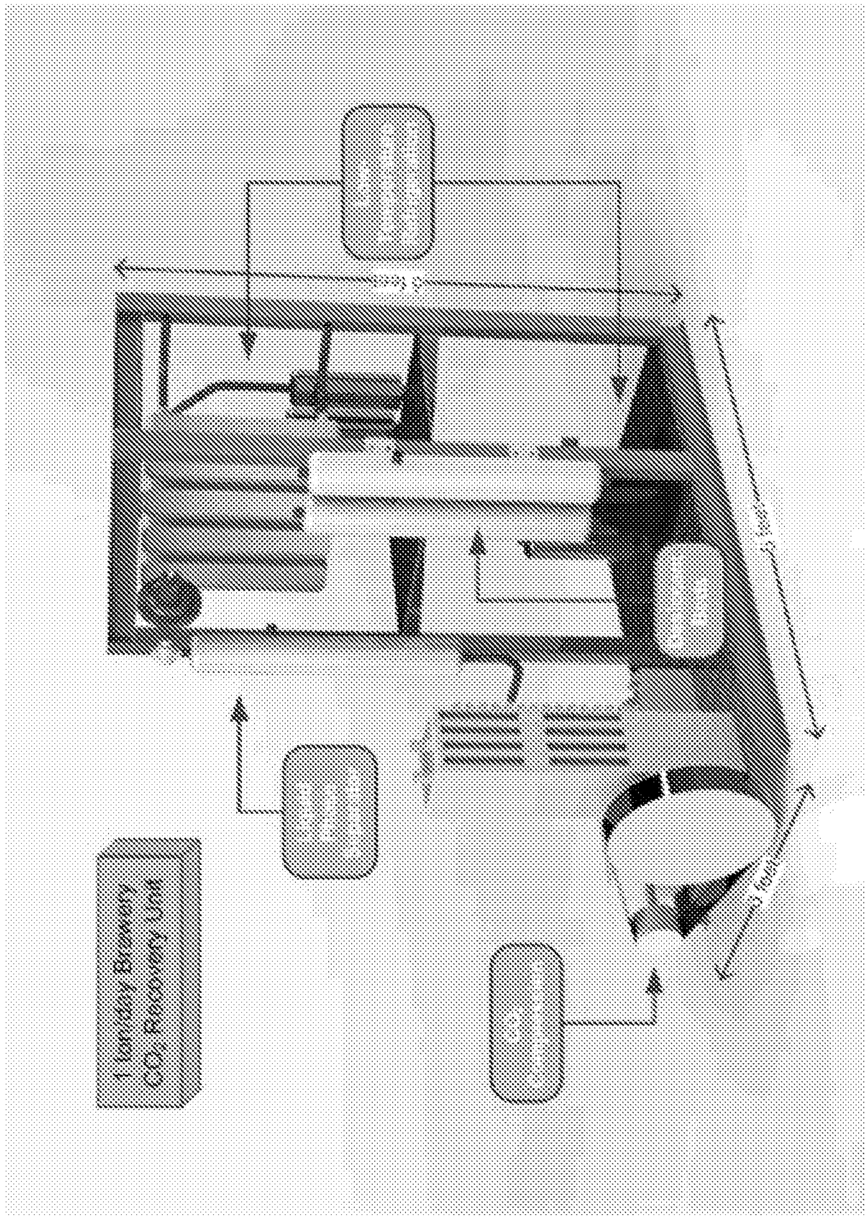


Fig. 4

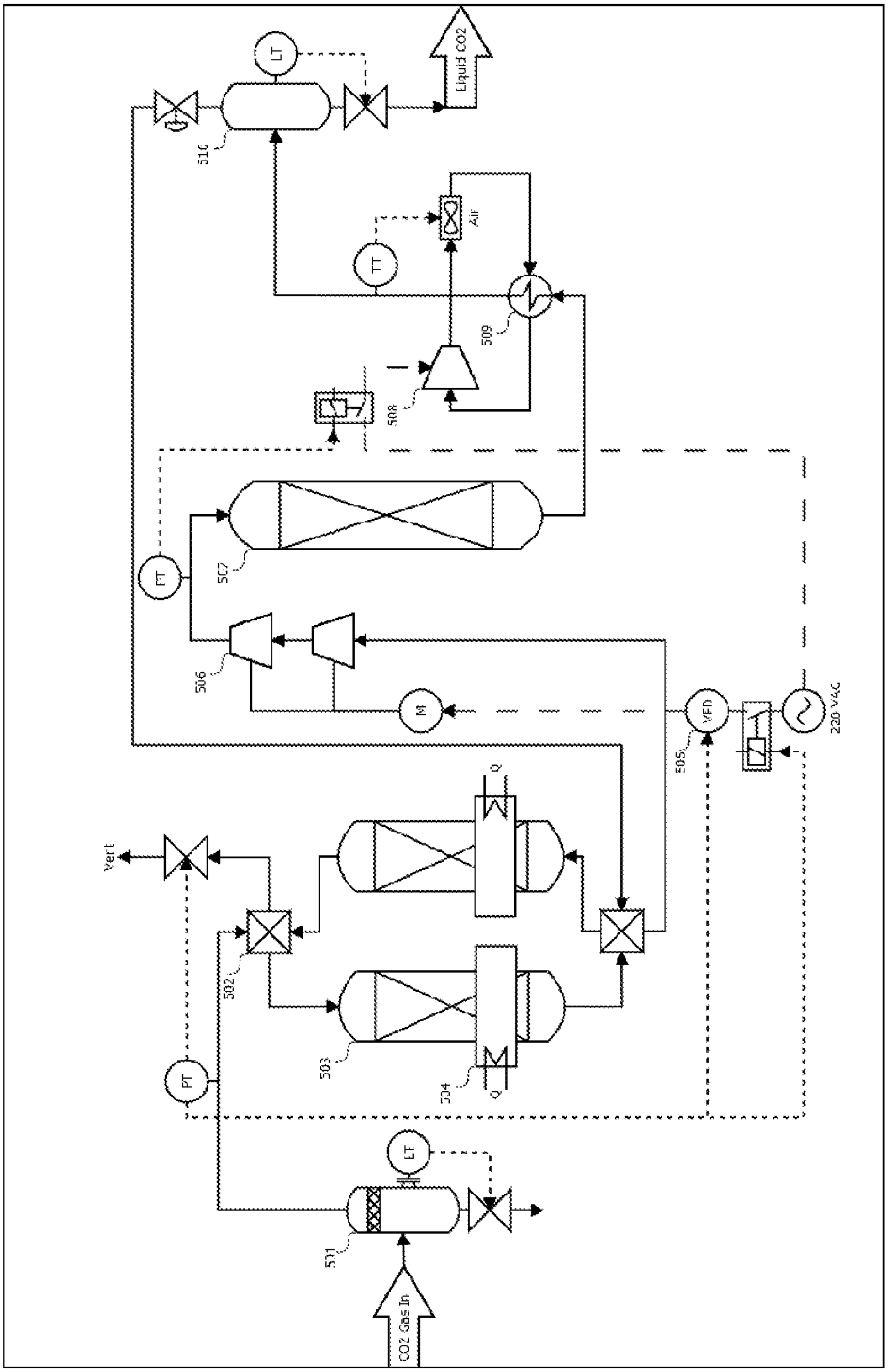

CO2 Gas In
501
LT
PT
502
503
504
Q
Q
Vent
505
VFD
220 VAC
M
506
FT
507
508
509
TT
Air
510
LT
Liquid CO2

Fig. 5

SYSTEMS AND METHODS FOR RECOVERING CARBON DIOXIDE FROM INDUSTRIALLY RELEVANT WASTE STREAMS, ESPECIALLY ETHANOL FERMENTATION PROCESSES, FOR APPLICATION IN FOOD AND BEVERAGE PRODUCTION

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/020,883 filed Jul. 3 2014 entitled "Systems And Methods For Recovering Carbon Dioxide From Industrially Relevant Waste Streams, Especially Ethanol Fermentation Processes, For Application In Food And Beverage Production" which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to enabling the recovery of carbon dioxide (CO2) from industrially relevant waste streams containing a sufficiently high concentration of CO2. The invention is most readily applicable to the burgeoning beverage alcohol industry (microdistilleries, craft vintners, and craft breweries) in the United States, most especially the craft beer brewing industry. In a craft brewery, carbon dioxide can be recovered from fermentation tanks, bright beer tanks, and other process vessels, tanks and lines. The recovered CO2 can then be used in forced carbonation, kegging, canning, bottling, purging, and other applications associated with production of packaged beer. More specifically, this invention relates to a modular system for separating carbon dioxide from non-condensable gases such as nitrogen and oxygen, while dehydrating, deodorizing, and purifying the carbon dioxide to a quality sufficient for beverage applications, and also liquefying the carbon dioxide and transferring it into a storage vessel so that it can be re-used (which would reduce the amount of carbon dioxide that is vented by breweries, as well as the reduce the amount of carbon dioxide that breweries have to purchase for plant operations).

BACKGROUND OF THE INVENTION

[0003] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0004] Large-scale recovery systems are commercially available for large producers of vented carbon dioxide waste streams. Processing capabilities of these systems exceed 50 kg/hr of CO2. These large and complex recovery systems require a permanent installation with extended utility lines (process water, waste water, cooling glycol, process heat, and electricity) to facilitate operation. The economics of such an installation are proportional to its size and complexity. The processing rate, space and infrastructure requirements, and cost make these commercially available CO2 recovery systems irrelevant for processes that generate waste CO2 streams of lesser magnitudes.

[0005] Because economic and space constraints are virtually limitless for conventional large-scale CO2 recovery systems and the large-scale conventional predominantly lager-producing breweries that house them, the process utilized to recover CO2 is not fully optimized for the application. Large breweries produce beer at a steadier rate when compared to smaller craft breweries who actively pursue seasonal and recipe variations in their production schedule. Given the reliability of upstream CO2 production and the consistency of utilities (heat, water, cooling glycol, and electricity) in a large brewery, conventional CO2 recovery systems are designed to run at steady-state at a single design point, with large-volume, ceiling-mounted balloons to account for small variations in CO2 production rates. This final detail is most certainly too costly, large, and unwieldy for potential clients producing moderate CO2 waste streams.

[0006] In most CO2 recovery applications, the recovered stream is liquefied for convenient, high-density storage. High pressure and low temperature are used by liquefaction processes that convert a chemical species from a vapor at standard temperature and pressure to a liquid at the process conditions. The designer engineer has a choice to provide either a higher pressure or a lower temperature to economically optimize the liquefaction process. In these conventional CO2 recovery systems where space and cost are inconsequential, the higher pressure option is chosen since there is enough floor space for a three-to-four stage compressor. A common process pressure in this application would be 250-300 psig. At 250 psig, pure carbon dioxide liquefies at −23° C. This enables the purchase and use of a conventional, off-the-shelf industrial refrigeration system which achieves a minimum evaporator temperature of −30° C. Common refrigerants in such a readily-available unit include propane, R-22, or R-404a.

[0007] Again, due to plentiful utilities and a fixed, static installation, these larger systems use a continuous aqueous scrubbing system to remove trace dissolved organics as part of the CO2 purification process. This consumption of process water imposes a high operations cost, and can be replaced by alternate methods as will be addressed. Also the presence of noncondensable gases is a problem in conventional CO2 recovery systems. Because the higher-pressure process is employed, dissolved gases have a much higher tendency to remain dissolved in the recovered CO2 product stream. The solution is to again use a costly plant utility, this time in the form of process heat and cooling glycol. A small distillation column with a reboiler and overhead condenser is employed to actively drive out noncondensable gases from the high-pressure product stream. The need for this is greatly reduced by opting for a lower-pressure process.

[0008] In the United States, the past ten years have seen a massive growth in the so-called craft beer industry. The Brewers Association is the prominent trade group associated with these breweries and defines a craft brewery as an operation that produces less than 6 million barrels of beer per year (1 US beer barrel=31 US gallons; Source: Brewers Association, Boulder, Colo., http://www.brewersassociation.org/statistics/craft-brewer-defined/, retrieved Jun. 22, 2014). This industry has nearly tripled in total production volume over the past ten years, from about 6 million barrels of beer produced in 2004 to over 15 million barrels brewed in 2013.

[0009] Beer (an aqueous solution of 3-10% ethanol by volume) is produced by the anaerobic fermentation of glucose by the yeast *Saccharomyces cerevisiae*. In this process every molecule of glucose yields two molecules of ethanol as the desired product, along with two molecules of carbon dioxide as a byproduct. This byproduct is not entirely unwanted however, since consumers of beer prefer to have the beverage carbonated. This carbonation step alone is not sufficient to utilize all the CO2 produced during a batch fermentation, but other applications around a typical brewery would be able to make use of such a recovered waste stream. Typical applications of a recovered carbon dioxide stream in a production brewery include carbonation of the final beverage product whether in bottles, cans, or kegs, purging all process lines and vessels to exclude air, dispensing beverages in the on-site tasting room or brewpub, and filling and reselling tanks of beverage-grade CO2 for other products such as soft drinks and carbonated water.

[0010] Currently carbon dioxide is being vented in large quantities at numerous locations by craft beer breweries. This activity entails significant loss of income that could be earned by recovering the vented carbon dioxide. Still more financial losses are entailed by purchasing carbon dioxide from industrial gas supply houses to support plant operations such as force carbonation, bottling (or canning or kegging) and purging tanks or process lines. Furthermore, the venting of carbon dioxide has raised environmental issues that could cause state and/or federal regulators to take action to fine, shutdown, or highly regulate their operations.

[0011] The fermentation of sugars by yeast to generate ethanol results in the formation of carbon dioxide as a byproduct. For each molecule of ethanol generated, a molecule of carbon dioxide is also generated. Thus the production of 1 barrel (31 gallons U.S.) of beer at 5% alcohol by volume (ABV) will generate 9.8 lb of carbon dioxide. Therefore, a brewery producing 10000 bands per year at 5% ABV will produce on average 270 lb CO2 per day, which must be released from the vessel(s) during the fermentation to avoid stalling the fermentation or mechanically overpressuring the fermentation tank.

[0012] The United States craft beer industry is expanding rapidly, with a near linear growth curve since 2007, accounting for the production of 15.6 million barrels of beer in 2013. (Source: www.brewersassociation.com Growth-infographic-main.png, 2014), This beer production level indicates carbon dioxide production in the range of 1.5-2.0 million lbs per year (depending on average ABV), and nearly all of it is vented to atmosphere, because up until the present invention no technology has been accessible to craft brewers to recover carbon dioxide from their beer production due to the size and economic constraints outlined earlier.

[0013] This venting produces significant quantities of harmful CO_2 emissions while producing no useful product. If this vented CO2 could be utilized to replace purchased CO2 for force carbonation, bottling, purging, and other plant uses, significant environmental and economic benefits would accrue. For example, the market value of purchasing industrial CO2 ranges from $0.10 to $0.50 per pound, depending on transportation and logistics factors. Recovery of this stream represents $200 to $1000 per ton of recovered CO2. This is a very significant savings for small to mid-sized breweries. However, this problem is not relegated to the contiguous United States. Craft and regional breweries are on the rise across other continents and on various island nations, often with significantly less infrastructure to facilitate the affordable transport of industrial CO2. Accordingly many small international breweries pay $0.50 to $2.00 per pound of CO2, making recovery of this precious commodity an economic imperative.

[0014] Furthermore, CO2 in craft breweries of average size is typically vented from the fermenter tank headspace, through a down coming blow-off arm directly into the plant where the cellar operators work. Carbon dioxide, being heavier than air, tends to accumulate on the floor space, presenting a significant workplace hazard. If sufficient air exchange is not available to keep CO2 concentrations below 5000 ppm, adverse health effects such as dizziness, confusion, and drowsiness are likely to occur. At still higher concentrations, asphyxiation is a possibility.

[0015] Most beers are force carbonated in the range of 2.2-2.6 volumes of CO2. A 'volume' of CO2 indicates the amount of CO2 contained in a given volume of beer, when it is expanded down to standard atmospheric conditions, compared to the volume of the beer itself. For example, 2.4 'volumes' of CO2 in a barrel of beer represents 2.4 barrels of CO2 per barrel of beer at atmospheric pressure and temperature, which is 1.2 lb of CO2. Therefore, a brewery producing 10000 barrels per year, force carbonating to an average of 2.4 volumes, will require 32 lb CO2 per day for force carbonation. In addition to force carbonation, there are other uses for CO2 in the brewery, namely bottling (or canning or kegging) and purging of tanks and process lines.

[0016] Typically, breweries utilize carbon dioxide purchased from industrial gas supply houses, which is acquired from ammonia/urea/fertilizer production and/or large scale fuel ethanol production. This industrial commoditized CO2 source is extensively processed to meet stringent beverage-grade purity standards. However, any variability in the purification steps to remove trace chemicals, hydrocarbons, nitrogen compounds, carbon monoxide, dissolved oxygen, or lubricating oils can result in a finished beer with unpleasant taste, odor, or even health consequences. CO2 produced from brewery fermentation, on the other hand, would be free of these contaminants, as it originates from a sterile fermenter with controlled conditions, and is produced from the same beer that is being carbonated, in an anaerobic fermentation environment. Economically this is a compelling case since the processing cost of purifying the recovered CO2 for reuse within beverage-grade specs (including <30 ppm dissolved oxygen) is greatly reduced by starting with a much cleaner feedstock when compared to conventional industrial CO2 feedstocks.

[0017] It is highly financially and environmentally disadvantageous to vent valuable carbon dioxide that could be utilized in the brewery for force carbonation and purging of tanks and process lines or packaged and resold to nearby consumers of beverage-grade CO2. It is even more financially and environmentally disadvantageous to utilize large quantities of carbon dioxide purchased from industrial gas supply houses, while perfectly useful CO2 of superior purity is already being produced in the facility.

[0018] Therefore, there exists an important need for a solution to address the problem of recovering carbon dioxide in the brewery to the maximum extent and to minimize or eliminate the purchasing of carbon dioxide generated outside the facility, while still being cost-effective and meeting beverage grade purity standards.

[0019] Accordingly, as recognized by the present inventors, what are needed are a novel method, apparatus, and system for recovering CO2 from brewery processes into a storage vessel that can be easily by the brewery for force carbonation, bottling (or canning or kegging), purging of tanks and process lines, and for other purposes. As recognized by the present inventors, what is also needed is a CO2 recovery apparatus that can recover the CO2 at a cost that is less than the cost of CO2 delivered from outside the facility, that can interface with a typical craft brewery facility, that can maintain beverage grade CO2 purity standards, and that can be of sufficient capacity to recover most if not all of the CO2 that is produced at the facility.

[0020] Due the required CO2 flow rates, space requirements, cost, complexity, and infrastructure requirements, commercially available conventional CO2 recovery systems are inapplicable to a new market segment that represents well over 1 million pounds of annual CO2 emissions.

Therefore, it would be an advancement in the state of the art to provide an apparatus, system, and method for cost-effectively recovering carbon dioxide from a craft-scale brewery that currently vents the CO2 produced at its facility. It would also be an advancement in the state of the art to provide a system that is accessible to craft breweries due to its cost-effectiveness, compatibility, and capacity to recover CO2 from said brewery.

[0021] It is against this background that various embodiments of the present invention were developed.

BRIEF SUMMARY OF THE INVENTION

[0022] The present invention is designed to enable the recovery of carbon dioxide (CO2) from industrial waste streams containing a majority of CO2. Processes that produce such streams include pharmaceutical synthesis via batch fermentation, fuel ethanol plants utilizing starchy feedstocks, anesthetic asphyxiation in slaughterhouses, ammonia production via steam reforming of natural gas, coal and biomass gasifiers, various thermochemical and Fischer-Tropsch-type gas-to-liquids conversions, soft drink bottling plants, plastics production facilities using the solvent properties of CO2 for materials property enhancements, coffee and tea decaffeination towers, so-called green dry cleaners, medical sterilization, and production of beverage alcohol products. Due to recent entrepreneurial market trends in the United States, many of these previously large-scale operations are being performed by various smaller businesses. Production plants of sufficient size and sophistication recognize the economic implications of recovering and utilizing a carbon dioxide waste stream. However, smaller operations often lack the capital required for installation of recovery equipment. Therefore, a technological gap exists between the laboratory and industrial scales for recovery, purification and storage of CO2 where it is currently being vented and wasted. The inventors have filled this gap by developing a novel process which is optimized for this economically relevant scale.

[0023] Whereas the problem of carbon dioxide recovery in breweries was previously recognized, systems have been previously developed for this purpose. Although the manufactures claim that systems can be built to accommodate small production volumes, the systems tend to be tailored to the needs of large production breweries outside of the craft beer arena. These systems are typically very expensive, have large footprints, require extensive facility modification, and are generally not accessible to craft breweries (production less than 6 million barrels of beer per annum).

[0024] Craft breweries face a number of challenges when evaluating CO2 recovery, most of which are related to the rapid growth of their market share of the beer brewing industry. In general, craft breweries are being forced to expand beer production rapidly to keep up with increasing demand. This means that brewhouses, fermentation tanks, bottling lines, packaging, and storage must all be expanded within existing production buildings. As a result, craft breweries are limited by the availability of working capital and physical space especially concerning equipment not directly related to beer production and packaging. Moreover, permanent modification of the facility and/or operations to accommodate a CO2 recovery system is generally not acceptable if it slows or interrupts the production of beer.

[0025] The system design presented in the present application solves the problems with existing systems provided by other manufacturers. The present system is intentionally designed to be cost-effective, compact, and compatible with typical craft brewery facilities. Most importantly, the system is intentionally designed to interface with the typical craft brewery operation in a minimally invasive way, which has no adverse effect on the rate of production of beer, while adding a only a minimal workload to brewery cellar operators.

[0026] The inventors realized that what is needed is a system that can draw CO2 from both fermentation tanks and bright beer tanks at operating conditions typically experienced in a craft brewery. Further, that the system can be interfaced into the brewery through flexible installations, and that the system can be compact enough to be easily relocated within a facility. Further, that the approach to the CO2 recovery can be designed to use less expensive processing equipment, to reduce up-front capital cost. Further, that the system can have variable capacity to match the rate of CO2 production to maximize the uptime of the system and the economic benefit. Further, that the system can recover CO2 at an energy cost much less than the cost of purchasing CO2 from a gas supply house. Further, that the system can treat the recovered CO2 to beverage grade quality standards. Finally, that the system can make available for storage and usage the recovered CO2 at a temperature and pressure that is useful in a brewery.

[0027] Accordingly, the inventors have invented an approach to draw the effluent gas (which is mainly carbon dioxide) from the fermentation and bright beer tanks, from pressures as low as 0 psig, and to separate the CO2 from any non-condensable gases present, and to dehydrate and deodorize the CO2, and to cryogenically (thus purifying via phase separation) liquefy the CO2 and to make the CO2 available for immediate use or transfer into bulk storage.

[0028] The inventors have invented a process in which the effluent gas (which is mainly CO2) is compressed to a pressure between 75 psia to 300 psia (and more preferably to between 130 psia to 160 psia), The CO2 is then cooled to a temperature of between −15° C. to −55° C. (and more preferably to between −37° C. to −43° C.) which causes liquefaction of the CO2.

[0029] One of several ways to achieve such a low temperature range is to utilize a unique refrigeration unit also invented by the present inventors. The unique autocascade refrigeration unit utilizes an autocascade refrigeration stage, in a compact, portable chassis for delivery to brewery. However, the present invention is not limited to utilizing the specific refrigeration unit shown and described.

[0030] Accordingly, one embodiment of the present invention is a system for recovering CO2 from fermentation and/or bright beer tanks, comprising a chassis or skid adapted to hold the system for installation in the brewery; a condensate trap for removing free water from the CO2 stream; a dehydrator for removing water from the CO2 stream; a carbon bed for deodorizing the CO2 stream; a compressor for compressing the CO2 stream to a pressure between 75 psia to 300 psia (and more preferably to between 130 psia to 160 psia); a refrigerator for lowering the temperature of the CO2 stream to an ideal temperature range, preferably approximately −15° C. to −55° C., (and more preferably −37° C. to −43° C.), which causes liquefaction of the CO2; and a storage vessel adapted to contain the liquefied CO2, and to vent non-condensable gases from its headspace. Because the CO2 is liquefied and stored and/or used, the CO2 is not vented to the atmosphere. Because the CO2 is liquefied and stored cryogenically, the CO2 is free from bacteria or other microbiological contaminants. Because the system relieves non-condensable gases, the liquefied and stored CO2 is of beverage grade quality standards, particularly with respect to oxygen content as well as common industrial contaminants that are not present inside sanitary beer fermentation vessels. As such, the stored and liquefied CO2 can be used in the brewery for force carbonation, bottling, and purging of tanks and process lines without further treatment, thus replacing CO2 purchased and delivered CO2 from outside the facility.

[0031] Yet another embodiment of the present invention is the system described above, further comprising a foam trap to remove free water and foam from the inlet stream, in place of the aforementioned condensate trap. Yet another embodiment of the present invention is the system described above, where the foam trap detects the presence of foam by way of an optical sensor and sprays water automatically to collapse it. Yet another embodiment of the present invention is the system described above, further comprising an automatic water drain to manage the free water level in the foam trap.

[0032] Yet another embodiment of the present invention is the system described above, wherein the dehydrator employs a desiccant bed, to dehydrate the CO2 stream. Yet another embodiment of the present invention is the system described above, wherein two desiccant beds are employed in alternation, wherein heat required to dry the two beds is provided by a process heater, which heats air that is provided by a blower to drive the hot air through the beds and dry them. Yet another embodiment of the present invention is the system described above, where the gas from the headspace of the CO2 storage vessel is heated and used for the regeneration of the beds.

[0033] Yet another embodiment of the present invention is the system described above, further comprising a boost blower upstream of the compressor to raise the suction pressure from a vacuum to at least 0 psig at the main compressor. Yet another embodiment of the present invention is the system described above, further comprising one or more variable frequency drives (VFDs) to control the speed of the main compressor and/or the boost blower, to track the rate of CO2 production in the facility.

[0034] Yet another embodiment of the present invention is the system described above, wherein the compressor compresses the CO2 stream to a pressure of no more than approximately 300 psia.

[0035] Yet another embodiment of the present invention is the system described above, where there is one single stage of refrigeration, having at least one heat exchanger for lowering the temperature of the CO2.

[0036] Yet another embodiment of the present invention is the system described above, wherein the refrigerator comprises a dual refrigeration loop, containing both a high-stage refrigeration loop having at least one heat exchanger for cooling the low-stage refrigeration loop, and possibly a second heat exchanger for lowering the temperature of the dehydrated CO2 stream; and a low-stage refrigeration loop having at least one heat exchanger for further lowering the temperature of the CO2 stream.

[0037] Yet another embodiment of the present invention is the system described above, wherein either the single stage refrigeration loop, (if applicable) or the low-stage of a dual refrigeration loop (if applicable) is an autocascade loop having mixed refrigerants. Yet another embodiment of the present invention is the system described above, wherein the mixed refrigerants are non-flammable. Yet another embodiment of the present invention is the system described above, wherein the mixed refrigerants are hydrocarbons.

[0038] Yet another embodiment of the present invention is the system described above, wherein the storage vessel is an insulated and/or refrigerated vessel, wherein the liquefied CO2 is filled into the vessel through a dip tube contained in the vessel, with a vent valve so that the non-condensable gases in the headspace are allowed to vent from the vessel to maintain its pressure. Yet another embodiment of the present invention is the system described above, where there is a phase separator that removes the non-condensable gases from the liquefied CO2 stream before the liquefied CO2 stream is stored or used. Yet another embodiment of the present invention is the system described above, where the phase separator is fitted with a liquid transfer pump to transfer the liquefied CO2 into a closed storage tank.

[0039] Yet another embodiment of the present invention is the system described above, wherein some or all of the various operations within the system are managed by automatic electro-mechanical control elements. Yet another embodiment of the present invention is the system described above, further comprising one or more microcontroller(s) programmed to automatically control some or all of the various operations. Yet another embodiment of the present invention is the system described above, wherein the control system is comprised of both electro-mechanical control elements and one or more microcontroller(s) programmed to maintain control over some or all of the various operations of the system. Yet another embodiment of the present invention is the system described above, further comprising a sensor network to provide feedback to the microcontroller(s).

[0040] Another embodiment of the present invention is a method for recovering CO2 in a brewery, comprising the following steps: (1) bringing a CO2 recovery system to a brewery venting CO2 and connecting the system to fermentation and bright beer tanks; (2) removing free water from the inlet using a condensate trap or removing both free water and foam using a foam trap, if necessary; (3) removing water vapor from the CO2 stream utilizing a dehydrator; (4) compressing the CO2 stream utilizing a compressor; (5) lowering the temperature of the CO2 stream utilizing a refrigerator, which causes liquefaction of the CO2; and (6) transferring the liquefied CO2 into a storage utilizing a vessel adapted to contain it.

[0041] Yet another embodiment of the present invention is the method described above, wherein the dehydration step employs desiccant beds. Yet another embodiment of the present invention is the system described above, wherein two desiccant beds are employed in alternation, wherein heat required to dry the two beds is derived from a process heater.

[0042] Yet another embodiment of the present invention is the method described above, wherein the refrigeration step utilizes an auto cascade refrigerator having mixed non-flammable refrigerants. Yet another embodiment of the present invention includes two stages of refrigeration. Yet another embodiment of the present invention is the method described above, wherein the refrigeration step cools the CO2 stream to a temperature range of −15° C. to −55° C.

[0043] Yet another embodiment of the present invention is the method described above, wherein some or all of the various steps of the method are controlled by an automatic control system. comprised of a combination of electro-mechanical and microcontroller-based control elements, and further having a sensor network to provide feedback to the control system.

[0044] Other features, utilities and advantages of the various embodiments of the invention will be apparent from the following more particular description of embodiments of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045] The invention will be understood by the following detailed description in conjunction with the accompanying drawings, wherein like reference numerals designate like structural elements, and in which:

[0046] FIG. **1** shows an engineering drawing of a CO2 recovery system relevant for craft breweries. System components and subsystems are labeled.

[0047] FIG. **2** shows a schematic for a typical installation in a craft brewery with a centralized CO2 manifold/foam trap already in place. The CO2 recovery system is plumbed in parallel to the main CO2 collection line headed to the foam trap. This ensures seamless operational transition to recovering CO2 under the purview of standard brewery practice.

[0048] FIG. **3** shows a simplified process flow diagram for capturing, boosting, drying, scrubbing, compressing, liquefying, and storing CO2 as required to recover this waste stream.

[0049] FIG. **4** shows a perspective view of one embodiment of a CO2 recovery system according to one embodiment of the present invention. This particular embodiment is designed to recover a nominal flow rate of 1 ton CO2 per day.

[0050] FIG. **5** shows a detailed piping and instrumentation diagram of a typical CO2 recovery system.

DETAILED DESCRIPTION OF THE INVENTION

[0051] The following description is merely exemplary in nature and is in no way intended to limit the scope of the present disclosure, application, or uses.

DEFINITIONS

[0052] The following terms of art shall have the below ascribed meanings throughout this specification, unless otherwise stated.

[0053] Throughout this disclosure a CO2 recovery "system," "unit," or "apparatus," or any reference to a single commercially viable module, will refer to an apparatus module that can process a given number of pounds (kilograms) of carbon dioxide per day. Volumetric flow rates of trace compounds including air, humidity, ethanol vapor, trace organics including higher alcohols, aldehydes, ethers, and esters are considered negligible. Multiple modules can be combined for higher gas flow rates and to address the cyclic behavior of manifolded fermenter effluent flow rates. Product flow estimates and sinusoidal characteristics are based on direct flow measurement of CO2 effluent from a batch fermentation of a typical ale product at a major craft brewery, and are provided for explanation purposes only, and are not intended to be limiting the scope of the present invention in any way. Different flow rates and characteristics associated with production variations between craft breweries as well as other CO2-venting industries will require different modular configurations to address the specific case and will by definition affect the quantities of products. It is important to note the quality of recovered CO2 will not vary appreciably due to the active purification steps taken in the recovery process.

[0054] The abbreviation CO2 always refers to the molecule carbon dioxide. The word "day" shall imply "a day of operations," which shall be a 24-hour day, but could also be an 8-hour day, a 12-hour day, or some other amount of operational time. Furthermore, time-based production numbers will assume the recovery system has sufficient inlet conditions and supporting utilities to run at 100% duty. Real variations in production will cause the flow control of the CO2 recovery system to adjust below the maximum operating rate, and will reduce the total processed quantity of CO2.

[0055] The terms fermenter effluent, blowoff, vent gas, headspace, carbonation, and fermentation gas all refer to CO2 that is produced in tandem with ethanol during anaerobic fermentation of glucose via glycolysis by the yeast *Saccharomyces cerevisiae*. This is an ideal waste stream that can be recovered by the outlined invention.

[0056] Desiccation describes the physical removal of water by a solid adsorption medium to reduce the humidity dew point temperature of the inlet CO2 gas to a value below the coldest possible process temperature. This ensures consistent operation by avoiding the potential for water ice accumulation and plugging inside the process.

[0057] Deodorization or scrubbing refers to heterogeneous adsorption by activated carbon of trace organic components present in fermentation CO2, especially esters, aldehydes, and terpenes. This ensures the purity of the recovered product so that it can be reused transparently regardless of the flavoring of the desired product.

[0058] Beverage-grade CO2 is an industry-specific classification that defines a baseline purity of CO2 gas for production of carbonated beverages. The primary distinction is 30 ppmv or less of oxygen contamination, but other purity specifications are implied, including the absence of other flavor, odor, condensable, and noncondensable species.

[0059] Industrial CO2 is nomenclature for commercially available conventional CO2. This commodity stream is recovered from large-scale industrial sources other than beverage-grade ethanol fermentations. Because the CO2 feedstocks for industrial CO2 are so varied and geographically disparate, the potential for contamination in the procurement and transportation chain is much higher than in-house recovered CO2. This is a distinct competitive and economic advantage of the proposed invention.

[0060] An autocascade refrigeration system is a single-condenser system containing a mixture of refrigerants which approximates the behavior of a conventional cascade refrigeration system yet in a smaller form-factor. This is one of the proposed solutions to achieving the cooling required in the liquefaction of recovered CO2.

Overview of the CO2 Recovery Process

[0061] It makes no financial or environmental sense to vent clean, valuable carbon dioxide (CO2) that could be used in-house to offset significant expenditures or sold to other manufacturers requiring beverage-grade CO2 at great profit. It makes no financial or environmental sense to pay elevated prices for a commodity feedstock of middling purity that is typically transported thousands of miles by truck, boat, or aircraft, requiring huge amounts of money on vehicle fuel for transportation and at the same time this feedstock is being vented in the very same facility requires it for manufacturing its products. The problem is that CO2 being vented in the facility is not suitable for reuse directly, due to low pressure, high humidity, high volume required for storage, and trace contaminants, including oxygen which will ruin the company's finished products. What is therefore needed is a mobile, modular system with a minimal footprint and minimal operational impact that can be installed in any typical craft brewery rapidly and with minimal hardware changes or associated installation costs. It is to meet this need that the inventors have developed a novel CO2 recovery process which is significantly different from conventional CO2 recovery technology to service the booming worldwide craft brewery industry.

[0062] In the CO2 recovery process, raw fermentation CO2 is first dehydrated and then compressed. The dry, compressed gas is then passed through an activated carbon bed which deodorizes the process gas by removing trace organic components. The dry, compressed, deodorized gas is then refrigerated down to optimally cold temperatures, causing the carbon dioxide to liquefy, while trace noncondensable gases remain in a dissolved gaseous phase. An optional two-phase separator with pressure control is then employed to separate non-condensable gases (mainly nitrogen and oxygen) from the liquid CO2 phase. Alternately, this action can be performed in an integrated storage vessel which further reduces the cost and complexity of the process. Because the liquid CO2 product is always at a colder temperature than ambient conditions inside a production facility, partial vaporization of the CO2 occurs, and some venting is permitted by the pressure control device. As this process continues, non-condensable gases are preferentially stripped from the liquid CO2 product stream and vented safely to atmosphere, further enhancing the purity of the recovered product. If this step is performed in a separate phase separator, the liquid CO2 product is then sent to an insulated liquid storage dewar by differential pressure balancing. Otherwise, the product is already been sent to the liquid storage dewar, also by differential pressure balancing. Eliminating a cryogenic product pump further simplifies the process and reduces cost when compared to conventional CO2 recovery technologies. Once the liquid CO2 product is stored in the onsite dewar, it is vaporized through a provided ambient vaporizer for direct use in the brewing process.

[0063] Therefore, this CO2 recovery process solves a large market gap that has existed for over two decades by providing an in-house CO2 recovery system appropriate for the small size of the vast majority of breweries worldwide. This allows these small, cash-strapped companies to see a much-needed savings on a major brewing commodity as well as address a major environmental concern and source of a workplace hazard.

[0064] The innovative design of the CO2 recovery system according to the principles of the present invention leverages a valuable in-house waste stream using a novel autocascade refrigeration subsystem. This design allows for very compact and cost-effective purification and recovery of fermentation CO2 inside a small-scale production brewery. The recovered liquid CO2 is stored on-site in a liquid storage dewar and can be vaporized and used directly in the brewing process, or used to fill vessels for sale at a profit to outside organizations. The unique design of the CO2 recovery process produces a system that can be sized to fit through doorways of standard dimensions. Craft breweries typically inhabit old repurposed buildings and are experiencing rapid production growth, which makes space in around the brewery a limited resource. The CO2 recovery system, which can process 300 pounds/day of fermentation gas, onto a cart with casters and a handle that measures 28 inches wide by 40 inches deep by 64 inches tall. Larger units can be manufactured that process up to approximately 600-900 pounds/day and still fit within a standard 36-inch-wide, 80-inch-tall door. CO2 effluent leaving beer fermenters in the active anaerobic phase measures >99% CO2 composition by volume on a gas chromatograph. The vented fermenter gas also contains other compounds such as water vapor, hydrogen sulfide, carbon monoxide, oxygen, and nitrogen, as well as trace organic compounds including alcohols, aldehydes, ethers, esters, ketones, and terpenes.

[0065] Beverage-grade CO2 is an exacting standard defined by the International Society of Beverage Technologists (ISBT; http://www.bevtech.org/) that requires a minimum 99.9% purity by volume, as well as a maximum 30 ppm by volume of oxygen contamination. The full specification is listed in Table 1. A brief skimming of the table shows contaminants that are not present in a beer fermenter to begin with, including ammonia, nitric oxide, nonvolatile residue, phosphine, and aromatic hydrocarbons. These compounds are however present in processes which are conventional sources of industrial CO2. Economically, industrially available CO2 requires a lot more effort and technology to produce a product consistent with the beverage CO2 specification. Therefore, tailoring a CO2 recovery system to accommodate craft breweries, there is an inherent superiority from both a purity and a transportation standpoint.

[0066] The process described in this patent application has been demonstrated to achieve a maximum oxygen contamination of 1.1 ppm by volume, with a corresponding inlet air contamination of 3%. Due to partial pressure concerns the minimum CO2 purity required for successful liquefaction in the present invention is 80%. If methane linear relationship is assumed between inlet air contamination and product purity, even an inlet air contamination of 20% will result in 7.3 ppm oxygen contamination, well below the industry standard of 30 ppm. The samples discussed were procured via CO2 recovery from active fermenters at a major craft brewery at two dates eight months apart, using two separately constructed systems implementing the proposed CO2 recovery system, and measured by an independent third-party lab with ion exchange chromatography. Other contaminant results include hydrogen which was undetectable at the instrument threshold of 0.1 ppm, a maximum of carbon monoxide at 0.1 ppm (cf. 10 ppm in the standard), and a maximum of 2 ppm nitrogen, which is considered a neutral contaminant. Indeed, in an effort to constantly innovate, craft breweries have begun serving beers carbonated with varying proportions of a CO2/nitrogen (N2) gas mixture. Full purity results are displayed it Table 2. The processes described in this patent application are distinguishable from conventional CO2 recovery technologies which operate at system pressures of 250-300 psig or higher. As noted in the introduction, ethane preferred embodiment of the present invention recovers CO2 at a significantly reduced pressure of 150 psig. This design modification provides a myriad of benefits, including process simplicity, opportunity for miniaturization, improved capital economics, lower ambient noise concerns, enhanced process safety, downstream equipment cost savings, and easier removal of noncondensable contaminants. Because no CO2 recovery solutions exists# for craft breweries, their purchased industrial CO2 is stored in higher pressure containers consistent with the conventional process. A lower pressure product consistent with the preferred embodiment of the present invention can't be transported into a higher pressure vessel without an active control element, which is absent from the design. This requires a separate lower pressure storage solution to receive the recovered product, and physically prevents any contamination of the two different CO2 sources. This is an important distinction which prevents clients from force-feeding their superior recovered CO2 into the higher pressure backup storage tank, which would violate leasing terms that are standard with gas supply companies. By incorporating a separate, lower pressure storage solution and vaporizer as part of the CO2 recovery system itself, purity, contractual, and process parameters are all maintained within specifications. This also makes a separate phase separator for removing noncondensable gases extraneous, which further lowers the capital cost of the system and simplifies the process. It is also much easier to drive out dissolved gases from a lower pressure liquid, and can even occur passively, instead of a higher pressure system which requires an active driving force to remove noncondensable gases to meet purity specifications. Therefore the lower pressure design point provides far-reaching economic benefits when compared with conventional technology, in addition to opening up a large, previously untapped market segment.

[0067] The present invention has already been designed, fabricated, tested, and installed in multiple typical production craft breweries. All the above benefits have been observed and supported, including the design processing rate of 12.5 pounds of CO2 per hour. The superior purity numbers reported in Table 2 were taken from installations of this CO2 recovery process in active production breweries. Furthermore, extensive taste testing of carbonated beverages (both water and flagship beer products) was performed by long-time employees in the industry with well-trained palates at three major craft breweries. All results indicated even or superior flavor and odor characteristics when sampling beverages prepared with CO2 recovered by a produced embodiment of the present invention when compared to samples prepared with conventionally purchased industrial CO2. This satisfies the odor and taste stipulations of beverage-grade CO2 as outlined in Table 1.

Potential Economics of Small-Scale CO2 Recovery

[0068] One of many illustrative scenarios is presented here to demonstrate the potential profitability of a CO2 recovery process representative of the present invention. In this scenario, the example brewery uses exactly as much CO2 as it is able to capture with the CO2 recovery system, thus replacing its entire expenditure on purchased CO2. Other scenarios would be if the brewery is able to capture more CO2 than it consumes, leaving excess inventory for sale, or if the brewery uses more CO2 than it can capture, in which case the make-up inventory would be provided by the existing gas supplier, but at a much reduced usage rate which is still a large economic improvement. This economic analysis is illustrative of the invention only and is not meant to limit the scope of the present invention.

[0069] In one embodiment, a CO2 recovery system processes 300 pounds of fermentation CO2 per day. Assuming a premium industrial peak electricity cost of $0.20/kWh and a negotiated industrial CO2 cost of $0.15 per pound (which can range to upwards of $0.50 or even $1.00 per pound, depending on geographic location), the CO2 recovery system will use an average of 600 Wh per kilogram of recovered CO2. The output produced by such a CO2 recovery unit will fall within beverage-grade CO2 purity specifications.

[0070] At the indicated prices, the purchased CO2 displaced by in-house recovery would be valued at $1,350 in a 30-day month. At an electricity consumption of 600 Wh/kg, this system would cost $491 to operate, yielding a savings of $859, or 64% of the previous cost associated with purchasing industrial CO2. This is a rather conservative economic scenario. For instance, many areas located next to regional power plants will have lower electricity rates. Craft brewers also experience negative economies of scale with their gas suppliers. Since they are relatively small clients, their independent negotiating power is less and they commonly pay $0.20-0.30 per pound of delivered industrial CO2. International and offshore craft breweries have such outrageous delivered CO2 prices that a purchase of a CO2 recovery system consistent with the present invention will realize full payback periods of six months or even less, all while utilizing a product of superior purity.

Preferred System Schematics of the CO2 Recovery System

[0071] The present invention in its various embodiments provides highly efficient and economic solutions to close the loop in production facilities which simultaneously vent one CO2 stream while purchasing another. In one embodiment, the CO2 recovery system is a mobile, modular system that can be rapidly installed in parallel within an existing craft brewery to recover CO2 for reuse in the beer production process.

[0072] FIG. **3** shows a schematic diagram of one embodiment of a process of CO2 recovery according to the principles of present invention. CO2 vented from the headspace of a bank of fermenters enters the recovery system from the vessel labeled "Fermenters." Depending on the specific configuration of the CO2 vent manifold in the brewery, the process gas is optionally boosted in pressure by the equipment labeled "Blower." This gas is first dehydrated in the unit operation labeled "Dry Bed," which is actually a pair of desiccant beds which removes humidity from the inlet CO2 via adsorption. One bed is being actively regenerated while the other is online and is drying the CO2 stream. The dehydration step is followed by the "Scrubber" which deodorizes the fermenter CO2 gas via adsorption with activated carbon. The dry, deodorized gas is then compressed at the "Compression" step which raises the pressure from the inlet fermenter pressure to the elevated process pressure. The dry, compressed gas is then refrigerated at "Refrigeration," causing the CO2 gas to liquefy, while the noncondensable gases become dissolved in solution but do not undergo a phase change. The liquefied CO2 product is then transferred into storage ("Liquid CO_2 Storage"). In this embodiment, the storage vessel doubles as the liquid-gas phase separator, which passively evolves the noncondensable gases from the liquid CO2 product. This is the simplest and most economical configuration which allows for separation of the noncondensable species by venting from the headspace of liquid storage to maintain pressure control. When the brewery has demand for CO2 gas in the process, the liquid CO2 product is sent through an ambient vaporizer, ensuring the headspace of the storage never gets used in the downstream brewery process.

[0073] FIG. **1** shows a constructed version of a preferred embodiment of the present invention. The relevant unit operations as referenced in FIG. **3** are clearly labeled. Two main additions to note in FIG. **1** are the "Control Panel" which contains the microcontroller-based and electromechanical-based control system which enables autonomous operation of the CO2 recovery unit and the "Foam Trap" which protects the adsorption beds on the system from krausen, foam, trub, malt solids, hop solids, wort proteins, and yeast which can become entrained in the fermenter blowoff. The foam trap acts as a catch-all liquid separator which will trap and drain all potential inlet liquids from humidity condensation to krausen. An optical sensor will observe and foam or liquid phase and then proceed to lower the liquid level in the vessel with a washdown cycle that sprays water from the top and pumps inventory out the bottom. The other unit operations of note that are shown in FIG. **1** are the "Dry Beds," "Activated Carbon," "Main Compressor," and "Refrigeration."

[0074] As mentioned, the system that is enclosed inside the container labeled "Refrigeration" is preferably a single-compressor autocascade refrigeration system. An autocascade is a closed-loop refrigeration cycle that relies on a single refrigeration compressor as its prime mover. The working fluid in an autocascade refrigeration cycle is a mixture of refrigerants, which can be either flammable or nonflammable, as required by the process requirements or safety standards associated with particular installations. The preferred embodiment of the invention uses a mixture of nonflammable refrigerants in the autocascade refrigeration cycle. The condenser used in the autocascade refrigeration cycle is air-cooled, which removes the need for a chilled glycol utility stream which would burden already overloaded glycol systems in craft breweries and advances the design intent of a mobile, modular system with minimal input/output connections and process utility requirements. Because an autocascade refrigeration system contains a mixture of refrigerants, a two-phase vapor-liquid system develops inside the refrigeration system. The liquid phase is then flashed across a pressure reducing device which further cools it, whereupon it exchanges heat with the vapor stream to partially condense the refrigerant in preparation for the final refrigeration evaporator heat exchanger. The autocascade configuration is preferred since this process has elected for a lower pressure operating point when compared to convention CO2 recovery technology. The autocascade refrigeration system is capable of achieving the low process temperature, ranging anywhere from −80 to −30° C., or colder or warmer as required. Furthermore, because an autocascade refrigeration system operates on a single compressor, it is a compact, space-saving subsystem which is required for the most economically relevant applications.

[0075] In an alternative embodiment a conventional cascade refrigeration system can be employed wherein two parallel refrigeration loops contain refrigerants of differing vapor pressures. These two refrigeration loops establish different operating temperatures, wherein the higher temperature loop exchanges heat with the lower temperature loop, which ultimately cools the process gas. These configurations can be air-cooled or glycol-cooled or process water-cooled, as required by the application.

[0076] FIG. **2** shows an example installation in a typical production craft brewery with an existing CO2 vent gas manifold. As can be seen the previous installation has the blowoff arms dropping down vertically from the vessels labeled "Fermenter" where they are then manifolded into a common line and leave the left side of the drawing to an existing, centralized foam trap. The installed CO2 recovery system is installed in parallel to the existing CO2 vent manifold with tees that are installed into the existing blowoff arms. Each individual fermenter is then run through a hand valve which allows brewery cellar operators to valve on fermenters that are actively producing CO2 and valve off fermenters that are idle or empty and presumably full of air, which would negatively affect the capture efficiency and product purity of the recovery process. FIG. **2** emphasizes the simplicity of installation and operation which is a core design principle and distinguishes this technology from commercially available solutions. CO2 gas enters the recovery system and liquid CO2 product leaves to storage. Water is made available to the optional foam trap which is used intermittently for washdown during inlet krausen events. The foam is simultaneously pumped to a floor drain or tote during the washdown cycle. Aside from electricity required to power the system, no other utilities are required or consumed by the recovery solution.

[0077] FIG. **4** shows a constructed version of an alternate embodiment of the present invention. This system is constructed to handle a higher capacity than the preferred embodiment, with the capability to liquefy 2000 pounds of CO2 per day. This system can also be operated at a slightly elevated pressure than the preferred embodiment, which allows for a warmer temperature in the refrigeration subsystem. This process temperature is achieved in the unit depicted by FIG. **4** with a standard cascade refrigeration system employing two separate refrigeration compressors. This configuration also has a liquid phase separator with pressure control which enhances removal of noncondensable gases at this elevated pressure before the CO2 is transferred into storage. These design parameters are typically favored for higher-throughput systems which are installed in larger breweries. Larger craft breweries usually have more floor space and process utilities which are required to support a CO2 recovery system of this design.

Process Parameter Selection

[0078] The CO2 recovery process takes an un-used, vented, fermenter CO2 gas stream, and produces a high purity, locally available liquid CO2 product suitable for reuse in the very same brewing facility. This process is unlike conventional CO2 recovery technology which requires a static installation occupying a large footprint and consuming valuable brewery utility streams, resulting in a much larger system and more costly operations. In conventional CO2 recovery technology, purification steps are complex and many, with liquid water scrubbers, actively heated stripping columns and overhead condensers. This creates a complex, expensive, and cumbersome system that is not mobile or modular and would not be useful in any craft brewery. Furthermore, the cost and complexity require an economy of scale of processing capacity which is an order of magnitude larger than what a craft brewery is capable of producing. In contrast, the present invention is able to achieve a high purity product and an efficient recovery rate without using a complex system comprising multiple unit operations with elaborate upstream and downstream infrastructure including high-volume, low-pressure, ceiling-mounted feed gas storage balloons, as well as a completely engineered and custom fabricated sanitary hard plumbing manifold leading from the fermenters. The inventors were able to achieve this previously unknown result by carefully selecting the process operations and process parameters as described in detail in this application.

[0079] In summary, the inventors have found that it is possible to achieve this type of efficient CO2 recovery and purification via liquefaction by running the refrigeration subsystem to achieve a process temperature preferably in the range of approximately −15° C. to approximately −55° C. (and even more preferably −37° C. to −43° C.), at a pressure preferably in the range of approximately 75 psia to approximately 300 psia (and even more preferably under about 130 to 160 psia). The inventors also realized that this can be achieved utilizing a novel refrigeration unit. The inventors have discovered that the process parameters described here allow this type of purification and recovery to occur at the craft brewery scale, something that has not been achieved before in CO2 recovery systems. By utilizing these process parameters, the inventors were able to optimize the design of the entire system that utilizes this process, allowing the inventors to simplify the system to the point where it can be made portable and modular. The inventors have found that when one compresses and cools to the temperature and pressure ranges described here, it is possible to achieve this significant purification and recovery result in a portable apparatus.

[0080] In one embodiment, the process works by reducing the temperature of the raw, fermenter CO2 stream to an ideal temperature range. Unlike a conventional refrigeration cycle of existing CO2 recovery systems, the temperature is colder in order to facilitate a lower operating pressure as well as ease of removal of non-condensable gases. However, it is not so cold (below −56.6° C.) in which the carbon dioxide freezes into a solid block which would plug the process plumbing and heat exchangers which would have to be disassembled to remove the blockage. The CO2 recovery process temperature and pressure parameters were finely calibrated by the inventors in order to achieve this efficient recovery process, making it feasible to make the process work on a portable scale suitable for craft brewers, a previously unserved and very large brewery market segment. Because of the ideal cold temperature range, a moderate process pressure is needed which can be achieved with a two-stage compressor. Existing CO2 recovery systems do not operate at this cold of a process temperature, and so are forced to achieve the liquefaction at a higher pressure. This requires a three- or four-stage compressor which entails more capital expenditure and a larger installed footprint. Furthermore, non-condensable gases are more soluble in the liquid CO2 product at elevated pressures and so require a distillation column with a heated reboiler and a chilled overhead condenser to remove oxygen contamination below the 30 ppm standard for beverage-grade CO2. This distillation column again adds significant cost, complexity, and space to the installed recovery CO2 system.

[0081] In addition, because of the ideal temperature range, the load the compressor is reduced and the need for a distillation column is eliminated, reducing system complexity and operating costs. In addition, because of the ideal temperature range, instead of a complete distillation column to protect against oxygen contamination in the final product, no active separation system is needed aside from the phase separation that happens passively in the bulk liquid CO2 storage vessel. A stripping column is the bottom half of a distillation column and includes a reboiler, while the top half above the inlet is referred to as a fractionating column and includes an overhead condenser. In an alternate embodiment of the present invention with a moderately higher operating pressure, a simple phase separator is sufficient to drive off some noncondensable gases before the product is sent into storage. (A distillation column is twice as complex as a stripping column.)

[0082] One unique feature of the present invention is an ideal temperature and pressure range of the process stream required to perform the liquefaction of the fermenter CO2 gas. This allows the liquid CO2 product to get separation from noncondensable gas contamination, especially oxygen. The inventors recognized that refrigeration is less expensive than compression in terms of capital equipment, but more expensive in terms of operating (power) costs; however, they realized that this is greatly beneficial since this is the only configuration that supports minimization of the process to suit installation and operation in a craft brewery. The inventors also recognized that by reducing the temperature of the raw gas stream to a lower temperature range than previously achieved in a mobile scale, a lower compression ratio (and hence operating pressure) is possible while still achieving desirable results. Such a lower operating pressure results in an overall lower capital cost for the entire system because lower-pressure components and subsystems can be utilized.

[0083] The ideal temperature and pressure ranges for the CO2 recovery process were selected as follows by the inventors. A most preferred temperature range for the process is −37° C. to −43° C., but temperature ranges from −15° C. to −55° C. are feasible, and more preferably between −30° C. and −45° C., and possibly between −20° C. to −50° C. There would be little benefit to going below −55° C. and a significant cost to go below that temperature, as dry ice starts to form at −56.6° C., and it is desirable to avoid forming any amount of solid CO2. Accordingly, based on the above temperature ranges, a most preferred pressure range is 130-160 psia, and preferably 120-175 psia. However, pressure ranges of 75-300 psia are possible in various embodiments of the CO2 recovery process. Higher pressures are also possible in some embodiments since CO2 liquefies at 930 psia at 25° C. Existing CO2 recovery systems utilize higher pressures because they have not been able to achieve such low process temperatures on any scale.

[0084] In addition, many single-brewery CO2 recovery systems rely on higher compression and moderate refrigeration temperatures to cool the process gas. Unexpectedly, the inventors found active refrigeration to offer many advantages, as described here. On a high level, the CO2 recovery process utilizes compression, refrigeration, and purification. If one were to assume that each of the three sub-processes have been optimized and has equal cost and complexity, what this implies is that by optimizing one of the three sub-processes, it is possible to save on the capital and operating costs of the other sub-processes. The inventors had the insight that by improving the middle of the three processes—namely, refrigeration—it was possible to significantly save on the cost and complexity of the two processes before and after it—namely, compression and separation. After the vented, dehydrated, deodorized CO2 fermenter gas is compressed and refrigerated to the ideal pressure/temperature ranges described above, there is a simple liquid/vapor separation either in the storage vessel in the preferred embodiment or in a separate phase separator in an alternate embodiment. The gaseous impurities that leave the liquid/vapor separator are vented safely to atmosphere. Meanwhile, the liquid CO2 product is ready for use from the liquid storage vessel after passing through an ambient vaporizer. That is, after compression and refrigeration, the stream components that remain are primed for removal of noncondensable contaminants without any further processing equipment.

[0085] In summary, the existing single-brewery CO2 recovery systems are able to recover and purify fermentation CO2, resulting in a liquid CO2 product in storage with significant cost, complexity, and footprint requirements. By carefully selecting the process parameters and utilizing a novel system design and a unique refrigeration system able to reach very cold temperatures on a mobile, modular system suitable for installation in a craft brewery, the inventors have been able to achieve something on the portable scale that is unprecedented in CO2 recovery technology.

[0086] In summary, the CO2 recovery process offers the following primary value propositions, which separate it from conventional CO2 recovery systems:

[0087] 1. Mobility, which is essential for installation in a craft brewery.

[0088] 2. The CO2 recovery system has minimal process inputs or outputs and a minimized reliance on process utilities from the installation facility. The minimal requirements for operation are electrical service to power the unit and fermentation CO2 gas to provide a feedstock to the system.

[0089] 3. The system is compact due to choice of ideal operating temperatures and pressures, which minimizes the installed footprint, which allows installation inside cramped, busy craft breweries.

[0090] 4. Using a novel configuration and application, the inventors are able to eliminate active purification unit operations, which greatly reduces capital cost and utilities consumption, while maintaining production of a very high purity liquid CO2 product.

Experimental Results

[0091] The inventors have built and tested several embodiments of the present invention. This section presents various experimental results from such tests.

[0092] The criteria required for a CO2 sample to meet beverage grade certification according to the International Society of Beverage Technologists (ISBT) are listed inTable 1 (Source: *Fountain Carbon Dioxide Quality Guideline*, International Society of Beverage Technologists, September 2006).

[0093] The initial hurdle to validate the present invention was to demonstrate purity results that are as good or better than industrially available CO2. Toward this end a pilot unit was constructed and installed in a major craft brewery for operational testing. Operations were satisfactory and a significant amount if liquid CO2 was recovered. A sample was collected and sent off for testing. Results are listed as Sample 1 in Table 2. A simplified analysis was performed since many contaminants can be eliminated simply by knowing they are not present in the fermenters to begin with. Noncondensable gases, especially oxygen, were the primary liability for contamination, and a result of 1.1 ppm is clearly a superior sample when compared to the 30 ppm allowed by the industry standard. Furthermore, a gas analysis typical of commercially available industrially sourced CO2 is shown in Table 3. The oxygen content listed in that assay is 1.570 ppm, which is nearly 50% inferior to the performance of the present invention. In addition. gas assay points are typically located at the beginning of the transportation chain, upon which the liquid product is transferred between multiple trucks and tanks of varying quality. There is a very real potential for contamination along the way. The sample recovered by the proposed CO2 recovery technology was sampled from the storage container at the brewery, guaranteeing on-site quality control. By miniaturizing CO2 recovery technology that connects the source to the application, a very real potential for human error is removed. Taste testing of water and major flagship beer products at this and two other major craft breweries of recovered CO2 with this pilot unit proved even or better than the industrial CO2 control samples.

[0094] The superior purity result permitted design, fabrication, construction, and installation of a production version of the present invention. This unit was installed at a larger scale major craft brewery again for operational testing and purity analysis. Once operations were deemed acceptable, hundreds of liters of recovered liquid CO2 were collected and stored for reuse in purging fermenters and bright tanks in the brewery cellar. A liquid sample was again drawn and sent off for analysis. Again, the species of interest given the surrounding cleanliness and sterility of upstream and downstream vessels was oxygen. Results came back very consistently at 1 ppm oxygen as shown under Sample 2 in Table 2. Again, the in-house recovered CO2 was significantly superior in quality to purchased industrial CO2.

TABLE 1

ISBT Guidelines for Beverage Grade Carbon Dioxide

Metric	Volumetric concentration threshold
Purity	99.9% min
Moisture	20 ppm max
Oxygen	30 ppm max
Carbon monoxide	10 ppm max
Ammonia	2.5 ppm max
Nitric oxide/nitrogen dioxide	2.5 ppm max each
Nonvolatile residue	10 ppm (weight) max
Nonvolatile organic residue	5 ppm (weight) max
Phosphine	0.3 ppm max
Total volatile hydrocarbons	50 ppm max
Acetaldehyde	0.2 ppm max
Aromatic hydrocarbon	20 ppb max
Total sulfur content	0.1 ppm max
Sulfur dioxide	1 ppm max
Odor of solid CO2	No foreign odor
Appearance in water	No color or turbidity
Odor and taste in water	No foreign taste or odor

TABLE 2

Ion-exchange chromatography results for noncondensable contamination of recovered CO2 from craft brewery fermenters.

	Sample 1	Sample 2
Date	Mar. 22, 2013	Nov. 18, 2013
Hydrogen	<0.1 ppm	<1 ppm
Oxygen	1.1 ppm	1 ppm
Nitrogen	<0.1 ppm	2 ppm
Carbon monoxide	0.1 ppm	<10 ppb

TABLE 3

Example purity assay of commercially available industrially-sourced liquid carbon dioxide.

	Volumetric Concentration
Moisture	0.260 ppm
Oxygen	1.570 ppm
Argon + Oxygen	0.160 ppm
Nitrogen	4.480 ppm
Carbon monoxide	0.120 ppm
Total hydrocarbon	0.810 ppm
Total sulfur	0.003 ppm
Ammonia	0.000 ppm
Acetaldehyde	0.000 ppm
Nitrogen oxides	0.000 ppm
Aromatic hydrocarbons	0.000 ppm

Detailed Schematic of the CO2 Recovery Process

[0095] A detailed process and instrumentation diagram (P&ID) for the recovery of vented CO2 is now described according to one embodiment of the CO2 recovery system as shown in FIG. **5**. The P&ID depicts the flow vented, wet fermentation CO2 through the various components of the recovery process. In brewery applications, the vented CO2 is obtained downstream of any air locks, trub buckets, or foam traps (not shown).

[0096] The CO2 recovery system is designed to receive vented carbon dioxide gas from the fermenters in a production craft brewery. The recovery system processes the vented fermenter gas into a liquid product stream that meets the stringent purity requirements required to be classified as beverage grade carbon dioxide.

[0097] The CO2 recovery process begins at an optional foam trap (**501**). This foam trap provides a second layer of protection of the process from liquid ingress. This is in addition to any upstream air locks or foam traps already installed in the brewery. Liquid entering the system would damage all downstream components, including the desiccant material, the deodorizing adsorbent, the compressor itself, and the refrigeration heat exchangers. Final product purity would also be compromised since only 20 ppm of water is permissible in the final product. The foam trap provides a collection volume for any humidity condensation or krausen foam that may travel from the fermenters' blowoff arms to the inlet of the recovery system. An optical sensor detects a high level of accumulation in the foam trap and begins a washdown cycle, which simultaneously mists liquid water into the foam trap and pumps it from the bottom of the vessel.

[0098] The humidified fermenter CO2 enters a regenerative adsorption desiccant system for dehydration that removes any water that exists in the process gas. The resulting CO2 gas has an aqueous dew point below −73° C. (lower than the coldest temperature in this embodiment) which reduces the potential for ice formation in the refrigeration or storage portions of the system. The maximum dew point can be adjusted based on the system's operating temperature at its coldest point (after the autocascade). One can see from FIG. **5** that there are two desiccant beds (**503**) in parallel, allowing one to be regenerated by dry, hot air or CO2 from other parts of the process while the other bed is valved into the main process line and is actively drying the inlet fermenter gas. The regeneration of the offline dry bed is accomplished with alternating process flow by actuating the four-way valves (**502**) and adding heat, which in this embodiment is accomplished with electric band heaters (**504**).

[0099] The conditions required for liquefaction of the CO2 stream begin at the two-stage compressor (**506**). The suction pressure is continually monitored by a pressure transmitter on the inlet gas downstream of the optional foam trap. The reading of the pressure transmitter informs the variable frequency drive (VFD; **505**) of an appropriate speed at which to operate the compressor, which determines the instantaneous processing rate of the entire process. The frequency output of the VFD drives the electric motor that is mechanically coupled to both stages of compression. The compressor is oil-free to maintain purity specifications and is air-cooled to reduce installation size, avoid reliance on plant utilities, and to simplify operation. In this embodiment, two stages of compression are used to bring the fermenter effluent to a sufficiently high pressure to enable liquefaction of the CO2. If the desiccant beds were not placed upstream of the compressor the rise in pressure of the humidified process CO2 would cause partial condensation of moisture content. This would lead to complications including microbial growth, corrosion of mechanical components, and potential damage to the compressor pistons due to the incompressible nature of liquid water. In short, compression occurs in two stages, where the compressor is air-cooled and on speed control, which tracks the variable CO2 flow rate leaving the fermenters. This flow control minimizes variations in the slightly positive fermenter pressure, which is a critical parameter for maintaining on-spec production of quality beer products. Once the gas is sufficiently dehumidified and at high pressure, it is sent through a deodorizing scrubber filled with activated carbon (**507**). The preferred type of activated carbon is ideal for removing trace organic compounds from a gaseous CO2 stream. The most preferred specification for the activated carbon is a particle size distribution with over 90% of the particles falling with the range of 2.00 mm (10 mesh) to 4.75 mm (4 mesh) and with an iodine number, mg/g, equal to 1050 minutes. The carbon bed will last for approximately 30 days of full-time operation with typical loading from common ale recipes produced by craft breweries. The activated carbon is then dumped and refilled. The loaded carbon is sent back to the manufacturer for regeneration within stringent conditions to preserve the pore size and internal microstructure of the activated carbon particles. The carbon can then be sent back to the client at a reduced rate to further improve the process economics.

[0100] Once the fermenter CO2 gas is dehumidified, compressed, and deodorized, it is now ready to begin the chilling process to liquefy the CO2 at the elevated operating pressure. In the preferred configuration and in FIG. **5** the optimally cold temperature is achieved by an autocascade refrigeration subsystem, described previously in greater detail. While FIG. **5** shows a simplified diagram of the refrigeration system omitting some of the details, the three major components are represented: compressor (**508**), air-cooled condenser, and process evaporator (**509**). In a preferred embodiment the air-cooled condenser is controlled by a feedback loop that measures the liquid CO2 product temperature and changes the fan speed accordingly. This is a technique to minimize energy consumption required to operate the recovery unit. Because dry ice can form at process temperatures in a low-pressure scenario, operation of the refrigeration system is locked out by a pressure transmitter that measures the discharge pressure of the compressor. Once the system pressure is sufficiently high to protect against dry ice formation, the refrigeration compressor is commanded on to commence liquefaction of the CO2 product.

[0101] The final process vessel (**510**) in FIG. **5** can represent either a standalone phase separator located prior to bulk storage or it can represent the final liquid CO2 storage dewar. In either configuration, the vessel is operated under level control, which prevents flooding of the liquid CO2 product into areas of the process or into the production facility. The headspace of the vessel is composed primarily of CO2 gas, but the majority of any noncondensable gases introduced to the process will reside here as well. The vessel is pressure relieved at a pressure near the operating pressure, which is near 160 psig for the preferred embodiment. This pressure is significantly lower than conventional CO2 recovery process, so the noncondensable gases easily leave through the natural venting process associating with internal pressure regulation. This removes an otherwise very complicated distillation column from the process which is required by the conventional process to remove noncondensable gases in solution to meet beverage grade purity standards.

[0102] Once the vented headspace gas leaves the top of the phase separator or storage vessel, it does not directly vent to atmosphere. Staying consistent with the design intent of a compact, self-sufficient design with minimal reliance on utilities and electricity consumption, the vent gas is leveraged to regenerate the offline desiccant bed. The vent gas travels through the pressure control regulator which greatly reduces its pressure. This low pressure, predominantly CO2 gas stream travels through one of two four-way valves (**502**) and into the offline desiccant bed, whereupon the gas becomes heated by the vessel heater (**504**), marked “Q” to represent heat input. The heater on the desiccant bed which is actively dehumidifying the inlet process gas remains off until the bed is saturated. Logic for transitioning the beds is based on a combination of inputs from temperature transmitters, flow transmitters, timers, and humidity transmitters. The combination of elevated temperature and the convective medium provided by the flowing gas desorbs water molecules from the desiccant material and transports the water vapor through second four way valve (**502**), whereupon it vents safely into the atmosphere. In an alternate embodiment, a regenerative blower can be added to augment the regenerating gas flow rate. In another embodiment the heaters can be applied directly to the regenerating gas prior to the vessels instead of heating the vessel walls directly.

[0103] The absence of a cryogenic liquid transfer pump should be noted as yet another example of an intentional simplification and cost reduction of the present invention.

Refrigeration Subsystem Embodiments

[0104] In order to achieve the ideal temperature range to achieve liquefaction and purification of CO2 at a moderate pressure as described in this application, a highly novel and original refrigeration system was designed, built, and tested. The refrigeration system allows for efficient, small-scale recovery of fermenter CO2 into a liquid product stream that meets the stringent purity specifications outlined in Table 1. In particular, it enables the efficient removal of noncondensable gases, especially oxygen (**02**), from the liquid CO2 stream, where its presence would unfavorably impact the taste and flavor characteristics of the packaged beer products.

[0105] Since temperatures lower than −40° C. are preferred in this invention, in some embodiments cascade and/or autocascade refrigeration systems may be used. In a preferred embodiment of the present invention, an autocascade refrigeration system is utilized, as shown and described in relation to FIG. **5**. Some of the features and advantages of such an autocascade refrigeration system is now discussed, along with alternative embodiments. In a typical refrigeration system, the maximum difference between the warm and cold temperature of a refrigeration cycle is limited by properties of the refrigerant and/or losses associated with the transport of the refrigerant. For larger temperature differences, one has to arrange several refrigeration cycles “above” each other, each cycle spanning a certain temperature difference. A typical cascade refrigeration system is made up of separate but connected refrigeration stages, each of which have a primary refrigerant wherein the refrigerants work in concert to reach the desired temperature. The principal is to condense refrigerants that are capable of achieving ultra-low temperatures that would otherwise not be able to condense at room temperature. The reason that two refrigeration stages are used is that a single stage cannot economically achieve the high compression ratios necessary to obtain the proper evaporating and condensing temperatures.

[0106] The cascade refrigeration system comprises two separate circuits, each using refrigerants appropriate for its temperature range. The two circuits are thermally connected by the cascade condenser, which is the condenser of the low-temperature circuit and the evaporator of the high-temperature circuit. Refrigerants that may be selected for the high-temperature circuit include R-22, ammonia, R-507, R-404a, and so forth. For the low-temperature circuit, a high-pressure refrigerant with a high vapor density (even at low temperatures) should be selected (such as ethylene).

[0107] The condenser of the first stage A, called the “first” or “high” stage, is fan cooled by the ambient air. In some embodiments, a liquid coolant may be used. The evaporator of stage A is used to cool the condenser of stage B, called the “second” or “low” stage. The unit that makes up the evaporator of stage A and the condenser of stage B is referred to as the “inter-stage” or “cascade condenser.” Cascade systems use two different refrigerants, one in each stage. The two-stage cascade system uses these two refrigeration systems connected in series to be able to achieve temperatures as low as −85° C.

[0108] In an autocascade refrigeration system, in contrast, a single compressor system that can achieve temperatures as low as −100° C. is utilized. An autocascade refrigeration system is a complete, self-contained refrigeration system in which multiple stages of cascade cooling effect occur simultaneously by means of vapor-liquid separation and adiabatic expansion of various refrigerants. Physical and thermodynamic features, along with a series of counterflow heat exchangers and an appropriate mixture of refrigerants, make it possible for the system to reach low temperature. The autocascade is a cooling/freezing system using one compressor and two or more different refrigerants and heat exchangers to reach a lower temperature, wherein the first refrigerant cools the next and so on. The components of an autocascade refrigeration system include a vapor compressor, an external air- or water-cooled condenser, a mixture of refrigerants with descending boiling points, and a series of insulated heat exchangers.

[0109] The autocascade refrigeration system uses mixed refrigerants along with internal heat transfer and phase separation to achieve optimally cold temperatures through a single compressor. The most basic autocascade cycle uses only a single phase-separator and one additional heat-exchanger (compared to a standard refrigeration cycle) to mimic the behavior of a conventional two-stage cascade refrigeration system.

[0110] The refrigerant in the autocascade cycle is compressed as a gas and then sent through a condenser where heat is removed to liquefy the refrigerant. Because an autocascade uses mixed refrigerants of differing vapor pressures, the condensation of the gas is only partial. The refrigerant with the higher vapor pressure remains predominately gaseous whereas the refrigerant with a lower vapor pressure is liquefied. This two phase flow is then sent to a vessel where the gas and liquid phases are separated. The liquid stream is dropped in pressure to provide a cooling effect which is used—in a heat-exchanger—to further chill and condense the gas stream. The gas stream (now liquefied) is then dropped in pressure to provide the final useful cooling duty desired. In this way, an autocascade cycle essentially replaces two stages of conventional cascade refrigeration.

[0111] The above description is of the simplest autocascade cycles possible. Significantly more complex cycles are possible for use with the present invention. In some embodiments of the present invention, additional "staged" phase-separation steps with their corresponding internal heat transfer cooling afterwards can be used to reach even colder temperatures.

[0112] As a result of its multiple refrigerants and unique design, the autocascade design of the present invention can attain colder temperatures in a single stage than possible in a conventional cascade refrigeration cycle, so much so that a single stage autocascade refrigerator can replace a two-stage (or more) cascade refrigerator. While such an autocascade unit would not be as energy efficient as a two-stage conventional cascade system, it would be simpler and cheaper to build and operate. Because the CO2 recovery system primarily needs to be very compact and affordable to obtain, the trade of reduced capital and operating costs at the expense of increased energy costs offered by the autocascade is potentially highly attractive and may be considered a preferred embodiment.

[0113] The temperatures reached by the autocascade may be altered by altering a composition of the mix of refrigerants. Depending a variety of conditions that vary between installations, including higher air contamination, elevated operating pressures, and excessive electricity rates, the CO2 recovery system may thus be tuned to reach appropriate temperatures for effective operation with the gas composition at hand.

[0114] In a preferred embodiment, the CO2 recovery system is an innovative air-cooled autocascade system, as discussed previously in relation to FIG. **5**. This allows for a more thermodynamically efficient design while keeping the system compact and portable. While the thermodynamic efficiency is not necessarily optimal, because the CO2 recovery system is installed in an environment where space and purchase price are at a premium, it is sensible to trade some thermodynamic efficiency for a more mechanically compact design.

[0115] In the autocascade system, one refrigeration compressor is employed, with the process gas temperature typically ranging from −15° C. to −55° C., depending upon the particulars of the design. In the preferred configuration, the refrigeration system is of an autocascade design. The refrigeration cycle utilizes air-cooled heatexchangers to eliminate the need for liquid coolant which may not be available at all operating sites. However, if water or chilled ethylene glycol is available, the refrigeration cycle can be modified to utilize this resource for enhanced refrigeration performance.

[0116] In one alternative embodiment not shown in the figures, the refrigeration system is a conventional cascade refrigeration which employs two separate refrigeration compressors. Both stages are air-cooled, and exchange heat between the two stages with a compact countercurrent heat exchanger. The first stage is similar to the warmer stage of a standard cascade refrigeration cycle (but with two evaporators, one for the process gas and one for the other stage of refrigeration) and the second, colder stage, is also a standard cascade design.

[0117] Yet another embodiment is very similar to the system described in the preceding paragraph. In this embodiment the warmer stage of the cascade refrigeration system does not exchange heat with the process gas in a pre-cooling step. The warmer stage only exchanges heat with the lower temperature cascade refrigeration loop and loses heat through an air-cooled condenser. The colder stage is the only refrigeration loop which exchanges heat with the process gas, achieving a process temperature suitable for liquefaction of CO2 in a single compact heat exchanger.

[0118] For improved thermodynamic efficiency, both refrigeration loops may be used, in series, to chill and liquefy CO2 from the inlet gas stream. This requires two evaporators on the warmer refrigeration loop (the cascade evaporator/condenser heat-exchanger and a second heat-exchanger whose duty chills the CO2 gas stream as well as provides some superheat to the vapor returning to the refrigeration compressor suction inlet). Various alternative designs can range from a simple, single stage refrigeration cycle to three or more stages of cooling. Further any stage of a single or multi-stage configuration could be of a cascade design, or alternatively, an autocascade refrigeration stage, or alternatively of the hybrid design according to the present invention.

Dehydration Subsystem

[0119] Dehydration is necessary to remove entrained water moisture and any trace humidity content from the raw fermenter CO2 gas stream before refrigeration to avoid water ice formation, which would damage or destroy equipment. Due to the very cold temperatures reached by the refrigeration system, as low as −70° C. in some embodiments, it is essential to remove any trace humidity content in the raw CO2 gas stream. Therefore, a very efficient dehydration system is needed to take the inlet CO2 gas (which is saturated with moisture at the fermenter temperature) to a humidity equivalent to having a dew point below the coldest process temperature which can be as low as −60° C. in some embodiments. The present desiccant system, described below, is able to remove any trace humidity content that is required by the very cold temperature refrigeration. The dehydration system should be tuned to produce processed gas that has a dew point that is lower than the coldest temperature produced by the refrigeration system.

[0120] In a preferred embodiment, some water condensation happens in the gas transmission lines leading from the bank of fermenters to the CO2 recovery system. Final dehydration occurs in desiccant dryer beds. Examples of desiccants used in the desiccant beds include silica, alumina, silica alumina, calcium oxide, molecular sieves (such as zeolites), activated charcoal/carbon, and other like materials.

[0121] According to the beverage-grade CO2 purity standard as defined by the ISBT and as outlined in Table 1, the moisture level permitted in the final liquid CO2 product is capped at 20 parts per million (ppm). In addition to this specification there is a process restraint which requires the dew point of the process gas to be reduced to a value below the coldest process temperature. The only method of water removal which satisfies these criteria is heterogeneous adsorption of water by a solid desiccant medium. The approach also provides a low pressure drop solution which improves overall process economics.

[0122] Dehydration is typically carried out in the prior art using a four (4) step process that is less effective operation, requires larger beds, and longer hold time. The beds of the present invention in its preferred embodiment are smaller and more efficient because the inventors have developed a novel 2½ step dehydration process. The prior art four-step process includes: (1) actively dehydration, (2) depressurizing, (3) regenerating, and (4) re-pressurizing. If four steps are used, then four beds are needed. But the inventors have developed a novel dehydration process using only two beds by optimizing the cycle into only 2½ steps. The 2½ steps of the dehydration process include: (1) actively dehydrating, (2) regenerating, and a ½-step re-pressurizing cycle, which is quick, but enough to operate with only two beds. It is important to mention that the ½-step re-pressurization only works due to the moderate pressure of the system, which is only feasible with the very cold refrigeration temperature. Four-way valves simplify switching between the two beds in the 2½ step process. During the valve switch momentary pressure communication occurs between the two beds to equalize the pressures at an intermediary value. Once the switch is complete the process quickly reestablishes itself at steady-state pressure values.

[0123] Adsorbent molecular sieves can achieve moisture contents as low as 0.1 ppm, thereby mitigating the risk of damaging process components located in the cryogenic section such as pipes, heat exchangers, and expansion devices by freezing water inside them. The molecular sieve material is typically distributed inside round vessels in a packed bed configuration. Like other desiccants, molecular sieves have limited adsorption capacity and must be replaced or regenerated at given service intervals. For continuous dehydration service, a multi-bed system must be utilized where one bed is in service while the other is being replaced or regenerated, and the beds can be seamlessly switched in and out of service.

[0124] In general, alternating two-bed systems are used where bed “A” is in service and the process stream is dehydrated. At the same time, a dry, hot regeneration gas is flowed through bed “B” in a counter-current direction to remove moisture from the surface of the adsorbent material. Once the regeneration is complete, a set of valves are actuated such that the process gas is directed into bed “B” and the regeneration gas is flowed through bed “A” countercurrent to the process flow. This cycle can be repeated indefinitely until the adsorbent exceeds its useful life, usually years.

[0125] Typically, the adsorbent beds are sized so that cycle times are on the order of hours. The packed bed diameter is tuned to provide an acceptable superficial velocity, and the height is adjusted to achieve the required holding capacity. The diameter is limited by pressure containment, and the bed height is limited by overall pressure drop and/or crush strength of the adsorbent material. Optimal sizing can be iteratively obtained by balancing the time required for regeneration with the time available to adsorb water before the holding capacity is reached.

[0126] Most regenerative dehydration units employ a temperature-swing process, where the regeneration gas is externally heated. The regeneration gas must carry enough energy to bring the adsorbent material to an elevated temperature, as well as to provide the heat of desorption of the water mass. Additional heat is required to overcome the thermal losses through the piping, vessel wall, and effluent gas. After the removal of the water at the regeneration temperature, the external heater is taken off line and the regeneration gas cools the bed back to the process temperature.

[0127] A standard valving arrangement requires four on-off valves per bed, to allow the process stream and regeneration gas to flow through one bed at a time in a counter-current fashion. During the switchover, all eight valves are actuated simultaneously to swap beds. If a pressure difference exists between the process stream and the regeneration gas, a pressure equalization valve between the two beds is required. Pressure equalization must be done gradually to avoid adsorbent attrition, adding to cycle time. If the process gas is not compatible with the regeneration gas, vent valves and inert purge valves may be required to expel the unwanted gas and condition the beds prior to pressure equalization and/or switchover.

[0128] In a preferred embodiment of the present invention, two 5 A molecular sieve adsorbent beds are used. The process stream is a predominantly CO2 gas stream containing up to 2% water by volume, at a maximum volumetric flow rate of 2 standard cubic feet per minute (CFM). The design inlet conditions are 78° F. and a pressure ranging from 0-2 psig; however the unit can operate satisfactorily at off-design conditions. The vessel is sized to provide a maximum superficial velocity of 35 ft/min at flow rates up to 2 CFM. The packed height is 18 inches, resulting in a cycle time of 6 hours at the maximum flow rate. Longer cycles are possible at lower flow rates.

[0129] In the preferred configuration, the regeneration gas is the vapor stream leaving the liquid CO2 storage dewar, which has trace amounts of noncondensable gasas at a temperature and pressure near ambient. The regeneration gas is actively heated with an electric band heater mounted directly onto the desiccant bed undergoing regeneration of its adsorbent inventory. The heater delivers thermal energy to the regenerating desiccant bend obtaining a satisfactorily regenerated isothermal temperature profile around 450° F. After 4.5 hour, the power to the electric heater is removed, and the bed is cooled from 450° C. to 40° C. by the unheated regeneration gas in 1 hour. There is 0.5 hour of standby time to execute the switchover between beds.

[0130] The process gas flows downward through the bed and the regeneration gas flows upward, lifting the adsorbed water from the bed. The system utilizes a simplified valve arrangement based on two 4-way cross-port valves (as seen in FIG. **5**). The process gas flows through one circuit of the valve while the regeneration gas flows through the other circuit in a counter-current direction. With this configuration, the function of eight simple on-off valves can be replicated by two 4-way valves placed at the entrance and exit of each bed. At the time of switchover, both valves turn simultaneously. Because both the process gas and the regeneration gas are predominantly CO2, no vent and purge step is necessary.

[0131] In summary, a preferred embodiment of the final dehydration subsystem is an alternating two-bed system, able to dry up to 2 CFM of moisture-saturated CO2 gas in 6 hour cycles. The system has several unique features that save on capital expense and conserve energy. Use of four-way valves instead of on-off valves simplifies piping and controls while saving space and expense. The location of the desiccant beds upstream of the compressor and using vented gas from storage as the regeneration gas eliminates a blower, while making the switchover process faster and more seamless. Finally, the system is designed to remain as compact and simple as possible, allowing enhanced opportunity for installation in a variety of cramped craft breweries.

[0132] Alternative embodiments of the CO2 dehydration system could employ systems involving more than two beds, and/or use other methods of moisture capture, including alternative desiccants, or water capture using coolers or freezers.

Controls Subsystem

[0133] An automatic control subsystem is a required element of any physical separation process, being necessary to manage the various components of the system, maintain a satisfactory performance in the case of changing conditions, and reduce the burden on the system operator to a reasonable level. The CO2 recovery unit utilizes a novel control system that is totally autonomous, requiring minimal operator oversight and intervention. The defining feature of the control system is the ability to automatically track changes in CO2 production in real-time, therefore avoiding large inlet buffer tanks, and maximizing the amount of CO2 captured.

[0134] Capacity control is achieved by varying the rotational speed of the compression subsystem in real-time. In the present embodiment, a pressure transmitter feeds back an electrical signal proportional to the pressure at the compressor inlet to a variable frequency drive (VFD). The VFD compares this signal to a user-adjustable pressure setpoint, and adjusts the speed accordingly to maintain the setpoint pressure. When CO2 production is insufficient to maintain the setpoint pressure at the lowest possible speed, an automatic interlock stops the compression equipment until the pressure rises to a satisfactory level, at which point the compression will resume under automatic capacity control.

[0135] The dehydration system is also managed by the automatic control subsystem. In the present embodiment, a humidity transmitter feeds back an electrical signal proportional to the relative humidity at the compressor inlet to a setpoint relay. If the humidity exceeds the setpoint, the relay will operate and suspend the compression and refrigeration equipment. During the interruption, regeneration of the other dehydration bed continues, and is indicated by the operation of a temperature switch. When the temperature switch operates, the regeneration is complete, and after a cool-down period the controller will operate the directional valves that switch dehydration beds, and automatically restart the compression and refrigeration equipment. In an alternative embodiment, the aforementioned elements could be controlled by timing relays instead of humidity and temperature transmitters.

[0136] An innovative feature of the control system is management of the refrigeration subsystem in the case of changing load and ambient temperature conditions. Since the refrigeration system is ultimately air-cooled, it is necessary to adjust the amount of air-flow across the air-cooled refrigerant condenser in order to maintain satisfactory condensing temperature and pressure, and adequate refrigeration capacity. In the present embodiment, a temperature transmitter feeds back an electrical signal proportional to the refrigerant condensing temperature to a setpoint relay, which can select between discrete fan speeds to maintain the refrigerant condensing temperature near the setpoint. In an alternative embodiment, the temperature transmitter could feed back to a VFD (or other type of motor speed control device) to maintain the refrigerant condensing temperature. In the present embodiment, when the CO2 production drops below the minimum required to fully load the refrigerator, a temperature switch set to a user adjustable setpoint in the liquid CO2 product line will suspend the refrigeration equipment in order to save energy until the product temperature rises to an adequate level, at which point the refrigeration equipment will restart under automatic control.

[0137] Another innovative control feature of the CO2 recovery process was introduced to prevent the formation of solid CO2 (dry ice) in the system, which is undesirable. Observing the CO2 phase equilibrium diagram, it can be seen that CO2 cannot exist as a liquid if its partial pressure is below 75.1 psia. Therefore, if the pressure at the refrigerant evaporator is below this threshold, a temperature switch will operate and lock-out the refrigeration equipment until the pressure rises above the threshold. Further noting the CO2 phase diagram, above the triple point pressure of 75.1 psia, liquid CO2 will begin to nucleate solid phase on surfaces having temperatures below −56.6° C. Therefore, if the temperature of the refrigerant at its coldest point drops below this threshold, a temperature switch will operate and suspend the refrigeration equipment for a period of time sufficient to allow the refrigerant to warm above the threshold and also melt any dry ice formed.

[0138] The control subsystem as described above was carefully designed to maximize process up-time and minimize operator monitoring and intervention. Thus, the control system was designed and constructed to be fully autonomous, having only one button press necessary to bring the process from full stop to full automatic operation (run mode), and only one further button press to safely shut down the system (stop mode). A network of electromechanical safety switches and process interlocks allow the system to operate safely and satisfactorily without continuous operator monitoring. However, process status, alarms, and maintenance reminders are displayed to the operator through an array of lights and other indicators mounted on the control panel.

Various Use Cases of the Present Invention

[0139] Several alternative use cases of the present invention are now presented. These use cases are illustrative of the possible applications of the present invention and are not meant to be exhaustive or limiting.

[0140] The present invention relates to enabling the recovery of carbon dioxide (CO2) from industrially relevant waste streams containing a sufficiently high concentration of CO2. The invention is most readily applicable to the burgeoning beverage alcohol industry (microdistilleries, craft vintners, and craft breweries) in the United States, most especially the craft beer brewing industry. In a craft brewery, carbon dioxide can be recovered from fermentation tanks, bright beer tanks, and other process vessels, tanks and lines. The recovered CO2 can then be used in forced carbonation, kegging, canning, bottling, purging, and other applications associated with production of packaged beer. More specifically, this invention relates to a modular system for separating carbon dioxide from non-condensable gases such as nitrogen and oxygen, while dehydrating, deodorizing, and purifying the carbon dioxide to a quality sufficient for beverage applications, and also liquefying the carbon dioxide and transferring it into a storage vessel so that it can be re-used (which would reduce the amount of carbon dioxide that is vented by breweries, as well as the reduce the amount of carbon dioxide that breweries have to purchase for plant operations).

[0141] Microdistilleries are another growing business model domestically and abroad which generates large volumes of vented CO2 produced during ethanol fermentation of glucose by yeast. Many small-scale distilleries use traditional techniques involving open fermenters which make capture of the CO2 gas difficult. However, many are investigating floating-head open fermenters which would allow CO2 recovery, and many others are starting with brewery-type closed sanitary fermentation vessels, which has been demonstrated as a feasible CO2 source. Many other microdistilleries source their wash from craft brewers who could potentially be utilizing CO2 recovery consistent with the present invention. A distillery could use CO2 around the production facility to purge tanks, vessels, and lines, drive pneumatic controls elements, and even produce some recently popular carbonated high-proof alcoholic beverages. Sales of superior quality CO2 to outside organization always remains as a viable revenue model.

[0142] Microvintner operations have become recently popular in the United States and other countries as regions look to capitalize on their local fruit crops. Wine fermentation is conducted in a variety of vessels similar to microdistilleries, with some designs more appropriate for CO2 recovery than others. But there still remains a largely unserved market for wine producers who vent CO2 from fermentation and purchase industrial CO2 to produce and sell sparkling wine-type alcoholic beverages. The present invention would be very appropriate for such an operation even with intermittent CO2 production from seasonal fermentations.

[0143] The present invention is designed to enable the recovery of carbon dioxide (CO2) from industrial waste streams containing a majority of CO2. Processes that produce such streams include pharmaceutical synthesis via batch fermentation, fuel ethanol plants utilizing starchy feedstocks, anesthetic asphyxiation in slaughterhouses, ammonia production via steam reforming of natural gas, coal and biomass gasifiers, various thermochemical and Fischer-Tropsch-type gas-to-liquids conversions, soft drink bottling plants, plastics production facilities using the solvent properties of CO2 for materials property enhancements, coffee and tea decaffeination towers, so-called green dry cleaners, medical sterilization, and production of beverage alcohol products. Some of these processes require food- and beverage-grade CO2 to produce their products, but others don't. Many industrial processes have a very real economic need for CO2 recovery at a small scale but do not operate within stringent food, beverage, or sanitary constraints. For these applications in alternate industries the purification steps can be removed, further simplifying, miniaturizing, and reducing cost of the CO2 recovery system.

Potential Macro-Environmental and Macroeconomic Impact

[0144] Previously, the impact of the technology on a single brewery was discussed to show that it would be highly profitable. This is the key to the propagation of the technology to a large number of craft breweries. In this section, the macro-environmental and macroeconomic effect of the technology is discussed once it has been put into broad use, showing that it could have a major impact in both increasing efficiency of operation, offsetting an expensive commodity cost, and reducing carbon emissions.

[0145] In the United States alone, almost 13 million barrels (bbl) of beer (1 US beer barrel=31 US gallons) by craft brewers in 2012, over 90% (12 million bbl/year) of which is produced by breweries producing 3000 bbl annually or greater. Due to certain limits on miniaturization of the process, the minimum brewery size that can be serviced is 3000 bbl/yr. Assuming a metric that a 60,000 bbl/yr brewery produces an average of 1 ton CO2/day, that is sufficient market, in the United States alone, for 1300 CO2 recovery systems units. If there was 50% market penetration then almost 100 tons of wasted high-quality CO_2 would be avoided. Meanwhile, an economic gain of $7 million to $36 million per year is expected industry wide by offsetting the cost to purchase and deliver industrially-sourced CO2 of inferior quality.

Long-Felt, Unsolved Need for Craft Brewery-Scale CO2 Recovery Technology—Trade Association Data

[0146] According to annual production numbers for craft breweries published by the Brewers Association, breweries which are currently producing 3000 bbl beer per year or greater combine to produce an average of nearly 200 tons of vented CO2 per day (396,000 pounds/day) in 2012. (Source: Brewers_Association_2012.xls, Brewers Association, Boulder, Colo., April 2013) This astounding figure demonstrates the long-felt and unsolved need for CO2 recovery technology at the craft brewery scale to address this issue. A survey of commercially available CO2 recovery systems tailored to brewers shows that no existing technology exists in a compact fashion, at this scale, and with the ability to preserve stringent purity requirements, all key innovations of the present patent application. This discussion is merely illustrative and exemplary, and is not intended to limit the scope of the present invention or its application or uses.

[0147] The inventors have completed the construction of a craft brewery-scale, production-quality CO2 recovery unit according to one of many embodiments of the present application, and have completed field testing in two major craft breweries near Denver, Colo., United States.

[0148] While the methods disclosed herein have been described and shown with reference to particular operations performed in a particular order, it will be understood that these operations may be combined, sub-divided, or re-ordered to form equivalent methods without departing from the teachings of the present invention. Accordingly, unless specifically indicated herein, the order and grouping of the operations is not a limitation of the present invention.

[0149] While the present invention has been particularly shown and described with reference to embodiments thereof, it will be understood by those skilled in the art that various other changes in the form and details may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. An apparatus for recovering via purification and liquefaction of carbon dioxide gas from a vented CO2 waste gas stream, comprising:

a chassis adapted for installation inside a space-limited production facility;

one or more compressors for compressing the raw CO2 gas stream;

one or more dehydrators for removing water from the compressed CO2 gas stream;

one or more scrubbers containing solid-state adsorbent for deodorizing and purifying the inlet CO2 gas stream;

a refrigerator having one or more stages for lowering a temperature of the dehydrated, deodorized, compressed CO2 stream; and

a separation subsystem system adapted to separate the liquefied CO2 product from any remaining contamination by non-condensable gases, especially oxygen.

2. The apparatus of claim **1**, wherein the final oxygen content is less than 30 parts per million.

3. The apparatus of claim **1**, wherein the final water content is less than 20 parts per million.

4. The apparatus of claim **1**, wherein the liquid CO2 product has no foreign color, taste, or odor.

5. The apparatus of claim **1**, wherein the liquid CO2 product meets a beverage-grade standard.

6. The apparatus of claim **1**, wherein the one or more compressors compress the raw natural gas stream to a pressure range of 75 psia to 300 psia.

7. The apparatus of claim **1**, wherein the chassis is mounted on a cart having one or more wheels.

8. The apparatus of claim **1**, wherein the refrigerator further comprises:

a high-stage refrigeration loop having at least one heat exchanger for lowering the temperature of the dehydrated, deodorized, compressed CO2 gas stream; and

a low-stage refrigeration loop having at least one heat exchanger for further lowering the temperature of the dehydrated, deodorized, compressed CO2 gas stream.

9. The apparatus of claim **1**, wherein the refrigerator further comprises:

an autocascade loop having mixed refrigerants for lowering the temperature of the dehydrated, deodorized, compressed CO2 gas stream.

10. The apparatus of claim **9**, wherein the mixed refrigerants are hydrocarbons.

11. The apparatus of claim **9**, wherein the mixed refrigerants are nonflammable refrigerants.

12. The apparatus of claim **1**, wherein the refrigerator cools the compressed CO2 gas stream to a temperature range of −15° C. to −55° C. sufficient to liquefy the entire CO2 stream in a single heat exchanger.

13. The apparatus of claim **1**, wherein one or more of the dehydrators employ a desiccant bed.

14. The apparatus of claim **13**, wherein two desiccant beds are employed in alternation, and wherein heat required to dry the two desiccant beds is derived from waste heat from a power generator that drives the compressors and the refrigerator.

15. The apparatus of claim **1**, wherein the separation subsystem comprises a phase separator.

16. The apparatus of claim **1**, wherein the separation subsystem comprises a liquid storage dewar.

17. The apparatus of claim **1**, wherein the separation subsystem comprises one or more cyclones to separate liquids from gasses.

18. A method for recovering a liquid CO2 product from a vented CO2 gas stream, comprising:

a compression step for compressing the raw CO2 gas stream utilizing a compressor to a pressure range of 75 to 300 psia;

a dehydration step for removing water from the compressed CO2 gas stream utilizing one or more condensers and one or more desiccant beds;

a deodorizing step for removing trace organic compounds, flavors, and odors from the dehydrated, compressed CO2 gas stream utilizing an appropriate solid-state adsorbent;

a refrigeration step for reducing a temperature of the dehydrated, compressed, deodorized CO2 gas stream utilizing a refrigerator having one or more stages to a temperature range of −15° C. to −55° C.; and

a separation step for driving the non-condensable gas contamination, especially oxygen, in the final liquid CO2 product below relevant purity standards.

19. The method of claim **18**, further comprising:

a transportation step for bringing a mobile CO2 recovery system inside a cramped production craft brewery that is venting fermenter gas; and

a deployment step for connecting said CO2 recovery system to a vented CO2 gas source.

20. The method of claim **18**, wherein the final oxygen content is less than 30 ppm.

21. The method of claim **18**, further comprising:

vaporizing the liquid CO2 product to purge tanks, vessels, and lines.

22. The method of claim **18**, further comprising:

vaporizing the liquid CO2 product to carbonate beverages intended for sale.

23. The method of claim **18**, further comprising:

Re-selling the liquid CO2 product to local consumers of high quality CO2.

24. The method of claim **18**, wherein the refrigeration step utilizes an autocascade refrigerator having mixed nonflammable hydrocarbon refrigerants.

25. The method of claim **18**, wherein the refrigeration step cools the natural gas stream to a temperature range of −37° C. to −43° C.

26. The method of claim **18**, wherein two desiccant beds are employed in alternation, and wherein convection required to dry the two desiccant beds is derived from CO2 gas vented from storage.

27. A system for recovering a vented CO2 gas stream into a liquid CO2 product of sufficient purity for the downstream application, comprising:

one or more compressors for compressing the vented CO2 gas stream;

a dehydrator subsystem for removing water from the compressed CO2 gas stream;

a deodorizing subsystem for removing trace organic compounds, flavors, and odors from the dehydrated, compressed CO2 gas stream;

a refrigeration subsystem for lowering the temperature of the dehydrated, compressed, deodorized CO2 gas stream to a low temperature, comprising an auto-cascade refrigeration loop having mixed nonflammable hydrocarbon refrigerants; and

a separation subsystem adapted to remove non-condensable contaminants from the liquid CO2 product to meet specific purity standards.

28. The system of claim **27**, wherein the dehydration subsystem employs two desiccant beds alternation, wherein convection required to dry the two desiccant beds is derived from CO2 gas vented from the liquid storage dewar.

29. The system of claim **27**, wherein the oxygen content in the liquid CO2 product is less than 30 ppm.

30. The system of claim **27**, further comprising a chassis for holding system components for brewery installation, said chassis mountable to a cart, an indoor floor, or an outdoor surface.

31. The system of claim **27**, wherein the refrigeration subsystem comprises:

a high-stage refrigeration loop having at least one heat exchanger for lowering a temperature of the dehydrated, compressed CO2 gas stream; and

a low-stage refrigeration loop having at least one heat exchanger for further lowering the temperature of the dehydrated, CO2 natural gas stream.

32. The system of claim **27**, wherein the refrigeration subsystem cools the vented CO2 gas stream to a temperature range of −15° C. to −55° C. sufficient to liquefy the entire process stream in a single heat exchanger.

33. A method for recovering vented CO2 gas, comprising:

compressing the raw CO2 gas stream to a pressure range of 75 to 300 psia;

reducing a temperature of the CO2 gas stream to a temperature range of −15° C. to −55° C.; and

separating non-condensable gas components from the liquid CO2 product in a phase separator or liquid storage vessel.

36. The method of claim **35**, further comprising:

removing water from the raw natural gas stream to achieve a final aqueous content below 20 ppm.

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