

PG&E GAS R&D AND INNOVATION

Cryogenic Separation Technical Analysis

7/27/2018



Together, Building
a Better California



“The opinions, findings, and conclusions in the whitepaper are those of the authors and not necessarily those of PG&E. Publication and dissemination of the whitepaper by PG&E should not be considered an endorsement by PG&E, or the accuracy or validity of any opinions, findings, or conclusions expressed herein.

In publishing this whitepaper, PG&E makes no warranty or representation, expressed or implied, with respect to the accuracy, completeness, usefulness, or fitness for purpose of the information contained herein, or that the use of any information, method, process, or apparatus disclosed in this whitepaper may not infringe on privately owned rights. PG&E assumes no liability with respect to the use of, or for damages resulting from the use of, any information, method, process, or apparatus disclosed in this report. By accepting the whitepaper and utilizing it, you agree to waive any and all claims you may have, resulting from your voluntary use of the whitepaper, against PG&E.”



Table of Contents

Background.....	4
Industry Cryogenic Technologies.....	4
Summary.....	4
Benefits.....	5
Limitations	5
R&D Opportunities	6
Comparison of Industry Cryogenic Technologies	7
Cryogenic Distillation	8
Cryo Pur System	11
Cryogenic Packed Beds	11
CryoCell® Separation.....	12
References.....	15

Table of Figures

Figure 1 UOP Russell modular cryogenic plant	7
Figure 2 Flow Diagram of Distillation Process [5].....	9
Figure 3 General schematic of Cryo Pur system [6]	11
Figure 4 Schematic of Cryogenic Packed Bed Recovery for Carbon Dioxide [4]	12
Figure 5 Process Flow Diagram for Low Carbon Dioxide / Lean Natural [7]	13
Figure 6 Process Flow Diagram for Low Carbon Dioxide / Rich Natural Gas [7]	13
Figure 7 Process Flow Diagram for High Carbon Dioxide / Lean Natural Gas [7].....	13
Figure 8 Process Flow Diagram for High Carbon Dioxide / Rich Natural Gas [7]	14

Table of Tables

Table 1 Comparative Analysis of Cryogenic Technologies	7
Table 2 Comparative Analysis for Cryogenic Distillation Methods [4]	10

Background

In order for PG&E to reach new sustainability targets, technology must be introduced that can upgrade natural gas in more efficient and environmentally friendly to be integrated into the gas grid. Cryotechnology, or cryogeny, for biogas production is one method in which natural gas can be upgraded and injected into Gas Operations' systems. Biogas is the mixture of naturally occurring gases that are often produced by the anaerobic decomposition of organic matter known as biomass in landfills and digester chambers such as garbage, crops, animal waste, sewage, etc. Biogas is a renewable resource and can be used as a substitute for natural gas via pipeline injection.

Cryogeny makes use of low temperatures and pressures at which various gaseous components condense. Traditional gas cooling utilizes equipment such as compressors, and heat exchangers. Traditional upgrading techniques include pressure swing adsorption, in which components are absorbed into an absorbent at high pressures, water absorption, which utilizes counter-current water scrubbing in a packed bed, chemisorption, chemical scrubbing, pressure swing adsorption (PSA), and membrane separation.

All cryogenic technologies are useful for the removal of contaminants such as hydrogen sulfide, water vapor, carbon dioxide, helium, oxygen, volatile organic compounds (VOCs), siloxanes, and nitrogen from natural gas flows. It is important that these contaminants are removed to ensure no complications downstream. These complications include and are not limited to decreased energy content of biogas, corrosion in pipelines, combustion, mineral deposits, and erosion. Furthermore, cryogenic technologies also aid in the production of liquefied natural gas and liquefied carbon dioxide that can be stored at much higher volumes than in gaseous form and can also be used as fuel for large diesel trucks [1].

Industry Cryogenic Technologies

Cryogeny has been studied extensively and implemented in many European energy sectors, although much of these efforts have been on a smaller scale. Currently there are companies in the U.S. that develop and provide services for modular cryogenic plant design and installation. While many cryogenic technologies exist in the industry, there are many factors in which they differ from one another. The following sections will observe the benefits, limitations, and R&D opportunities in relation to emerging cryogenic technologies.

Summary

Cryogenic technologies are often used in biogas upgrading; however, they can also be utilized in natural gas streams. Before biogas can be upgraded, biomass must first go through a pretreatment process. Benefits of pretreatment

include increased biogas yield, and increased anaerobic digestion of raw materials. The type of pretreatment the biogas receives depends on the biomass from which it is derived. Traditionally, biomass is pretreated using mechanical, chemical, biological, or thermal methods. For example, food waste must be grinded and sorted to remove bones prior to being injected into a digester chamber. Once pretreated, biogas can then be effectively upgraded to biomethane [2].

Biogas is upgraded by lowering system temperatures to extremely low temperatures that range between -90 degrees centigrade and -125 degrees centigrade. This process is ideal for large volumes of gases with high concentrations of carbon dioxide as more traditional methods such as membrane separation or water scrubbing require multiple stages and aren't as effective in carbon dioxide removal. Higher concentrations of carbon dioxide can be found in wetlands, landfills, sewers, farm lands, etc.

There are many methods in which cryogenics can be utilized either as a separate process or in tandem with other forms of more conventional upgrading technologies. Each method provides different benefits and advantages over other forms of technology that may not be as energy efficient or cost effective. In addition, conditions such as the quality of the biogas being upgraded, the location of gas pipelines, gas loads, maintenance costs, etc. will affect the ability to implement cryogenic technologies as not all pipelines are ideal for pipeline injection.

Benefits

Cryotechnology can be used in areas where no gas grid is present which reduces the amount of limitations due to location. The process of upgrading biogas has been found to be generally preferred over direct power generation since this technology is very flexible and utilizes energy more efficiently. Because the process of liquefying natural gas is very energy intensive, a large amount of excess heat is produced. This excess heat can then be recovered as electric or thermal energy which can be utilized elsewhere. Because the biomethane produced is meant for pipeline injection into existing infrastructure, there is virtually no need to design new pipelines as long as there are cryogenic plants that are already connected and providing biomethane to the gas grid; otherwise, new pipelines will need to be developed that can connect to sources of biomethane. In this case, having the liquefied natural gas transported to facilities for pipeline injection may be an easier option.

Limitations

The use of cryogenic technology in the production of LBG and LNG is much more explored than its use for biogas upgrading. While data provided by various companies and research groups assert that no methane will be lost in the cryogenic process, it is impossible to eliminate methane losses altogether, although they can be greatly reduced.



Biomass will need to be made readily available for pretreatment and digestion. While this may not be an issue in landfills, waste from food crops and animals may not be as abundant since farmers typically don't have enough resources to meet such high demands.

Prior to pipeline injection, certain quality standards must be met and permits may need to be acquired beforehand which would incur additional costs. These requirements differ based on where the biogas is being collected and how it is being used and upgraded. In addition, the process of interconnecting new biomethane supplies is time consuming and incurs large project management costs. The use of cryogenic technology tends to be the most cost effective when utilized for large gas loads. Upgrading biogas is more expensive than simple biogas cleaning or purification. Cryogenic technology is capable of both purifying and upgrading natural gas and so will incur additional costs. It is more expensive to upgrade biogas for pipeline injection into the gas grid than for electricity generation or connection to power lines. Cryogenic plants, and cryogenic technology in general, are very expensive although they are energy efficient [3] There is very little information that gives an accurate estimation for the costs of cryogenic upgrading technologies; however, it is estimated that the initial investment cost is approximately 3,455,430 USD and the annual cost is approximately 388,131.66 USD [1].

R&D Opportunities

Biogas upgrading is an area in which there is much room for new developments and improvements. Presently, there are opportunities to conduct research around safe methods of pipeline injection of biomethane in PG&E's gas grid. It is also beneficial to conduct research around ways in which liquefied byproducts can be utilized throughout gas operations. Since there is no raw data readily available regarding domestic providers or cryogenic plants, biogas, etc. it would be beneficial to acquire the data to get an accurate understanding of the cryogenic technologies that are readily available. There are currently opportunities to research different combinations of traditional and cryogenic upgrading technologies (hybrid methods) to improve efficiency and cost effectiveness. These newly developed methods will require new models that accurately demonstrate cryogenic processes and provide the data necessary for further study and improvements.

Injected biomethane will only constitute a small percentage of the natural gas supply and if the injected biomethane is well-mixed in the pipeline, quality should not be affected. Cryogenic technology has not primarily been applied to large scale processes and it will be necessary to determine how to scale up different cryogenic processes for industrial use. Presently, there is an opportunity to research ways in which dilute carbon dioxide streams can benefit from this technology as the use of cryotechnology for rich carbon dioxide streams has proven to be the most cost effective. To improve efficiency of cryogenic plants, modular plants are often used to compensate for differences in gas

compositions at different locations. To completely convert to biomethane and other renewable forms of natural gas and liquefied natural gas, it will be necessary to continue creating roadmaps as well as new methods and procedures that are able to sustain this change.

Comparison of Industry Cryogenic Technologies

Domestic companies that provide cryogenic services include [Morse Electric Incorporated](#), [Cryogenic Industries](#), [Linde Engineering North America Incorporated](#), [Freeman and Curiel Engineers](#), [Enerflex](#), [Chart Industries](#), [McDermott](#), [UOP Russell](#), etc. Companies such as these can install modular cryogenic plants and develop new cryogenic processes. Some cryogenic processes include the Cryo Pur system, cryogenic distillation, cryogenic fractionation, cryogenic packed beds, CryoCell® separation, and others. It is important to note that all cryogenic processes have similar steps and outcomes.



Figure 1 UOP Russell modular cryogenic plant

Table 1 Comparative Analysis of Cryogenic Technologies

Cryogenic Technology	Pros	Cons
Cryogenic Distillation	<ul style="list-style-type: none"> • Low methane losses • Works well for carbon dioxide concentrated streams • Methane and carbon dioxide purity between 94.5% and 99.7% 	<ul style="list-style-type: none"> • More expensive than traditional upgrading technologies • Does not work well for dilute carbon dioxide streams • Possibility of solid formations in column at different pressures



Cryo Pur System	<ul style="list-style-type: none"> • Low methane losses • Integrates biogas upgrading and biomethane liquefaction • Integrates cryogenic distillation column • Easily scalable • High heat recovery • Liquid methane and carbon dioxide purity of 99% 	<ul style="list-style-type: none"> • More expensive than traditional upgrading technologies • Not domestic • Suitable for large gas flows at high concentrations • Energy intensive • High maintenance costs
Cryogenic Packed Bed	<ul style="list-style-type: none"> • Low methane losses 	<ul style="list-style-type: none"> • More expensive than traditional upgrading technologies • Chance for choking and blockage in operation
CryoCell® Separation	<ul style="list-style-type: none"> • Low methane losses • Multiple configurations for different types of gas streams • No foaming or corrosion potential • Scalable 	<ul style="list-style-type: none"> • More expensive than traditional upgrading technologies • High maintenance costs

Cryogenic Distillation

Cryogenic distillation is the most common approach used to upgrade biogas. There are many methods in which to carry out this type of process: flash, single column, double column, two column, and three column systems. Cryogenic distillation makes use of the fact that carbon dioxide condenses and freezes before methane. Here the carbon dioxide can be removed as a solid or as a liquid. The gas is usually first compressed between 18 and 30 bar and cooled to -45 to -59 degrees centigrade via a heat exchanger until different gaseous components liquify. Higher pressures ensure that carbon dioxide will not sublimate. Once methane is in liquid form it can then be separated from gaseous nitrogen and oxygen. This method takes advantage of the differences in volatility, or ability to be distilled, between different components [4].

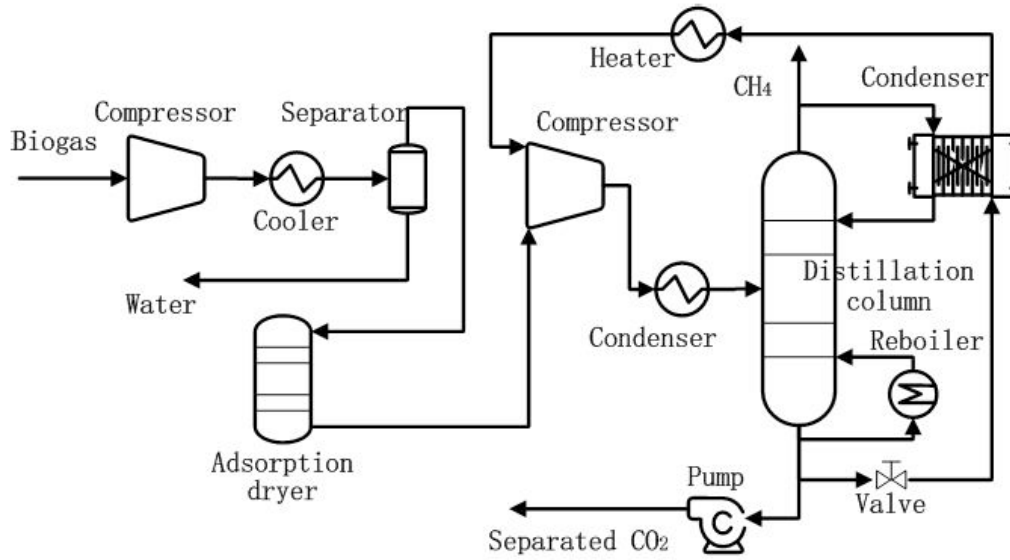


Figure 2 Flow Diagram of Distillation Process [5]



Table 2 Comparative Analysis for Cryogenic Distillation Methods [4]

Process	Pros	Cons
Flash Distillation	<ul style="list-style-type: none">• Simplest process• Well suited at low pressure	<ul style="list-style-type: none">• Not capable of achieving purity necessary for rejection to atmosphere• Low recovery
Single Column Distillation	<ul style="list-style-type: none">• Purity of gas components maintained• Theoretically can treat gas at any purity• High hydrocarbon recovery	<ul style="list-style-type: none">• Higher energy consumption• Requires refrigeration cycle
Double Column Distillation	<ul style="list-style-type: none">• Energy efficient• High hydrocarbon recovery	<ul style="list-style-type: none">• Low tolerance of carbon dioxide / impurity presence• Limited range of nitrogen content in feed• Not suitable for low pressure feeds
Two Column Distillation	<ul style="list-style-type: none">• Energy efficient• Tolerant of carbon dioxide / impurity presence• Wide range of nitrogen content in feed	<ul style="list-style-type: none">• Not suitable for low pressure feeds
Three Column Distillation	<ul style="list-style-type: none">• High hydrocarbon recovery• Tolerant of carbon dioxide / impurity presence• Wide range of applications	<ul style="list-style-type: none">• Not suitable for low pressure feeds

Cryo Pur System

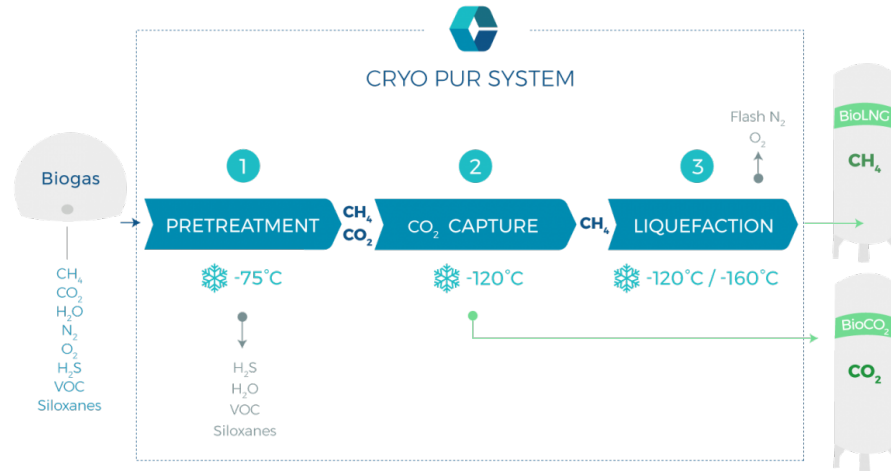


Figure 3 General schematic of Cryo Pur system [6]

The Cryo Pur system is a cryogenic process combined with a liquefaction step. This system is suitable for gas loads with high concentrations of nitrogen and oxygen making it ideal for landfill biogas. Some advantages of the Cryo Pur system, as reported by the company itself, include low power consumption, high heat recovery, a liquid carbon dioxide purity above 99.99% and a liquid biomethane purity above 99%.

The biogas entering the system is first preheated using activated carbon which removes hydrogen sulfide. After, the gas is cooled down to -40 degrees centigrade and water is frosted and defrosted in a heat exchanger to remove VOCs and siloxanes. To end the pretreatment process, biogas is then cooled to -75 degrees centigrade. Next, carbon dioxide is captured and separated in liquid form at -120 degrees centigrade and can be directly used as a liquefied product. Biomethane is compressed and cooled at 15 bar and -120 degrees centigrade respectively and the bio-LNG produced can be stored away [6].

Cryogenic Packed Beds

This process is based on a water-carbon dioxide interface in a cryogenically cooled packed bed. First, in the cooling step, the packed bed is cooled down to -120 degrees centigrade. During the capture step, flue gas is then fed to the packed bed where it is cooled allowing water to condense and carbon dioxide to sublime leaving nitrogen throughout the packed bed. In the recovery step, carbon dioxide is recycled for carbon dioxide recovery and air is recycled for

water recovery. This process is compatible with low gas flows and must be carried out using at least three beds in parallel [4].

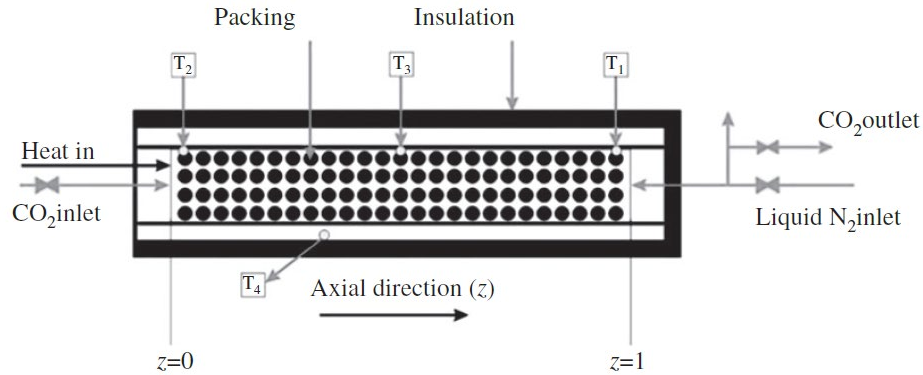


Figure 4 Schematic of Cryogenic Packed Bed Recovery for Carbon Dioxide [4]

CryoCell® Separation

The CryoCell® process can be modified to meet the following conditions [7]:

- Low Carbon Dioxide / Lean Natural Gas
- Low Carbon Dioxide / Rich Natural Gas
- High Carbon Dioxide / Lean Natural Gas
- High Carbon Dioxide / Rich Natural Gas

This process follows a typical thermodynamic operating path in which the gas stream is initially cooled near to the freezing point of carbon dioxide. Part of the stream is condensed and then flash across a Joule-Thompson valve so the stream is separated into a liquid, vapor, and solid. The stream is sent to a separator where the light and dense phases are separated from each other such that the vapor phase has a low carbon dioxide concentration and the dense phase has a high carbon dioxide concentration that is suitable for disposal.

Solid carbon dioxide is melted to mix with the liquid phase and be removed from the system. The hydrocarbon, carbon dioxide, and ethane concentrations must meet certain specifications before and after entering the separator to ensure that the products are ready to be sold. Some advantages of this process include the elimination of water consumption, usage of chemicals, corrosion, and foaming potential [7].

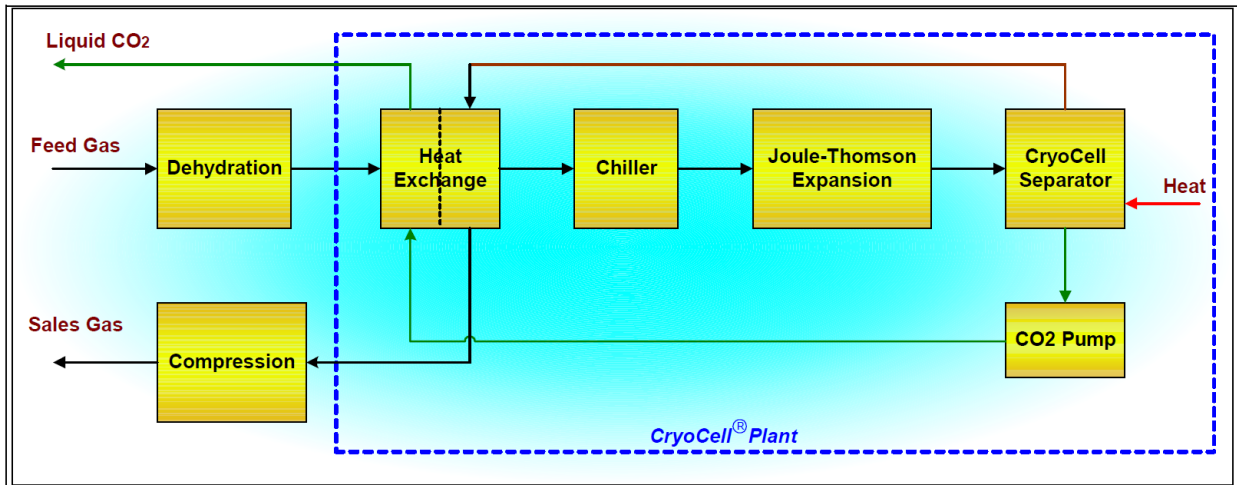


Figure 5 Process Flow Diagram for Low Carbon Dioxide / Lean Natural [7]

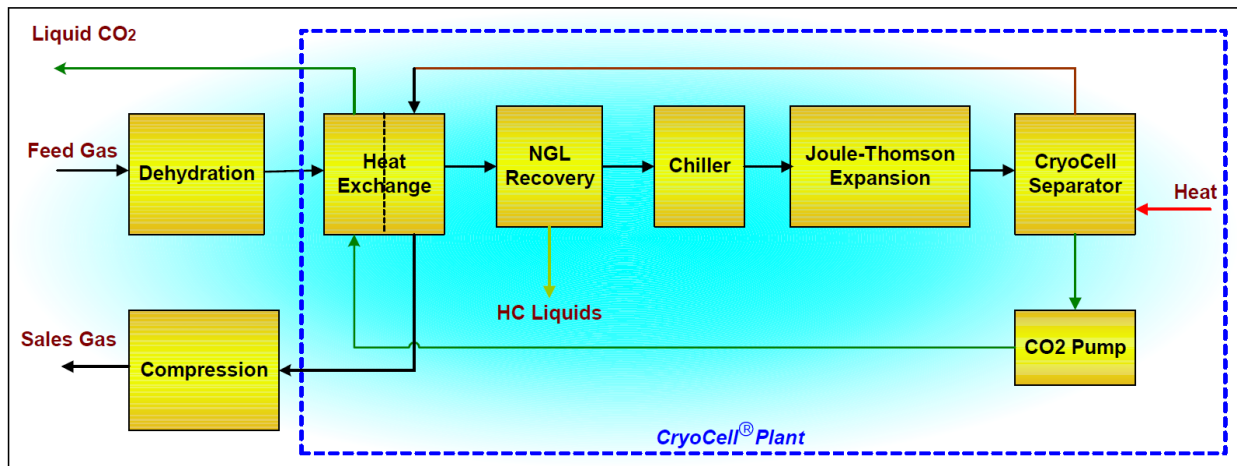


Figure 6 Process Flow Diagram for Low Carbon Dioxide / Rich Natural Gas [7]

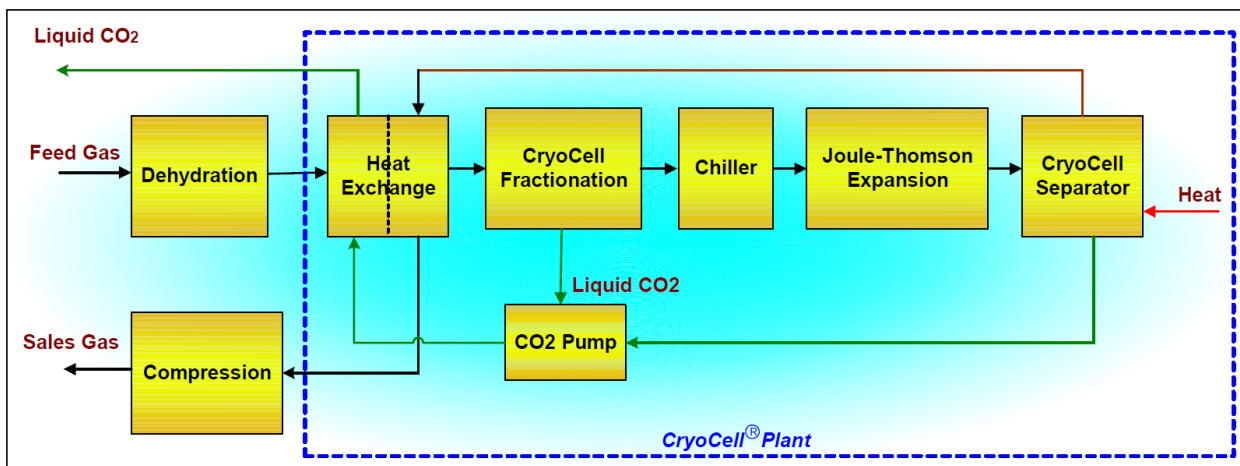


Figure 7 Process Flow Diagram for High Carbon Dioxide / Lean Natural Gas [7]

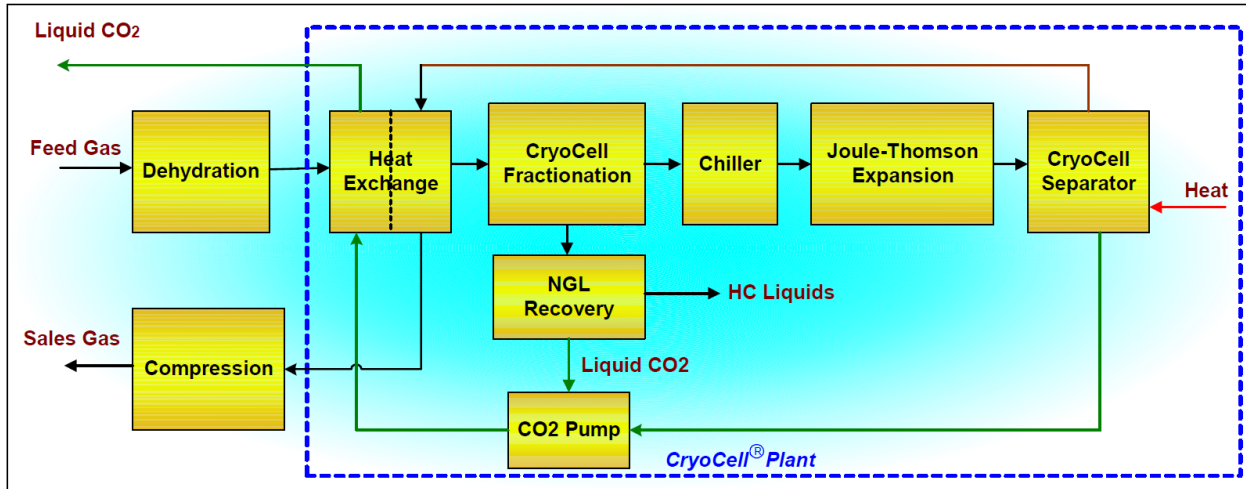


Figure 8 Process Flow Diagram for High Carbon Dioxide / Rich Natural Gas [7]

References

- [1] Brendeløkken, Hanne Wasmuth. Upgrading Technologies for Biogas Production Plants. 2016, pp. 1–59, Upgrading Technologies for Biogas Production Plants.
- [2] Johansson, Nina. “Production of Liquid Biogas, LBG, with Cryogenic and Conventional Upgrading Technology.” Lunds Universitet, Dec. 2008, pp. 6–12.
- [3] Miltner, Martin & Makaruk, Aleksander & Harasek, Michael. (2016). Selected Methods of Advanced Biogas Upgrading. Chemical Engineering Transactions. 52. 463-468. 10.3303/CET1652078.
- [4] Maqsood, Khuram & Mullick, Aditi & Ali, Abulhassan & Kargupta, Kajari & Ganguly, Saibal. (2014). Cryogenic carbon dioxide separation from natural gas: A review based on conventional and novel emerging technologies. Reviews in Chemical Engineering. 30. 453-477. 10.1515/revce-2014-0009.
- [5] Tan, Yuting, et al. “Cryogenic Technology for Biogas Upgrading Combined with Carbon Capture - a Review of Systems and Property Impacts.” Energy Procedia, vol. 142, 2017, pp. 3741–3746., doi:10.1016/j.egypro.2017.12.270.
- [6] Berg, Benjamin. “Efficient Liquid Biomethane Production with Cryogenic Upgrading.” Gas for Energy, no. 1, 2017, pp. 1–29.
- [7] Hart, Allan, and Nimalan Gnanendran. “Cryogenic CO₂ Capture in Natural Gas.” Energy Procedia, vol. 1, no. 1, 2009, pp. 697–706., doi:10.1016/j.egypro.2009.01.092.