

CHALMERS



Liquefied Synthetic Natural Gas from Woody Biomass

Investigation of Cryogenic Technique for Gas Upgrading

Master's Thesis within the Industrial Ecology programme

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Division of Heat and Power Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2013

MASTER'S THESIS

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Chalmers Reproservice
Göteborg, Sweden 2013

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ABSTRACT

Biomass-based liquefied natural gas (bio-LNG) is very valuable renewable fuel as it has high energy density and transportability. Bio-LNG requires liquefaction of the synthetic natural gas (bio-SNG). Cryogenic technology is a promising option for integration of the gas upgrading and liquefaction streams with the main biomass gasification and methane synthesis plant. This thesis investigates the feasibility of this technology for future commercial bio-SNG production plants based on indirect gasification technology, similar to that adopted by Göteborg Energi for the GoBiGas project. Two process configurations for production of bio-LNG from woody biomass are investigated: (1) an integrated configuration which uses cryogenic technology for gas upgrading and liquefaction integrated with the gasification and SNG synthesis plant; (2) a base case which uses a traditional gas upgrading (chemical adsorption) and a stand-alone liquefaction unit located downstream of the main Bio-SNG plant. Both cases are simulated with Aspen Plus to obtain mass and energy balances. Pinch analysis is conducted for both cases to investigate utility demands as well as the potential to convert excess process heat to shaft work to improve the energy performance of the processes. The cryogenic unit investigated achieves the targeted product specifications and capacity, and the calculated performance is comparable to published data for commercial cryogenic units in terms of specific power demand and methane loss. The simulation results show that the integrated plant configuration with cryogenic technology has a higher power requirement than the base case. Shaft power outputs are estimated for both the integrated and base cases assuming a steam cycle combined heat and power unit which recovers process excess heat. The estimated work outputs are more than sufficient to cover the process power demands for both cases; thus the excess power can be exported to the grid. The base case achieves a slightly higher overall energy efficiency compared to the integrated case, whereas the cold gas efficiency is higher for the integrated case due to low methane loss. Cryogenic technology is still under development, therefore there is a high potential for performance improvement by application of energy efficiency measures. In addition, high purity liquid CO₂ is produced at very low temperature as a by-product which could generate additional revenue.

Key words: Cryogenic technology, bio-SNG, bio-LNG, gas upgrading, liquefaction

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Notations

In this section, a description of used abbreviations and different terms used in this report are summarized to ensure a common and clear terminology.

Biogas	Gas mixture from biomass via anaerobic digestion
Bio-SNG	Synthetic natural gas produced from biomass
Bio-LNG	Liquefied bio-SNG
CNG	Compressed natural gas
kWh	Kilowatt-hour
LBG	Liquefied biogas
LCO ₂	Liquid carbon dioxide
LNG	Liquefied natural gas
LHV	Lower heating value
Nm ³	Volume at normal conditions (1 atm, 0°C)
SMR	Single mixed refrigerant

1 Introduction

There is an ecological overshoot in which society is using more resources than nature can regenerate. Overconsumption and the resulting scarcity of resources, has caused environmental and economic consequences. These problems have resulted in new regulations and policies that have stimulated research that has led to a wide variety of solutions ranging from technical improvements to completely new process routes for energy conversion and material production processes.

Energy supply security is a challenge due to the world's population growth and the increased energy demand (MEA, 2005). The conversion of energy from renewable sources plays a major role for energy supply security as well as to reach climate and energy targets that were established by the European Commission's directive on the promotion of the use of energy from renewable sources (the "Renewable Energy Directive"). These mandatory targets are often referred to as the 20-20-20 targets which are planned to be achieved by 2020. The aim of these targets is reduce future dependency on fossil fuel imports, decrease energy costs and reduce the emissions of greenhouse gases from the energy and transportation sectors. EU energy consumption from renewable sources is set to reach 20% share and in the case of transport sector it will be a 10% share (EU, 2009).

On the market at present, energy supply remains dependent on fossil fuels which include coal, petroleum and natural gas. Fuel supply is limited; thus, in order to have an alternative energy supply as well as to reach EU targets, the production of renewable fuels is a promising pathway.

Renewable fuels refer to fuels produced from renewable biomass or waste feedstock. They can be used for heat or electricity production and as a motor vehicle fuel as well. Bio-SNG (renewable substitute natural gas) has similar quality to fossil natural gas but it is produced from renewable sources.

Bio-SNG produced by biomass gasification can replace fossil natural gas; however, it has to be cleaned and upgraded before final use. Among other commercial upgrading techniques, cryogenic method has drawn attention recently. It makes use of the difference in condensation points of the gases in bio-SNG; the gases are separated from each other by consecutive cooling, condensation and separation units. It is an interesting option for both gas upgrading and bio-LNG (renewable liquefied natural gas) production with the additional benefit of producing high-purity liquid CO₂ as a by-product. Bio-LNG is a valuable product since it has higher energy density compared to bio-SNG. Thus, it is easier to transport which is highly favourable especially in the case of use as a vehicle fuel.

1.1 Objective

The objective of the thesis is the investigation of cryogenic method for bio-SNG upgrading and liquefaction. Evaluation is done by employing performance indicators in terms of energy requirement and efficiencies.

1.2 Methodology

The methodology adopted for this work consists of three parts; study of literature data, simulation of process flowsheet based on literature data, and evaluation of selected process configurations using process integration tools.

Cryogenic technology and the production of bio-LNG are not well-known yet but there are a few commercial plants which employ cryogenic technology as well as published studies and pilot plants in operation. There is not much written about the technology, since there is little experience available. However, there are reports from the Swedish Gas Centre (SGC) that focus on cryogenic technology as an upgrading method and LNG as an option for Sweden. They have been used as a base for cryogenic unit design in this thesis in addition with the information from a patent for liquefaction process (Dubar, 1997). Bio-SNG production process data based on process simulation is available from earlier studies held in Chalmers University of Technology (e.g. Arvidsson et al. 2012).

Two cases are defined and simulated; an *integrated case* in which the cryogenic upgrading and liquefaction process is integrated with the main Bio-SNG process, and a reference *base case* in which gas is upgraded using conventional gas upgrading (chemical adsorption) and a stand-alone liquefaction unit located downstream of the main Bio-SNG plant. Both cases have the same final product and capacity; 100 MW of bio-LNG. Simulation of the process configurations investigated is performed using flowsheeting software Aspen Plus to establish Energy and mass balances for the process as well as input data for a detailed heat integration analysis study used to assess the potential energy performance of the process.

1.3 Content

The thesis begins with an introduction to renewable fuels, bio-SNG and its production process (chapter 2) followed by a description of cleaning and upgrading technologies available today (chapter 3). Cryogenic upgrading and liquefaction processes are described in detail (chapter 4). After these three background chapters the thesis continues with methodology followed for cryogenic process design, integration and evaluation (chapter 5). Then follows discussion and results where energy balances are shown and designs are evaluated (chapter 6). Then, it is completed with conclusions in chapter 7.

2 Background

2.1 Renewable fuels

First generation renewable fuels consist of ethanol, biodiesel and biogas produced from raw material containing sugar, starch, oil or animal fats while second generation renewable fuels include bioethanol, synthetic biofuels, biodiesel, bio-methane and bio-hydrogen produced from lignocellulosic biomass such as wood, grasses and forest residues. Since production of first generation renewable fuels has limitations due to their relatively low resource efficiency, which threatens food supply and biodiversity, second generation renewable fuels such as bio-SNG via biomass gasification have been suggested as a viable alternative (IEA Bioenergy, 2008).

Contrary to fossil fuels, the combustion of renewable fuels is considered 'carbon neutral' over the life cycle, because the amount of CO₂ released during combustion is the same amount that was captured by the plant (biomass) during its growth. In addition to environmental benefits, it also contributes to energy security, since renewable fuels can be produced where they are consumed.

2.1.1 Bio-SNG

Bio-SNG (renewable substitute natural gas) can be used as a replacement for fossil natural gas. It consists of carbon dioxide and methane, and small amounts of impurities such as water, hydrogen and hydrogen sulphide. However, methane is the only fraction with an economic value. By upgrading bio-SNG to achieve natural gas quality, it can be distributed via the existing grid for use within existing appliances or as a transport fuel.

As a transport fuel, bio-SNG can be distributed in the form of CNG (compressed natural gas) or LNG (liquefied natural gas). LNG has many advantages when it comes to longer distances transportation because it has high energy density which increases the efficiency of its transport. In fact, LNG contains three times more energy per volume compared to CNG (Lidköping Biogas). Therefore, bio-LNG (liquefied bio-SNG) is a valuable product. It is relatively expensive and complex to produce; however, its advantages make it competitive, especially in places where there are limitations for grid pipeline natural gas distribution.

2.2 Göteborg Energi and the GoBiGas Project

Göteborg Energi is Sweden's fourth largest energy company and the market leader in Western Sweden. Since 2006 they are running a large project called Gothenburg Biomass Gasification (GoBiGas). The aim of the project is to produce bio-SNG using indirect biomass gasification technology and to distribute the product gas in the gas grid, thereby reducing import and combustion of fossil natural gas.

According to GoBiGas planning, the concept is to be implemented in two stages. The first phase is a demonstration plant with a capacity of 20 MW_{gas} that will be commissioned at the end of 2013. When the first phase is proven successfully, the construction of the second stage will take place in which it is aimed to produce about 80-100 MW_{gas} (Göteborg Energi). Indeed, the GoBiGas plant will be the world's

largest indirect gasification-based bio-SNG plant with a planned annual capacity of around 800 GWh. The technology that will be implemented in the second stage of GoBiGas project is not decided yet and cryogenic technology for gas upgrading and possible liquefaction could be an interesting option.

Göteborg Energi collaborated in the construction of the first plant in Sweden to produce biogas in liquefied form; the plant is called Lidköping Biogas. The plant produces mainly liquefied biogas from natural resources through anaerobic digestion. The raw biogas is upgraded using water scrubbing and pressure swing adsorption; then, it is cooled down to -163°C using nitrogen in an advanced refrigerator in order to obtain LBG (liquefied biogas). Its annual capacity of production is 60 GWh LBG (Lidköping Biogas).

Currently, there are two LNG filling stations that are mainly used for trucks in Göteborg and Stockholm, and two other are planned to be built in Jönköping and Malmö (Lidköping Biogas). Therefore, gas liquefaction is very important considering future aspects.

2.3 Bio-SNG production via biomass gasification-GoBiGas Project

General process steps for bio-SNG production are illustrated in Figure 1 and a schematic illustration of GoBiGas plant can be seen in Figure 2.

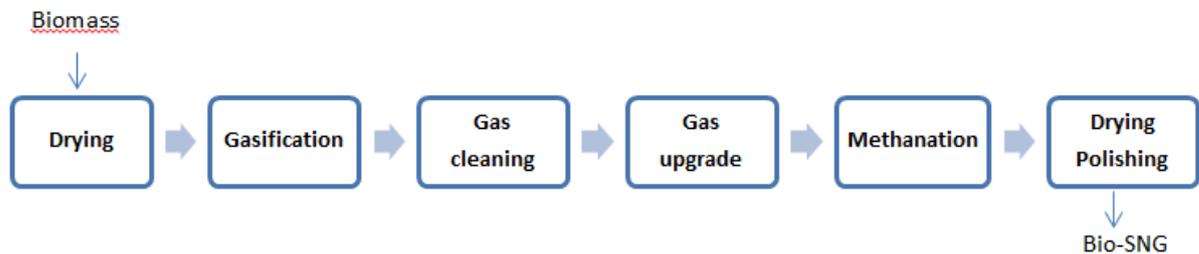


Figure 1. Schematic illustration of bio-SNG production via biomass gasification

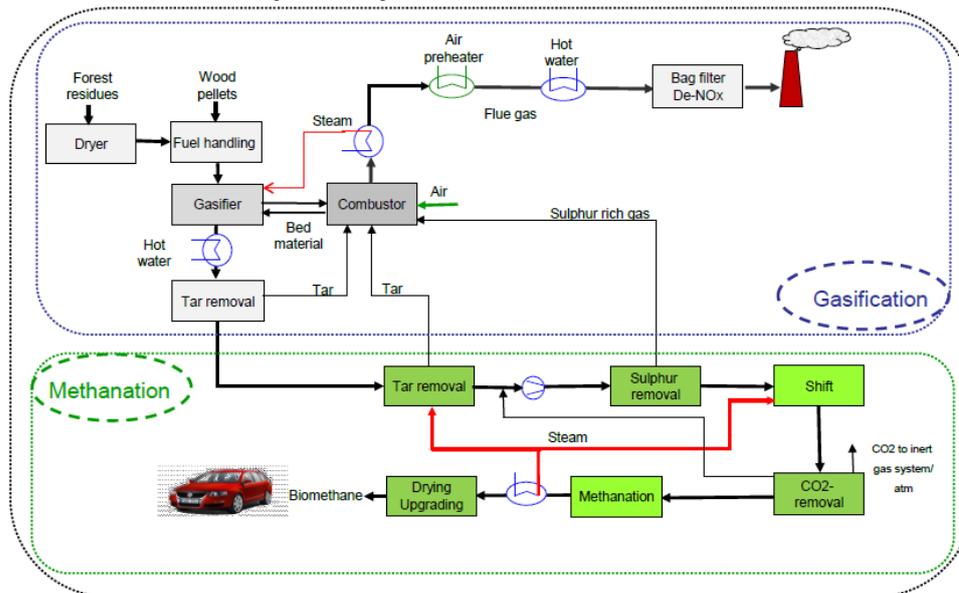


Figure 2. Process overview diagram (Gunnarsson, 2011)

The first generation GoBiGas plant used wood pellets as feedstock but, as a plan for future developments of the process, feedstock can be wet forest residues which would require drying process prior to gasification process. After biomass pre-treatment, the incoming biomass is gasified and a gas mixture is obtained which needs to be cleaned from contaminants such as tars, water, sulphur compounds etc. Subsequently to gas cleaning, CO₂ removal is an important step in order to provide good conditions for methanation in which methane is produced. The gas stream from methanation step is raw bio-SNG, which is dried and polishing is applied if necessary.

A brief overview of the main steps in the base case study is provided below

2.3.1 Drying

High temperatures are required in the gasification process; thus, in order to decrease the energy input, moisture content is decreased. Moisture content of incoming biomass is about 50 wt-% and it has to be decreased to about 10-20 wt-%, which is the optimal moisture content for an energy efficient gasification process (Cummer and Brown, 2002).

2.3.2 Gasification

Gasification is a chemical decomposition of the biomass particles into syngas, char and tars in a confined reactor in the presence of an external oxidizing agent. Syngas consists of a mixture of carbon monoxide, methane, water vapour, carbon dioxide and hydrogen. The most common gasification medium used is air, steam, oxygen, flue gas or product gas (Heyne, 2013).

One feedstock that is used in several commercial gasification processes is coal. In comparison with coal, biomass is more reactive and can be gasified at lower temperatures, but at the same time its composition is heterogeneous which leads to extra equipment for gas cleaning and solid handling (IEA, 2005).

Direct gasification technologies such as fixed bed gasification partly combust the biomass in order to provide the necessary heat for gasification. Instead, in indirect

gasification technologies this heat is transferred by the circulating bed material whose temperature is increased in a separated combustion chamber. In biofuels synthesis indirect gasification is suitable because of the low nitrogen content in the gas produced. Therefore, indirect gasification for bio-SNG production is assumed in this thesis. The flow diagram of indirect gasification used in this thesis is illustrated in Figure 2.

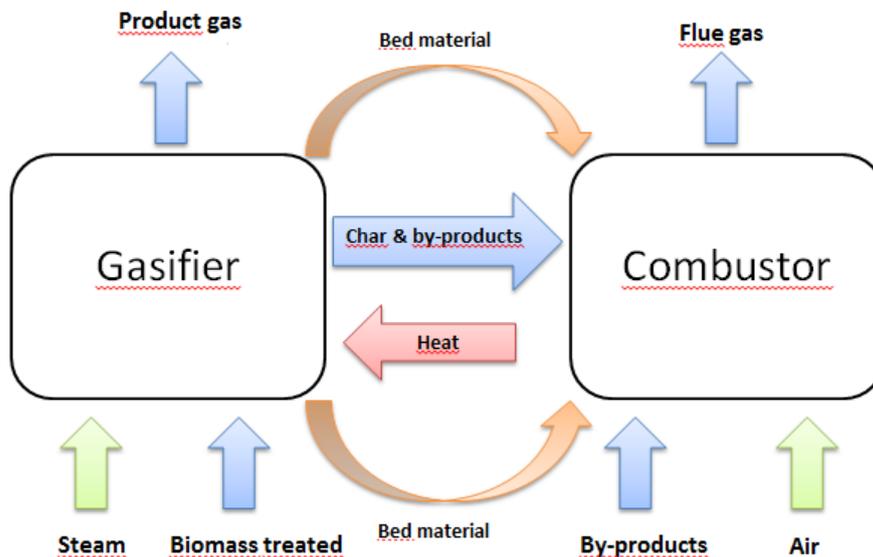


Figure 3. Flow diagram of indirect gasification

After biomass pre-treatment, the dried feedstock is decomposed in a yield reactor prior to gasification. As can be seen in Figure 3, the necessary heat in the gasifier is supplied by the combustor and steam. The bed material of the gasifier is circulated between the gasifier and the combustor to deliver heat. Unconverted char and by-products from the tar and sulphur removal units are burned to cover the heat demand of the gasification process. Flue gas from the combustor is to be treated before discharge.

2.3.3 Gas cleaning

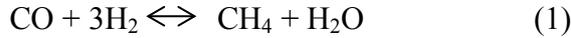
Syngas which contains chars and tars is the product gas stream obtained from gasification and it needs further treatment. Gas cleaning is the removal of the contaminants from syngas. Compounds such as H₂O, tars, H₂S, bed particles, ash and nitrogen and sulphur compounds are removed in this step. Most common technologies for the removal of each component are described in Chapter 3.1.

2.3.4 Gas upgrade

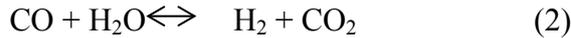
Upgrading is the removal of CO₂ to increase energy content of gas stream. There are currently several gas upgrading techniques commercially available and many are in research and development phase. In Chapter 3.2., most common upgrading technologies are thoroughly described.

2.3.5 Methanation

During methanation, the main reaction is the conversion of carbon monoxide and hydrogen to methane and water (Eq.1).



As can be seen in Eq.1, the optimal H₂/CO ratio is 3. However, after gasification this ratio is lower; thus, before methanation and CO₂ removal the cleaned feed stream is sent to a water gas shift reactor in order to achieve the desired H₂/CO ratio.



Carbon monoxide in the feed stream reacts with steam (water vapour) to form carbon dioxide and hydrogen (Eq.2). After the shift reactor, carbon dioxide is removed from the product stream and syngas is sent to the methanation reactor.

2.3.6 Gas Drying

Methanation product is still to be treated further before end use in order to achieve the purity requirements. Its water content is removed by gas cooling, separation of the condensed water and drying.

2.4 CO₂ as a by-product

CO₂ in liquid or solid phase has many commercial applications. CO₂ is obtained with high purity as by-product in cryogenic technology.

Solid CO₂ is usually known as *dry ice*. This product can be used as a refrigerant for the replacement of CFCs and HFCS which are highly contaminant refrigerants. *Dry ice* or LCO₂ can also be used as an alternative to fossil fuels, in wastewater treatment, in fire extinguishers and in food industry (Johansson, 2008).

Two applications of CO₂ as an alternative to fossil fuels are cryogenic transport temperature control and fertilizing in greenhouses. Instead of diesel-driven cooling system with fluorinated refrigerants which is the conventional way of cryogenic transport temperature control, CO₂ is used as an *environmentally friendly* alternative. Another interesting possibility could be to place a greenhouse close to the production plant in order to utilize CO₂. It is a replacement of fossil fuel in places where fossil fuels are burnt to provide heat and CO₂ to the greenhouses. The benefit of LCO₂ obtained from cryogenic technology is that it has high purity so that it does not need treatment before final use (Johansson, 2008).

3 Gas Cleaning and Upgrading

Product gas can be utilized to fuel vehicles or to inject into the natural gas grid for use in any application connected to the grid after gas cleaning and upgrading (SGC AB, 2013).

The most common technologies are water scrubbing, PSA and amine scrubbing. Full list of biogas cleaning and upgrading plants in Sweden can be seen in Appendix 1 (IEA Bioenergy Task 37, 2012).

This chapter is based on a literature survey that has been done by Nina Johansson regarding the most commonly used technologies for gas cleaning and upgrading.

3.1 Description of the available gas cleaning techniques

Cleaning of the product gas stream is required for safety issues in order to avoid fouling of the heat exchangers, corrosion and contamination of the catalysts (Johansson, 2008).

Available gas cleaning techniques for damaging compounds such as H_2S , H_2O , halogenated compounds, dust and particles are described below.

3.1.1 Hydrogen sulphide - H_2S

H_2S is produced as a result of biomass decomposition during the gasification process. Hydrogen sulphide is corrosive to several different types of metals. Its reactivity is proportional with concentration, pressure and high temperature, and increases where water is present (Johansson, 2008). Thus, its existence might deactivate metal based catalysts such as Nickel based catalyst in methanation reactor and inhibit the reaction. In addition to that, it is poisonous when inhaled, consequently harmful to people. It is also corrosive in contact with water which is a great problem for internal parts of the plant (Hullu et al, 2008).

Catalytic oxidation reaction on activated carbon can be applied to remove hydrogen sulphide. The main products of the reaction are elementary sulphur, S, and water. Rate of reaction can be enhanced by carbon enrichment with sulphuric acid and/or potassium iodide. Activated carbon might be saturated; in that case, it is possible to regenerate it or replace it with new material. This method is applied mostly in case a PSA (Pressure Swing Adsorption) is used (Persson and Wellinger, 2006).

Another method used to remove hydrogen sulphur is chemical absorption on a material which contains metal oxides. Iron hydroxide and zinc oxide sorbents are commonly used for this purpose (Johansson, 2008).

3.1.2 Water vapour – H_2O

Water is formed and added to be used in different steps in bio-SNG production process, so that there is considerable amount of it in the product gas stream. In the presence of CO_2 and H_2S , water can cause severe corrosion problems which can damage equipment (Persson, 2003).

According to Persson, the most common technology for water removal is adsorption on the surface of a drying agent such as hygroscopic salts, zeolites, silica gel or aluminium oxide.

3.1.3 Other components

Trace amounts of halogenated compounds can be produced during bio-SNG production. They are considered corrosive since their reactions e.g. burning might yield dioxins and furans. Adsorption on enriched activated carbon is often used for removal of halogenated compounds (Persson, 2003).

Dust and particles can be removed from the gas mixture by filtering which takes advantage of different particle size of different compounds and materials. Filters with different mesh sizes are used for this purpose, and they can separate small amounts of water and even oil from the gas mixture (Persson and Wellinger, 2006).

3.2 Description of the available gas upgrading techniques

There are currently several gas upgrading techniques commercially available and many are in research and development phase. Upgrading stands for increasing the energy content of gas through removal of CO₂. In this chapter, the most common upgrading technologies are described. They are absorption, adsorption and membrane separation.

3.2.1 Absorption

Absorption employs the different binding forces of different chemical compounds for separation. In raw bio-SNG, carbon dioxide and hydrogen sulphide are more polar compared to the other compounds. Thus, they dissolve in polar absorption solution easier than methane, since it is non-polar. Water and organic solvents are mostly commonly used absorption fluids (Persson and Wellinger, 2006).

3.2.1.1 Water scrubbing

The most common upgrading technology for gas upgrading from anaerobic digestion in Sweden is water scrubbing in which water is the absorption fluid (Johansson, 2008). Carbon dioxide is removed from the raw bio-SNG by employing solubility differences of different gases in water. First, carbon dioxide is dissolved in water within an absorption column which operates at high pressure. Then, it is sent to the desorption column where it is released from the water by using air which is at atmospheric pressure (SGC AB, 2013). Schematic illustration of the system can be seen in Figure 4.

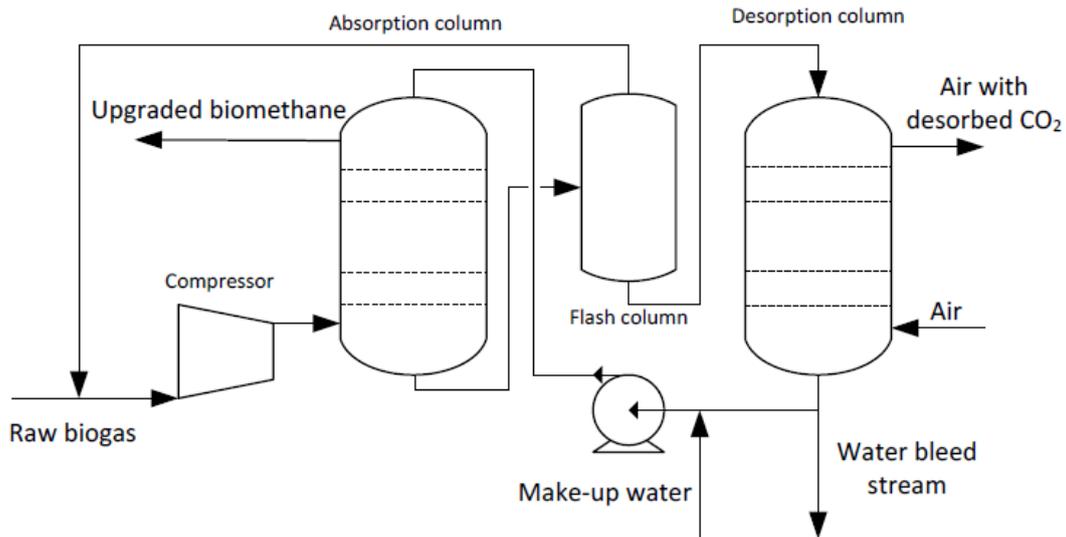


Figure 4. Schematic illustration of water scrubbing system (SGC AB, 2013).

As can be seen in Figure 4, upgraded gas with a purity of 97% methane is saturated with water and it leaves the absorption column from the top.. Water stream leaves the column from the bottom with a high amount of CO₂; however, it has trace amounts of methane which is dissolved in water. The water stream is then sent to a flash column where the pressure is decreased and this makes the dissolved methane release and separate. And then, the separated methane is mixed with the raw biogas inlet and sent back to the absorption column in order to reduce CH₄ losses (Persson and Wellinger, 2006).

3.2.1.2 Chemical absorption

Absorption fluid is an organic solvent in chemical absorption in which CO₂ is separated by means of chemical reactions. Mostly, aqueous solutions of amines which are the chemical compounds with carbon and nitrogen are used in chemical absorption applications. Product of chemical absorption reaction can be in molecular or ionic form (SGC AB, 2013). Methyldiethanolamine (MDEA-tertiary amine), diethanolamine (DEA-secondary amine) and monoethanolamine (MEA-primary amine) are the amines used the most in chemical absorption for carbon dioxide and hydrogen sulphide removal (Kohl and Nielsen, 1997).

The process has limitations in terms of loading and has high energy requirement as well as problems concerning corrosion and degradation (Jonsson and Westman, 2011). A descriptive process layout of the chemical absorption can be seen in Figure 5.

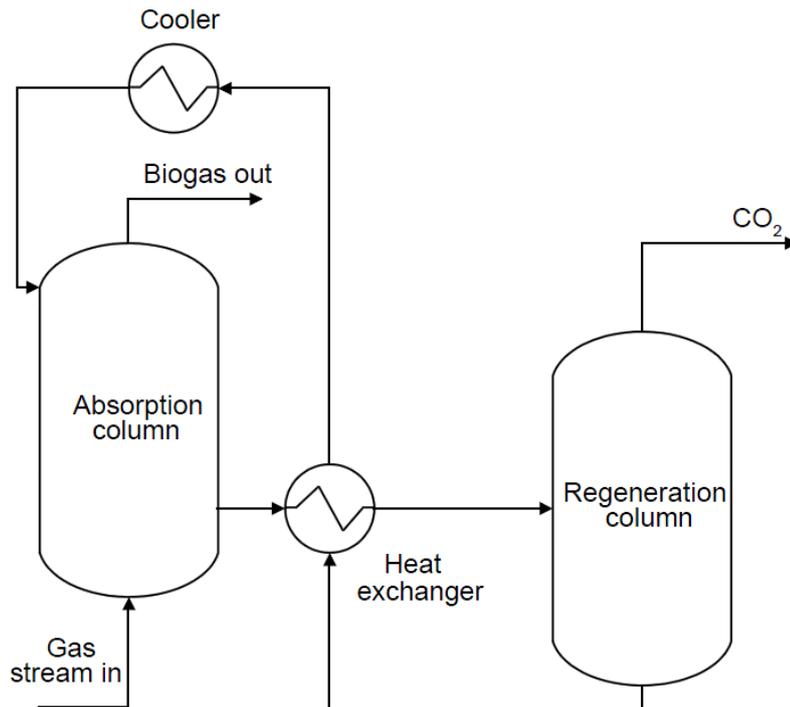


Figure 5. Schematic illustration of chemical absorption system (Hullu et al, 2008).

The raw bio-SNG flows through the absorber where it is mixed with an absorbent. CO₂ binds chemically with the absorbent and upgraded biogas consisting of mainly CH₄ leaves the absorber. The upgraded biogas can be purified to CO₂ concentrations below 0.5%. The process is regenerated by submitting the CO₂ rich liquid to a desorber where the temperature is increased. The CO₂ is released from the absorbent which can be reused in the absorber. The regeneration requires heat, but for economic reasons this is preferable compared to replacing the absorbents (Jonsson and Westman, 2011).

3.2.2 Adsorption

During adsorption, carbon dioxide is adsorbed on a surface of a material by employing the difference in particle size of different compounds. Commonly used adsorption materials are activated carbon and molecular sieves (Johansson, 2008).

There are several different adsorption techniques commercially available for removal of carbon dioxide from biogas. The names of the different techniques indicate the method used to regenerate the adsorption process (Jonsson and Westman, 2011). Three different methods are described in this section, namely:

- Pressure Swing Adsorption (PSA)
- Temperature Swing Adsorption (TSA)
- Electric Swing Adsorption (ESA)

The most common adsorption process, and the second most common gas upgrading process in Sweden, is Pressure Swing Adsorption, PSA (Johansson, 2008). In PSA, the raw bio-SNG is compressed to an elevated pressure, and then fed into an

adsorption column which retains the CO_2 but not CH_4 . When the column material is saturated with CO_2 , the pressure is released and CO_2 can be desorbed, and then led into an off-gas stream. For continuous production, several columns are needed as they are closed and opened consecutively (SGC AB, 2013). A simplified process diagram for a PSA upgrading unit is shown in Figure 6.

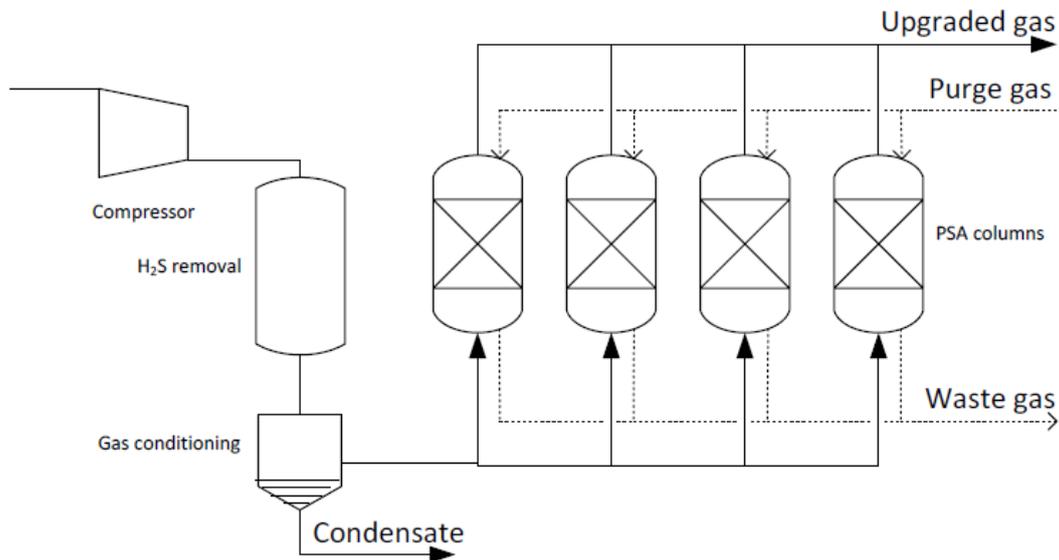


Figure 6. Schematic illustration of pressure swing adsorption system (SGC AB, 2013).

TSA works under a different principle. Instead of adjusting the pressure it adjusts the temperature. The technique is usually applied to gas drying, where the water content is first adsorbed at around $40\text{ }^\circ\text{C}$ and the process regenerates at temperatures above $120\text{ }^\circ\text{C}$ (Jonsson and Westman, 2011).

Electric Swing Adsorption regenerates by the means of temperature increase. It uses a low voltage electric current to heat the adsorbing material by the direct Joule effect. This process cannot use waste heat for the regeneration which is a disadvantage (Grande and Rodrigues, 2007 in Jonsson and Westman, 2011).

3.2.3 Membrane separation

CH_4 and CO_2 can also be separated by using a membrane. Because of the difference in molecule size and/or affinity, certain molecules pass through a membrane while others do not. The difference in partial pressure between gases is the driving force behind this process. The properties of this separation method are strongly dependent on the type of membrane used. Many different membranes are available each with its particular specifications (Hullu et al, 2008).

The membrane separation stage is designed differently depending on the manufacturer of the system and the type of membranes they are using (SGC AB, 2013). Three of the most common designs are shown in Figure 7.

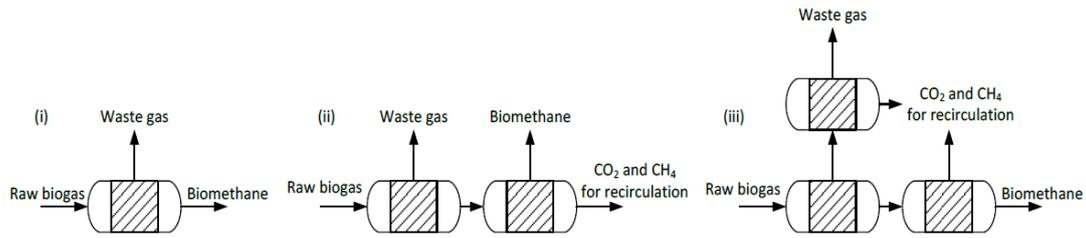


Figure 7. Schematic illustration of three most common membrane separation designs (SGC AB, 2013).

Design (i) does not have internal circulation of the raw gas, so there is lower energy requirement for the compressor. In this design, there will be high methane loss though; therefore high selectivity membranes should be preferred. Design (ii) has better performance in terms of the methane recovery compared to design (i). In this design, the raw gas is cleaned in the first membrane and the permeate stream (the stream running through membrane) of it is removed from the system while the permeate from the second membrane is fed back to the system inlet to have a lower methane slip. In design (iii), the retentate (the gas stream which does not run through membrane) from the first membrane is cleaned via the second membrane to have a product stream with a methane content of 97%. In addition to the design (ii), the permeate of the first stage is purified in another membrane (third membrane) to have a minimal methane content in the off-gas stream; this also minimize the amount of the gas sent to the compression. The permeate of the second membrane and the retentate stream of the third one are mixed and fed back to the compressor (SGC AB, 2013).

3.3 Additional gas polishing techniques

Gas polishing is necessary in case cleaning and upgrading are not enough to meet purity requirements. Techniques explained above can be used for further purification. H_2 can be captured since it is a useful by-product.

Conventional hydrogen separation techniques are pressure swing adsorption, temperature swing adsorption, electrical swing adsorption and membrane separation of which operation principles described in previous chapter (EERC, 2010).

Most hydrogen separation membranes operate on the principle that only hydrogen can penetrate through the membrane because of the inherent properties of the material. The mechanism for hydrogen penetration through the membrane depends on the type of membrane. Most membranes rely on the partial pressure of hydrogen in the feed stream as the driving force for permeation, which is balanced with the partial pressure of hydrogen in the product (permeate) stream (EERC, 2010).

4 Cryogenic Upgrading and Liquefaction

Cryogenic technique has been used for different purposes and the following are the most common three tasks where it is employed:

- Landfill gas cleaning; trace contaminant removal
- Gas upgrading; CO₂ removal
- Liquefaction of upgraded gas

Regarding cryogenic technique, very few technical data has become available since it is not a mature technology yet (SGC AB, 2013).

4.1 Cryogenic gas upgrading

Since CO₂ and CH₄ condensate at different temperature-pressure domains; it is possible to separate them by cooling and compressing the raw bio-SNG gas mixture. Pure CO₂ has a desublimation temperature of -78.5°C at atmospheric pressure, while methane condenses at -161°C. CO₂ can be separated by adjusting the temperature of the gas in order to condensate or desublimate CO₂. The gas stream without carbon dioxide is then received. Depending on the temperature of the process different purity grades can be reached. A lower temperature results in a higher removal efficiency of carbon dioxide (Jonsson and Westman, 2011).

Compared to other upgrading techniques, cryogenic approaches have the following potential or expected benefits (SGC AB, 2013):

- No contact between gas and chemicals
- Production of pure CO₂ as by-product
- Possibility to liquefy upgraded gas

4.1.1 Available cryogenic systems

There are three commercial cryogenic unit providers which are Scandinavian GtS, Prometheus-Energy, and Terracastus. Their designs are briefly explained below.

In 2007, *Scandinavian GtS* was established via partnership with Dutch company Gas treatment Services (GtS). The system is designed to produce liquefied biogas from landfill and digester gas. It consists of four units and a schematic illustration of the system can be seen in Figure 8 (Scandinavian GtS, 2008).

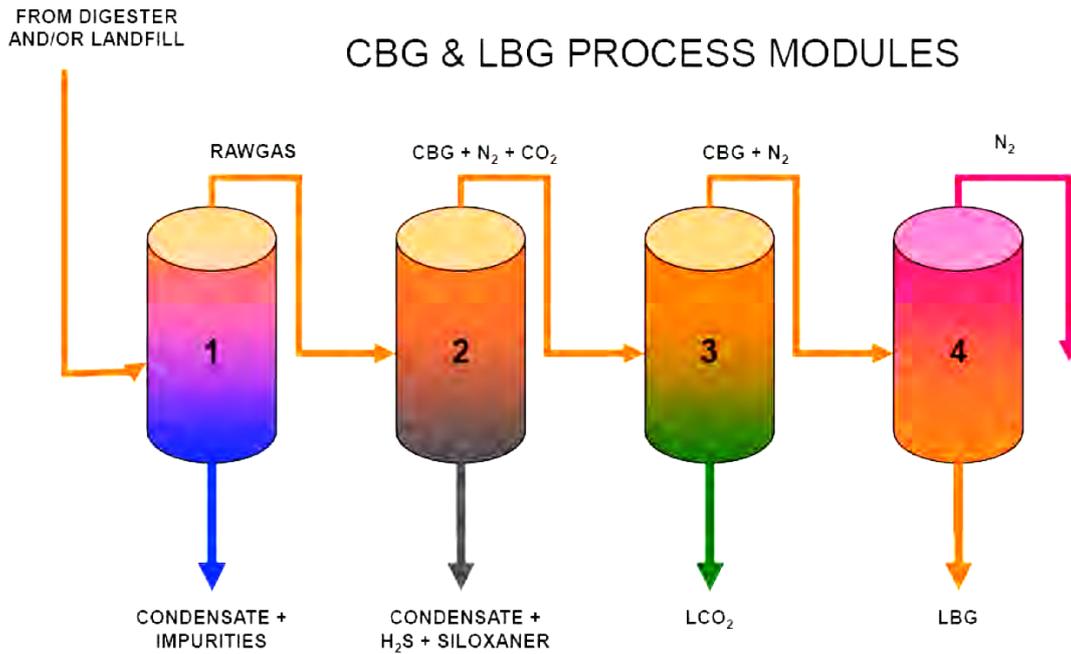


Figure 8. Schematic illustration of Scandinavian GtS cryogenic system design (Scandinavian GtS, 2008)

In 1st unit, the gas stream is cooled down to 6°C to condense and remove moisture content with some other contaminants. In the 2nd, the gas is further cooled to -25°C to freeze out the remaining moisture and condensate siloxanes. And, a filter is used to clean the gas from traces of hydrogen sulphide and siloxanes. In the 3rd unit, carbon dioxide is frozen out and separated by chilling the gas stream to -78°C. Separated carbon dioxide can be liquefied and used since it is a valuable by product. The stream leaving the unit is clean enough to be compressed and used as CBG (compressed biogas gas). The gas is further processed in the 4th unit where LBG (liquefied biogas) is produced by cooling down to -190°C. The product is LBG which has more than 99% of methane (Scandinavian GtS, 2008).

Prometheus-Energy is an American company which produces LNG from overlooked sources like landfill sites, stranded gas wells, wastewater treatment facilities and coal mines (Prometheus-Energy, 2008a). Prometheus-Energy does not want to reveal any technical details about their present technology; however, there is process flow diagram of the pilot plant at Hartland Landfill which can be seen in Figure 9.

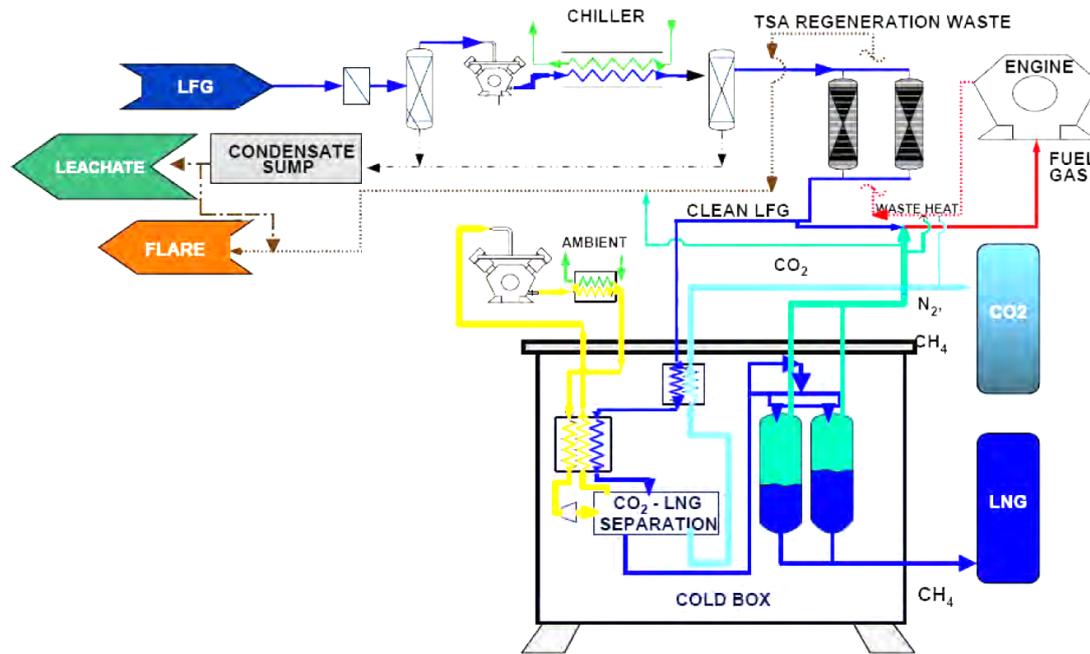


Figure 9. Schematic illustration of Hartland Landfill cryogenic system design (Pettersson et al, 2006).

LFG (landfill gas) is first compressed and chilled in the chiller for removal of water and heavy organic compounds which are vaporized and burned in the flare. The remaining contaminants are then removed in the TSA (temperature swing adsorption) columns. Then, it is sent to the cold box where CO₂ is separated from the gas stream by condensation in the heat exchangers and sent to LCO₂ (liquid CO₂) storage. And then, CH₄ is condensed and the cold for the condensation of CO₂ and CH₄ is produced in a closed Brayton cycle. Any N₂ is separated from LBG in the blue/green columns. N₂ concentration in the raw gas at Hartland Landfill varies between 14-38 %, which is a very high N₂ concentration, resulting in a high CH₄ concentration in the flash vent. This vent is sent to the gas engine driving the process (Pettersson et al, 2006).

Acrion is a company based in USA and their expertise area is separation and upgrading of gases with high carbon dioxide content (> 10%) and the utilization of separated carbon dioxide as a working fluid for separation and upgrading. Their process is a combination of cryogenic technique and existing conventional technology. Distillation column (CO₂ Wash®) is used to clean the raw gas via two membranes and a liquefaction step to produce LBG. Schematic illustration of the process can be seen in Figure 10 (Johansson, 2008). Today, Terracastus has the global rights to the CO₂ Wash® technology (SGC, 2013).

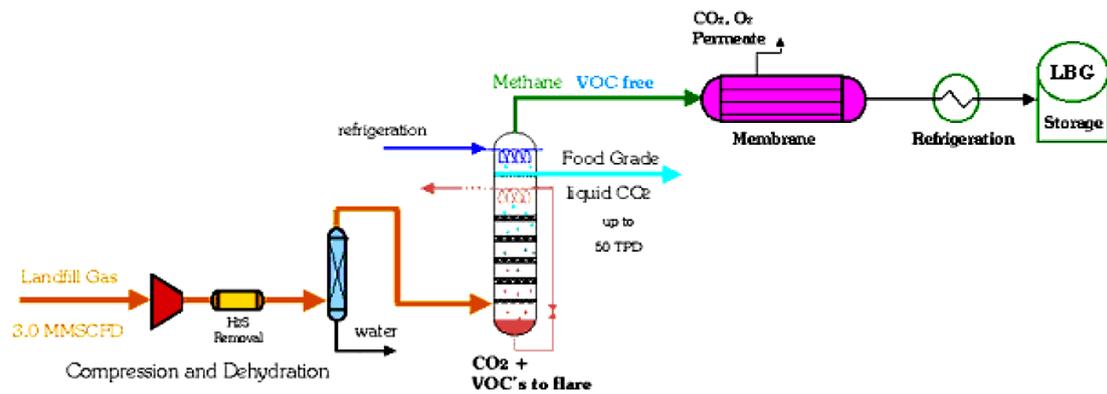


Figure 10. Schematic illustration of CO₂ Wash® technology for LBG production from raw gas (Johansson, 2008).

The compressed, cleaned and dried gas is fed into the distillation column. There two streams leaving the column from the top. One is the liquid CO₂ stream which has a purity of 99.99 %. The other one is the clean gas stream containing CH₄, CO₂ (approximately 25%), O₂ and N₂. Since CO₂ can freeze during liquefaction, the clean gas stream from CO₂ Wash® has to be further processed. CO₂ and remaining O₂ are separated via membranes. Gas leaving the membranes still has a CO₂ content of 1-2 %. Before the refrigeration, the last CO₂ removal is achieved by a mol sieve and the CO₂ concentration is reduced down to 100 ppmv. Remaining N₂ is separated and flashed in the refrigeration plant. The methane is then liquefied by applying a refrigeration cycle as explained in Chapter 2.2.3 (Johansson, 2008).

4.2 Cryogenic gas liquefaction

Cryogenic gas liquefaction is the process to produce bio-LNG from raw bio-SNG or upgraded bio-SNG by cooling down to condensation point of methane. Liquefaction system has strict inlet condition requirements in terms of purity, since it operates at extreme conditions e.g. low temperatures and high pressures. Thus, the gas upgrading unit should fulfil these requirements for smooth operation of the system. Requirements can be seen in Table 1. If the upgrading process does not reach these requirements, an extra polishing step is needed after upgrading and before liquefaction (Johansson, 2008).

Table 1. Purity requirements for the liquefaction of bio-SNG (Flynn, 2005)

Compound	Requirement
H ₂ O	0,5 ppm (v)
H ₂ S	3,5 ppm (v)
CO ₂	50-125 ppm (v)

Bio-LNG can be produced by combining cryogenic upgrading and liquefaction or can be upgraded first with commercial upgrading methods as explained in previous chapter and then liquefied by cryogenic liquefaction (Johansson, 2008).

Existing small-scale liquefaction methods which are commonly used are explained in Chapter 4.2 to provide a better insight for cryogenic liquefaction process. Small-scale liquefaction techniques can be classified into two groups: closed cycles and open cycles which are explained below.

4.2.1 Open cycles

The refrigerant which is used as cooling agent in liquefaction can be considered as a part of the gas stream in open cycles. General outline of an open cycle process can be seen in Figure 11. The feed gas is compressed with a compressor (CP in figure) and then cooled down to ambient temperature via heat exchanging units (HE in figure). Cooled gas liquefaction is achieved via a turbo expander (TEX in figure), and work which can be utilized within the process is produced during expansion. Finally, liquefied gas is sent to a flash tank in order to remove its N₂ content (Johansson, 2008).

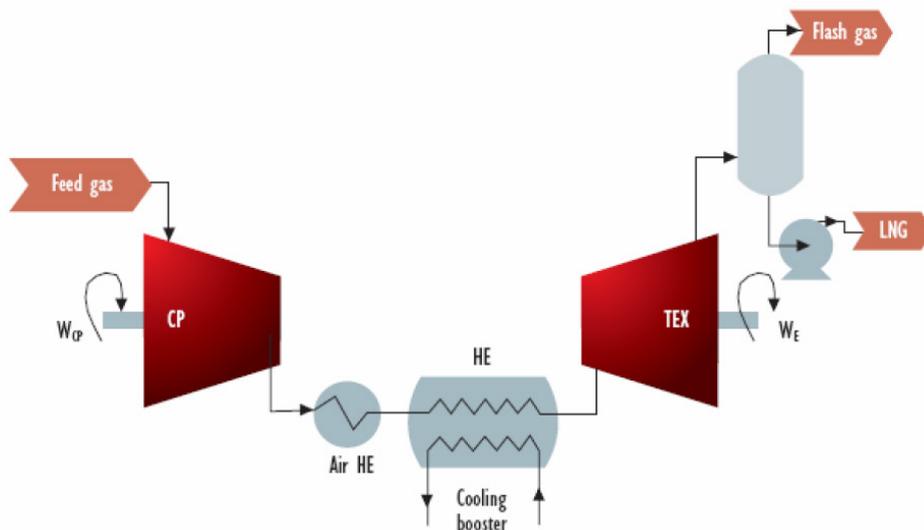


Figure 11. Open cycle (Pettersson et al, 2007)

4.2.2 Closed cycles

In contrast to open cycles, the refrigerant is not a part of the gas stream in closed cycles. The refrigerant is supplied externally. General outline of a closed system can be seen in Figure 12. The refrigerant is compressed first (CP in figure), then cooled down via a heat exchanger (HE in figure) and cooled further in a cryogenic heat exchanger (MCHE in figure). Refrigerant leaving the cryogenic heat exchanger is expanded (TEX or E-V in figure) to obtain low pressure refrigerant at low temperature and work is produced at the same time to drive the compressor. The expansion can be achieved either by a throttle valve which simply acts as an isenthalpic orifice, or an isenthalpic expansion engine. The difference between these two is that throttling provides only cooling while an expansion engine produces work in addition to cooling (Smith, 2005).

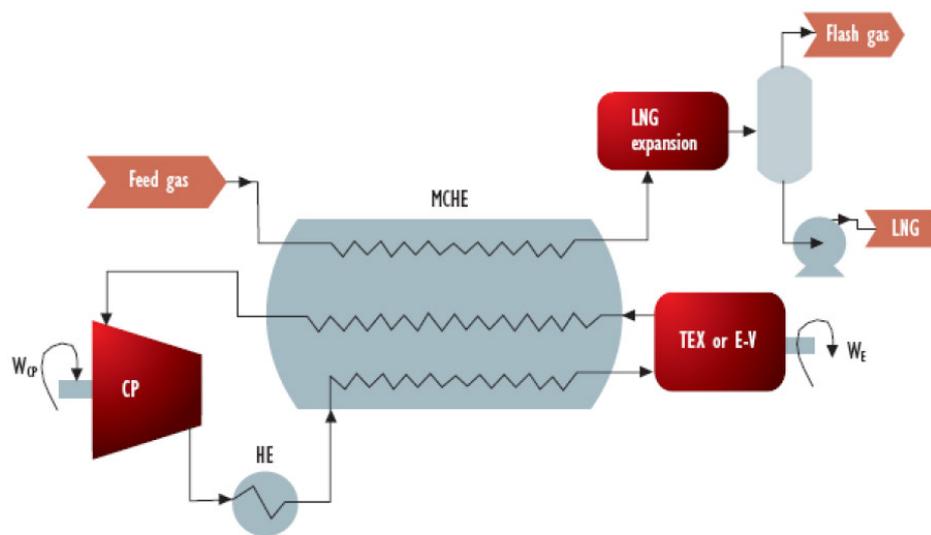


Figure 12. Closed cycle (Pettersen et al, 2007)

Closed cycles are more complex compared to open cycles but also safer since it reduces the number of process steps in natural gas applications. Natural gas is flammable and can damage the turbo expander if there are any condensing or solidifying components (Kidnay and Parrish, 2006).

Brayton cycle

The ideal closed-loop cycle is the Brayton cycle which consists of four internally reversible processes (Lane, 2001) that are illustrated in Figure 13:

- 1-2 Isentropic compression
- 2-3 Isobaric heat addition
- 3-4 Isentropic expansion
- 4-1 Isobaric heat rejection

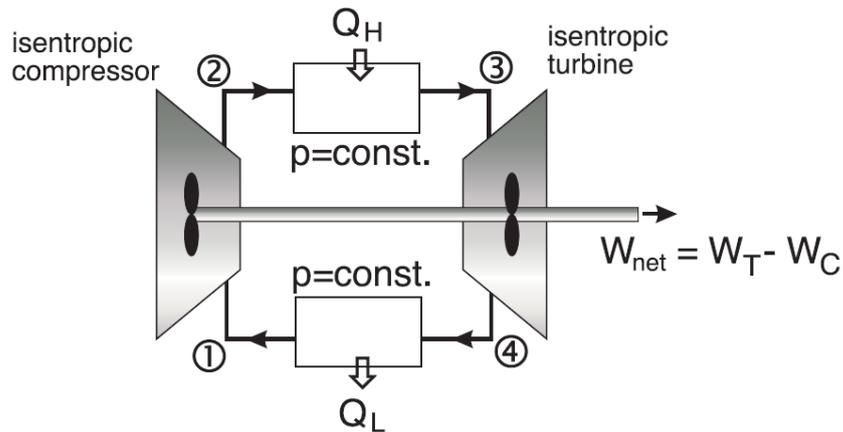


Figure 13. Brayton cycle (Lane, 2001)

Contrary to other refrigeration cycles, the refrigerant remains as in gas phase throughout Brayton cycle. As there is no phase change, the specific heat transferred is almost constant; thus, an increase in the refrigeration flow rate is required in order to fulfil the liquefaction of natural gas.

A parameter used to measure the efficiency of the refrigeration cycle is the coefficient of performance, which corresponds to the heat extracted from the system in relation to the mechanical work done by the system.

$$COP = \frac{|Q_L|}{W_{net}}$$

The real reverse Brayton cycle differs from the ideal one and operates with some losses due to:

- i. Non-isentropic compression and expansion processes
- ii. Pressure drop in heat exchangers

4.2.3 Description of the available liquefaction techniques

According to Smith, lower cooling temperature leads more complexity in the refrigeration process (Smith, 2005). Refrigeration processes developed for natural gas liquefaction can be classified into three main categories depending on the equipment used and the refrigerant. These processes are explained below (Wonsub et al, 2013).

4.2.3.1 Expander process using gas phase refrigerants

The simplest liquefaction process is based on the reverse-Brayton cycle explained in Chapter 4.2.2, which uses nitrogen in gas state as a refrigerant in a closed expander cycle. The efficiency of this process is low due to the fact that a single refrigerant is used in a single phase (gas). Besides that, it is used over a wide range of temperatures. Thus, the temperature difference in some temperature domains is large which leads to thermodynamic inefficiencies and hence higher power requirements (Bronfenbrenner et al, 2009). In 2012, Air Liquide Advanced Technologies commissioned their first plant for the liquefaction of biogas in Lidköping based on a nitrogen expander process (SGC, 2013). The plant is a good example for similar applications.

4.2.3.2 Cascade process using pure refrigerants

A way of improving efficiency is the use of several separate refrigeration cycles with different refrigerants for cooling at different temperature levels and be as close as possible to the natural gas cooling curve. Each cycle of the cascade operates at a lower temperature than the previous one. Energy efficiency is improved by the increase of stages of refrigeration; however, it also increases the complexity of the process and the equipment required (Bronfenbrenner et al, 2009). According to Flynn, the most common refrigerants are propane, ethylene and methane (Flynn, 2005).

4.2.3.3 Single mixed refrigerant process

In this process a mix of refrigerants with different condensation temperatures is used. It consists of hydrocarbons and nitrogen and its composition is adjusted to match as close as possible the natural gas cooling curve (Smith, 2005). A scheme illustrating cascade process and SMR process are shown in Appendix 2.

Moreover, another possibility is to use a cascade process with several mixed refrigerants in each cycle so as to improve energy efficiency. However, it leads to many problems when leading with two phases in multicomponent mixtures (Flynn, 2005).

5 Methodology

A literature study was conducted in order to gather data required to establish a simulation model of a bio-LNG production process. In this chapter there is a detailed description of the process modelling including the employed limitations, specifications, assumptions and the procedure for its simulation. Material and energy balances are solved in the commercial flowsheeting software Aspen Plus from Aspen Technology.

In this thesis two different cases are defined in order to investigate cryogenic technique for gas upgrading; base case and integrated case. In the *Base case*, bio-LNG is produced in a liquefaction plant located immediately downstream of the main Bio-SNG process, as shown in Figure 14. In the *integrated case* a cryogenic unit is implemented directly within the process instead of conventional gas upgrading technology. Both processes are based on the capacity assumption of 100 MW of bio-LNG and are inspired by GoBiGas design which is explained in Chapter 2.3 with addition of gas liquefaction unit.

Process integration tool pro_PI is used to conduct pinch analysis with simulation results for both cases. Minimum cold and hot utility demands as well as theoretical maximum work outputs are investigated.

Schematic representations of base case and integrated case can be seen in Figure 14 and 15, respectively.

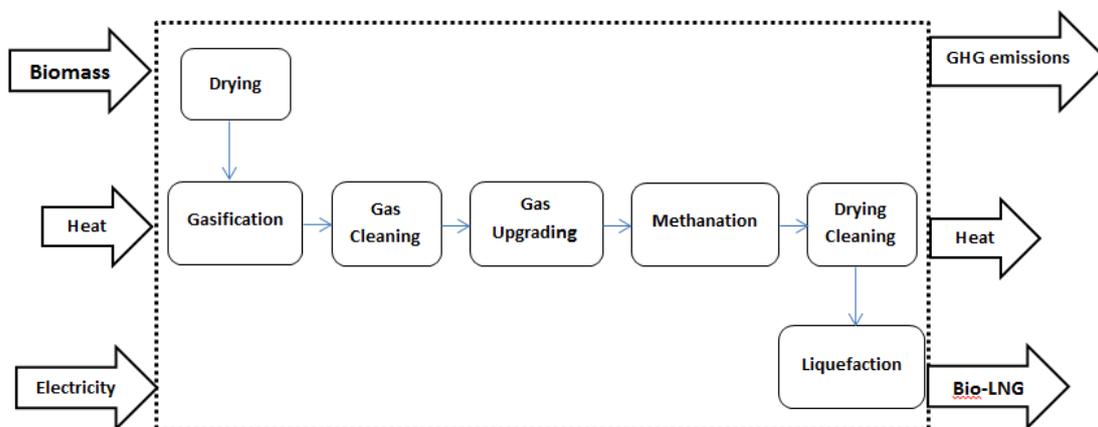


Figure 14. Schematic representation of base case bio-LNG production process

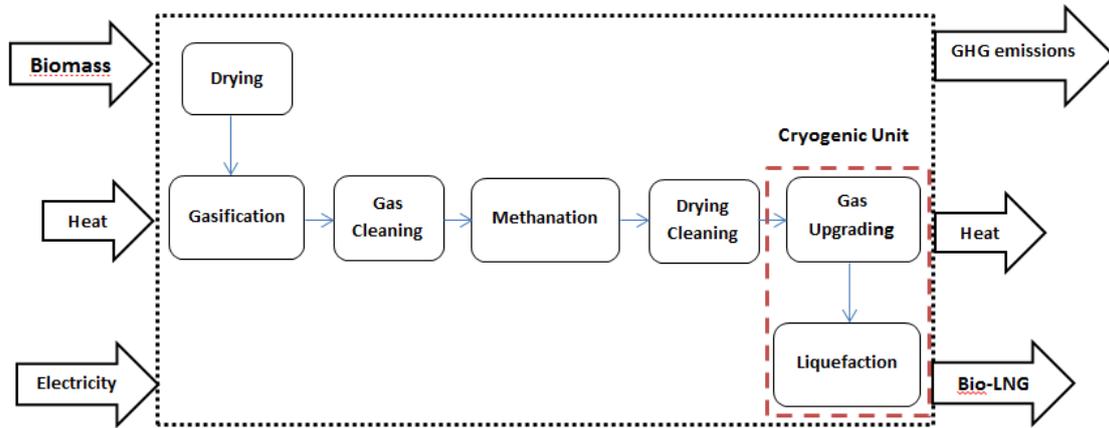


Figure 15. Schematic representation of integrated case bio-LNG production process

The major difference between the designs is the upgrading unit. In the base case, it is kept as the same as in GoBiGas project which is chemical absorption technique applied before methanation while in the integrated case cryogenic method is applied after drying and cleaning.

5.1 Process modelling

Aspen Plus provides a rich property database, equations of state for different conditions and different models for common unit operations. Peng-Robinson equation of state with Boston-Mathias extension was chosen as a property method as recommended by guidelines in Aspen Plus for gas handling processes and cryogenic operations. For water and steam processes, steam tables are used instead.

Components

Biomass inlet consists of wet wood and it is modelled as a non-conventional solid (Heyne, 2013). Raw bio-SNG is produced after gasification and gas cleaning and it mainly consists of carbon dioxide, methane and trace amounts of hydrogen, carbon monoxide and water. Other existing components during the process that are removed are char, hydrocarbons, tars, sulphur compounds and trace compounds such as N_2 and HCl. Final product is bio-LNG that is primarily methane in liquid state.

Limitations

In this thesis cryogenic unit for gas upgrading and liquefaction processes are simulated. The rest of the process simulation is based on Arvidsson et.al (2012) whose explanations and modelling assumptions are summarized in Appendix 3. Liquefaction process modelling is considered for the base case whereas cryogenic technique modelling together with liquefaction is considered for the integrated case.

Process specifications and assumptions

During process modelling for bio-SNG production and more specifically during cryogenic unit for upgrading and liquefaction simulation, the following assumptions and process specifications used in both cases are:

- Process capacity: $100 \text{ MW}_{\text{bio-LNG}}$

- Final delivery bio-SNG pressure in GoBiGas project: from 5 bar to 10 bar (Gunnarson, 2011)
- Final product delivery conditions:
 - Pressure: 7.5 bar
 - Temperature: -163°C
- Purity requirements for the liquefaction of bio-SNG (Table 1)
- Pressure drop in the heat exchangers: 2%
- Maximum compressor stage compressor ratio: 3
- Isentropic efficiency of compressors: 0.85
- Isentropic efficiency of turbines: 0.90
- Minimum temperature difference in multiple heat exchangers: 2°C
- Cooling water is used for cooling requirements down to 20°C
- Pressure ranges in the refrigeration cycle (Dubar, 1997):
 - Low: 5-20 bar
 - Intermediate: 15-25 bar
 - High: >25 bar

5.1.1 Base case

The employed technology for bio-SNG liquefaction is based on a reverse nitrogen Brayton cycle which is explained in Chapter 4.2.2.

5.1.1.1 Nitrogen as a gaseous refrigerant

Nitrogen is used as a refrigerant in gas phase, which has some advantages and disadvantages in comparison to mixed refrigerants that are summarized in Table 2.

Table 2. Advantages and disadvantages of nitrogen in gas phase as a refrigerant (Bronfenbrenner et al, 2009).

Advantages	Disadvantages
<ul style="list-style-type: none"> ✓ Nitrogen is a safe non-flammable refrigerant whereas hydrocarbons in large amount that are used in mixed refrigerants are flammable ✓ It is readily available as opposed to mixed refrigerants in which large amounts of some components must be extracted from the natural gas feed ✓ The process is simpler and less equipment items are required 	<ul style="list-style-type: none"> ✗ Nitrogen refrigerant warming curve cannot be aligned as closely to the natural gas cooling curve as SMR and cascade process ✗ Heat transfer coefficient is lower because there is no phase change

5.1.1.2 Process description

The flow sheet of cryogenic bio-SNG liquefaction used in Lidköping in which our study is based on is shown in Figure 16.

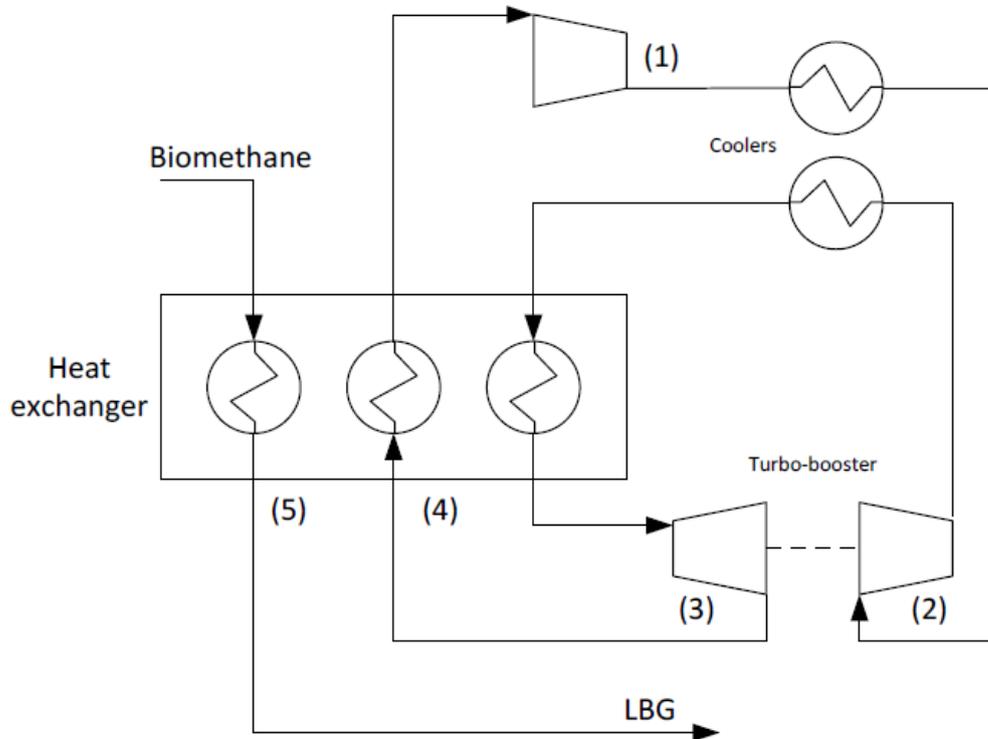


Figure 16. Schematic illustration of cryogenic gas liquefaction by nitrogen expander process (SGC AB, 2013).

The process can be explained following the steps below (SGC AB, 2013):

1. Nitrogen is compressed to an intermediate pressure. Since it is warmed by the compression process, after compression nitrogen stream is cooled with ambient air or water in order to return the refrigerant back to ambient temperature.
2. After cooling the compressed nitrogen, it is then over-pressurised in a turbo-booster. Then, the high pressure nitrogen is cooled down to ambient temperature with air or water following further cooling in the heat exchanger by the same refrigerant in expanded form.
3. The high pressure nitrogen stream is expanded to a low pressure to cool it further. When the refrigerant is expanded through a turbine, this work is used to recover the energy required to compress the refrigerant.
4. The low pressure stream flows back in the multiple heat exchanger and cools down both bio-SNG and the high pressure nitrogen stream by counter-current exchange.
5. Bio-SNG is liquefied.

One key variable in liquefaction is *pressure*. As can be seen from a pressure-enthalpy diagram, liquefying at high pressure is beneficial since the heat to be removed is reduced with increased pressure (Luber, 2009). In order to study the advantages and disadvantages of liquefying at high pressure, two designs that operate at different pressures are modelled in Aspen: high pressure case at 40 bar and low pressure case at 8 bar that is in the range of the delivery pressure in GoBiGas plant (5-10 bar). A pressure-enthalpy diagram for methane is illustrated in Figure 17 showing the two pressure levels chosen and their respective heat rejected during liquefaction.

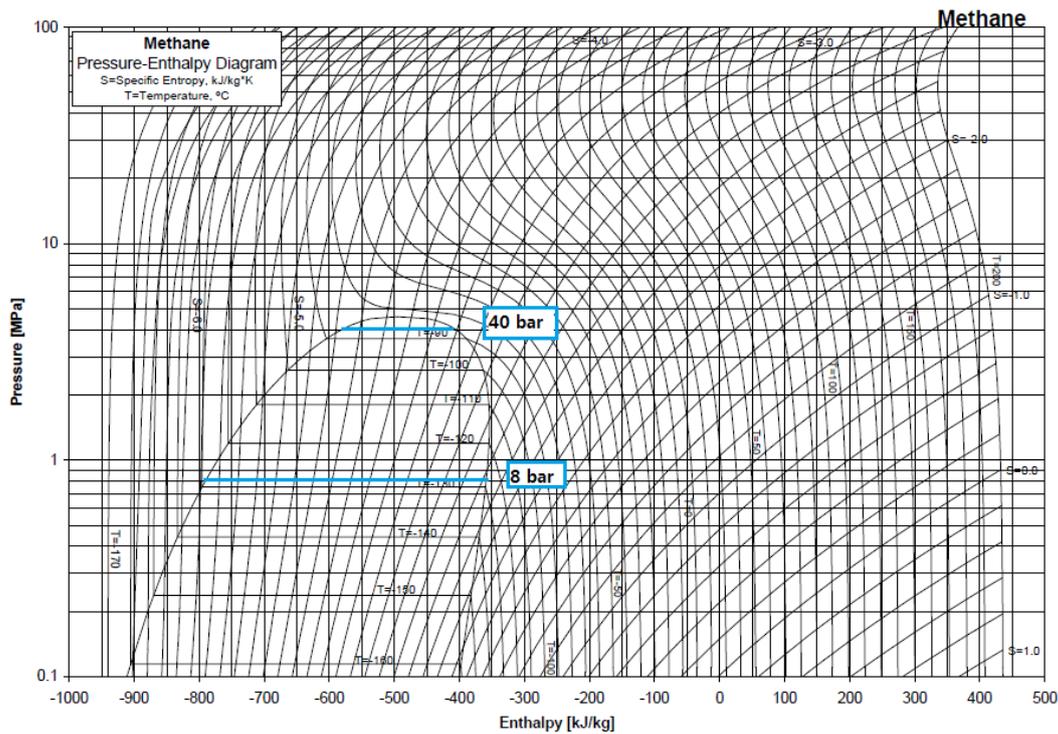


Figure 17. Pressure-enthalpy diagram for methane (Luber, 2009)

Another aspect to take into account is the exergy losses, which lead to excess work done by the refrigeration cycle. A way of decreasing these exergy losses is to match as close as possible the cooling curve of bio-SNG/High pressure N_2 with the warming curve of low pressure N_2 (Luber, 2009).

5.1.1.3 Liquefaction at 8 bar

Since bio-SNG coming from drying and gas cleaning and entering the liquefaction process is at 8 bar, liquefaction occurs at -130°C (Figure 17). The liquefaction simulation flow sheet at 8 bar is based on the technique used in Lidköping plant commissioned by Air Liquide; it is shown in Figure 18.

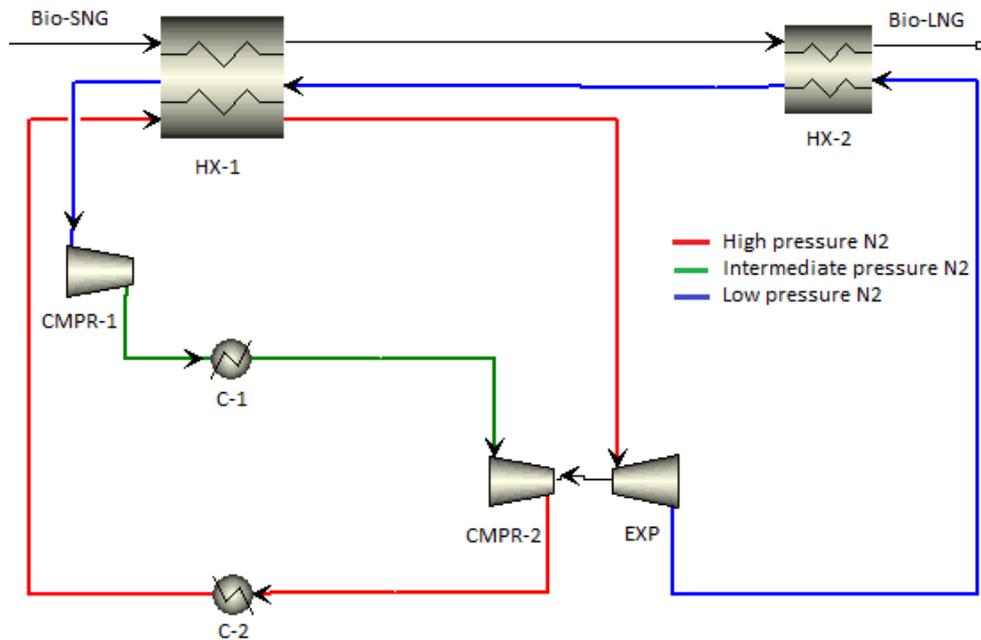


Figure 18. Flowsheet for bio-SNG liquefaction at 8 bar

In HX-1 the low pressure N₂ cools down the bio-SNG and the high pressure N₂ to -92.5°C in order to achieve the desired specification of a minimum temperature difference of 2°C in the hot side of HX-1. Both hot streams after HX-1 are considered to be at the same temperature. In HX-2 liquefaction of bio-SNG occurs. Mass flow of refrigerant is decided according to the warming curve of N₂ and cooling curve of bio-SNG in HX-2, which should match as close as possible while having a ΔT of 2°C so that exergy losses are reduced. In order to have a ΔT of 2°C in the cold side of HX-2, a calculator block is set to adjust the pressure in the expander. Both coolers decrease refrigerant temperature to ambient temperature and the pressure in the compressors is in the ranges determined in process specifications (PCMPR-1= 20 bar; PCMPR-2= 55 bar).

5.1.1.4 Liquefaction at 40 bar

In this case liquefaction occurs at -88°C (Figure 17). Hence, it is not required to expand all refrigerant to the lowest temperature because the lowest temperatures are only required for bio-LNG sub-cooling. In this temperature domain the warming curve of the refrigerant is not able to be closely matched with the cooling curve of bio-SNG. Thus, one way of improving the process efficiency is to introduce a second expander stage in which it is only expanded to the lowest temperature the volume of refrigerant required for the sub-cooling part. A dual N₂ expander process is described in the patent from Dubar (BHP) which is shown in Figure 19.

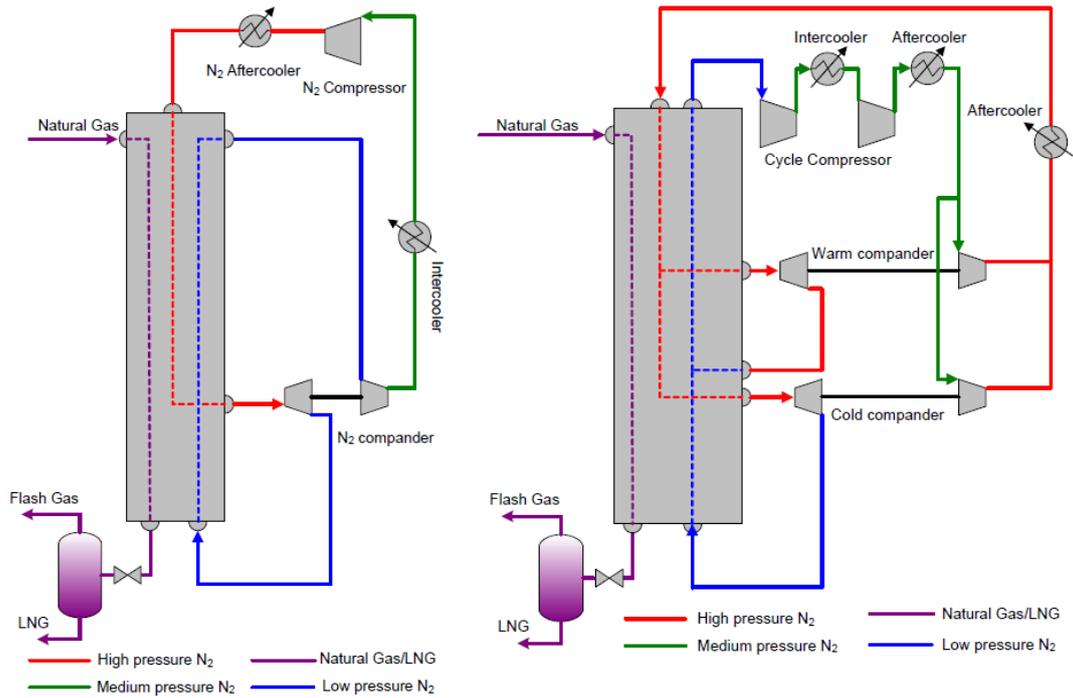


Figure 19. A single N2 expander (left) and a dual N2 expander (Dubar, 1997).

The implementation of a second expansion level comprises two different gradients in the warming curve of the refrigerant so that its combination is more closely matched to the cooling curve of natural gas which brings on energy savings. This difference is illustrated in Figure 20.

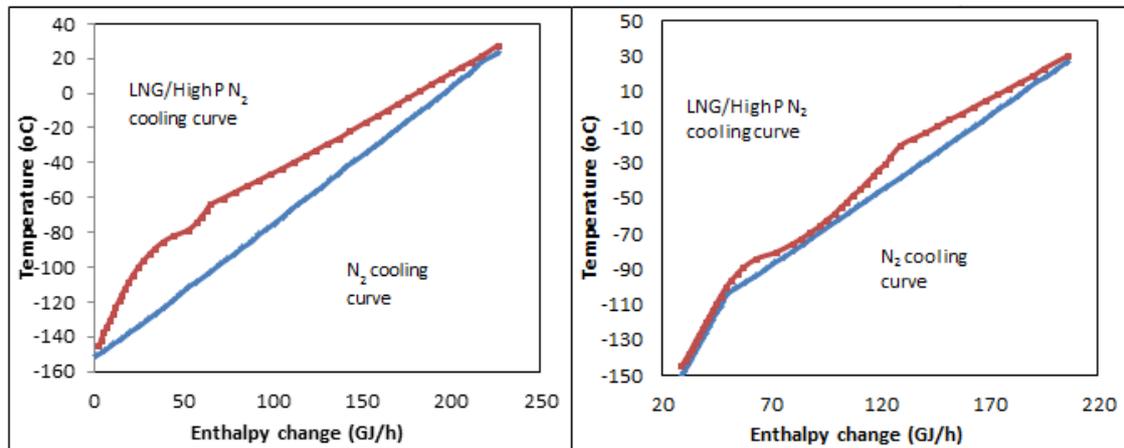


Figure 20. Nitrogen warming curve in comparison to the LNG/nitrogen cooling curve for the single N2 expander (left) and for a dual N2 expander (right) (Dubar, 1997).

Therefore, a dual nitrogen expander is modelled for liquefaction at 40 bar. The simulation flow sheet is shown in Figure 21.

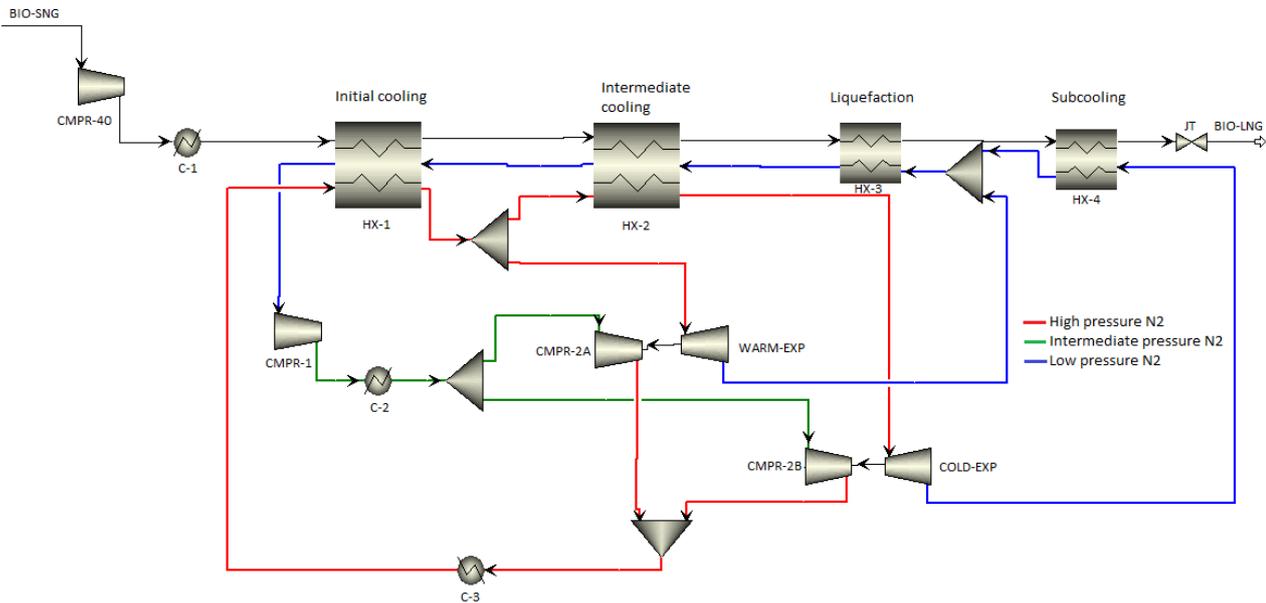


Figure 21. Flowsheet for bio-SNG liquefaction at 40 bar

Bio-SNG is compressed to 40 bar and cooled down to ambient temperature before entering the refrigeration cycle. As can be seen in Figure 21, there are two levels of expansion and only the amount required for sub-cooling is expanded to the lowest temperature.

Operating conditions for all the coolers and the compressors are kept as in liquefaction at 8 bar. The same calculator block is applied for the pressure in the cold expander using the same criteria applied previously. Both expanders are considered to have the same pressure and both hot streams after HX-1 and HX-2 are estimated to be at the same temperature.

Split fraction is an important parameter that divides high pressure nitrogen stream into two different streams: the amount required for sub-cooling and the rest which is mixed before liquefaction with the outlet low pressure nitrogen stream from sub-cooling. This parameter is chosen in order to avoid excess work done by the process. Split fraction and temperatures ranges for liquefaction simulation are selected according to the patent from Dubar (BHP) and are summarized in Table 3.

Table 3. Split fraction and temperature range for liquefaction simulation at 40 bar (Dubar, 1997)

Nitrogen stream	Split fraction (%)
Fraction expanded to the lowest temperature	20 - 50
Bio-SNG stream	Temperature range (°C)
After initial cooling ($T_{\text{BIO-SNG-1}}$)	-10°C to -30°C
After intermediate cooling ($T_{\text{BIO-SNG-2}}$)	-70°C to -90°C
After liquefaction ($T_{\text{BIO-SNG-3}}$)	-85°C to -100°C

The bio-SNG temperature after every heat exchanger is kept as in Dubar patent ($T_{\text{BIO-SNG-1}} = -20^\circ\text{C}$; $T_{\text{BIO-SNG-2}} = -84^\circ\text{C}$; $T_{\text{BIO-SNG-3}} = -90^\circ\text{C}$). Split fraction is chosen so that ΔT in the hot side of HX-4 (sub-cooling) is 2°C and mass refrigerant flow is selected in order to achieve a 2°C temperature difference in the hot side of HX-1.

5.1.2 Integrated case

Integrated case is designed to produce bio-LNG from raw bio-SNG by applying cryogenic technique. First, raw gas is upgraded to decrease CO_2 content, and then liquefied. Nitrogen Brayton cycle liquefaction unit is designed to supply refrigerant to the upgrading unit and liquefy bio-SNG. Aspen model of the cryogenic process can be seen in Figure 22.

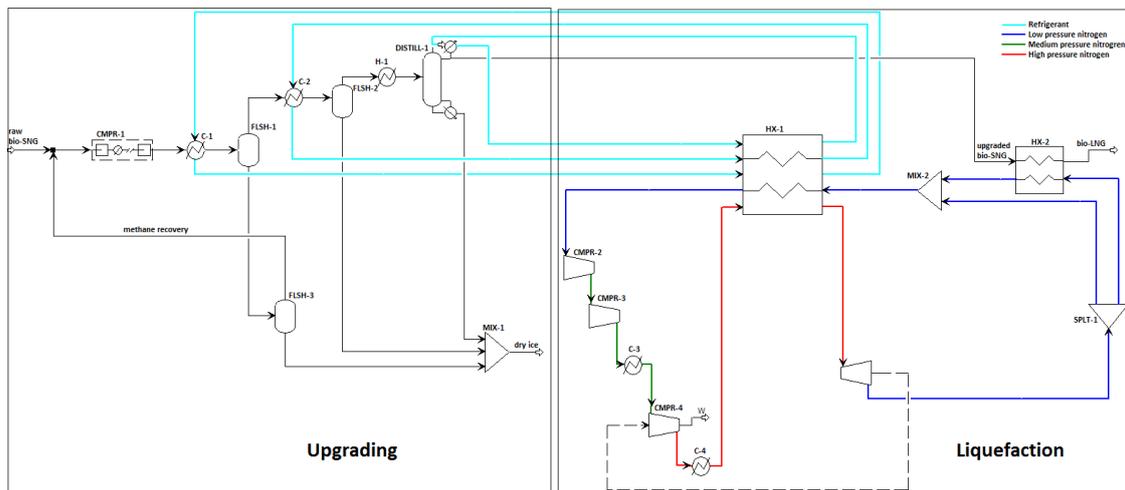


Figure 22. Integrated case Aspen model

5.1.2.1 Process Description of Gas Upgrading Unit

Aspen model of the cryogenic upgrading unit which can be seen in Figure 23 is based on a model designed by Swedish Gas Center and the data was published in 1997. The reference model can be seen in Appendix 3 (SGC, 1997).

As can be seen in Figure 23, raw gas is compressed to 65 bar with a multi stage compressor with inter cooling first. Compressed gas stream is cooled to $-51\text{ }^{\circ}\text{C}$ and flashed where first CO_2 separation is achieved. Bottom stream of the flash tank, FLSH-1 is flashed further in FLSH-3 for methane recovery, and recovered methane is mixed with inlet raw bio-SNG stream. Top stream of the flash tank, FLSH-1 is cooled to $-56\text{ }^{\circ}\text{C}$ and sent to another flash, FLSH-2 where more CO_2 is separated. Product stream with high methane content is heated to sublimate solid CO_2 content of it and fed to a distillation column to meet inlet purity requirement of the liquefaction unit.

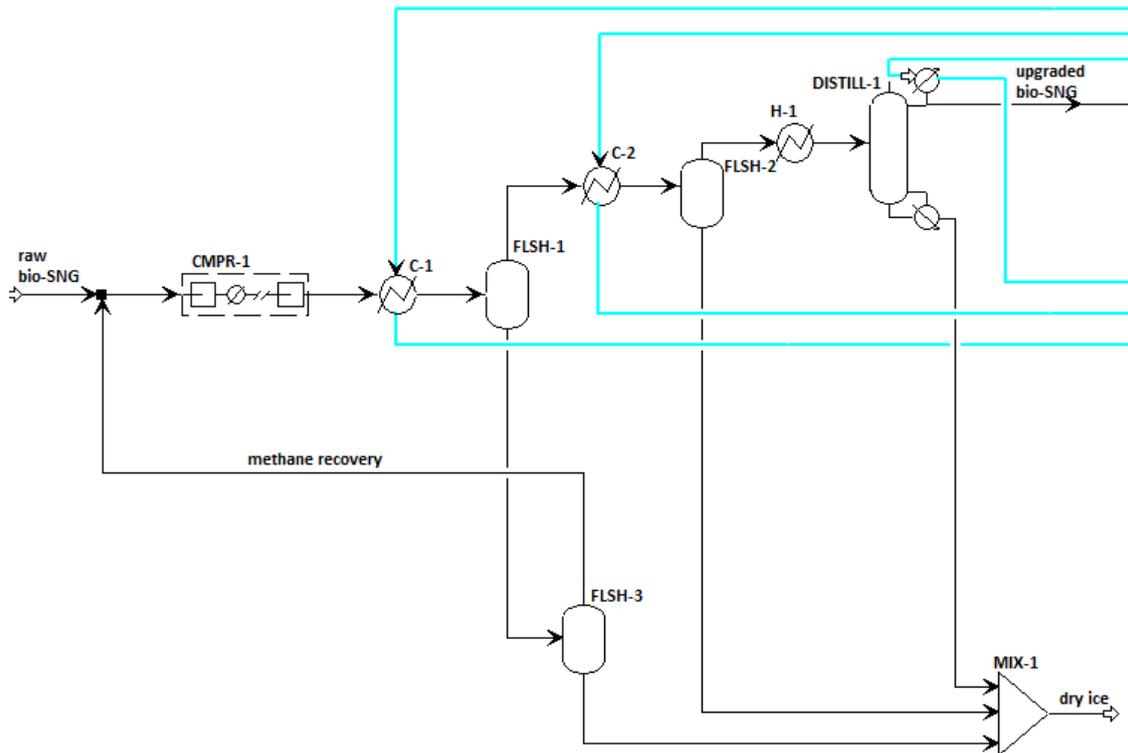


Figure 23. Cryogenic upgrading unit Aspen model

5.1.2.2 Design parameters of gas upgrading unit

Design parameters are chosen according to literature values, personal communications and sensitivity analysis done by using Aspen Plus.

Product stream (upgraded bio-SNG) should not have more than 125 ppm CO_2 , thus it is a limitation considered in design (Flynn, 2005). Methane loss (percentage of methane loss compared to inlet) is set to be kept below 2% which is the highest value available in literature for cryogenic upgrading (Johansson, 2008). Purity of the dry ice (separated CO_2 from raw bio-SNG) is also taken into account when choosing design parameters. High purities of the upgraded bio-SNG and dry ice streams indicate a good level of separation, thus good performance for upgrading unit.

Operating conditions are chosen carefully so that dry ice (solid CO_2) formation in does not occur since it might cause problems in heat exchangers and compressors. Therefore, operating temperature of the second cooler, C-2 is set to -56°C at which CO_2 is in liquid or vapour phase as can be seen in phase diagram of CO_2 , Figure 24.

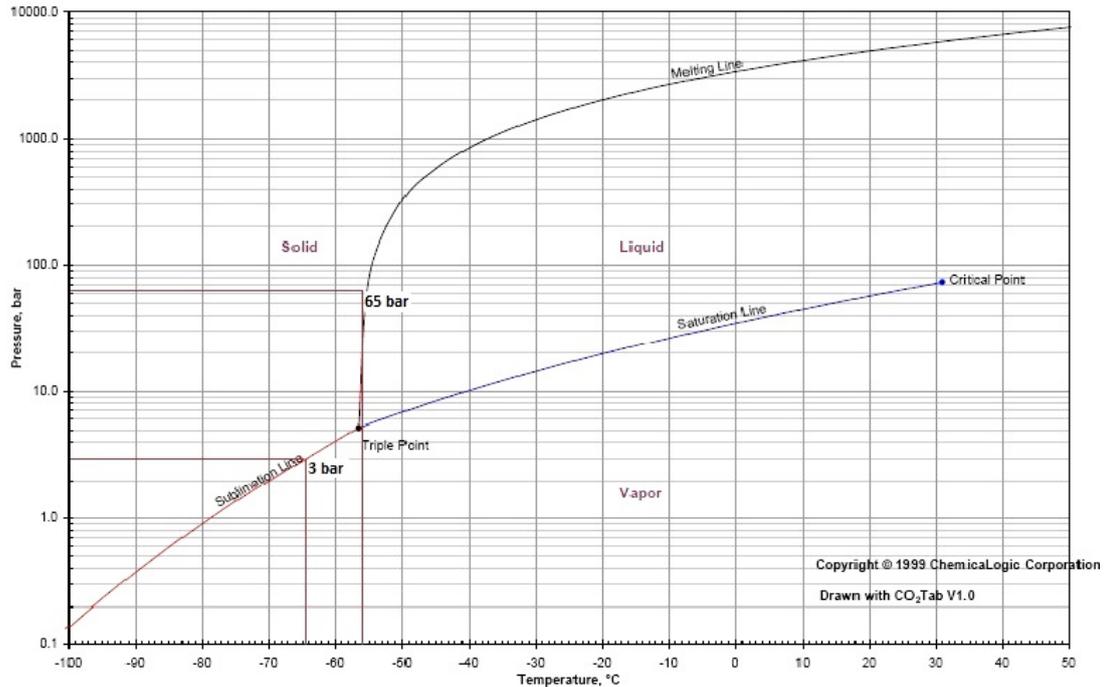


Figure 24. Phase diagram of CO₂ (ChemicaLogic, 1999)

Operating pressure is chosen as 65 bar for CMPR-1 since the range is suggested as 65-80 bar (Heyne, 2013), and 65 bar gives the best separation results. Operating condition of flash, FLSH-1 is chosen as suggested in the reference model (SGC, 1997) which is 0 pressure difference. Sensitivity analysis are held to choose operating temperature of C-1, operating pressures of flash tanks FLSH-2 and FLSH-3, and D:F (distillate to feed ratio) of distillation column, DISTILL-1. The resulting design parameters are summarized in Table 4, and the details of the sensitivity analysis can be seen in Appendix 3.

Table 4. Sensitivity analysis results for design parameters

Unit	Parameter	Value
C-1	Temperature (°C)	-51
FLSH-2	Pressure (bar)	2
FLSH-3	Pressure (bar)	1
DISTILL-1	D:F	0.922

5.1.2.3 Process description of gas liquefaction unit

Both liquefaction of upgraded bio-SNG and refrigerant production for upgrading are achieved in the liquefaction unit. Aspen model of the process can be seen in Figure 25. Refrigeration is provided by a nitrogen Brayton cycle by consequent compression, cooling and expansion as explained more in detail in Chapter 5.1.1.3.

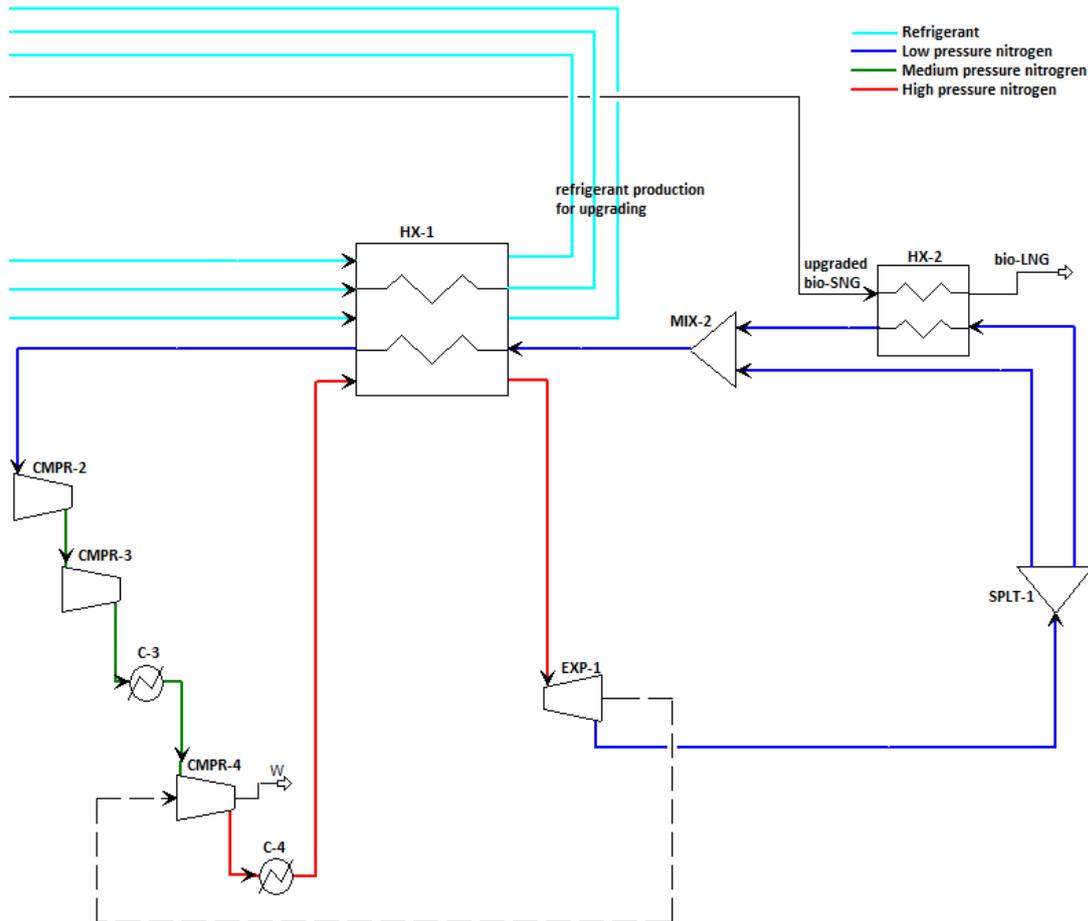


Figure 25. Liquefaction unit Aspen model

5.1.2.4 Design parameters of liquefaction unit

Upgraded bio-SNG enters the liquefaction process at 7.65 bar, and -129°C . Final product, bio-LNG, is in the same conditions as in base case which are 7.5 bar and -163°C as stated before in process specifications.

Design parameters for the nitrogen cycle are chosen the same as in base case 1 (liquefaction at 8 bar) since upgraded bio-SNG (at 7.65 bar) liquefies at the same temperature. However, heat duty of HX-1 is higher due to extra refrigerant production for upgrading unit while HX-2 has lower duty since inlet bio-SNG is at lower temperature which needs less refrigerant. Thus, nitrogen flow rate is higher compared to base case 1 to compensate the difference in heat exchanger duty.

A splitter and a mixer are placed to optimize nitrogen flow in the cycle, since higher flow rate results in higher power consumption. Cold nitrogen from expander, EXP-1

is splitted into two streams; one is sent to HX-2 as cold stream for bio-SNG liquefaction and the other stream is mixed (MIX-2) with the outlet cold stream from HX-2 and sent to HX-1. Split fraction is chosen considering minimum ΔT of 2°C in heat exchangers.

In order to have a ΔT_{\min} of 2°C in the cold side of HX-2, a calculator block is set to adjust the pressure in the expander. Both coolers C-3 and C-4 decrease refrigerant temperature to 20°C. All design parameters are shown in Table 5.

Table 5. Design parameters for liquefaction

Unit	Parameter	Value
CMPR-2	Pressure (bar)	10
CMPR-3	Pressure (bar)	25
CMPR-4	Pressure (bar)	55
C-3	Temperature (°C)	20
C-4	Temperature (°C)	20
SPLT-1	Split fraction	0.78

5.2 Process integration

Process integration is a tool used in process design that analyse the energy use of a system as a whole. Instead of optimising process units separately, interaction between different unit operations is considered in order to minimise resource use (Smith, 2005). In this thesis heat integration within the process is investigated using Pinch technology.

5.2.1 Pinch technology

Pinch technology refers to the combination of pinch analysis and process design based on pinch rules. It is used for determination of the minimum heating and cooling demand of a process, and to identify potential process energy efficiency improvements (Heyne, 2013).

For the pinch analysis, an Excel add-in called pro_PI is used. First step is mapping the process streams. Inlet and outlet temperatures as well as heat heating and cooling demands for each stream are identified. Grand composite curve (GCC) is constructed with the process data by using pro_PI. GCC is a plot of the net heat flow against the interval/shifted temperature, which is shifted so as to take into account ΔT_{\min} which is necessary for heat exchange as driving force (Svensson, 2012). Figure 26, an illustrative example of a GCC is shown.

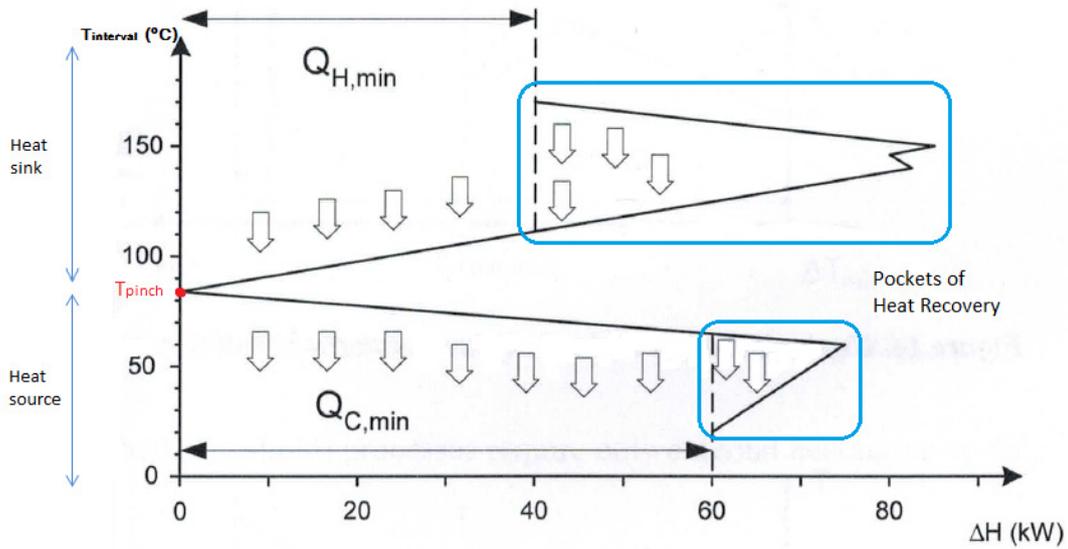


Figure 26. The Grand Composite Curves (GCC) (Svensson, 2012)

Pinch point is the only point where ΔT_{\min} occurs; above pinch, the curve represents a deficit of heat and below pinch, it represents an excess of heat. As shown in Figure 26, minimum external cooling and heating demand can be seen in GCC. Furthermore, the heat pockets are shown in GCC which represent potential for internal heat exchange that is necessary to achieve minimum utility demand (Svensson, 2012).

Exergy concept using Carnot efficiency based curves is applied in combination with Pinch Analysis which enables targeting for shaft power savings in low temperature processes (Hackl and Harvey, 2012). Exergy is defined as the theoretical useful work (shaft work or electrical work) obtainable as two systems interact to equilibrium or the minimum theoretical work required to bring matter to a specified state (Bejan et al., 1995).

Carnot-based GCC is a variation of GCC which is constructed with Pro_PI. The main difference to conventional and combined exergy Pinch Analysis is that the y-axis of GCC shows Carnot efficiency corrected temperature instead of temperature. It is used for screening the mechanical work that can be extracted from a process is given as the integral area below the curve. This mechanical power is represented by a heat source at a temperature T that rejects heat to the environment T_0 in a Carnot cycle (Heyne, 2013). The y-axis is replaced by the Carnot efficiency (θ) that is defined as:

$$\theta = 1 - \frac{T_0}{T} \quad (1)$$

Even if this calculated area extracted from the Carnot-based GCC overestimates the power production, it can be used to have a fair comparison between different process alternatives.

Exergetic efficiency of a turbine system indicates the ability of a real system to harness the theoretical potential for shaft power output. Therefore, it is possible to estimate the actual shaft work generated by using exergetic efficiency. Based on a study of the integration of a steam cycle for combined heat and power (CHP) production to the SNG production process, values for exergetic efficiency close to 0.7

can be expected for cases with a high level of thermal integration making use of internal heat pockets of the process (Heyne, 2013).

5.3 Process evaluation

After process simulation and pinch analysis, both cases are evaluated using some performance indicators that are explained below. Employing these indicators, power requirement and external heating and cooling demand, a comparison is held in order to identify the most promising process technology.

5.3.1 Performance indicators

Since the main difference between the two cases defined in this thesis is the gas upgrading technique, methane loss is an important factor to evaluate when comparing both techniques. Methane loss is defined as the fraction of methane contained in the raw gas that is not supplied to the grid but is leaving the plant together with the off-gas flow.

$$\text{Methane loss} = \frac{(CH_4 \text{ entering upgrading unit} - CH_4 \text{ in the product})}{CH_4 \text{ entering upgrading unit}} \cdot 100 \quad (1)$$

Methane loss does not have a strong influence in energy consumption but it represents a loss of income and an emission of methane that is a greenhouse gas (Johansson, 2008).

Important factors that are also discussed in this study are methane purity in bio-LNG product, CO₂ recovery and the use of LCO₂ in external processes.

The CO₂ recovery factor ϕ_{CO_2} compares the amount of CO₂ extracted as a by-product \dot{m}_{LCO_2} to the CO₂ content in the raw bio-SNG $\dot{m}_{CO_2,raw \text{ bio-SNG}}$ (before gas upgrading).

$$\phi_{CO_2} = \frac{\dot{m}_{LCO_2}}{\dot{m}_{CO_2,raw \text{ bio-SNG}}} \quad (2)$$

Dry ice which can be utilized in either solid or liquid form (LCO₂) is obtained as a by-product when using cryogenic upgrading technology as explained in Chapter 5.1.2.2.

LCO₂ as explained in Chapter 2.4 can be used as a replacement for diesel in cryogenic transport temperature control. CO₂ can replace around 1.5 litres of diesel/h. Considering good vehicle insulation and a right temperature of the goods, CO₂ consumption is around 20-25 kg/h (Johansson, 2008). The calculations for LCO₂ utilization as replacement of diesel can be seen in Appendix 4.

In order to evaluate the energy consumption of both techniques, cold gas efficiency and overall energy efficiency are defined.

The cold gas efficiency (η_{cg}) is a measure that relates the heat produced in the final product depending on the energy input of the biomass inlet (Heyne, 2013):

$$\eta_{cg} = \frac{\dot{m}_{bio-LNG} \cdot LHV_{bio-LNG}}{\dot{m}_{wet \text{ wood}} \cdot LHV_{wet \text{ wood}}} \quad (3)$$

where \dot{m} is the mass flow and LHV the lower heating value

The overall energy efficiency (η) can be defined as the useful heat transferred in relation to the energy supplied:

$$\eta = \frac{\sum \dot{m}_{products} \cdot LHV_{products} + \sum \dot{W}^- + \sum \dot{Q}^-}{\sum \dot{m}_{input} \cdot LHV_{input} + \sum \dot{W}^+ + \sum \dot{Q}^+} \quad (4)$$

where \dot{Q}^- and \dot{Q}^+ represents useful heat departing or entering the system whereas \dot{W}^- and \dot{W}^+ the mechanical power

In this study power production from excess heat is estimated and it is considered in overall energy efficiency.

Processes are also compared with energy demands in terms of primary energy. Energy input is given in primary energy using a primary energy factor for Nordic electricity mix (1.6) and 100% represents the energy content in bio-LNG product, which is 100 MW.

The designs simulated in the thesis are compared with commercial unit to provide an insight. Cryogenic technology is still under development, therefore very little information is available in literature. There are a few suppliers of the technology available as presented in Chapter 4.1.1; however, they don't reveal the details of the processes due to confidentiality reasons. Therefore, comparisons are held with available published data of the commercial units.

6 Results and Discussion

In this chapter, the results obtained from process modelling and integration are presented and discussed. The stream data of the Aspen simulations can be seen in Appendix 3. Results for both base case and integrated case that are explained in Chapter 5 are evaluated with data gathered from literature. However, not all suppliers reveal technical details of their designs, thus comparisons are made with available data.

6.1 Process simulation results

6.1.1 Products and by-products

When comparing gas upgrading techniques, methane loss is a key factor. Data from cryogenic technology suppliers, Scandinavian GtS and Terracastus which are explained in Chapter 4.1.1 are presented in order to make a comparison with the cases simulated in the thesis. In Figure 27, methane losses of upgrading units for different cryogenic designs and base cases (chemical adsorption, MDEA) are shown.

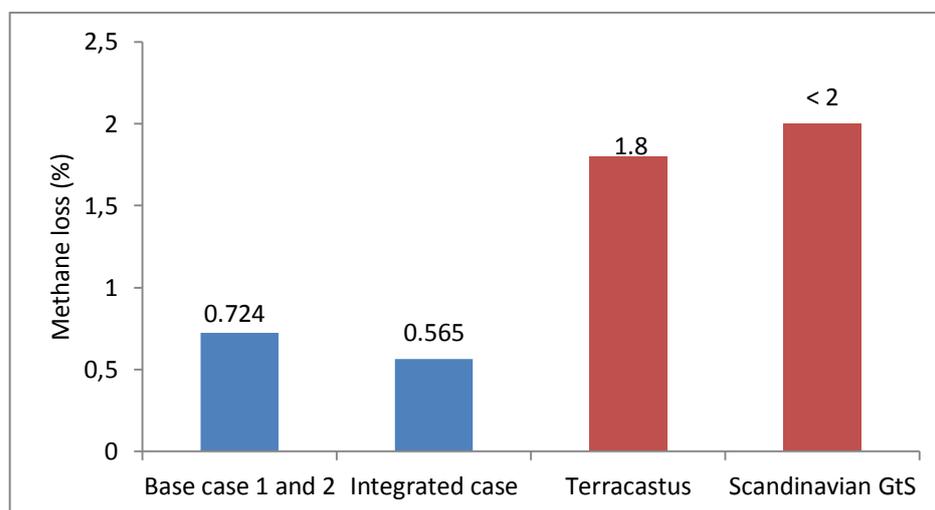


Figure 27. Methane loss in gas upgrading for four different cases (SGC, 2013; Johansson, 2008)

As can be seen in the figure, the cryogenic design used in the integrated case has the lowest methane loss which represents lower profit losses. In simulated cases, methane loss only considers the amount which leaves the system in liquid form with separated CO₂ streams. Since the data of commercial cryogenic units are from pilot plants, results of the cases simulated in the thesis might be more optimistic regarding the simulation assumptions e.g. dissolved methane in carbon dioxide or methane leakage from process units and pipes is neglected. The sources of methane loss are not specified in the published data for the commercial units, therefore it is not known how much methane is released to the atmosphere or left the system with separated CO₂ streams; only total methane loss is given. Thus, comparison of the cases in terms of greenhouse gas emissions caused by methane released from the system is not considered.

Biogas which has different gas composition than bio-SNG is upgraded in the commercial units shown above which might cause difference in the results as well.

The final products for both cases are in the same conditions: -163°C and 7.5 bar. They both produce 100 MW bio-LNG; however, they have different CO₂ concentrations which are shown in Table 6.

Table 6. CO₂ concentration of product streams

	CO₂ concentration (ppm)
Base case 1 and 2	58
Integrated case	13

CO₂ is removed by upgrading in both cases and the concentrations are lower than the limit (125 ppm) required for liquefaction (Flynn, 2005). However, the lower the concentration is, the easier the maintenance of the process. This is mainly due to dry ice formation which causes clogging in the heat exchangers. Thus, integrated case is more favourable.

In Table 7, performance indicators regarding CO₂ and CH₄ are summarized for different cryogenic technologies. Product stream of integrated case has only 13 ppm impurity (CO₂) and rest is CH₄, so the purity is shown as 100%.

Table 7. CO₂ recovery, liquid CO₂ purity and CH₄ purity for three different cryogenic technologies (SGC, 2013; Johansson, 2008)

	Specification	CO₂ recovery (%)	LCO₂ purity (%)	CH₄ purity (%)
Integrated case	Raw bio-SNG to bio-LNG	100	99.8	100
Terracastus	Raw biogas to LBG	30-50	99.99	99.99
Scandinavian GtS	Raw biogas to LBG	25	100	>99

Cryogenic technology achieves high methane purity which is always above 99% in all designs shown in Table 7. Concerning the production of LCO₂ as by-product only cryogenic technologies are considered due to the fact that in base case upgrading unit, CO₂ recovery is not achieved. Integrated case is the most interesting option for LCO₂ production since it has the highest CO₂ recovery with the highest purity.

6.1.2 Power demand

A main constraint in GoBiGas Project is the power requirement (Gunnarson, 2011). Thus, it is considered as a key factor in this study. For base cases, total power demand is the sum of power demand for upgraded bio-SNG production and its liquefaction. For integrated case, it is the sum of power demand for raw bio-SNG production, and the cryogenic technology (upgrading and liquefaction). Total power demands which are the sum of all power consuming devices e.g. pumps, compressors are directly taken from simulation results and are shown in Table 8.

Table 8. Total power demands of base case 1 and 2, and integrated case

	Upgraded bio-SNG production (MW)	Bio-SNG liquefaction (MW)	Total power demand (MW)
Base case 1	7.74	4.61	12.35
Base case 2	7.74	3.89	11.63
	Raw bio-SNG production (MW)	Bio-SNG upgrading and liquefaction (MW)	Total power demand (MW)
Integrated case	7.50	9.71	17.21

As can be seen in the table, integrated case has higher power demand due to the fact that cryogenic technology requires high pressures (65 bar) as separation is achieved by expansion in flash tanks. Furthermore, the refrigerant that is needed in the process is produced in the refrigeration cycle, which leads to more refrigerant mass flow, thus higher power demand in the compressors of the nitrogen cycle.

Difference between the base case liquefaction power demands is because of the operating pressure. Base case 1 (8 bar) requires more refrigerant due to higher heat of evaporation as explained in Chapter 5.1.1.2. The difference is illustrated by constructing Bio-SNG cooling curve and N₂ cooling curve for liquefaction at 8 bar and 40 bar, and they are shown Figure 28 and 29, respectively. As can be seen in the figures, liquefaction at 8 bar has higher duty, thus higher refrigerant mass flow. And, more refrigerant results in higher power consumption in compressors. Moreover, the area between the curves indicates a higher temperature difference between the streams and in consequence more degradation of energy quality e.g. exergy losses. Therefore, liquefaction at 40 bar has a better energy performance since the warming and cooling curves are matched better.

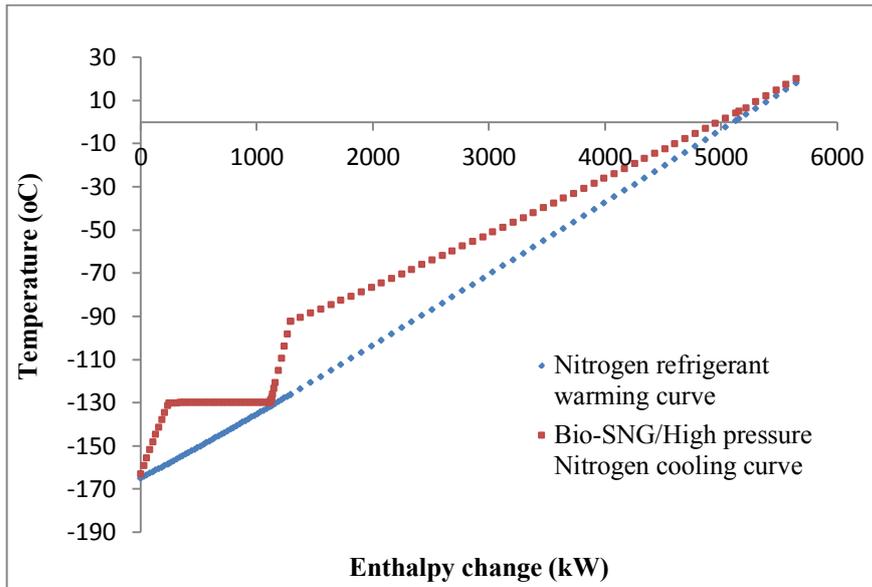


Figure 28. Nitrogen warming curve and bio-SNG/nitrogen cooling curve for liquefaction at 8 bar in base case 1

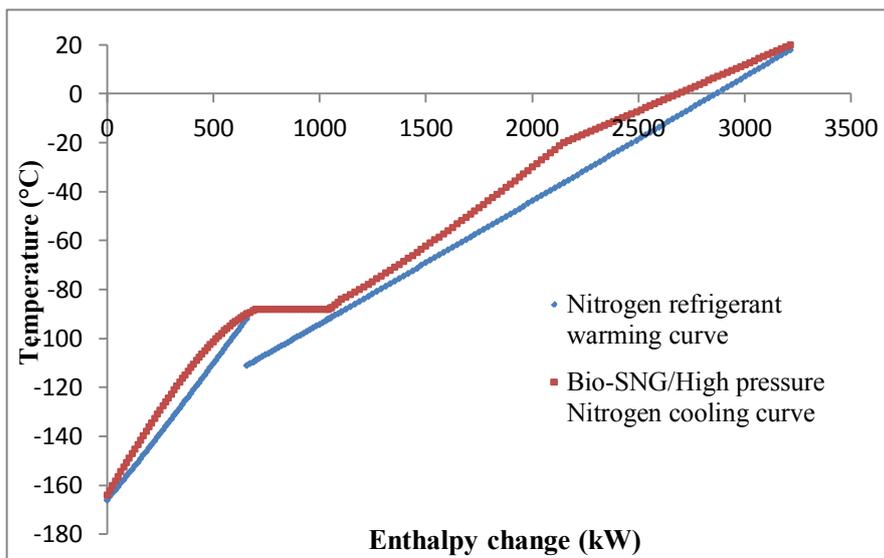


Figure 29. Nitrogen warming curve and bio-SNG/nitrogen cooling curve for liquefaction at 40 bar in base case 2

Concerning power demand, liquefaction at 40 bar has a better performance; however, more equipment is required which leads to higher investment costs. Moreover, high operating pressure of the process results in higher operating costs for control and safety.

Specific power demand data for commercial cryogenic units and integrated case design are shown in Table 9. All of them achieves both upgrading and liquefaction from raw gas.

Table 9. Specific power demands and capacities for different cryogenic technologies (SGC, 2013; Johansson, 2008)

Cryogenic technology	Specification	Capacity (Nm³raw gas/h)	Specific power demand (kWh/Nm³ raw gas)
Integrated case	Raw bio-SNG to bio-LNG	16900	0.57
Scandinavian GtS	Raw biogas to LBG	50-2400	0.45
Terracastus	Raw biogas to LBG	230-930	0.76
Prometheus Energy	Raw biogas to LBG	90-930	1.54

As can be seen in the table, integrated case has a similar power demand compared to commercially available technologies. Moreover, relation between the capacity and power demand is seen clearly; increased capacity leads to lower specific power demand.

Specific power demand data for a commercial small-scale liquefaction unit and base case design are shown in Table 10.

Table 10. Specific power demands and capacities for different liquefaction units (SGC, 2013)

Liquefaction technology	Specifications	Capacity (Nm³LBG /h)	Specific power demand (kWh/Nm³ LBG)
Airliquide	Includes polishing step Reverse nitrogen Brayton cycle	765	1.12
		(Nm ³ bio-LNG /h)	(kWh/Nm ³ bio-LNG)
Base Case 1	Reverse nitrogen Brayton cycle	10008	0.46
Base Case 2	Reverse nitrogen Brayton cycle	10008	0.39

Both base cases are designed inspired by Airliquide, thus they have the same refrigeration system. Base case designs have lower power demand due to higher capacity as shown in the table.

6.2 Process integration results

6.2.1 Heating and cooling demand

Minimum heating and cooling demands are estimated from Grand composite Curves (GCC). GCCs are constructed by following the procedure explained in Chapter 5.2. Since the liquefaction for base cases are designed as stand-alone units, heat integration between bio-SNG production part of the process and liquefaction unit is not possible. Thus, GCCs are plotted separately for bio-SNG production, and liquefaction units at 8 bar and 40 bar which can be seen in Figures 30, 31 and 32, respectively.

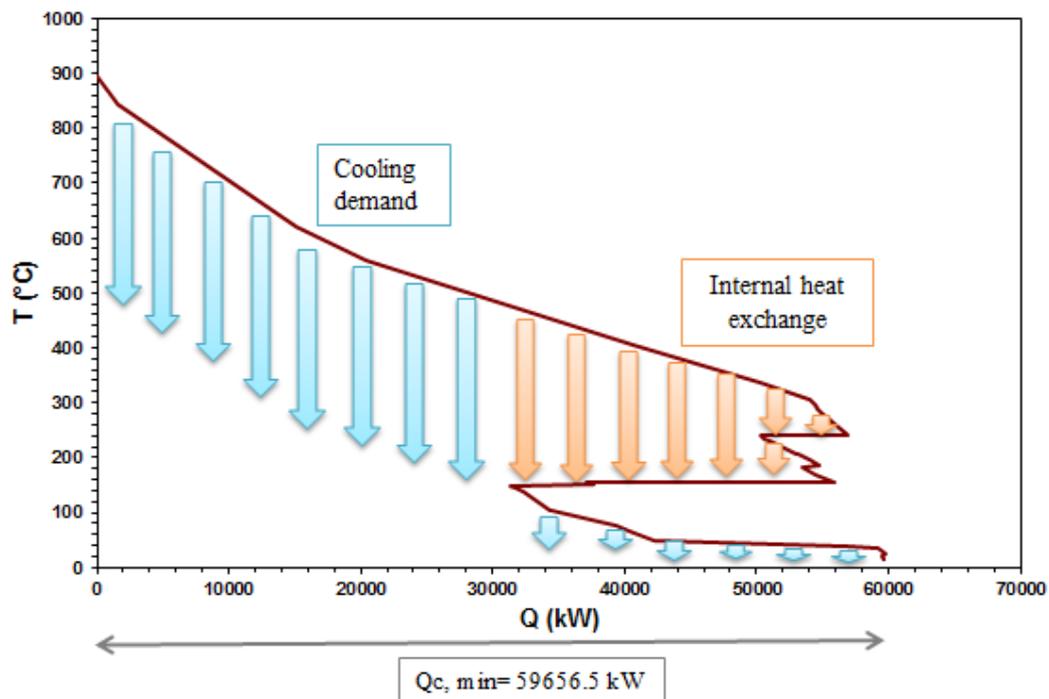


Figure 30. GCC for bio-SNG production for base case 1 and 2

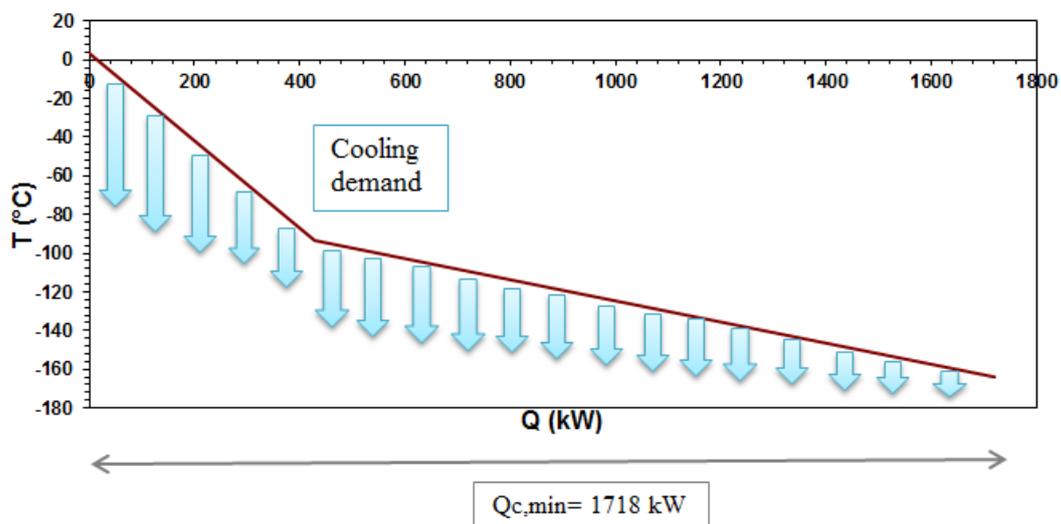


Figure 31. GCC for the liquefaction of bio-SNG at 8 bar in base case 1

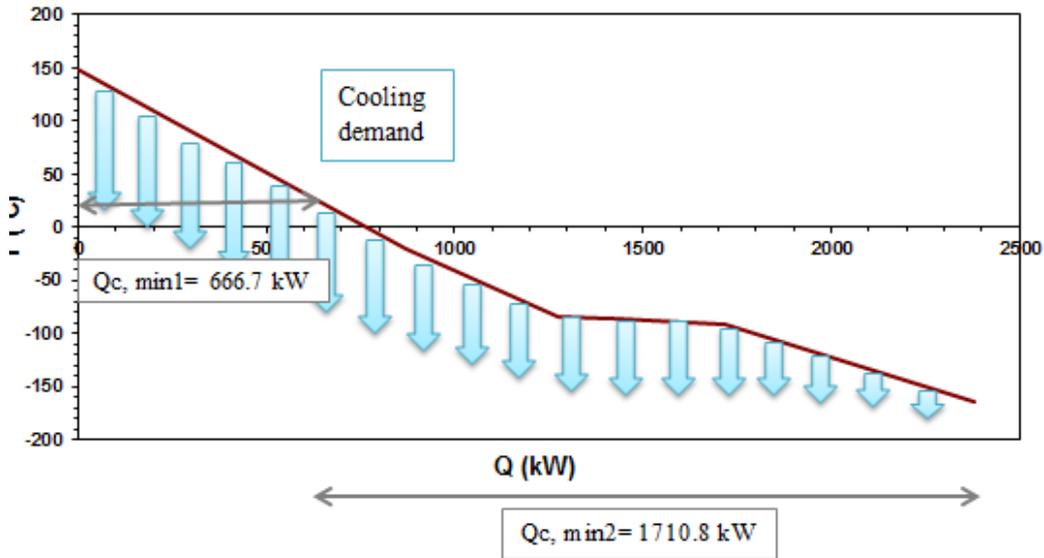


Figure 32. GCC for the liquefaction of bio-SNG at 40 bar in base case 2

As can be seen in the figures, there is no external hot utility demand, because heat demands of the bio-SNG production process streams are covered by internal heat exchange (Figure 30) and liquefaction units do not require heating (Figure 31 and 32). Heat pocket shown in Figure 30 represents the internal heat exchange.

Minimum cold utility demands can be seen in Figures 30, 31 and 32. Cold utility demands are shown in the figures at above and below ambient temperature (T_{amb} : 20°C), since refrigeration is required for cooling below T_{amb} . Bio-SNG production process only requires cooling above T_{amb} (Figure 30) while liquefaction at 8 bar requires only refrigeration (Figure 31), and liquefaction at 40 bar needs both (Figure 32) due to the operating conditions. Liquefaction at 40 bar requires cooling above T_{amb} , since inlet bio-SNG stream is warmed up during compression and has to be cooled down.

GCC for integrated case is constructed which includes all the streams of bio-SNG production, upgrading and liquefaction. The curve can be seen in Figure 33.

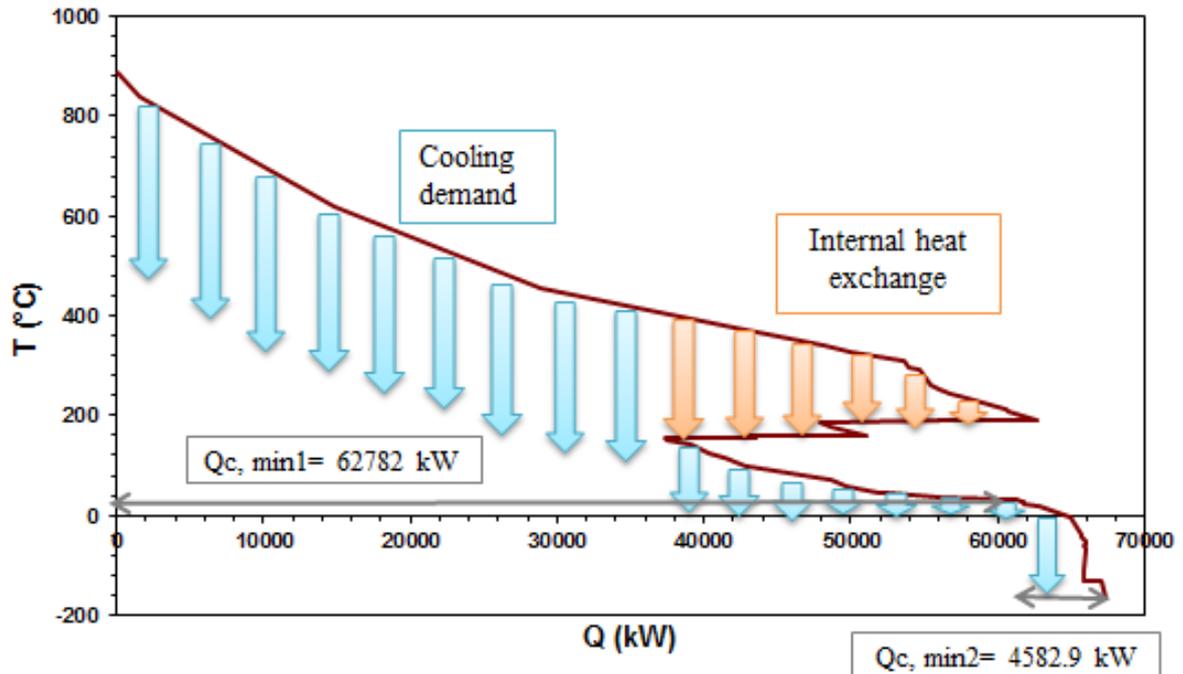


Figure 33. GCC for the integrated case

Figure 33 shows a similar trend as Figure 30 since bio-SNG production parts for both cases are the same except the gas upgrading; bigger heat pocket in Figure 30 indicates the heat utility demand of upgrading unit which is recovered by internal heat exchange. Moreover, higher cold utility demand of integrated case is due to heat streams of cryogenic unit. Cryogenic unit streams which are at low temperatures constitute lower part of the GCC (Figure 33) which requires refrigeration e.g. cooling below T_{amb} . Cooling demands of three cases (base case 1 and 2, and integrated case) are summarized in Table 11.

Table 11. Minimum cold utility demands of three cases

Case	Cold utility demand below $T_{amb}(20^{\circ}\text{C})$ (kW)	Cold utility demand above $T_{amb}(20^{\circ}\text{C})$ (kW)	Total minimum cold utility demand (kW)
Base case 1	1718	59657	61375
Base case 2	1711	60324	62035
Integrated case	4583	62782	67365

6.2.2 Potential Power Production

Maximum potential work outputs are estimated from Carnot Grand Composite Curves. Curves are constructed by following the procedure explained in Chapter 5.2. Theoretical potential for mechanical work extraction of a process can be determined by integration of the area below the curve. Carnot GCC for base case is plotted only for bio-SNG production part of it since it is the part which has great amount of excess

heat available for work output. Carnot GCCs are shown in Figure 34 and 35, for base case and integrated case, respectively.

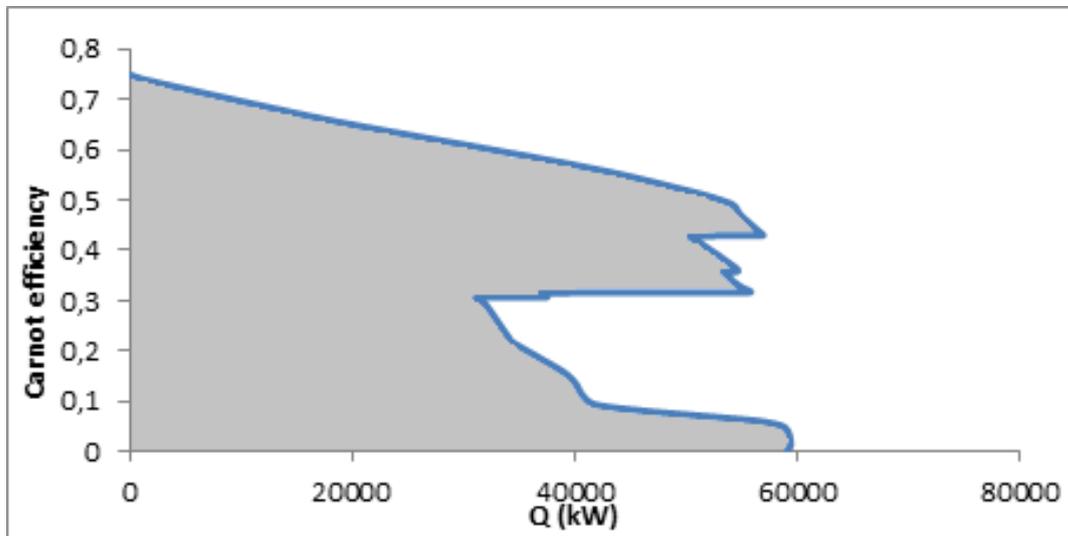


Figure 34. Carnot GCC for base case

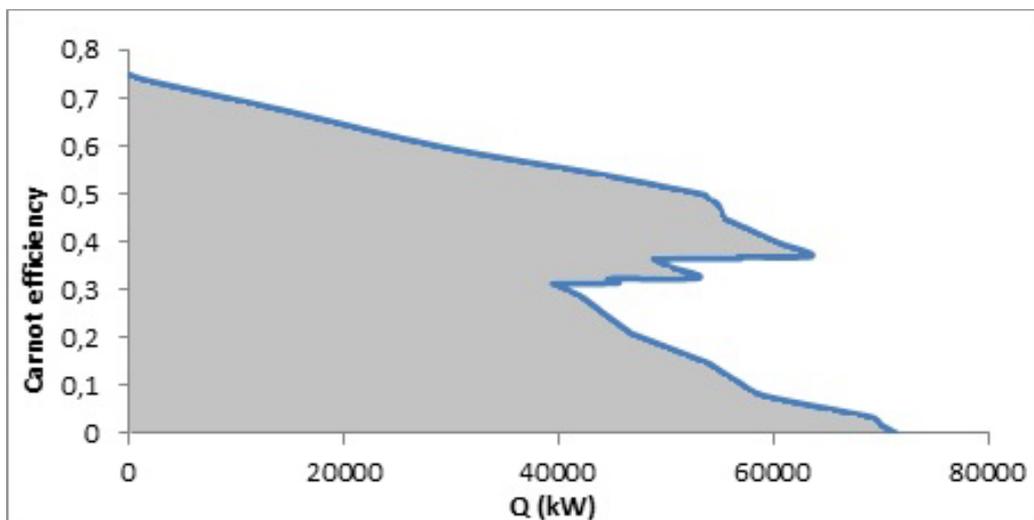


Figure 35. Carnot GCC for integrated case

The difference in the shapes of the curves is mainly due to gas upgrading of base case (chemical adsorption) which requires heating at constant temperature and the cooling requirement of streams of methanation units; gas mixture entering the methanation reactors have different gas concentrations and flow rates (CO_2 is removed by gas upgrading before methanation in base case while it is removed after methanation in integrated case) which effect cooling demand. Thus, different properties of process heat streams reflect on the shapes of the curves as can be seen in Figure 34 and 35.

Exergetic efficiency of 0.7 is used for the estimation of the power production from the recoverable excess heat for the different cases investigated here (Heyne, 2013). Results are obtained by assuming that all excess heat is recoverable for power production via a steam cycle. In fact, there are process restrictions e.g. limitations due to impurities in the hot streams or maintenance issues in power cycle; however, this method still gives a good estimation of the differences in power production potential of the processes as they have same characteristics.

Maximum useful work outputs are estimated by multiplying the areas (29.65 MW for base case, 33.57 MW for integrated case) under the Carnot GCCs with exergetic efficiency; 12.35 MW for base cases and 23.50 MW for integrated case.

As total power demands are known, net power demand can be estimated by extracting the production from total demand. Results are shown for all three cases in Figure 36.

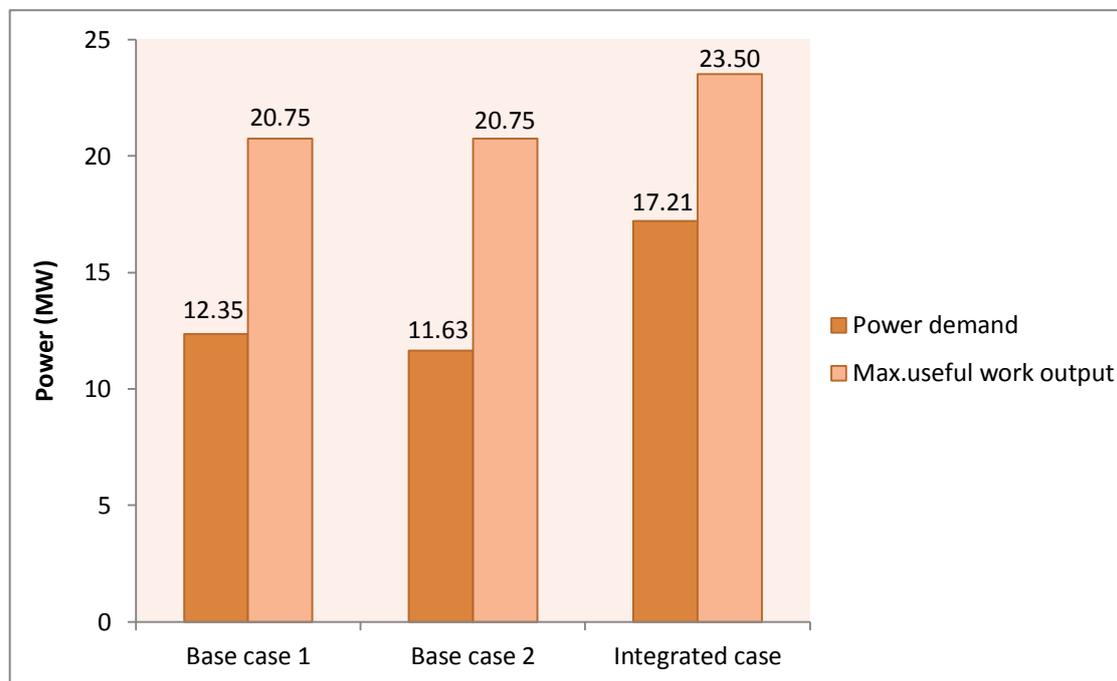


Figure 36. Total power demands, power productions and net power demands for three cases

As can be seen in Figure 36, all three cases have excess power which can be exported. Power production for integrated case is higher than base cases; however, its total power demand is the highest so that net power demand is the lowest. Base case 2 is the most feasible one as it has the maximum net power demand.

6.3 Efficiencies

Cold gas efficiency and overall energy efficiency are calculated for three cases as described in Chapter 5.3.1. Required data for efficiency calculations and the calculation results are shown in Table 12.

Table 12. Data required for efficiency calculations and calculation results for three cases

		Base case 1	Base case 2	Integrated case
Fuel Input (wet wood)	MW _{LHV}	155.658*	155.658*	155.31*
Bio-LNG production	MW _{LHV}	100	100	100
Total power demand	MW	12.35	11.63	17.21
Power production	MW	20.75	20.75	23.50
Net power output	MW	7.80	9.12	6.30
Cold gas efficiency	%	64.24	64.24	64.39
Overall energy efficiency	%	69.25	70.10	68.44

*LHV (MJ/kg wet biomass) = 8.55 (Heyne, 2013)

Cold gas efficiency of integrated case is slightly higher than base cases. Since methane loss is lower in integrated case as shown in Figure 27, less biomass is required for the same production capacity (100 MW bio-LNG).

Energy content of the product and the feed (biomass) are almost the same for all three cases as shown in Table 12. Moreover, useful heat entering or leaving the system is represented in terms of power in overall energy efficiency, since the excess heat is utilized for power production as described in Chapter 6.4. Therefore, power demand and production are the key variables in calculating the overall efficiency values. To be able to do the comparisons, all data used in the energy balances have been converted to primary energy. And, with the converted values, energy demand distribution relative to product energy content is illustrated for three cases in Figure 37.

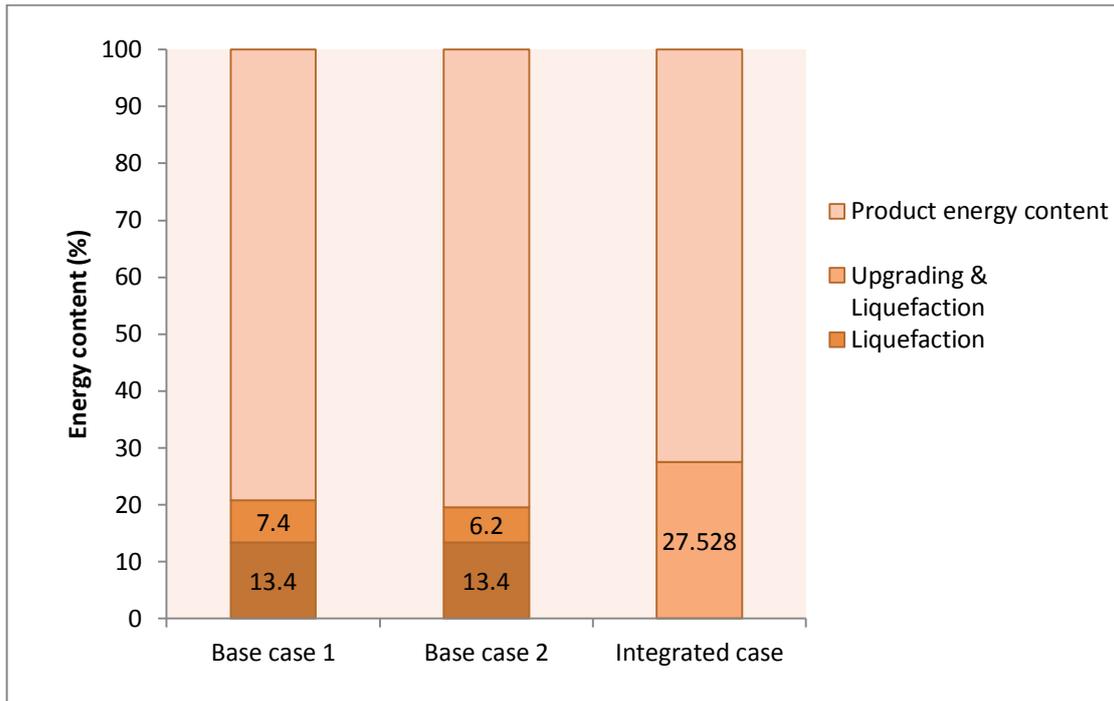


Figure 37. Energy demand distribution relative to product energy content for three cases

Product energy content is $100 \text{ MW}_{\text{bio-LNG}}$ which is defined for all three cases as the capacity. Energy demands of gas upgrading and liquefaction units are shown as a percentage of the product energy content to provide an insight for comparing the cases studied in terms of primary energy. Figure 37 shows that cryogenic unit (integrated case) requires 27.528% of energy produced in form of bio-LNG while base case upgrading and liquefaction units need less due to maturity of the technology used.

7 Conclusions and Discussion

The cryogenic unit investigated achieves the targeted product specifications and capacity, and the calculated performance is comparable to published data for commercial cryogenic units in terms of specific power demand and methane loss.

The analysis shows that the process with integrated cryogenic gas upgrading and liquefaction has a slightly better cold gas efficiency in comparison with the base case which employs a traditional upgrading gas upgrading and stand-alone liquefaction. The resulting cold gas efficiencies are 64.24% for two base case configurations and 64.39% for the integrated case. The main reason for the difference in efficiency is to lower methane loss for the integrated case. The calculated overall energy efficiencies are 69.25% for base case 1, 70.10% for base case 2 and 68.44% for the integrated case. The integrated case is thus competitive in terms of energy performance with an added benefit of LCO₂ production. In addition, cryogenic technology is not mature yet, therefore there is a high potential for performance improvement by improved technology and enhanced process integration.

According to process simulation results, cryogenic upgrading technology results in very low CH₄ losses which are connected to the flash separation. However, there is uncertainty due to simulation assumptions which might neglect other sources of CH₄ loss. CH₄ loss is loss of income but, in addition to that, it results in emissions of a greenhouse gas, 20 times stronger than CO₂ in case of CH₄ leakage to the atmosphere from the system. However, they have small influence on the energy balance.

Very clean dry ice (or LCO₂) is produced at very low temperature (-114°C) as by-product that could be used in external processes. However, the disposal of this CO₂ is very site specific, and it might require extra equipment e.g. dry ice has to be liquefied for collection and distribution as in the case of this study. Dry ice can be used within the process to take advantage of its exergy content since it is at low temperature, or it can directly be sold. To be able to sell the separated CO₂ the bio-LNG producers might have to invest in a distribution vehicle and a LCO₂ buyer has to be situated close by. Moreover, continuous LCO₂ supply should be ensured to secure customer, thus the profit gained from it.

In a country like Sweden, where the gas network is limited and the interest of using bio-LNG as a vehicle fuel is growing, it is a good alternative to fossil fuels. The production is energy intensive; however, it results in a more valuable product as it becomes available for a bigger market. The use of cryogenic technology also opens for more smart solutions where LCO₂ and rejected heat could replace fossil fuel sources in external applications, affecting the energy balance in a positive way. Bio-LNG can also be used to fuel heavier vehicles, since it can be stored in its liquid state, therefore significantly increasing the driving range.

Details of the second stage of GoBiGas project is not decided yet. Results obtained in this study shows that cryogenic technique would be an interesting option for gas upgrading and liquefaction with an addition of cogeneration of power from the excess heat via a steam cycle to improve energy performance of the system.

8 Future Work

Future work for the thesis should focus more on system optimization to improve energy performance of the system since it is the most important drawback. And as illustrated in the process integration chapter, there is a great potential which deserves more attention and further study. Dry ice utilization is another important point which can provide further performance enhancement and extra income. Further study can be held to identify the sources and consequences of methane loss and overcome the uncertainties related to that. In addition to that, more data can be gathered from existing commercial and pilot plants to provide a better insight with more knowledge and expertise. These improvements would promote deployment of the technology.

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Personal Communication

Stefan Heyne

Appendix 1

Table 1. List of upgrading plants in Sweden.

Country	Place	Substrait	Utilisation	Methane (%)	Technology	Plant capacity (Nm ³ /h raw gas)	In operation since
Sweden	Linköping	Sewage sludge, biowaste	Vehicle fuel	97	Water scrubber	330	1997
Sweden	Eslöv	Biowaste, sewage sludge	Vehicle fuel	97	Water scrubber	80	1999
Sweden	Kristianstad	Biowaste, manure, sewage sludge	Vehicle fuel	97	Water scrubber	280	1999
Sweden	Jönköping	Biowaste, sewage sludge	Vehicle fuel	97	Water scrubber	300	2000
Sweden	Laholm	Biowaste, manure	Gas grid	97	Water scrubber	500	2000
Sweden	Helsingborg	Biowaste, manure	Vehicle fuel, gas grid	97	PSA	350	2001
Sweden	Trollhättan	Biowaste, sewage sludge	Vehicle fuel	97	Water scrubber	400	2001
Sweden	Uppsala	Sewage sludge	Vehicle fuel	97	Water scrubber	400	2001
Sweden	Borås	Biowaste, sewage sludge	Vehicle fuel	97	Chemical scrubber	450	2002
Sweden	Bromma, Stockholm	Sewage sludge	Vehicle fuel	97	PSA	250	2002
Sweden	Linköping	Sewage sludge, biowaste	Vehicle fuel	97	Water scrubber	1400	2002
Sweden	Skövde	Sewage sludge, slaughter house waste	Vehicle fuel	97	PSA	140	2002
Sweden	Bromma, Stockholm	Sewage sludge	Vehicle fuel	97	PSA	250	2003
Sweden	Eskiltuna	Biowaste, sewage sludge	Vehicle fuel	97	Water scrubber	330	2003
Sweden	Nynäs gård	Manure	Vehicle fuel	97	Water scrubber	10	2003
Sweden	Ulricehamn	Sewage	Vehicle	97	PSA	20	2003

		sludge	fuel				
Sweden	Henriksdal, Stockholm	Sewage sludge	Vehicle fuel	97	Water scrubber	600	2004
Sweden	Norrköping	Sewage sludge	Vehicle fuel	97	Water scrubber	250	2004
Sweden	Västerås	Biowaste, sewage sludge	Vehicle fuel	97	Water scrubber	650	2004
Sweden	Lilla Edet			97	PSA	25	2005
Sweden	Skellefteå	Sewage sludge	Vehicle fuel	97	Water scrubber	250	2005
Sweden	Henriksdal, Stockholm	Sewage sludge	Vehicle fuel	97	Water scrubber	800	2006
Sweden	Kristianstad	Biowaste, manure, sewage sludge	Vehicle fuel	97	Water scrubber	600	2006
Sweden	Norrköping	Distiller's waste, energy crops	Vehicle fuel	97	Water scrubber	240	2006
Sweden	Östersund	Sewage sludge	Vehicle fuel	97	Water scrubber	200	2006
Sweden	Bjuv	Biowaste, manure	Gas grid	97	PSA	500	2007
Sweden	Boden	Sewage sludge, manure	Vehicle fuel	97	Water scrubber	360	2007
Sweden	Falköping	Sewage sludge	Vehicle fuel	97	Water scrubber	200	2007
Sweden	Göteborg	Biowaste, sewage sludge	Gas grid	97	Chemical scrubber	1600	2007
Sweden	Helsingborg	Biowaste, manure	Vehicle fuel, gas grid	97	Water scrubber	650	2007
Sweden	Helsingborg	Sewage sludge	Gas grid	97	Water scrubber	250	2007
Sweden	Örebro	Sewage sludge	Vehicle fuel	97	Water scrubber	450	2007
Sweden	Kalmar	Sewage sludge, manure	Vehicle fuel	97	Chemical scrubber	200	2008
Sweden	Malmö	Sewage sludge	Gas grid	97	PSA	500	2008
Sweden	Plönninge	Manure	Vehicle fuel	97	Water scrubber	20	2008
Sweden	Falkenberg	Biowaste, sewage sludge, energy crops	Gas grid	97	Chemical scrubber	750	2009

Sweden	Himmerfjärden, Stockholm	Sewage sludge	Vehicle fuel	97	Chemical scrubber	800	2009
Sweden	Katrineholm	Sewage sludge	Vehicle fuel	97	Water scrubber	80	2009
Sweden	Motala	Sewage sludge	Vehicle fuel	97	Water scrubber	80	2009
Sweden	Västervik	Sewage sludge	Vehicle fuel	97	Water scrubber	130	2009
Sweden	Örebro	Sewage sludge	Vehicle fuel	97	Water scrubber	2000	2009
Sweden	Jönköping	Biowaste, sewage sludge	Vehicle fuel	97	Water scrubber	600	2010
Sweden	Karlstad		Vehicle fuel	97	Chemical scrubber	120/500	2010
Sweden	Katrineholm	Manure, co-digestion	Vehicle fuel	97	Water scrubber	800	2010
Sweden	Käppala (Stockholm)	Sewage sludge	Vehicle fuel	97	Water scrubber	1000	2010
Sweden	Lund	Sewage sludge	Gas grid	97	Water scrubber	200	2010
Sweden	Norrköping	Sewage sludge Distiller's waste	Vehicle fuel	97	Water scrubber	400/800	2010
Sweden	Visby	Energy crops	Vehicle fuel	97	Water scrubber	550	2010
Sweden	Lidköping		LBG	LBG	Water scrubber	2000	2011
Sweden	Sävsjö			97	Chemical scrubber	700	2011
Sweden	Brålanda	Manure, biowaste	Vehicle fuel	97	Water scrubber	300	2012
Sweden	Gävle		Vehicle fuel	97	Water scrubber	300	2012
Sweden	Mörnum	Biowaste	Vehicle fuel	97	Water scrubber	300	2013
Sweden	Skövde		Vehicle fuel	97	Water scrubber	800	2012

Appendix 2

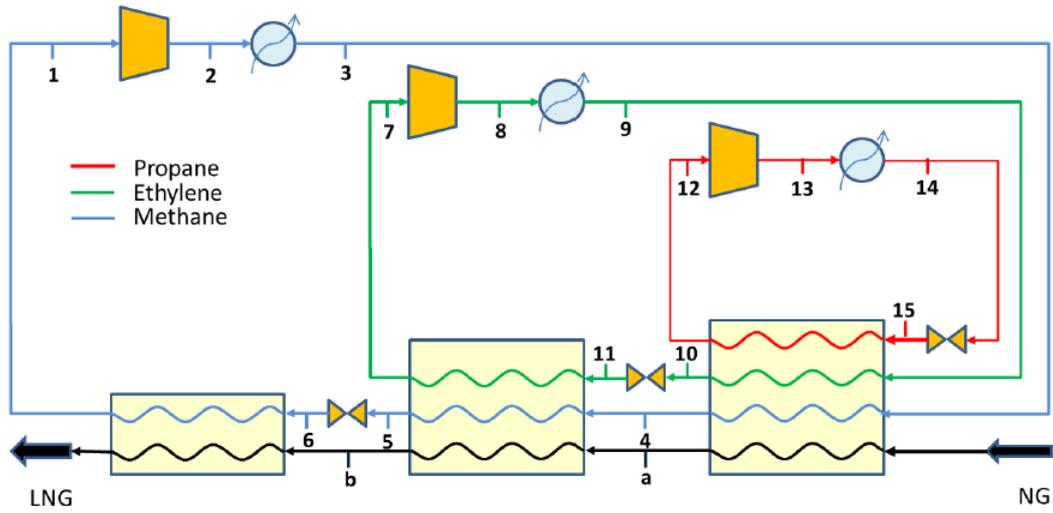


Figure 1. Triple cascade liquefaction process using propane, methane and ethylene (Trigilio, 2012)

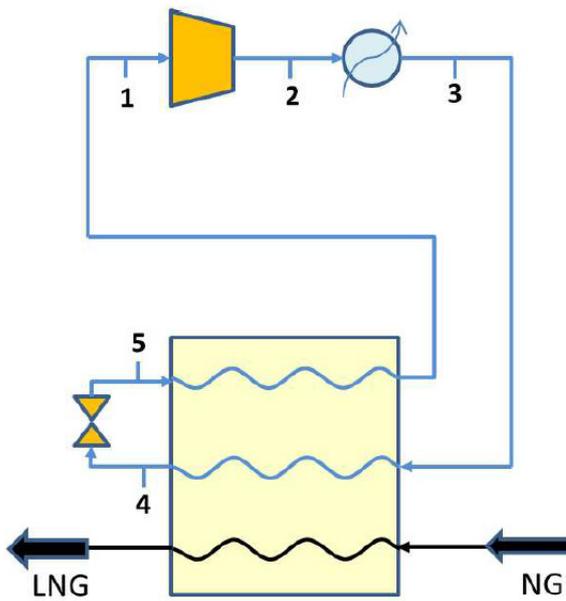


Figure 2. Simple liquefaction cycle using mixed refrigerant (Trigilio, 2012)

Appendix 3

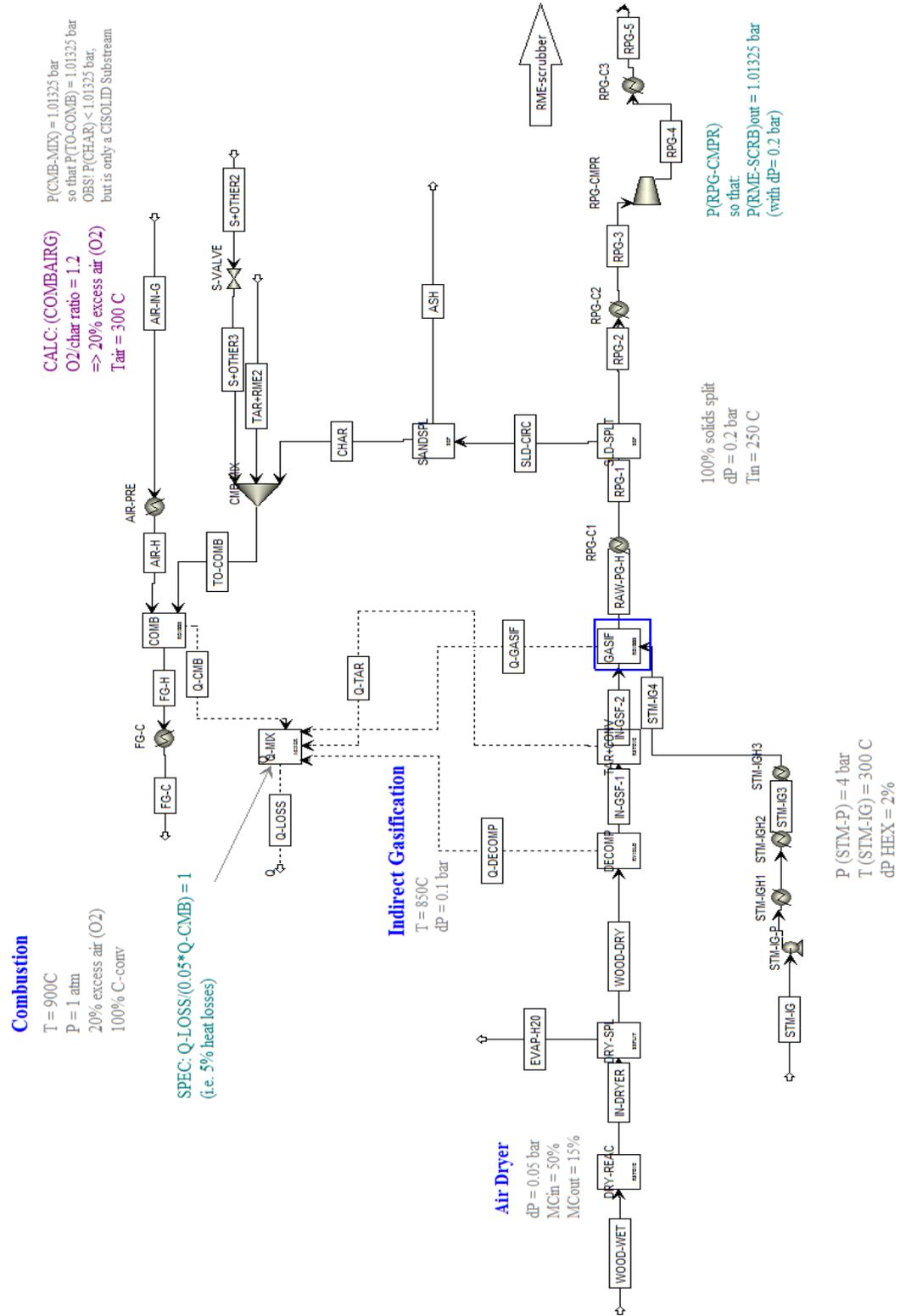


Figure 3. Flowsheet for bio-SNG production (1). From biomass inlet to RME-scrubber

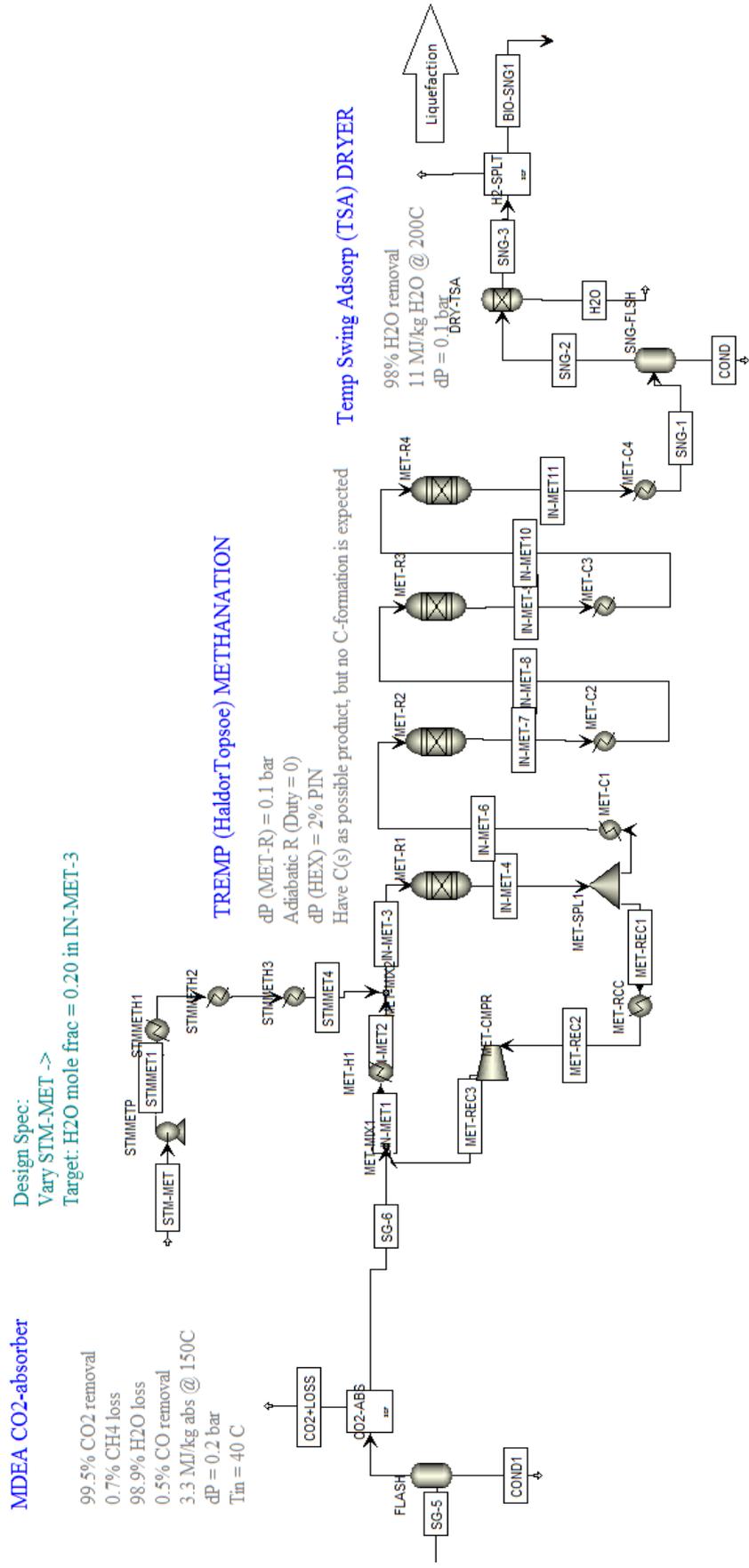


Figure 5. Flowsheet for bio-SNG production (3). From CO₂ removal to liquefaction

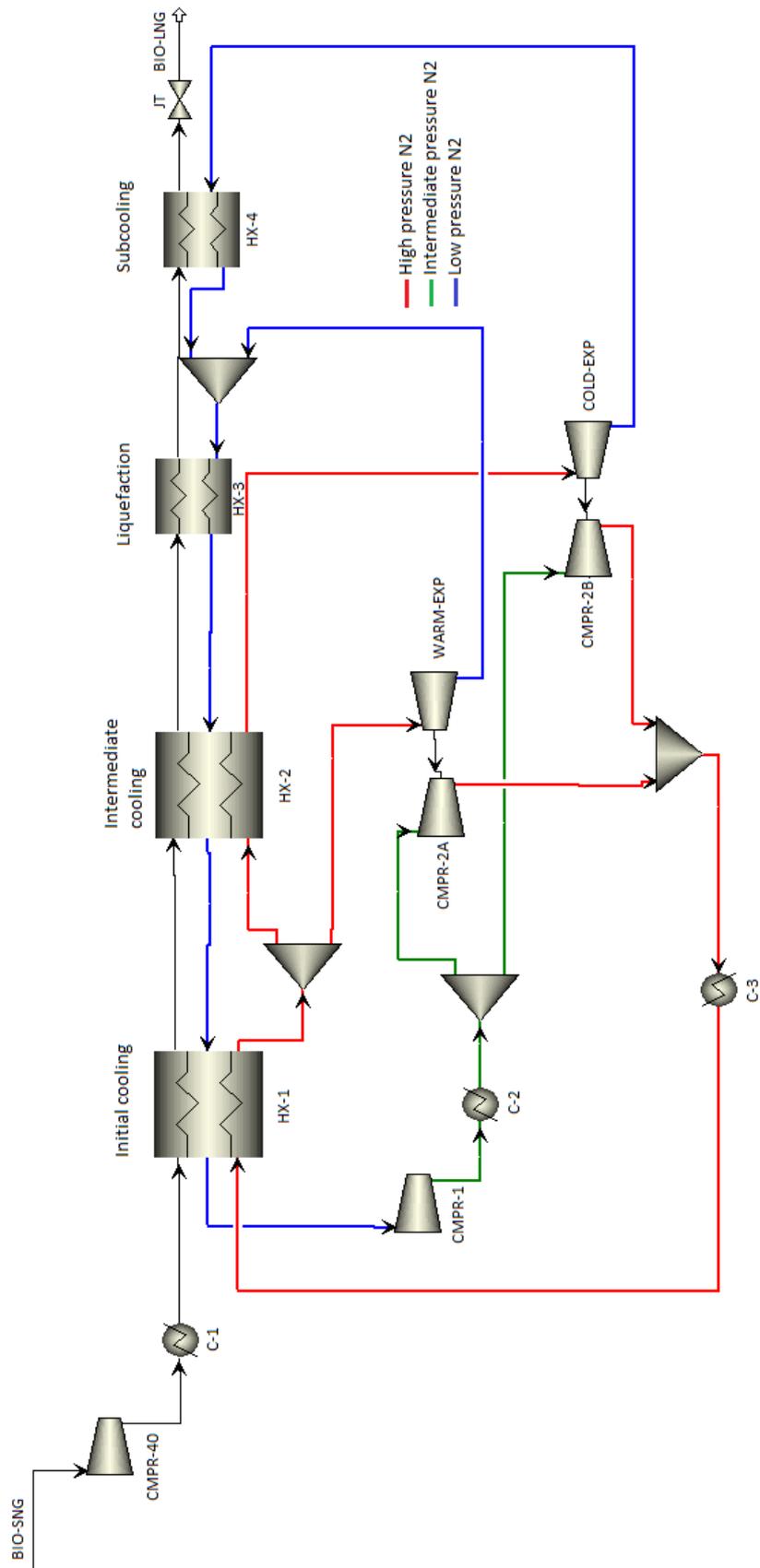


Figure 6. Flowsheet for bio-SNG liquefaction at 40 bar

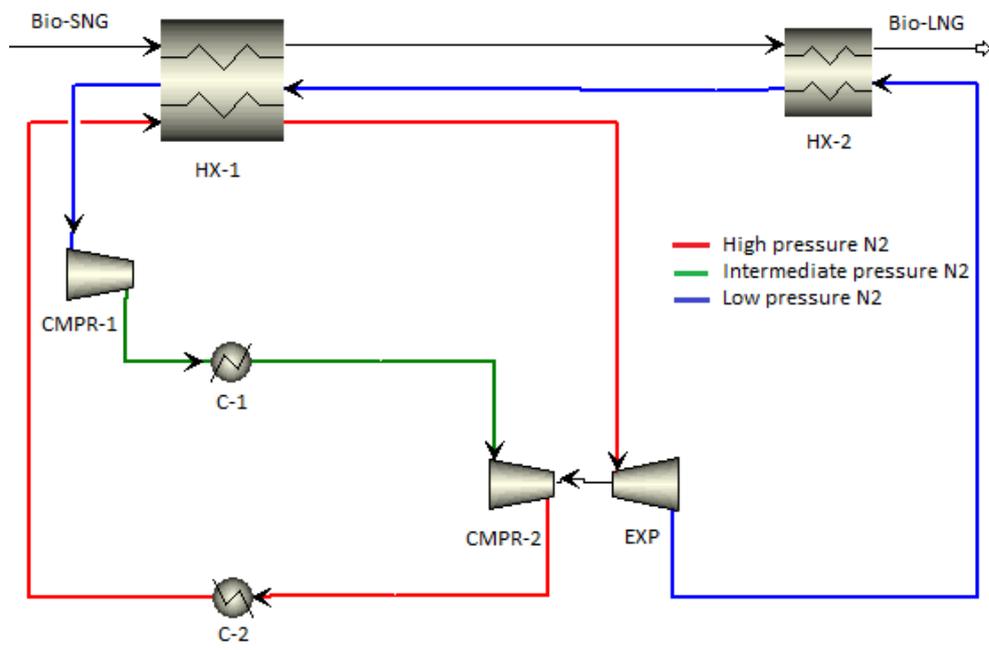


Figure 7. Flowsheet for bio-SNG liquefaction at 8 bar

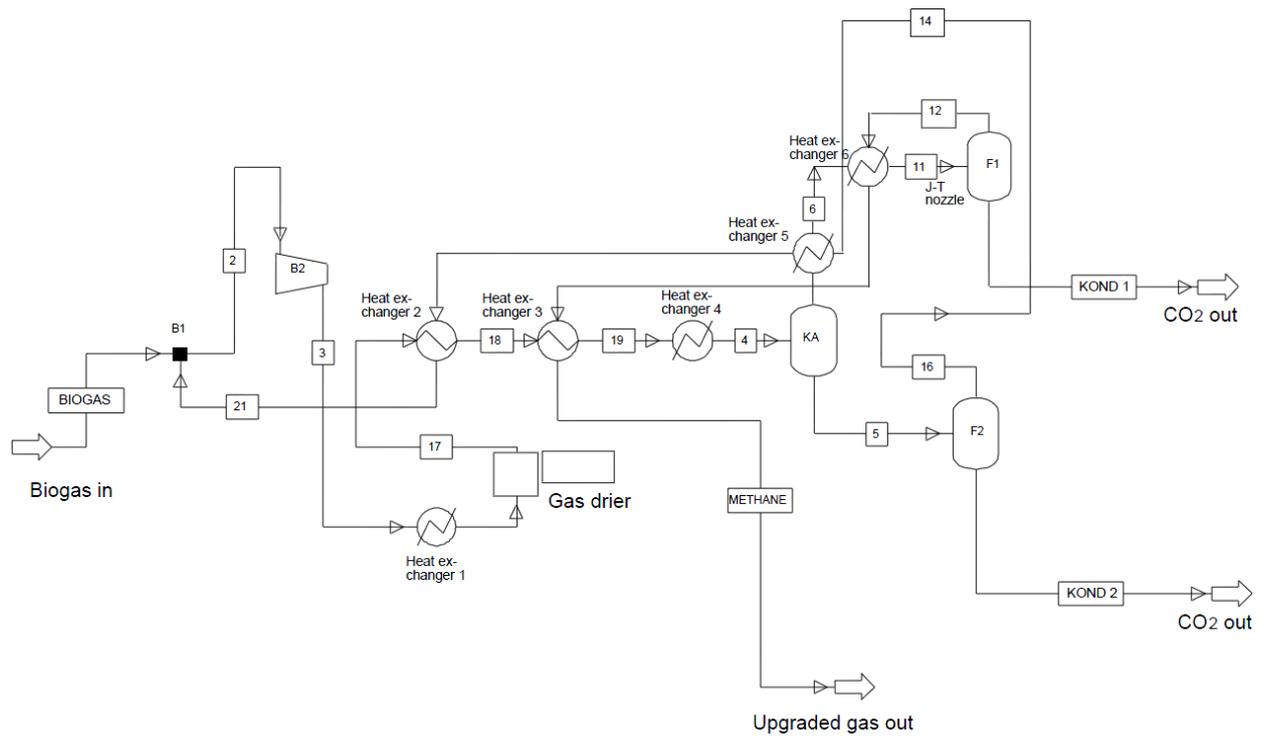


Figure 8. Cryogenic gas upgrading unit (SGC, 1997)

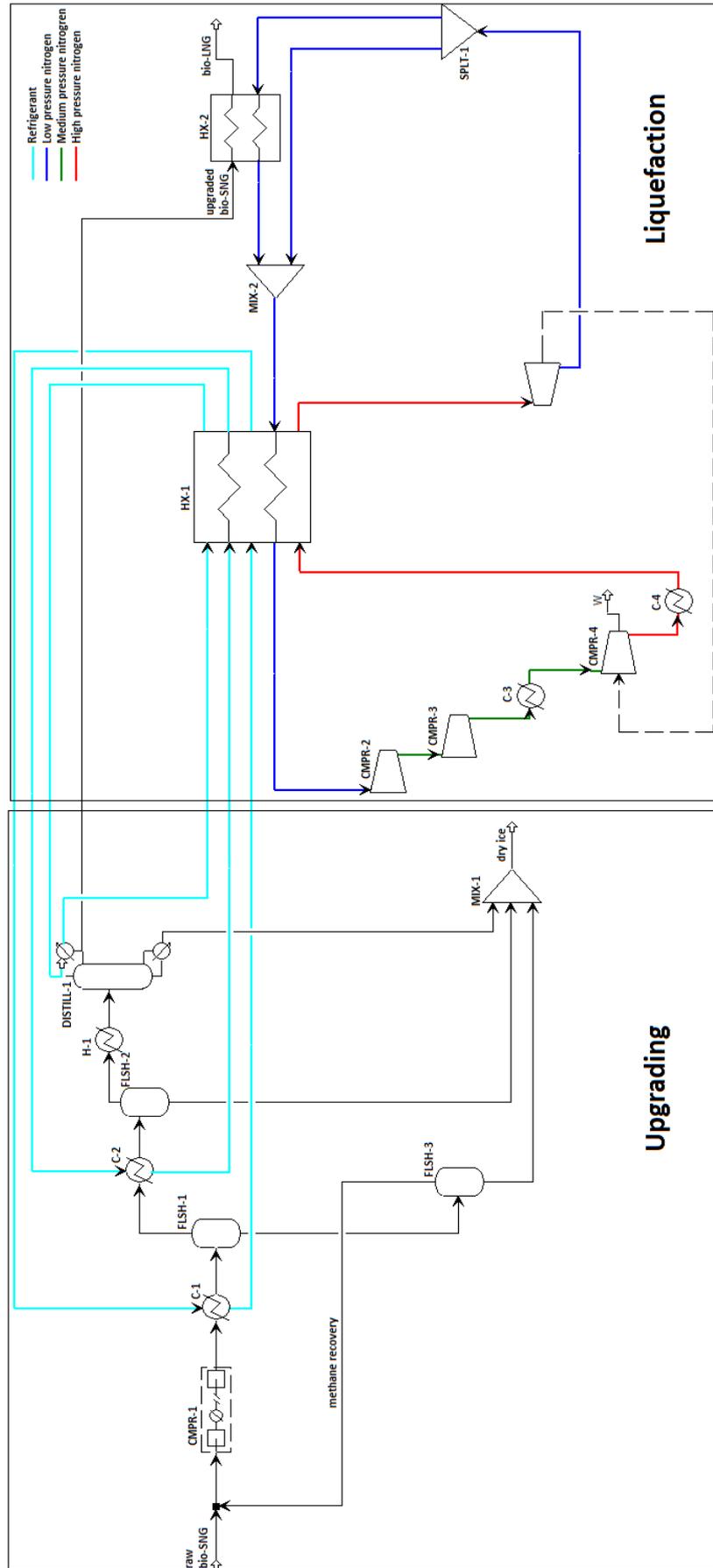


Figure 9. Cryogenic unit in integrated case Aspen model

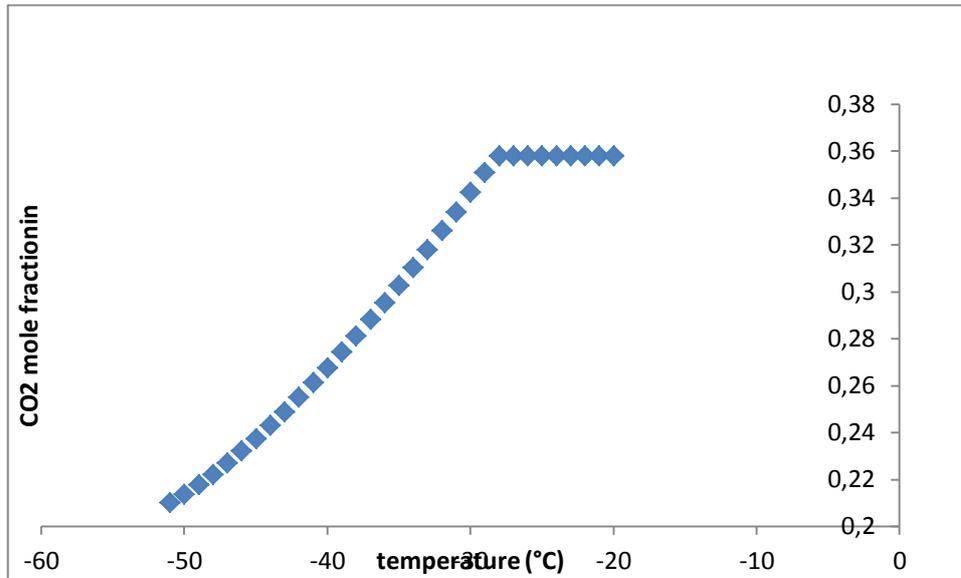


Figure 10. Sensitivity analysis results for C-1(CO2 mole fraction in the top stream of FLSH-1)

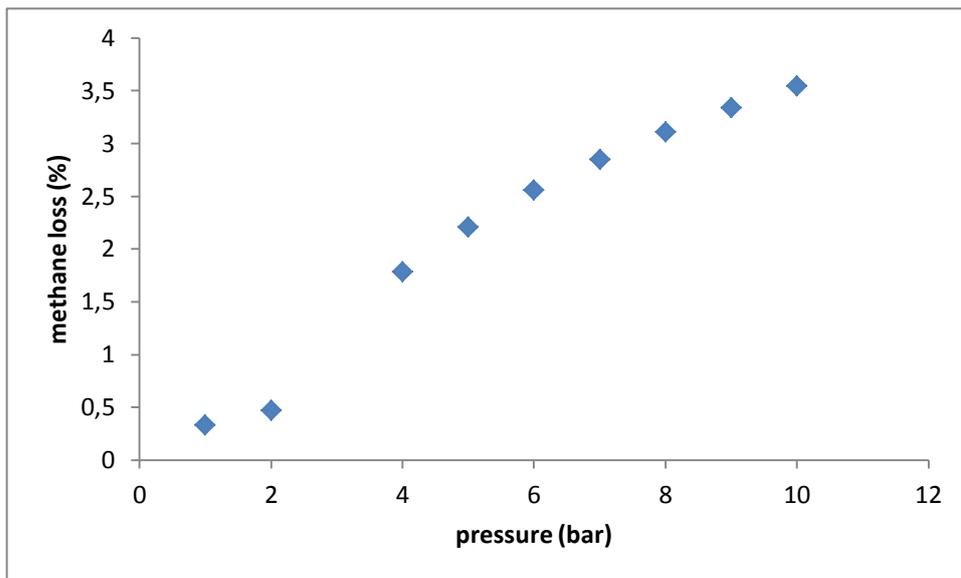


Figure 11. Sensitivity analysis results for FLSH-2

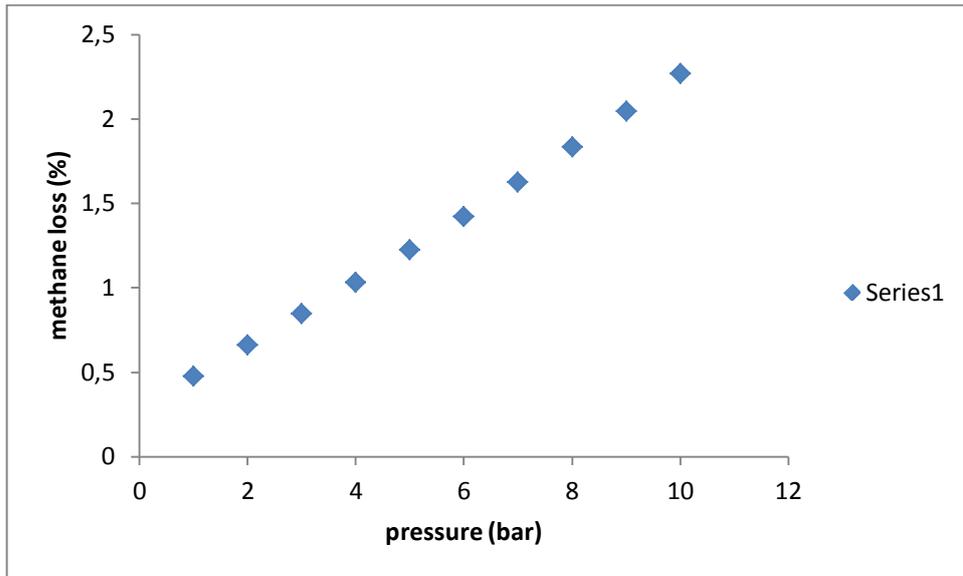


Figure 12. Sensitivity analysis results for FLSH-3

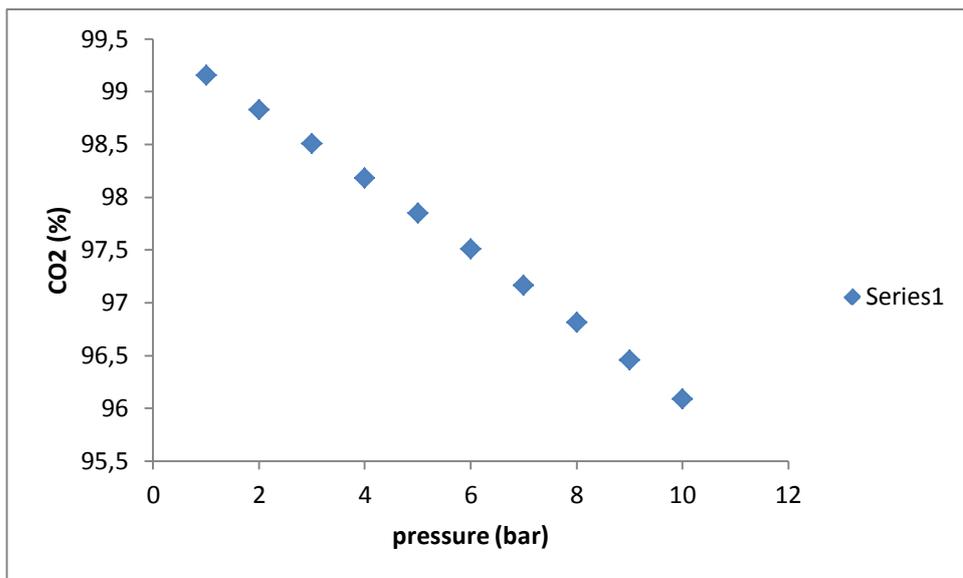


Figure 13. Sensitivity analysis results for FLSH-3

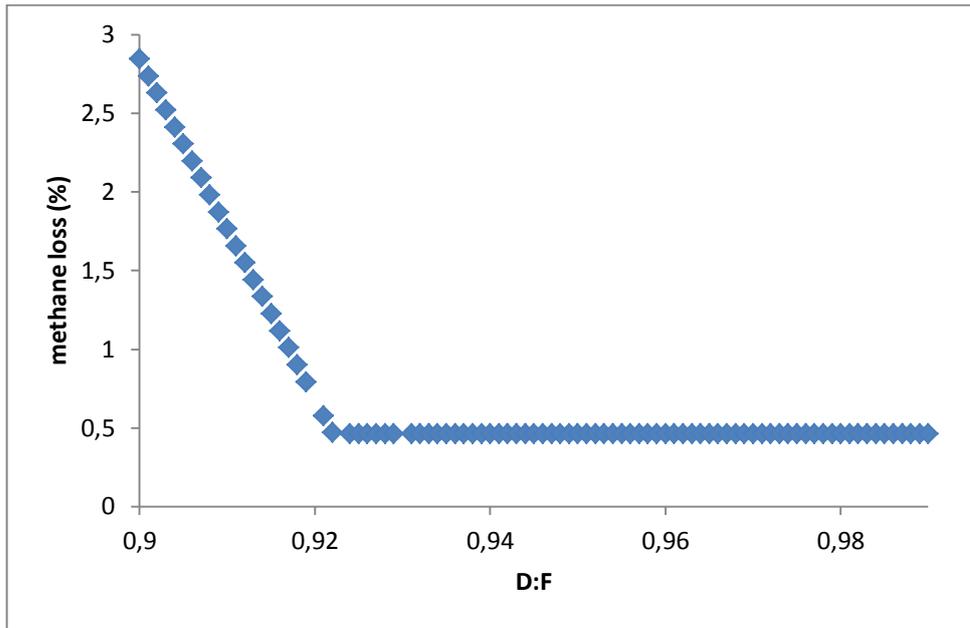


Figure 14. Sensitivity analysis results for DISTILL-1

Table 2. Stream data for bio-SNG production in base case 1 and 2

Stream	Type	Tstart °C	Ttarget °C	Q kW	Comment
Wood wet	Cold	15	60.29	1703.41	Wood drying
Raw-PG-H	Hot	850	250	17213.94	Gas cooling after gasification
STM-IG1	Cold	15.11	144.32	1737.50	Steam preparation 1
STM-IG2	Cold	144.32	145.32	6485.06	Steam preparation 1
STM-IG3	Cold	144.32	300	910.92	Steam preparation 1
AIR-IN-G	Cold	15	300	6905.2	Heat demand before combustion
FG-H	Hot	900	150	23679.43	Flue gases cooling from combustion
RPG-2	Hot	249.95	144	2380.96	Syngas cooling in RPG-C2
RPG-4	Hot	285.25	110	3942.98	Syngas cooling in RPG-C3
RMESCRBF	Hot	107.24	30	9466.51	Syngas cooling before sulphur removal
SG-1	Hot	109.91	80	470.06	Compressor cooling stage 1
SG-1a	Hot	173.04	80	1486.59	Compressor cooling stage 2
SG-1b	Hot	173.18	40	2765.12	Compressor cooling stage 3
S-reboil	Cold	150	151	8555.06	MDEA reboiler in sulphur removal
S-cool	Hot	55	40	6844.05	Syngas cooling in sulphur removal
STMSHFT1	Cold	15.98	234.81	3726.40	Steam preparation 2
STMSHFT2	Cold	234.81	235.81	6613.75	Steam preparation 2
STMSHFT3	Cold	234.81	300	529.55	Steam preparation 2
IN-SHFT2	Cold	156.06	330	2577.14	Heat demand before water shift reactor
IN-SHFT4	Hot	625.11	80	15499.30	Syngas cooling after water shift reactor
SHFTOUT	Hot	70.37	40	1278.76	Syngas cooling after mixing in SHFTMIX2
CO2-reb	Cold	150	151	10341.26	MDEA reboiler in CO ₂ removal
CO2-cld	Hot	55	44	8273.01	Syngas cooling in CO ₂ removal
IN-MET1	Cold	231.77	300	2511.33	Syngas cooling before methanation 1
STMMET1	Cold	15.58	178.21	506.69	Steam preparation 3
STMMET2	Cold	178.21	179.21	1407.18	Steam preparation 3
STMMET3	Cold	177.35	300	168.95	Steam preparation 3
MET-REC1	Hot	565.08	300	7685.43	Gas cooling after recycle in methanatio 1
IN-MET-5	Hot	565.08	200	4192.32	Gas cooling after methanation 1
IN-MET-7	Hot	408.97	235	1850.14	Gas cooling after methanation 2
IN-MET-9	Hot	293.75	235	589.60	Gas cooling after methanation 3
IN-MET-11	Hot	239.12	5	6742.86	Gas cooling after methanation 4
SNG-2	Cold	200	200	25.21	Dryer before liquefaction

*Global ΔT difference= 10K

Table 3. Stream data for liquefaction at 8 bar

Name	Type	Tstart °C	Ttarget °C	Q kW	Comment
BIO-SNG1	Hot	4.74	-92.5	429.28	Heat exchanger 1
BIO-SNG3	Hot	-92.5	-163	1289.82	Heat exchanger 2

*Global ΔT difference= 2K for multiple heat exchangers, 10 K for the rest

Table 4. Stream data for liquefaction at 40 bar

Name	Type	Tstart °C	Ttarget °C	Q kW	Comment
BIO-SNG2	Hot	149.33	20	666.77	Cooling of bio-SNG at high pressure
BIO-SNG3	Hot	20	-20	202.56	Heat exchanger 1
BIO-SNG4	Hot	-20	-84	405.78	Heat exchanger 2
BIO-SNG5	Hot	-84	-90	445.99	Heat exchanger 3
BIO-LNG1	Hot	-90	-164	656.62	Heat exchanger 4

*Global ΔT difference= 2K for multiple heat exchangers, 10 K for the rest

Table 5. Stream data for bio-SNG production in integrated case

Name	Type	Tstart °C	Ttarget °C	Q kW	Comment
Wood wet	Cold	15	60.29	1703.41	Wood drying
Raw-PG-H	Hot	850	250	17104.81	Gas cooling after gasification
STM-IG1	Cold	15.11	143.60	1680.14	Steam preparation 1
STM-IG2	Cold	143.6	144.6	6310.56	Steam preparation 1
STM-IG3	Cold	142.89	300	893.28	Steam preparation 1
AIR-IN-G	Cold	15	300	6895.46	Heat demand before combustion
FG-H	Hot	900	150	23630.01	Flue gases cooling from combustion
RPG-2	Hot	249.95	144	2364.75	Syngas cooling in RPG-C2
RPG-4	Hot	262.1	110	3383.64	Syngas cooling in RPG-C3
RMESCRBF	Hot	107.24	30	9277.57	Syngas cooling before sulphur removal
SG-1	Hot	124	80	693	Compressor cooling stage 1
SG-1a	Hot	189.4	80	1752	Compressor cooling stage 2
SG-1b	Hot	189.5	40	3029	Compressor cooling stage 3
S-reboil	Cold	150	151	8481.14	MDEA reboiler in sulphur removal
S-cool	Hot	55	40	6785	Syngas cooling in sulphur removal
STMSHFT1	Cold	15.3	181.3	2333.97	Steam preparation 2
STMSHFT2	Cold	181.3	182.3	6921.41	Steam preparation 2

STMSHFT3	Cold	234.81	300	817.34	Steam preparation 2
IN-SHFT2	Cold	164.6	330	2333.97	Heat demand before water shift reactor
IN-SHFT4	Hot	629.2	80	14627.29	Syngas cooling after water shift reactor
SHFTOUT	Hot	69.8	40	1215.92	Syngas cooling after mixing in SHFTMIX2
IN-MET1	Cold	249.8	300	3123.63	Syngas cooling before methanation 1
STMMET1	Cold	15.583	178,21	3004.37	Steam preparation 3
STMMET2	Cold	178.21	179.2	8328.19	Steam preparation 3
STMMET3	Cold	177.4	300	999.86	Steam preparation 3
MET-REC1	Hot	466.8	300	8467.17	Gas cooling after recycle in methanation 1
IN-MET-5	Hot	466.8	320	3209.10	Gas cooling after methanation 1
IN-MET-7	Hot	383.9	320	1352.33	Gas cooling after methanation 2
IN-MET-9	Hot	339	300	806.73	Gas cooling after methanation 3
IN-MET-11	Hot	308.5	5	18737.44	Gas cooling after methanation 4
SNG-2	Cold	200	201	38.03	Dryer before cryogenic unit

*Global ΔT difference= 10K

Table 6. Stream data for cryogenic unit in integrated case

Name	Type	Tstart °C	Ttarget °C	Q kW	Comment
1	Hot	54	40	483.48	Inter cooling of multiple compressor
2	Hot	135	40	1036.51	Inter cooling of multiple compressor
4	Hot	-51	-56	149.12	Cooler 2
5	Cold	-108.7	-60	226.94	Heater 1
6	Hot	-128.9	-129.85	878	Condenser of distillation column
8	Hot	20	-56	2766.68	Heat exchanger 1
11	Hot	-129.9	-163	244.63	Heat exchanger 2
13	Cold	-51.46	-51	7.58	Reboiler of distillation column

*Global ΔT difference= 2K for multiple heat exchangers, 10 K for the rest

Appendix 4

Replacement of diesel with LCO₂ in cryogenic transportation:

The CO₂ density is 1.978 kg/Nm³ (Air Liquide, 2013) and the worst case is considered in which CO₂ consumption is 25 kg/h. The volume of CO₂ consumed corresponds to:

$$25 \frac{kg CO_2}{h} \cdot \frac{1 Nm^3}{1.978 kg} = 12.64 \frac{Nm^3 CO_2}{h}$$

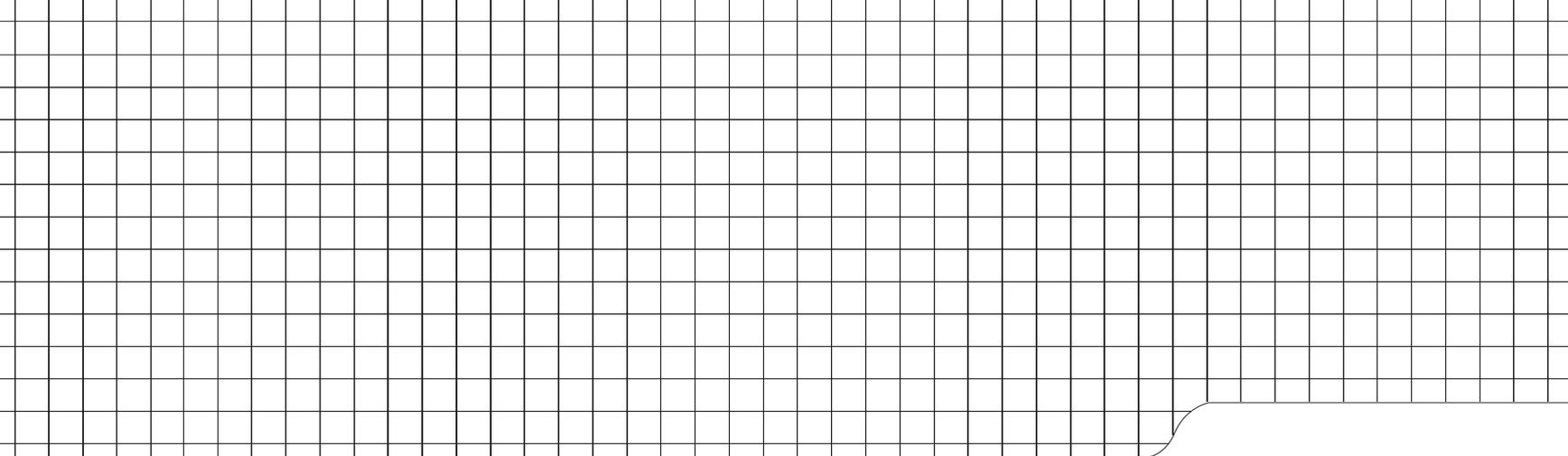
Thus, the amount of replaced diesel per Nm³ of LCO₂ is calculated as:

$$\frac{1,5 \frac{l diesel}{h}}{12.64 \frac{Nm^3 CO_2}{h}} = 0.12 \frac{l diesel}{Nm^3 CO_2}$$

Energy content in a liter of diesel corresponds to 9.8 kWh (SGC, 2007). Taking into account a primary energy factor of 1.05 (Johansson, 2008), replaced primary energy corresponds to:

$$\frac{9.8 kWh * 1,05}{1 l diesel} \cdot 0.12 \frac{l diesel}{Nm^3 CO_2} = 1.22 \frac{kWh primary energy}{Nm^3 CO_2}$$

In integrated case, the amount of LCO₂ produced is 11102 kg/h. Thus, the quantity of primary energy that can be replaced using LCO₂ for cooling temperature-controlled goods during transportation is **6.85 MW**.



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