



Norwegian University of
Science and Technology

Production, Liquefaction and Transport of Low-Processed Natural Gas

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Master of Science in Product Design and Manufacturing

Submission date: July 2010

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Problem Description

The main objective for this Master thesis is to make a systematic survey and analysis of value chains for natural gas based on un-processed or low-processed natural gas in liquid phase (possibly with a solid fraction). The survey should evaluate and focus on energy efficiency, complexity (both in development, design and operation), uncertainty elements, need for technology qualification and the realism of the concepts.

1. A high level survey of different published, known, patented as well as possible/imaginable concepts for production and transport of un-processed or low-processed natural gas.
2. An evaluation of different solutions for processes and equipment related to such concepts for gas transport with emphasis on gas pre-treatment and liquefaction. This will also require a search in the patent literature.
3. To establish energy and material balances for relevant concepts and value chains based on process modeling tools (process simulators). The level of detail should be increased for the more promising concepts.
4. To analyze and discuss the results (see the objective section) and compare with realistic figures for conventional production and transport solutions.

Assignment given: 11. February 2010
Supervisor: Truls Gundersen, EPT

EPT-M-2010-27

MASTER THESIS

for

Stud.techn. Haakon Andreas Hveding
Spring 2010

Production, liquefaction and transport of low-processed natural gas

Produksjon, kondensering og transport av lav-prosessert naturgass

Background

Processing and liquefaction of natural gas to LNG require considerable pre-treatment (CO₂-removal, drying, extraction of heavier hydrocarbons, mercury removal), and the power requirements for the cooling process are large since natural gas is liquefied at atmospheric pressure. For exploration and transport of natural gas from “unfriendly” or remote regions, often combined with floating production systems, it is highly desirable to simplify the process and reduce power consumption. Concepts have been proposed for value chains for natural gas based on pressurized LNG (Heavy LNG – HLG or Pressurized LNG - PLNG), where the condensation temperature is set above the highest freeze-out temperature – normally for CO₂. This type of process will reduce power demand, but still requires some pre-treatment.

A more extreme idea is to let CO₂, heavier hydrocarbons and possibly also water to freeze out during cooling/expansion of natural gas, and thus produce a “slurry” that can be transported by ships to a receiving terminal for processing and export. One example of such a concept is “LUWS” – Liquefaction of Unprocessed Well Stream, which is currently investigated in a knowledge building project with industrial contribution (KMB) funded by the Research Council of Norway (RCN) with IFE as the project leader. Other partners in the project are NTNU, SINTEF and Statoil.

One of the challenges with LUWS and similar ideas is to develop complete, consistent and realistic analyses for the entire natural gas value chain from reservoir to gas export (pipeline or LNG), where energy efficiency, complexity, need for technology qualification and realism of the concepts are considered and compared with conventional solutions. Such analyses of different “LUWS” concepts must include natural gas production, potential need for drying or other (minor) pre-treatment, liquefaction/expansion process, power production, power supply, transport and storage of slurry and “post” treatment. Several different process concepts have been proposed for liquefaction/expansion and these will result in different challenges related to freeze-out problems, amounts and conditions for flash gas, need for compression, special requirements for equipment as well as energy efficiency, power requirements and fuel gas demand. Selection of transport/storage pressure is a parameter that has a strong impact on both

process and equipment. When it comes to expansion processes, one could consider different solutions for integration of water separation (vortex/twister solutions) and also separation of CO₂ (Cryex process, etc.) as part of the process.

Objective

The main objective for this Master thesis is to make a systematic survey and analysis of value chains for natural gas based on un-processed or low-processed natural gas in liquid phase (possibly with a solid fraction). The survey should evaluate and focus on energy efficiency, complexity (both in development, design and operation), uncertainty elements, need for technology qualification and the realism of the concepts.

The following issues should be considered in the Master thesis:

1. A high level survey of different published, known, patented as well as possible/imaginable concepts for production and transport of un-processed or low-processed natural gas.
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4. To analyze and discuss the results (see the objective section) and compare with realistic figures for conventional production and transport solutions.

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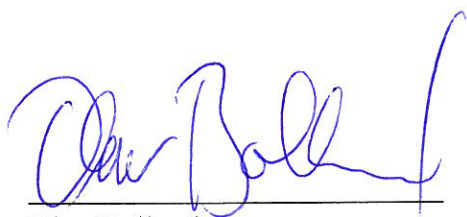
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Department of Energy and Process Engineering, 1 February 2010



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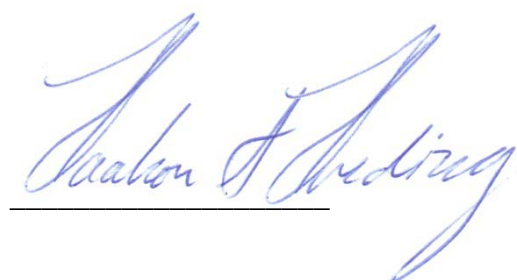
Preface

This Master Thesis was written as the final work in the last semester of the quinquennial Product Design and Manufacturing program at the institute of Energy and Processing, NTNU, in the spring of 2010.

As the thesis is not a continuation of the project assignment in autumn 2009, a great deal of time was spent on getting an overview and gather and evaluating different patents from the concepts described, as well as patents that potentially could have been used.

I would like to express my gratitude to my supervisor Truls Gundersen at NTNU for great follow-up and always being available for consultation. I would also like to thank the industrial contacts at Statoil, Jostein Pettersen and Arne Olav Fredheim for giving me input and information during the semester, and taking the time to arranging feedback meetings along the way. In addition I would like to thank Petter Neksa, Jacob Stang and Yves Ladam for input on the LUWS concept status and Longman Zhang for calculations and advice on freeze out concentration limits for water and CO₂.

Trondheim, 06.07.2010



A handwritten signature in blue ink, reading "Haakon A. Hveding". The signature is written in a cursive style and is positioned above a horizontal line.

Haakon A. Hveding

Summary in English

The pre-processing and liquefaction of LNG is very energy demanding in addition to having a high level of complexity. This motivates for finding alternative value chains and technologies for gas transportation and various concepts have been proposed based on natural gas in liquid phase. These can be split into two main principles; liquefaction with solids formation, and storage under pressure. Due to the increased temperature and solubility, freezable components will not form solids as easily in the pressurized concepts allowing less pre-treatment of the gas. The evaluated concepts in this thesis are Liquefied Unprocessed Well Stream (LUWS) with controlled solids formation, and three pressurized storage concepts; Aker Solutions' Heavy Liquid Gas (HLG), ExxonMobil's Pressurized Liquefied Natural Gas (PLNG) and Chevron's Liquefied Heavy Gas (LHG). All are presented in a high level survey together with similar ideas and patents in the first part of the thesis.

Value chain evaluations are carried out for the different concepts and positive contributions, uncertainty and possible difficulties are discussed. The different patents filed, with solutions to some of the difficulties associated with the concepts, are also explained and presented. As the different gas products will have a less pure composition compared to LNG, the gas treating part of the value chains will be moved downstream of the liquefaction for all the new concepts.

Through simplified simulations in PRO/II, energy requirements and specifications of the product liquid for the different concepts are found. The gas composition is adjusted to avoid freeze out of any kind for the pressurized liquids. The power needs for liquefaction are drastically decreased with increased pressure, giving smaller and less complex liquefaction plants. For a HLG concept at 20 bars, the power need is around halved, while for LHG at 50 bars it is between 25-39% compared to LNG, depending on the amount of heavy hydrocarbons in the LHG. The amount of flash gas needed for power production is as a direct result reduced by 70%.

Water removal will still be necessary for all the concepts as hydrates will form easily at high pressures and low temperatures. The only exception is for the LUWS concept, where a smaller amount of water possibly could be allowed to form hydrates in a controlled way together with hydrocarbons and CO₂.

The reduced requirements for the gas means alternative processes for pre-treatment can be utilized and the thermal energy needs for these decreased at the liquefaction site. CO₂ removal may be done by a membrane system or similar as the CO₂ concentration can be around 1,4 and 6 mole% for a pressure of 12 and 50 bars respectively without the forming of solids. At the receiving site, a system similar to the CRYEX process can be implemented to remove the CO₂ and allow storage of gas as LNG at atmospheric pressure.

Estimations of the weight of the steel pressure vessels have been calculated for all the pressure levels. Due to the extremely high weight and the large amount of steel needed, the vessels must be constructed by an alternative building material for the high pressure ranges. A fiber reinforced plastic is suggested used with a steel or aluminum liner retaining the liquid. If successfully manufactured, these vessels would significantly reduce the weight and make HLG/LHG possible to implement.

Sammendrag på norsk

Før-prosesseringen og flytendegjøringen av LNG er veldig energikrevende i tillegg til å ha en høy grad av kompleksitet. Dette gir motivasjon til å finne alternative verdikjeder og teknologier for gasstransport og ulike konsepter har blitt lagt frem basert på naturgass i flytende form. Disse kan deles inn i to hovedgrupper; flytendegjøring med utfrysning, og transport under trykk. På grunn av forhøyet temperatur og løselighet vil komponenter som vanligvis ville frøset ut kunne forbli i væskeform i de trykksatte konseptene, som igjen reduserer kravene til før-prosessering av gassen. De drøftede konseptene i denne oppgaven er: Liquefied Unprocessed Well Stream (LUWS) med kontrollert utfrysning, samt tre trykksatte konsepter; Aker solutions Heavy Liquid Gas (HLG), ExxonMobils Pressurized Liquefied Natural Gas (PLNG) og Chevrons Liquefied Heavy Gas (LHG). Alle blir presentert i en oversikt sammen med lignende ideer og patenter i begynnelsen av oppgaven.

Verdikjedebetraktninger for de ulike konseptene har blitt utført og positive virkninger, usikkerhet samt mulige vanskeligheter blitt diskutert. Forskjellige patenter med mulige løsninger til nevnte vanskeligheter forbundet med konseptene har også blitt presentert og gjennomgått. Siden den transporterte væsken vil ha en mindre ren komposisjon enn LNG, gassbehandlingsdelen av verdikjeden vil bli flyttet nedstrøms av produksjonen og flytendegjøringen for alle de nye konseptene.

Gjennom forenklete simuleringer i PRO/II har energibehov og spesifikasjoner for væskeproduktene til de forskjellige konseptene blitt funnet. Gasskomposisjonen blir justert slik at ingen utfrysning finner sted i de trykksatte væskene. Kraftbehovet for flytendegjøring blir drastisk redusert med økning i trykknivå noe som gir mindre prosessanlegg og reduserer kompleksiteten på dem. For HLG konseptet ved 20 bar blir kraftbehovet rundt det halve, mens LHG ved 50 bar gir et krav på mellom 25-39% i forhold til LNG varierende med mengden tyngre hydrokarboner i væskeproduktet.

Fjerning av vann før flytendegjøringen vil fremdeles være nødvendig for alle konseptene da gasshydrater lett vil oppstå ved høye trykk og lave temperaturer. Eneste unntak er for LUWS konseptet hvor en mindre mengde vann muligens kan tillates å forme hydrater på en kontrollert måte sammen med hydrokarboner og CO₂.

Det reduserte kravene til renhet på gassen fører til at alternative prosesser til førprosessering kan bli tatt i bruk og de termiske energibehovene redusert ved prosesseringsanlegget. CO₂ fjerning kan bli utført ved hjelp av en membran eller lignende siden CO₂-konsentrasjonen kan være rundt 1,4% og 6% for trykk ved henholdsvis 12 og 50 bar uten å danne fast stoff. Ved mottagsstedet, kan et system ikke ulikt CRYEX prosessen bli brukt til å fjerne CO₂ og dermed tillate lagring av noe av gassen som LNG ved atmosfærisk trykk.

Noen estimat for vekten av trykkbeholderene laget av stål er satt opp for alle trykknivåer. Grunnet den ekstremt høye vekten og den store mengden stål, må trykkbeholderene bli utført i et alternativ byggemateriale for de høyeste trykkene. Fiberarmert plastikk beholdere med et foringsmateriale av aluminium eller stål er foreslått. Hvis disse blir vellykket produsert til en rimelig pris vil dette muliggjøre realisering av konsepter slik som HLG/LHG.

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Nomenclature

LNG	Liquefied Natural Gas
NGL	Natural Gas Liquids
LPG	Liquid petroleum Gases
PLNG	Pressurized LNG
HLG	Heavy Liquid Gas
LHG	Liquid Heavy Gas
LUWS	Liquefied Unprocessed Well Stream
FPSO	Floating Production Storage and Offloading
HHV	Higher Heating Value
GCV	Gross Calorific Value
HHC	Heavy Hydrocarbons
DP	Dew Point
JT	Joule-Thomson
MEA	Mono ethanol amine
FRP	Fiber Reinforced Plastic
ppm	Parts per million
C1	Methane
C2	Ethane
C3	Propane
iC4	I-Butane
nC4	N-Butane
iC5	I-Pentane
nC5	N-Pentane
C6	Hexane
CX+	Hydrocarbons over X C-atoms
Hg	Mercury
s	Specific entropy
e	Specific exergy
h	Specific enthalpy

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1 Introduction

1.1 Objective

The main objective for this thesis is to give an overview of concepts and alternative processes for production, liquefaction and transport of low-processed natural gas in a liquid phase. The value chains for such concepts are to be presented and evaluated with special emphasis on pretreatment and liquefaction, so that a basis of the feasibility and complexity can be given for the different concepts.

The energy requirements for liquefaction and recompression in addition to the compositions of the different products are to be found through simple simulations in PRO/II. The results of these will then be compared to a conventional LNG process. Estimations of transport vessel sizes and weights will also be calculated and the different vessel options and building material discussed.

1.2 Background

A large amount of natural gas around the world is currently not being produced because of its economic, physical or geographic unsuitable qualities [1]. This gas, so called stranded gas, has a huge potential of becoming a future energy source once the technical difficulties are mastered. Known areas today are found all around the world e.g. Alaska, Siberia and Brazil, with different complications varying heavily. Many possible future discoveries are situated in arctic areas and under the ice cap of the North Pole. With the receding ice layers experienced today, options for developing energy resources in these regions must be evaluated and improved.

Regions far away from gas markets depend today mostly on LNG as the transportation method due to the alternative of building a gas pipe, would be too costly. Traditional LNG however, can be impractical in many cases because of the necessary pre-processing of the natural gas and the consequential cost of the equipment. This is especially the case for offshore liquefaction plants (FPSO's), where the space used for processing also has a high expense and should be limited to an absolute minimum.

To make field developments more economical feasible, different methods for alternative storage and transportation have been developed. Among these are Compressed Natural Gas (CNG), Natural Gas Hydrates (NGH), Gas To Liquids (GTL), Liquefied Unprocessed Well Stream (LUWS) and Pressurized Liquefied Natural Gas (PLNG). There are advantages and disadvantages for all of them and some are more suited for various areas than others.

The two alternatives involving gas in a liquid cryogenic phase are LUWS and pressurized LNG. These can both also be liquefied with a reduced, or no requirement for pre-processing of the gas stream depending on the feed gas composition. The advantages of this are obvious resulting in a lower equipment count and space requirements. In addition, the latter will dramatically reduce the power requirements for liquefaction.

1.3 Limitations

There are a lot of unpredictable variables in all the concepts and the comparison between them will not be a correct depiction of what the actual outcome might be, if they are allowed to be realized. However, since the simulations will be done on the same assumptions, the numerical values of these will be comparable, even though they are simplified and not optimized. The technical difficulties associated with them are discussed, but since there is high uncertainty with regard to many aspects of these, there cannot be drawn absolute conclusions in the comparison.

As there are many different alternatives and aspects to go through, the analyses will have a more high level character than one on a specific part of a process. A lot of time was used for finding and getting insight in the different patents and concepts. This limited the time available for thorough process simulations.

2 Conventional LNG production

In 1941, the first commercial LNG plant started liquefying gas in Cleveland, Ohio, and in 1959, the first trans-Atlantic LNG shipment proved the possibility of a large scale global trade of natural gas. Since then, and especially in the last ten years, there has been an extensive expansion in worldwide production and demand. At the end of 2008, the total produced LNG reached 377,4 million m³ (172 mill. tons) and the number of transport vessels passed 300 [2]. The future projections predict an annual increase of natural gas demand of 1,6% per year until 2030 [2].

The high level value chain for LNG will consist of the five sections shown in Figure 1.

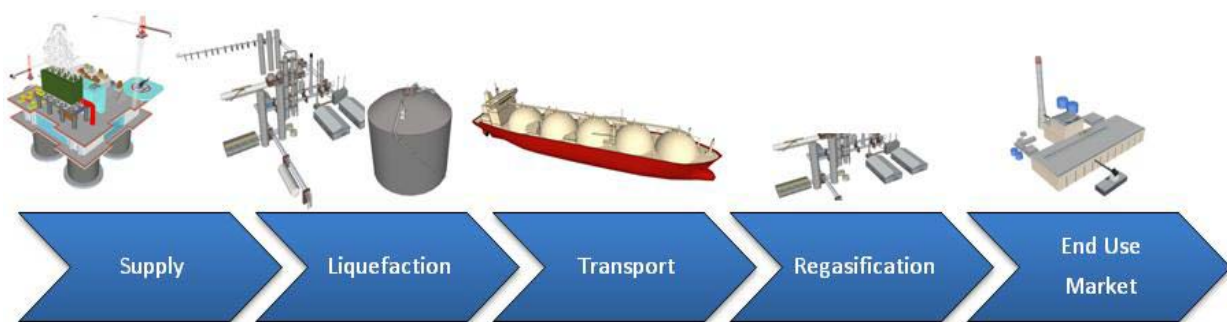


Figure 1: LNG General Value Chain

The delivered gas composition will need to be adjusted to the market it is delivered to and the requirements vary around the world. The requirements include:

- Heating value
- Wobbe Index
- Water Dew Point
- Hydrocarbon Dew Point
- Nitrogen Content
- CO₂ Content
- H₂S Content

The specification in this thesis is set to EASEE's Harmonized Pipeline Specifications and can be found in the appendix.

The liquefaction of gas requires a much purer gas than the pipe specifications due to freeze out at low temperatures. Some of the concentration limits are extremely low and the design of the plant becomes a great deal more complex than a pipe gas treatment facility. The result of this is an extensive pre-processing procedure that all LNG plants will have implemented in some way or the other. The typical gas specifications before liquefaction are presented in Table 1.

CO ₂	H ₂ O	HHC	Hg	H ₂ S
50-100 ppm	0,1-0,5 ppm	1-10 ppm	0,01µg/Nm ³	4 ppm

Table 1: LNG Specifications

Transportation of LNG is for the most part done by large well insulated tankers, but it can also be distributed with tank trucks or by train to smaller customers. Practically all transport of LNG today is done under atmospheric pressure and at a temperature of about -160°C. The liquefaction reduces the volume to around 1/600 compared to transportation in a gaseous state, making worldwide shipment possible at competitive costs.



Figure 2: LNG Tanker [4]

Site specific variations

The technical installations will have to be adjusted depending on site specific variables:

- The available ambient cooling water or air temperature can vary greatly between arctic conditions and the tropics influencing the work requirements. In warmer climates, the daily variation may also be big.
- The well stream composition will affect the choice of processes for treatment. This can be the amount of heavy hydrocarbons, but especially the CO₂ and H₂S amounts are important as these can vary widely.
- CO₂ recovery and disposal obligations will vary with the geographical placement of the plant and the political agreements here. This is especially true where a high CO₂ content is present in the feed.

The diagram in Figure 3 shows the cost distribution associated with the LNG value chain with both a minimum and maximum percentage wherein the cost usually lies. As we can see, the LNG plant including gas treating, liquefaction, LPG extraction and storage takes up a large fraction of the total cost. In addition, the LNG shipping costs can vary between 10 and 30% of the total, and may in some cases have a large influence on the total cost [3].

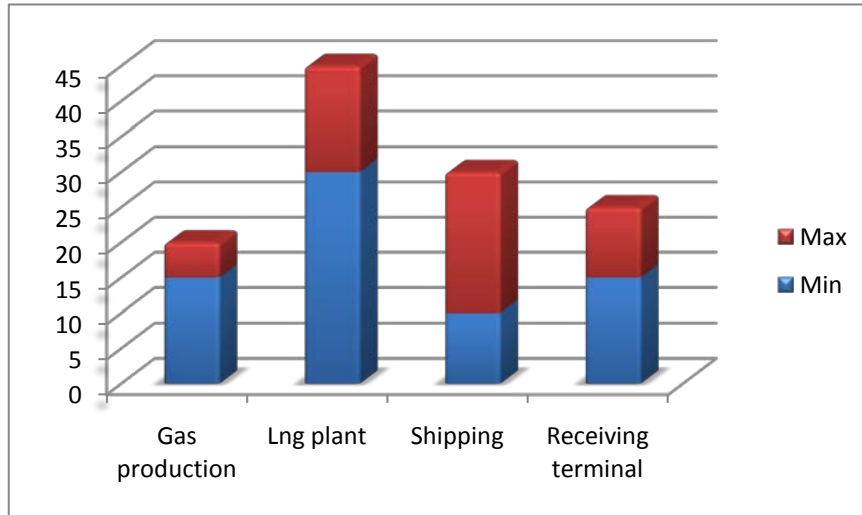


Figure 3: LNG cost distribution

An extended value chain for LNG can be represented by a simple box diagram shown in Figure 4. This includes both the extensive pre-processing as well as the treatment at the receiving site.

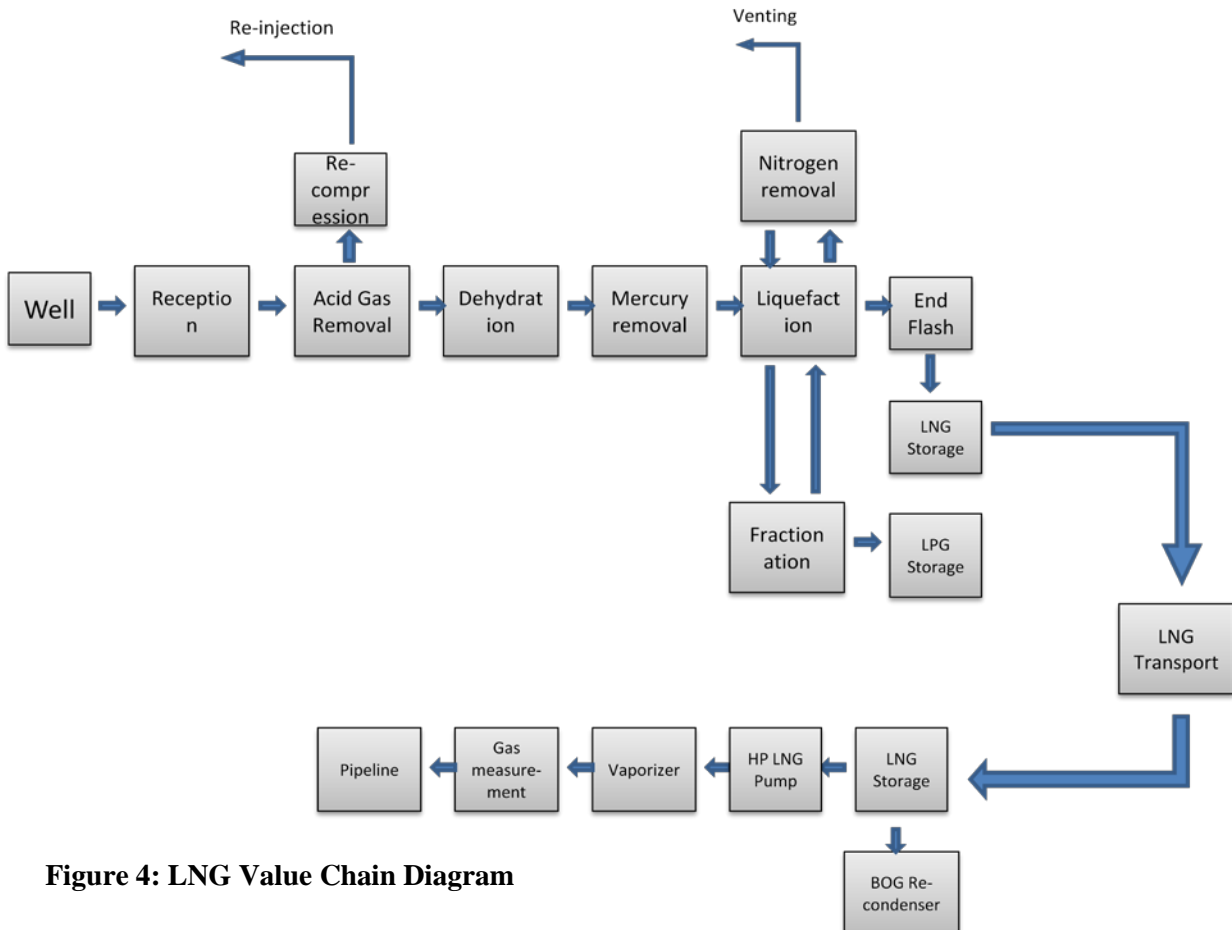


Figure 4: LNG Value Chain Diagram

When the gas arrives at the inlet facilities, both the temperature and the pressure have been reduced from the well heads. This results in condensation of both water and heavy hydrocarbons (HHC's) which are removed from the stream and treated separately. In addition, the hydrate inhibitors injected at the wellhead are regenerated here and sent back to the well.

The next step is removing the acid gases CO_2 and H_2S . This can be done in numerous different ways with amine treatment and molecular sieves being the most common. Amines are usually solved in water which means that the gas is saturated with it after the sour gas treatment. Therefore, the dehydration of the gas in most cases has to be placed subsequent to this process.

Water removal is for LNG plants mostly done by molecular sieves which can take the gas to extreme dryness. All of these steps ensure, in addition to the sales specifications, that there is no freeze out during the liquefaction.

Also, mercury (Hg) removal is especially needed for LNG production due to the corrosive effects it has on aluminum. Most LNG heat exchangers are made of aluminum and the presence of Hg will strongly effect the lifetime of these. The recommended maximum amount of Hg in the gas is typically set to ten nano-grams per cubic meter [4].

The last step of the pre-processing is the removal of heavy hydrocarbons. This can be done by a simple refrigeration cycle and a separator or by more complex fractionation processes. The more thorough removal of the smaller droplets is done by a scrubber.

The gas is then cooled down below the dew point by an appropriate cooling cycle. The selection of the type of cooling process will be carefully evaluated as this is heavily dependent on location, size and power supply among others. Some nitrogen rich gas is flashed off at the end for fuel before the liquid is stored in tanks.

Arriving at the receiving terminal the LNG is pumped to storage tanks. A high pressure pump increases the pressure of the liquid to the pipeline specifications before it is vaporized by either air or water heated vaporizers. The last part of the delivery chain consists of measurements and quality control before it is sold to the customer. A flow diagram of a typical LNG receiving facility is shown in Figure 5 [5].

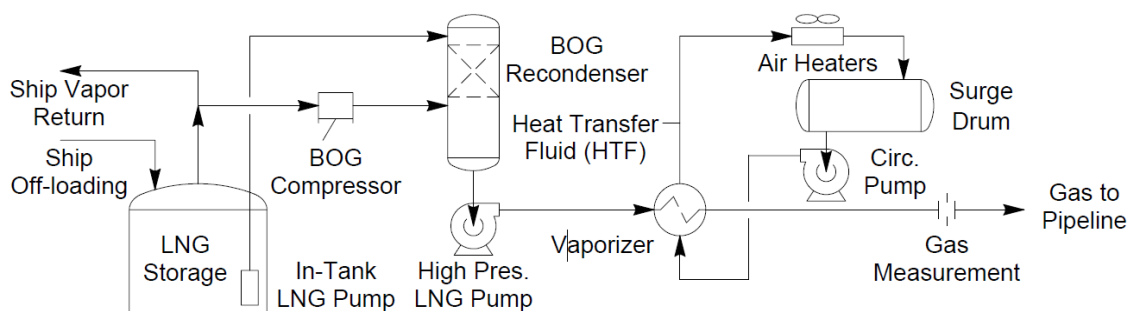


Figure 5: LNG Receiving Facility [5]

3 Survey of Concepts

As there are numerous patents, publications and possible solutions associated with the different concepts, a brief summary of these will be presented in this chapter and will be more thoroughly dealt with further on.

Liquefaction with solids formation

Methods have been suggested of liquefying gas directly from the well stream without any, or with only marginal pre-processing. The liquid produced will contain solids of various substances e.g. CO₂ and C₆+, depending on the gas specifications. In the most extreme ideas, the product will also contain solids of water and even sand. In this way the amount of equipment required for liquefaction is significantly reduced, resulting in a less complex and less expensive process. The main obstacle for this concept is the method of handling the generation of solids in the actual liquefaction. Some suggested solutions have been presented but the technology verification of the method however, is not yet satisfactory and the commercial applications are still unclear. In addition, the total profitability when considering transportation, storing and post-processing adds to the uncertainty.

3.1 LUWS

Liquefied Unprocessed Well Stream, or LUWS for short, is the result of a knowledge building project (KMB) funded by the Research Council of Norway in cooperation with IFE, NTNU, SINTEF and Statoil. Guttorm Olav Endrestøl is the project leader of this study which started in summer 2006 and is due to finish within 2010. A post doc position, employing Andre Fettouhi at the Technical University of Denmark, is funded by the same financiers and commenced in 2007 supervised by Kaj Thomsen. Fettouhi has mostly done work on developing software for freeze out issues in connection with the project. The basis of the concept-patent filed in 2003 in connection with this project is shown in Figure 6 and illustrates the basic steps for obtaining the specified liquid natural gas.

With this concept it would be possible to liquefy and transport the well stream gas without any pre-processing at all. The transported weight and volume might then include sand, water, HHC's, CO₂ and the light liquid hydrocarbons. The substances that will freeze out are allowed to do so but in a controlled way and in a predicted location in the process. By not needing to separate the water, removing the CO₂ content and other prerequisites as one need for conventional LNG, the process would be a great deal less complicated. The reduced processing equipment might make smaller gas fields possible to develop with special

emphasis on utilizing FPSO's. Part of the cooling for liquefaction would come from an expansion of the well stream by decreasing the pressure down to atmospheric levels. In the patent, a few possible patented expanders are mentioned that could handle the solids forming during the expansion. The mentioned are a dynamic expander with patent No. 4,771,612, and two static ones with patent No. 5,083,429 and 6,372,019 [6]. The latter is a Supersonic Separator described later. None of the expanders have been proven to handle solids.

Additional cooling will be required even for the highest well pressures as expansion does not deliver enough cooling to liquefy the whole stream. This can either be achieved by recompressing the remaining gas phase, cooling and expanding again or by solely cooling through a heat exchanger and an external cooling loop. The main focus for the KMB has been on heat exchanger freeze out and a test rig has been built for this purpose. The rig can handle pressures up to 500 bars and temperatures down to -170°C covering all possible areas of interest [7]. The key problem to the tests is related to the water content in the feed and has proved to be a difficult element to handle and predict.

The original thought for cooling is depicted in a ph-diagram in Figure 7. State 6 shows the wellhead conditions before the stream is expanded through 3 and ending at state 2. Part of the stream will here be liquefied and the remaining gas cooled to storage state 1.

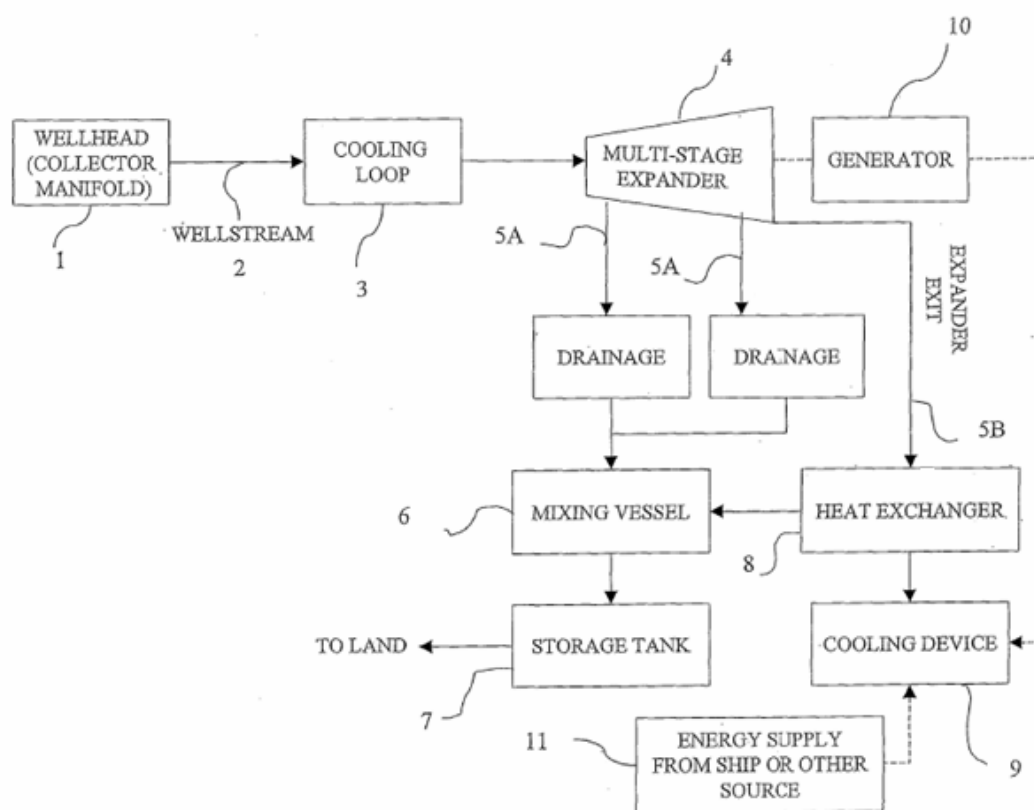


Figure 6: LUWS Patent diagram [6]

An alternative route has been proposed aiming at avoiding the phase envelope entirely and expanding the product in liquid phase thus preventing some of the challenges associated with the gas phase. Water however, is still a problem here and the formation of gas hydrates is of great concern.

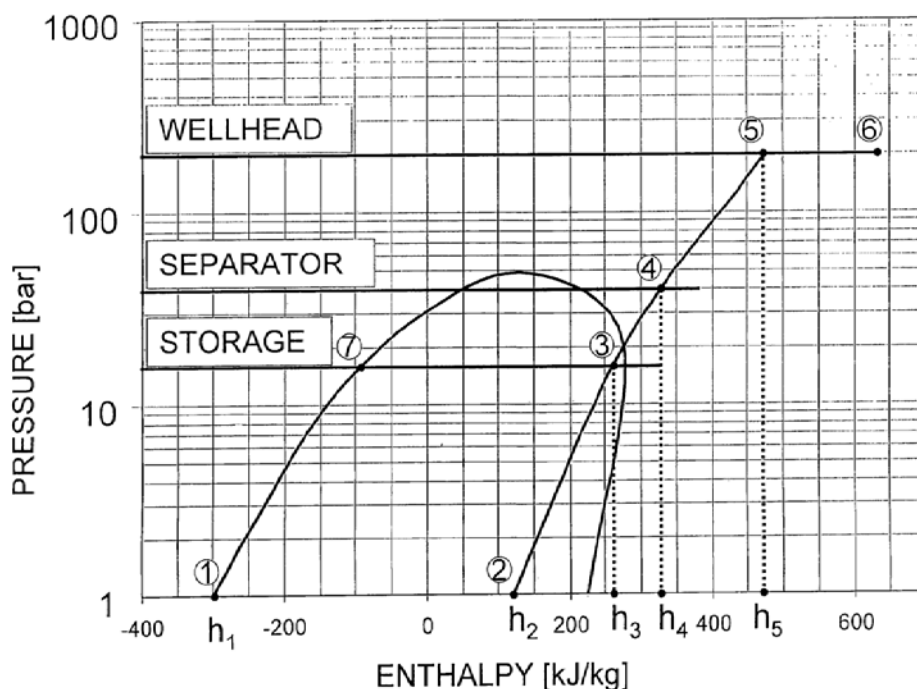


Figure 7: LUWS Patent PH diagram [6]

LUWS process description

The unprocessed well stream is led through a cooling loop to set the temperature to a few degrees above the temperatures at which hydrates would start forming. The typical range would be 10-30°C depending on the pressure of the stream. This cooling can be achieved by leading the gas through extra coiled pipes on the seabed or a similar arrangement. After entering the processing plant or FPSO, the stream is expanded and cooled through a multi stage expander resulting in parts of the gas condensing. This expansion is done in multiple stages and at each stage liquid is drained off. All the drained liquids from the expansion are routed to a mixing vessel.

The remaining gas, which will consist of the lighter components and mostly methane, is fed to a heat exchanger where it is further cooled and liquefied by an external cooling device. All the liquids are collected in a storage tank before it is shipped ashore. The expansion can power a generator that can supply the cooling cycle and reduce the amount of external energy required for liquefaction further.

3.2 Idaho National Laboratory: "Compact High Efficiency Natural Gas Liquefier"

Idaho National Laboratory, INL, has developed a method for producing LNG directly from transmission lines without the need for pre-treating the gas e.g. removing CO₂ and lowering the water dew point. This technology is very compact and in the patent being claimed to be competitive with some of the major LNG plants around the world. In 2000, INL went into a Cooperative Research and Development Agreement with Pacific Gas and Electric and Southern California Gas Company. In this cooperation, the construction of a 38m³ per day prototype plant took place and the tests of it verified the efficiency and uses. This method was mainly thought to be of small scale, but could just as easily be applied to bigger plants according to the patent. In addition, it was meant to be placed at a pressure let-down station where the high pipeline pressure is decreased to fit the transportation pressures downstream. Utilizing the power and the cooling on expansion, this method indicates a possibility of liquefying some of the gas without the need for further removal of contaminants. The well stream is in this concept mixed with methanol or a similar water absorbing substance to prevent hydrates from forming during the cool down. CO₂ is allowed to freeze out during the expansion to form a slurry comprising of liquefied gas and solid CO₂. The slurry is then separated by a hydro cyclone to form the LNG product and a thick slush of mostly solid CO₂. Although this patent suggests removing all the solids for reinjection or venting, one could imagine the possibility of transporting the slurry without any further processing mixed with the liquefied gases.

On May 5th 2005, Battelle Energy Alliance filed for a patent on the invention and the uses of it. Patent No. US 7,219,512 B1 [8].

Idaho Process description

Feed gas is firstly filtrated to remove any objects of some size (e.g. sand or other solids), which can obstruct the flow in the plant. The feed is then split into two separate streams, one cooling stream and one process stream. The cooling stream is expanded through a turbo expander giving a cold, low pressure stream. The power generated from the expander is used to further compress the process stream. The process stream is then cooled down by the cooling stream in a heat exchanger giving a cold, high pressure stream for further processing.

The process stream is then again split into a second cooling stream, CS₂, and the process stream. The CS₂ is expanded and further cools the process stream. The final product stream is then expanded to form a mixture of liquid, vapor and solids. This mixture can again be separated and the product will be a liquid-solid mixture comprising of CO₂, HHC and LNG. The expansion valve in this patent is a Joule-Thomson valve. However, the patent does not suggest or point out any manufacturers of such a valve. Nor does it indicate how the valve may cope with the formation of solids following the pressure decrease. The process flow diagram is shown in Figure 8.

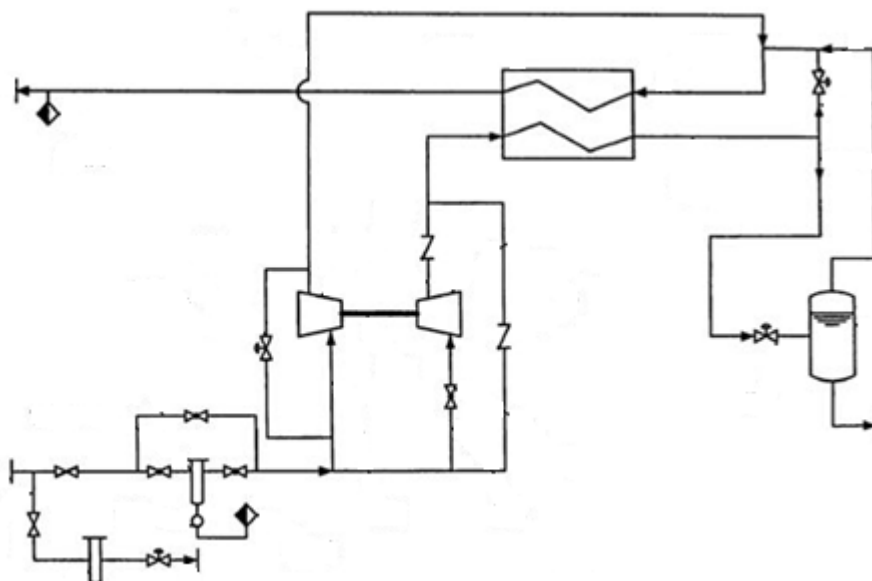


Figure 8: Idaho Process Flow Diagram [8]

3.3 Cool Energy Limited and the MicroCell/CryoCell technology

In January 1999, Professor Robert Amin working at Curtin University, Australia, began research on a method for removing CO₂ from a well stream as a part of the cryogenic process of liquefying natural gas. This study resulted in a process called MicroCell or Curtin Contamination Tolerant Process (CCTP). This process would remove CO₂ and other freezable components like H₂S by letting them form solids in a specially designed contactor vessel after being expanded through a JT-valve. His work on the topic in cooperation with Mr. Tony Kennaird of Core Laboratories made the basis of what became CryoCell in 2005 [9]. The patent for the early work done by professor Amin claimed the use of separating these contaminants in US patent No. 7,325,415 [10]. This patent describes a possible device for liquefying natural gas without pre-processing shown in Figure 9. The basic principal for the device is having a vessel constructed of a non adhesive material and expanding the gas stream into this. In addition, a vortex inside the container is provoked by injecting a sub stream of LNG for controlling the freeze zone. Successful tests of the device have been completed in conjunction with the filed patent.

The technology is now under ownership of Cool Energy Limited with Shell Technology Ventures Fund 1 as the major stock holder and is still being developed further under the name CryoCell [9]. Although the CryoCell technology is primarily designed as a CO₂ removal process, it would also allow the production of a LNG-slurry for transportation.

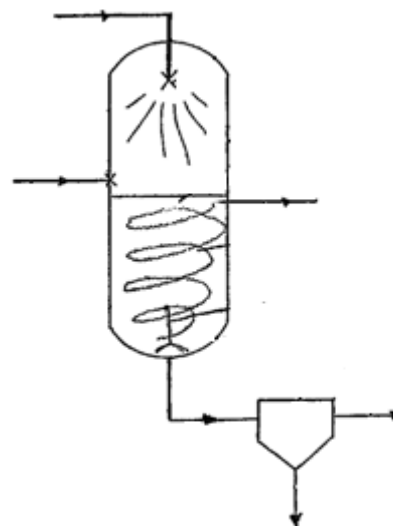


Figure 9: MicroCell Patent Vessel [10]

Liquefied Natural Gas under pressure

LNG under pressure is a new concept for transportation of natural gas and some value chains for this have been proposed by different parties. The motivation for production of LNG under pressure is the decrease of power requirements for liquefaction. Depending on the level of increased pressure, the saturation temperature will be higher than that of gas at atmospheric conditions. In addition, it has the positive side effect of increasing the solubility of the contaminants liquid resulting in a lower requirement for pre-processing without running the risk of freeze out. The main difficulties in connection with this concept are the means of containment in storage and transportation. Due to the low temperatures, ordinary steel container walls would need to be thick in addition to running the risk of rupturing due to the low temperature. A couple of companies have evaluated the possibility of implementing such gas transportation method resulting in numerous patents. ExxonMobil has especially put down a substantial effort in the evaluation, but also Aker Solutions and Chevron have their own processes and patents.

3.4 PLNG - Pressurized Liquefied Natural Gas

Pressurized Liquefied Natural Gas, or PLNG, is ExxonMobil's name for their new transportation method for natural gas involving above atmospheric pressures. Their first patent referring to PLNG was filed in 1998 and since then many solutions to various difficulties have been suggested and patented.

Unlike conventional LNG production, the whole delivery chain of PLNG is done under pressure. The pressure can be in the range of 1-7,6 MPa, but ExxonMobil suggests an optimal selection to be around 1,7 MPa corresponding to a -115°C dew point. The liquefaction can either be done by a refrigeration system and heat exchangers or by an expansion process. Because of the increased temperature of the product, the required power for liquefaction is about halved compared to conventional methods, again depending on the pressure. This results in a substantial reduction in expensive equipment i.e. heat exchangers, compressors and turbines, making the production less expensive.

The greatest savings might come from the reduction or possible elimination of CO_2 treating by an amine process. The increased pressure and elevated temperatures increases the solubility of CO_2 to about 2% when stored at 1,7 MPa. With a well stream containing less than this amount the amine treatment would be superfluous. The reductions in space and heat requirements due to this can be extensive. The solubility of aromatics and HHC's are also increased and the usually required scrub tower might also be unnecessary. The potential reduction in process equipment is represented in Figure 11, where the yellow areas represent the potential reductions.

Due to the plants compactness it would be ideal for implementing on an FPSO where space is costly. It could also make smaller gas fields more attractive to develop.

The PLNG is proposed transported in a 220x33x49 meter single insulated compartment on a specially designed ship shown in Figure 10.

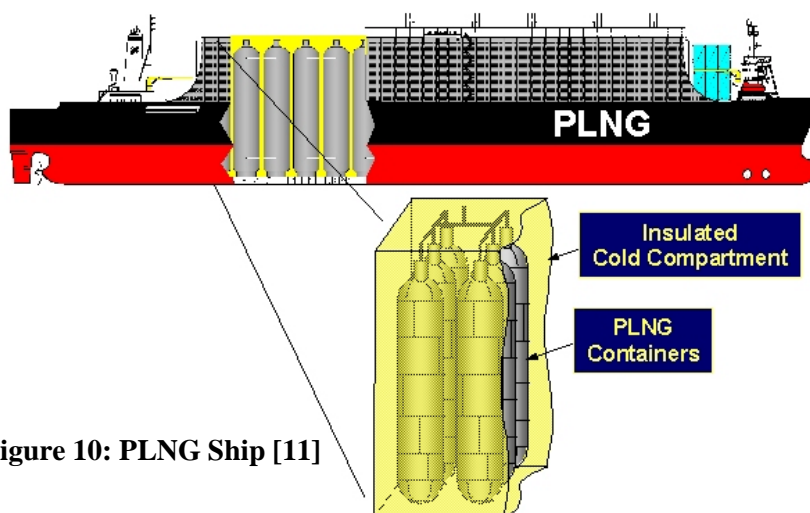


Figure 10: PLNG Ship [11]

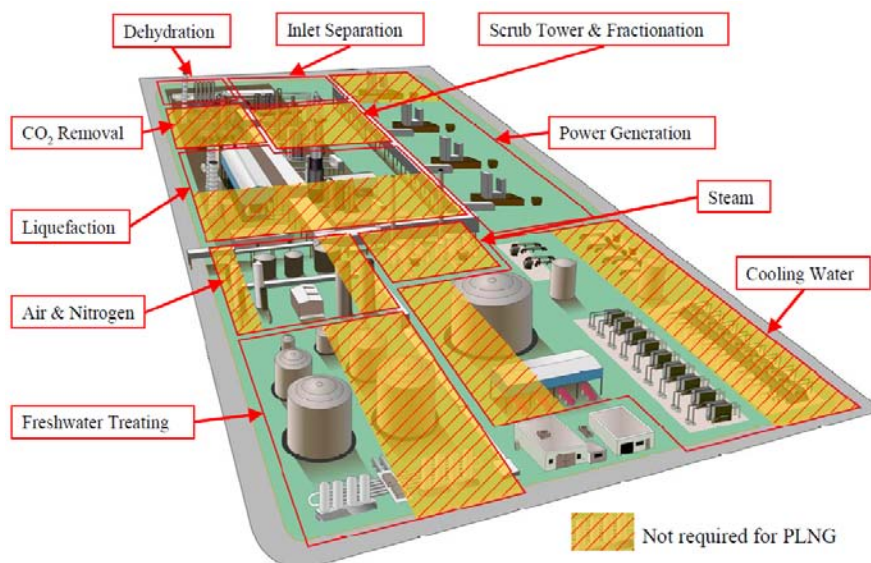


Figure 11: PLNG Reduced Space Requirements [11]

The high pressures at the cryogenic temperatures require special containers for storage and transportation. Ordinary cryogenic steels do not have the strength for handling these pressures without having a large wall thickness, resulting in a massively heavy ship. ExxonMobil has developed and patented a so called High Strength, Low Temperature steel, or HSLT steel, for this purpose and claims to be able to produce this at a relatively low cost. A prototype of the new containers has been built and tests of it have been successful [11].

ExxonMobil presented the technology at the GasTech convention in Bilbao, Spain in 2005 and the delivery chain from this presentation is shown in Figure 12.

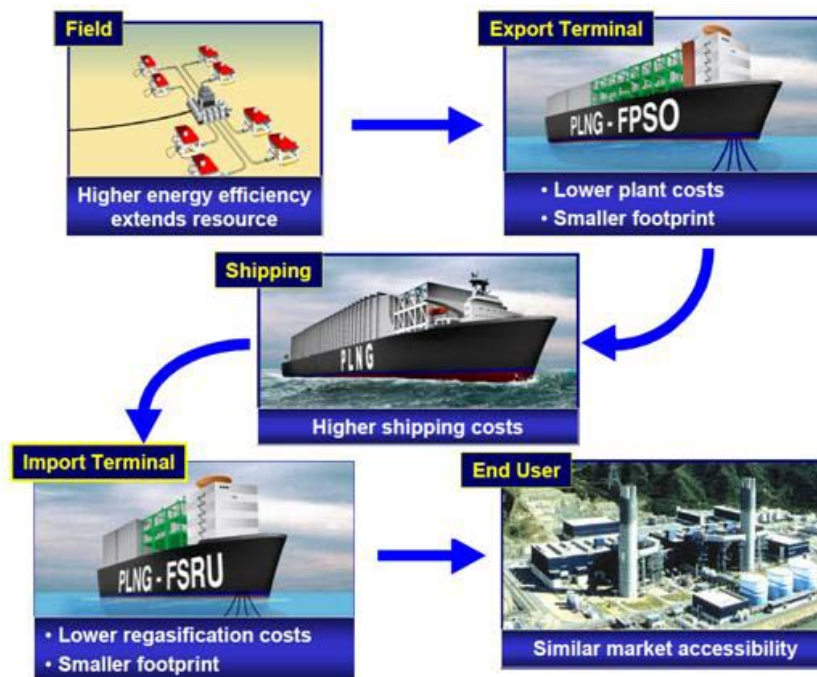


Figure 12: PLNG delivery Chain [11]

The main difference from a conventional LNG chain is the import terminal. This will need to be specially designed for PLNG which again sends the gas into a pipeline. This can be placed on a barge or a ship as to make the trading of the gas more flexible and can be positioned near a LNG terminal for ensuring gas supply between shipments. Another option that has been looked into is the possibility of storing the gas underground in salt caverns. The PLNG is then vaporized at the import terminal and injected into the caverns for storage. This would give a steady gas supply in addition to reducing storage costs.

A large number of patents have been filed by ExxonMobil Upstream Research Company with M. Minta and R. Bowen as the main contributors during their evaluation of the technology. Some of the main patents are shown below with connected flow diagrams.

Process for making pressurized liquefied natural gas from pressured natural gas using expansion cooling:

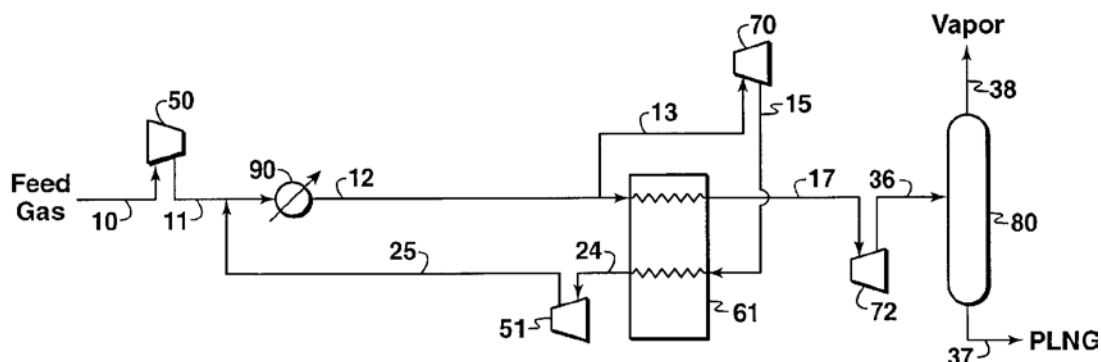


Figure 13: US Patent No. 6,378,330 B1 Apr. 30, 2002

Process for liquefying a natural gas stream containing at least one freezable component

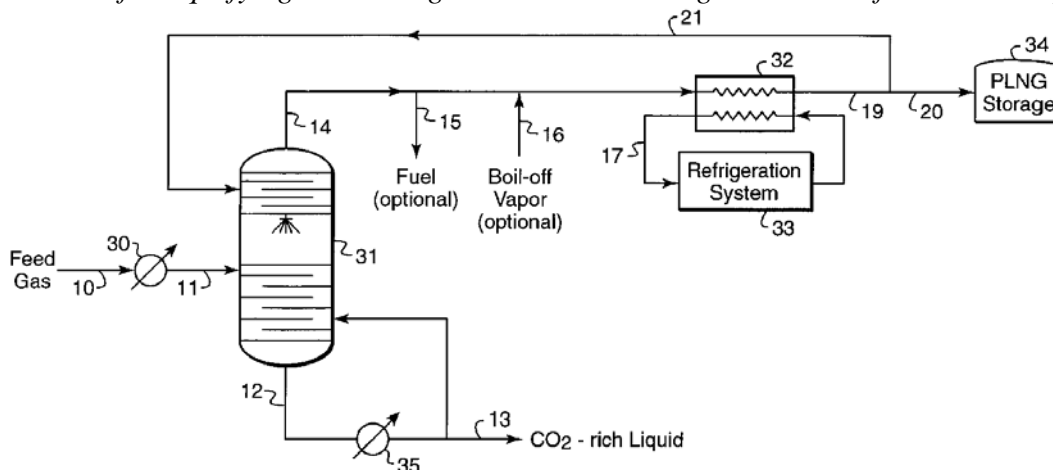


Figure 14: US Patent No. 5,956,971 Sept. 28, 1999

Process of manufacturing pressurized liquid natural gas containing heavy hydrocarbons

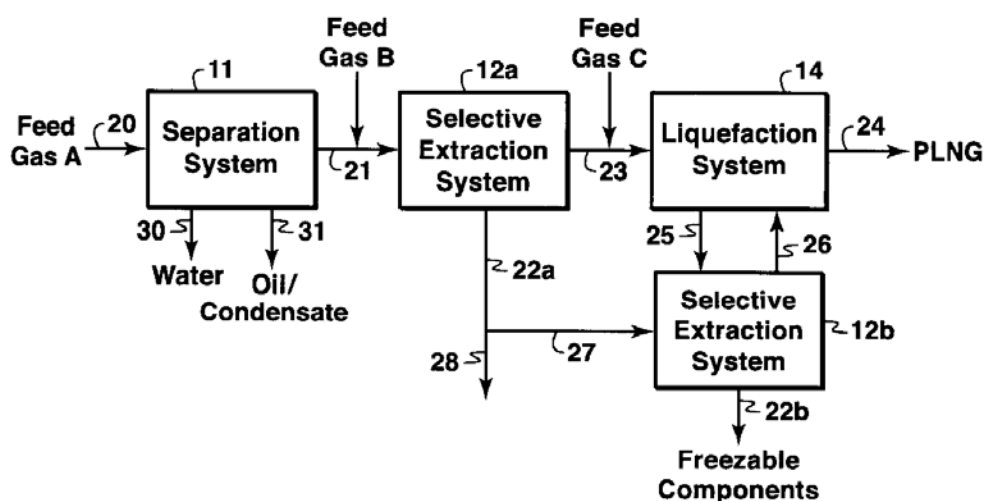


Figure 15: US Patent No. 6,539,747, B2 Apr. 1, 1999

3.5 HLG - Heavy liquefied gas

In 1992 Ugland Engineering filed patent US 5,199,266 “*Unprocessed petroleum gas transport*” which is shown in Figure 16 below. The patent explains a method for producing what is called heavy liquefied gas, or HLG, with minimal pre-processing and is similar to ExxonMobil’s PLNG. The well stream entering the plant is here removed of its solids and liquids before it is dried and cooled. The cooling is done under pressure and produces a liquid natural gas with a temperature above -120°C . The HLG is then stored at a pressure of between 10-30 bars corresponding to temperatures of -100°C to -120°C . Transportation must be done in a suitable vessel specially made to withstand the pressures. A concept diagram from the patent is shown in Figure 16.

In recent years Aker Kværner, now Aker Solutions, has pursued the method based on Ugland Engineering's work and from 2007 - 2009 the Norwegian Science Council has been funding the project. In addition, Statoil, Vigor and DNV have also participated in the development.

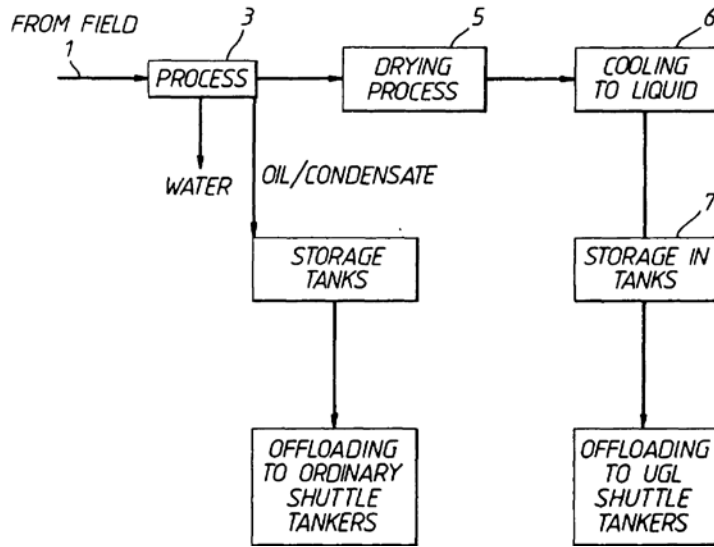


Figure 16: HLG Patent Figure

In connection with the project a case study was done based on producing 4 Mill Sm² gas per day and transporting it 1000 nautical miles for further processing. A suggested FPSO is modeled in Figure 17 containing both liquefaction, storage and offloading system. The case study concluded that HLG is competitive with pipeline transport above 1000nm if compression and dehydration facility is available and 500 if not. The topside area was estimated to be 5000m² depicted in Figure 18 [12].

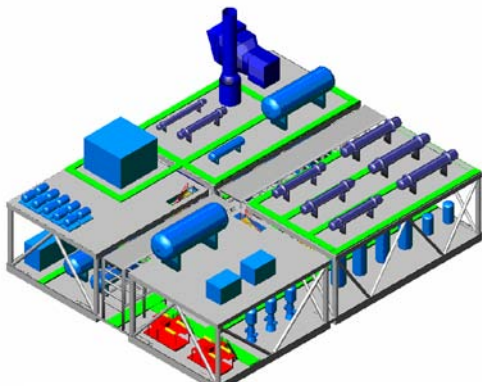


Figure 18: HLG Topside [12]

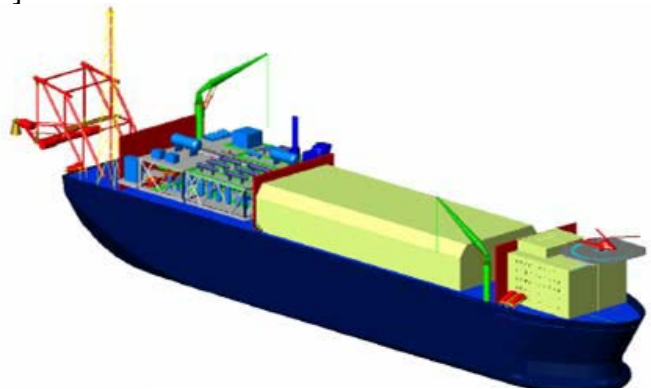


Figure 17: HLG FPSO [12]

A suggested receiving terminal was also modeled shown in Figure 19. The storage capacity of this is 32000 m² constructed in 9% nickel steel.

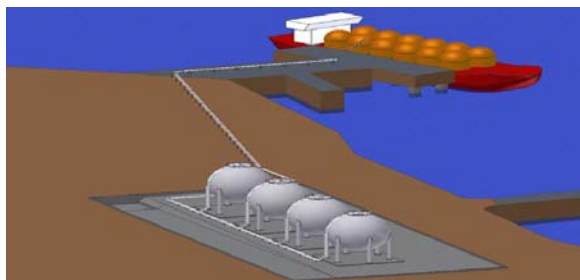


Figure 19: HLG Receiving facility [12]

3.6 Chevron LHG

Chevron filed for a patent (Application No. 20090095020) in 2008, regarding a method for producing liquefied gas from the associated gas generated during crude oil production. The liquefied product is called Liquid Heavy Gas or LHG. Where the practice has been to flare these gases, this method aims at utilizing them. The main mechanisms are drawn in Figure 20 showing the path from the oil field to the LHG storage tank. The end pressure suggested in the method is between 15 and 52 bars and the temperature above -48°C . At these conditions the process can handle CO_2 concentrations up to 5mole% with a 2% concentration being preferred. This again will eliminate the need for CO_2 removal allowing for a more economical production in remote areas. The LHG will according to the invention consist of between 30% to 70% methane and ethane, or $\text{C}_2\div$ components. The high concentration of heavy hydrocarbons in the gas mixture will result in the condensation pressures and temperatures of $\text{C}_2\div$ to be moderate compared to the other mentioned processes.

The relatively high temperatures make the use of ordinary transportation vessels for Liquid Petroleum Gases (LPG) possible for the LHG. These tankers have the capability of transporting liquids with a temperature above -48°C at pressures under 34 bars according to the patent. Consequentially the cost for developing transportation containers is significantly reduced. The LHG is shipped to an onshore processing plant for fractionation to pipeline gas and LPG's. All of the associated methane and ethane can however not be transformed to liquids for the LHG process for most fields without lowering the dew point too much. The surplus light hydrocarbons will be used as fuel for turbines and compressors at the production site as well as other utility energy demands like a refrigeration cycle. If there still is leftover gas this is suggested compressed to CNG or similar for storage or transportation. The proposed gas chilling for the process can be any expansion process (JT process, turbo expansion) or an external refrigeration process.

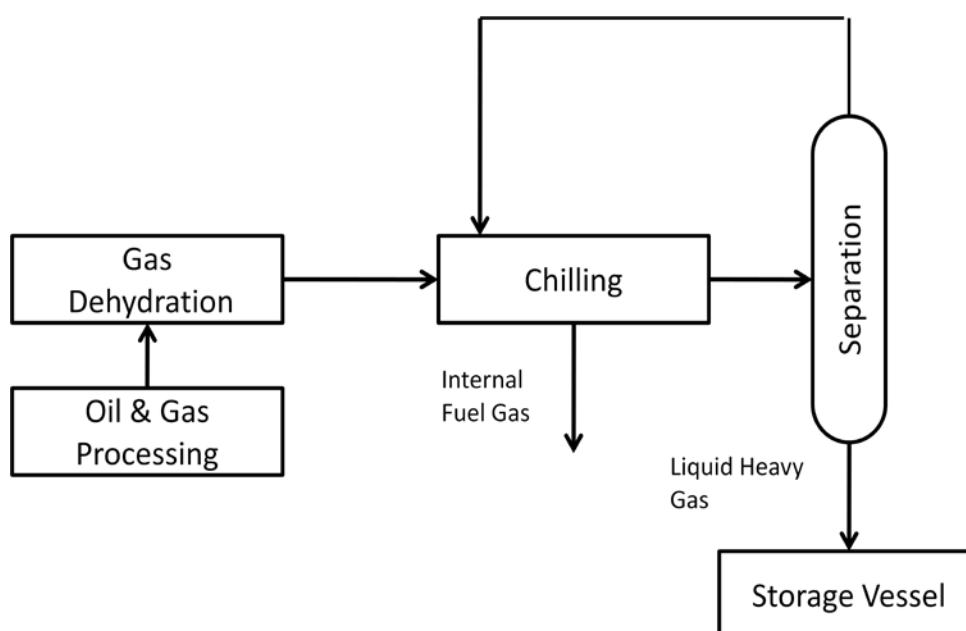


Figure 20: LHG Patent Diagram

4 Untraditional Separator Technologies

The new concepts can radically change the conditions of the end liquid product as well as the gas purity requirements. This will open for replacing the pre-processing technologies usually utilized today with new untraditional ones or even develop new custom technologies to be implemented. Presented in this chapter are some processes thought suitable for separating water and removing acid gas from the feed stream in the low processed gas value chains.

4.1 3S - Super Sonic Separator Technology

A new expansion process concept has been developed called Super Sonic Separation or SSS. The expansion in this device is near isentropic, not unlike known turbo-expanders, but combine these qualities in a way that make separation of the gasses and liquids formed during expansion it possible. Whereas the usual configuration for expansion is using a turbo-expander to right above the dew point and then expanding through a JT valve, the SSS technology can handle the formation of liquids. Since the JT expansion valve is an isenthalpic process, the product temperature is higher than the minimum attainable for an isentropic process like the turbo-expander. The main difference for the SSS process is that the expansion work is not transformed to shaft work but to kinetic energy in the form of a vortex in the tube as presented in Figure 21. After entering the SSS tube, the gas flow is transformed into a high vorticity, concentric swirl by static guide vanes. A Laval nozzle will then expand the gas to a supersonic velocity at low temperatures resulting in water and HHC's condensing in the stream. The concentric swirl in the tube makes it easy to remove the liquids as they are heavier than the gasses and will be forced to the walls.

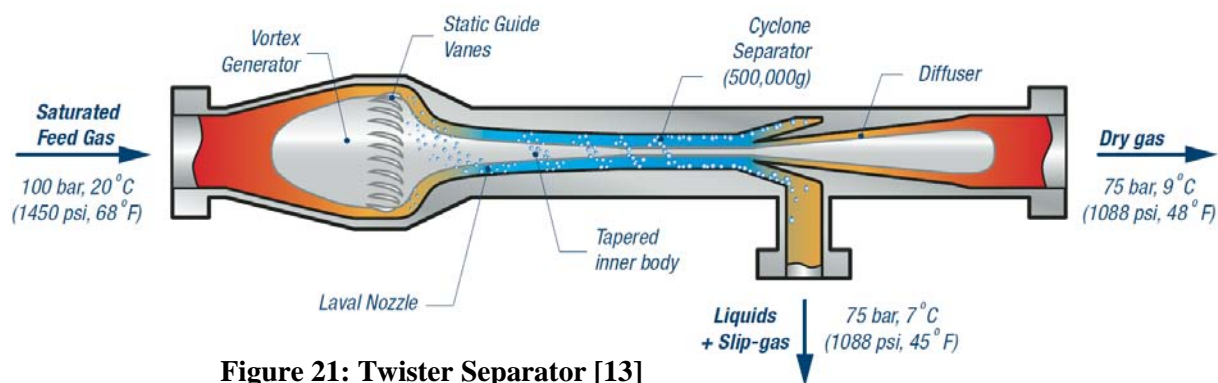


Figure 21: Twister Separator [13]

To recover the pressure allowing for a higher dry gas value, the streams are slowed down in diffusers before being discharged. The diffusers can recover around 80% of the free pressure in the stream [13].

The SSS technology has been developed by two separate parties with TransLang Technologies Ltd. on one side and Twister BV on the other. This has resulted in two different devices; 3S and Twister respectively. Both apparatuses rely on the same principles and are similar in construction. Twister is the result of a joint venture between Shell Technology Ventures and other investors with co-funding from the EU and The Netherlands. The separator has been vigorously tested and has now been successfully commissioned at two gas plants, one at the offshore B11 plant in Malaysia (2003) and one at the onshore Okoloma plant in Nigeria in 2009. Both the plants have six Twister tubes in parallel to support various mass flows engaging the amount of tubes required for a given flow [13].

Future potential for SSS Technology

Twister BV is now looking into the possibilities of extending their application of the device to new areas of gas processing. Studies are being executed on the possibility of CO₂, H₂S as well as mercury removal with the device in addition to installation subsea [9]. Having more tubes in series opens for extracting different substances in each processing step, avoiding problems with freeze out. This process line up might also require recompression between the stages. If a more durable device is manufactured, even solid formation within the gas vortex maybe tolerated expanding the area of use to concepts like LUWS.

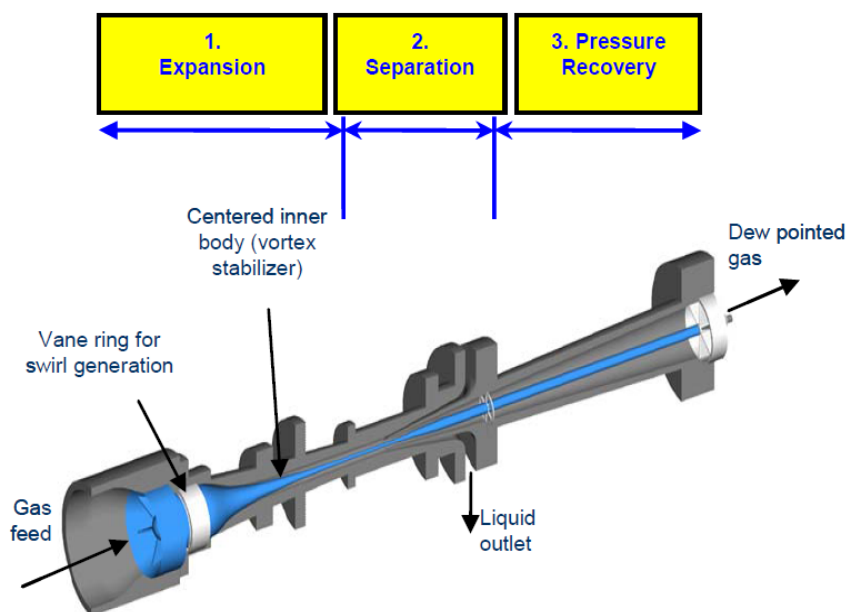


Figure 22: Twister Separator Stages [13]

4.2 CRYEX - Cryogenic Extraction

CRYEX is Chicago Bridge and Iron Company's (CB&I) patented process for separation of CO₂. This method is based on letting the CO₂ remain in the gas when it is dried and liquefied for later to be extracted as small solid particles on expansion. The main difference for the actual condensation part of the plant is that it has to be done under high pressure as opposed to conventional LNG production. The first commercially utilized CRYEX process was at the Newport LNG plant in Oregon in 1977 [14]. The technology is well proven with four peak shaving plants successfully installed in the USA.

The CRYEX Process

The CRYEX process needs a dehydrated feed gas as it cannot handle the formation of gas hydrates. Therefore, a water removal plant needs to be installed upstream of the CRYEX process. The condensation is done under pressure to raise the solubility of CO₂ in the liquid and to avoid the deposit of solids in the same way as for HLG/PLNG/LHG. The maximum concentration depends as mentioned earlier on the pressure levels and corresponding temperature as well as the composition of other components present. This creates an upper limit of the possible amount of CO₂ present in the feed gas which is approximately 5 mol% corresponding to a 42 bar pressure. When the gas is in a liquid state with dissolved CO₂ it is expanded through a JT valve decreasing the pressure to atmospheric levels and thus lowering the temperature to around -160°C. This pressure let-down is done in a specially designed CRYEX vessel where the CO₂ is allowed to form small solid particles. At the bottom of this drum the solids deposit and a slurry of CO₂ and LNG can be extracted. This slurry will consist of between 20-28 mol% CO₂ and based on plant specifications and energy demand is either separated or evaporated and used as fuel gas [15].

When depressurizing into the Cryex vessel, the mixture will move down into the phase envelope evaporating some of the LNG. This gas will have to be recompressed and mixed with the feed gas before again being condensed. At the top of the CRYEX vessel the product LNG is drawn off and pumped into a storage container. This LNG will have around 350 ppm CO₂, which is higher than conventional LNG and very small solid particles will float around in it [15]. This is however not a problem for the downstream shipping and processing. The schematics for the CRYEX process can be in Figure 23.

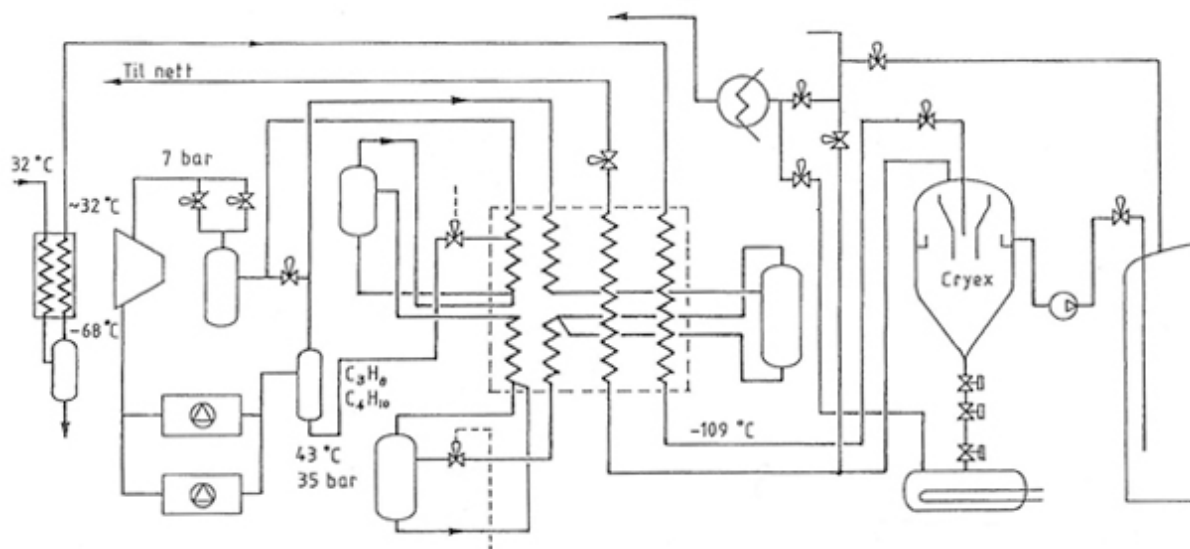


Figure 23: CRYEX Flow Diagram [15]

4.3 CryoCell

CryoCell is a novel CO₂ separation process patented by Cool Energy Limited based on the Micro-Cell technology mentioned earlier. The process has been tested in a demonstration plant at the AWE Xyris site and the results look promising for reducing costs and complexity of acid gas treating. Cool Energy is currently cooperating with Great Artesian Limited and Beach Petroleum Limited for a CryoCell plant in the Cooper Basin which will handle 20MMcsfd of gas [16]. The plant schematics are shown in Figure 24 and show how the gas is cooled before it is expanded through a JT-valve and into a container. Here CO₂ freezes and falls to the bottom of the column where it is heated and melted to a liquid before extracted. The liquid CO₂ can then easily be pumped up to the CO₂ storage pressure and sent for reinjection.

Due to the simplicity of the process, the capital costs can be reduced as much as 20-40% depending on the CO₂ content compared to conventional amine treatment [17]. The heat demand associated with the regenerative process in an amine plant is also eliminated saving huge amounts of thermal energy. Even though it can handle a wide range of CO₂ content, the process requires a very dry feed gas, so dehydration of the gas is an absolute necessity. Currently, the commercialized plant design can only reduce the CO₂ content to pipe specifications, but future development for LNG pre-treatment is anticipated [17]. The minimum CO₂ content achieved is around 200 ppm which is by far enough for a pressurized LNG product like PLNG or HLG that can tolerate 1-3 mol percent CO₂. The maximum successfully tested feed CO₂ concentration is 60% [9].

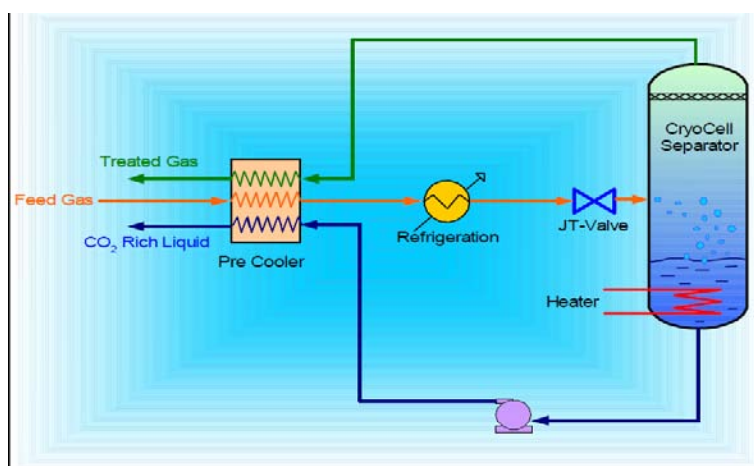


Figure 24: CryoCell Flow Diagram [9]

The technology is still under development and its durability and reliability is not yet tested in a large scale production site. This makes the device less attractive when considering integration with the low processed gas value chain and especially combined with other unproven applications.

5 Evaluation of processes and equipment

The different concepts will have a wide range of variables which will influence the value chains in positive as well as negative ways. The number of units of equipment will vary heavily and the complexity and uncertainty elements are also important factors to consider. In this chapter the value chains for the different concepts will be discussed and elements in them evaluated.

5.1 Concept groups

The concepts described in the earlier chapters can be categorized into groups. One group will consist of liquid hydrocarbons transported at elevated pressure and include HLG, PLNG and LHG. The value chains for these will be similar in structure even though LHG in some cases may be significantly simplified in the pre-processing step. The second group will be where the freezable components are allowed to form solids in a controlled manner. Here, this will include LUWS or any other possible arrangements which include solids discussed previously. The different concepts are plotted in Figure 25: Concept P-T diagram together with conventional LNG and a compressed natural gas option. The HLG concept has been divided into two pressure levels; one at 12 bars and another at 20. This can of course be optimized when the final gas composition etc is known. Even though we operate at relatively high pressures for the LHG concept, we can see that it is far from getting close to the CNG pressure which is around 200 bars.

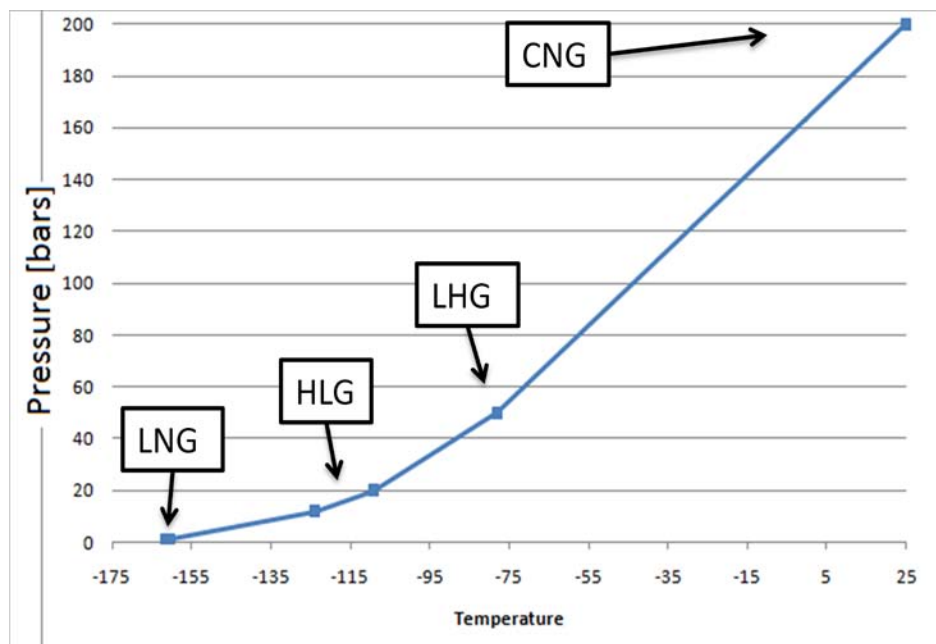


Figure 25: Concept P-T diagram

5.2 Value chain for LUWS

The original idea for the LUWS concept was to liquefy and transport all of the substances that come from the well and in this way eliminate all the pre-processing equipment. The product would then contain even sand, mud and water. As the well stream can contain a large portion of these unwanted contaminants and the removal of some of them is fairly straight forward, separation of at least sand and mud is seen as a necessity [7].

As we see in the box diagram in Figure 26, the operations usually found in the pre-processing stage for LNG is now shifted further down the chain at the receiving site. This will have a large impact on the value chain and the considerations when evaluating it. In the diagram, the red colored boxes are the areas with possibly the most difficulties and uncertainty, while the green area is the reduced requirements, compared to LNG.

The main area of application for LUWS is not proposed to be big base-load plants, but smaller remotely situated gas fields where the available infrastructure is scarce. The plant could be installed on a FPSO or onshore, with a floating alternative being the most practical for extracting gas from smaller reservoirs.

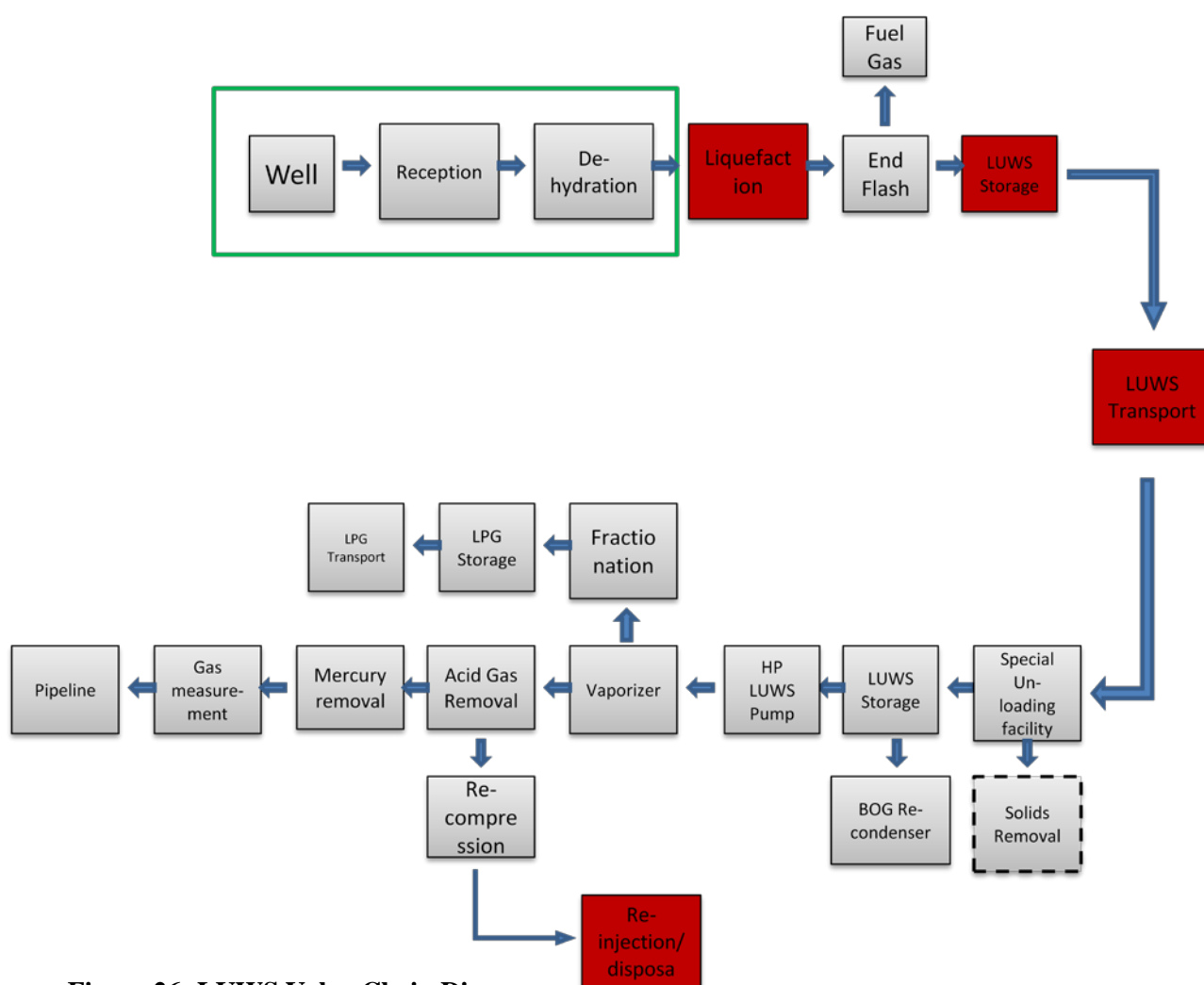


Figure 26: LUWS Value Chain Diagram

5.2.1 Dehydration

Removing the water content from the feed stream was not part of the original idea for LUWS as this would complicate the process. Nevertheless, the problems arising dealing with natural gas alongside water at low temperatures, might cause bigger problems than the savings when excluding it. Typical water content for the well stream is around 3% so including the water in the transported product will directly reduce the useful products accordingly [4]. At least the condensed water before cooling should be removed leaving only water saturated gas at around 20°C. Removing the water will contribute to a more profitable shipping part in the chain, but the most important motivation for dehydration is the prevention of gas hydrates formation. In the presents of water, gasses in the feed will form gas hydrates under certain conditions. At -161°C formation of such hydrates will take place under any pressure and can constitute large problems when doing so. Removing the water will also eliminate the most challenging component in regard of freeze out during the liquefaction.

While for LNG the water content should be reduced to under 150-50 ppm, it may be possible to leave more water in the gas for a LUWS concept. As we are already prepared for solids formation in the liquefaction, a small amount of water could be allowed to form hydrates without causing problems. This opens for larger options when selecting the dehydration process and a vigorous adsorption system may not be required. The hydrates will form early during the cooling and will make the freeze out difficult to predict.

In the case of a glycol absorption process like Tri-Ethylene Glycol (TEG), problems will arise for a process with as little pre-processing as LUWS. Acid gas and condensate is normally removed before the dehydration, but because we want to leave these in the product they will be at least partially present through the absorption. Both acid gas and aromatic hydrocarbons will be absorbed along with the water and would have to be handled when regenerating the glycol [18]. Since CO₂ and HHC's are a significant part of the feed stream to the dehydration, a large amount of these substances will have to be separated from the condensed water. In addition, the liquid hydrocarbons entering the process will cause extensive chemical foaming in the unit.

5.2.2 Liquefaction

The main obstacle for accomplishing a technically feasible LUWS chain lies in the liquefaction part of the process and how to predict and control the freeze zone. This has also been the main area of research [7]. In principle, there are two ways of removing the heat from the gas; heat exchange or an expansion cycle.

Heat exchange

Cooling the gas down to -160°C will require a system similar to well proven LNG systems, but the heat exchangers will need to be significantly changed to handle the solid formation. The build material of the heat exchangers should be changed by one that limits the adhesion of passing solids as well as frosting of the components on the cold surfaces inside. A non-sticky surface with a high heat transfer coefficient is needed or the solid formation should take place away from any surface.

Heat exchangers are built with relatively small tubing sizes to maximize the contact surface and reducing the size of the unit. The small tubing will cause problems if there are solids

flowing are over a certain size. Together, these can merge and form a solid blockage in the heat exchanger which would lead to downtime.

Another possibility is to keep the pressure at a high level throughout the liquefaction preventing the temperature dropping below the freeze out points. After all the feed is condensed it can be sub-cooled and expanded through a valve letting solids form in much the same way as a CRYEX process. This would require the same dehydration as for conventional LNG.

Expansion process

A way to avoid having freeze-out problems in the heat exchangers is to provide the cooling through expansion cooling. Utilizing a Joule-Thomson valve or a turbo expander, the temperature will drop and a part of the gas will liquefy. A near isentropic expander should be used in preference to a valve, as it gives a bigger temperature drop.

The gas will have a higher inlet pressure than for other processes due to the absence of pre-processing requirements such as the amine stripper. This gives a lot of free energy for cooling but is far from being enough to liquefy more than a small fraction of the gas. The remaining warm flash gas will again need to be cooled by heat exchange or by recompression and expansion. This gas will now consist of the lighter components, mainly methane and nitrogen, and far less of the freezable ones as these will form solids at higher temperatures. An arrangement with a contactor vessel like the MicroCell could control the freeze out zone.

5.2.3 Storage

The produced product is thought to be stored close to atmospheric pressures and therefore the tanks will have a lot in common with conventional LNG storage tanks. The temperature will also be in the same region, about -160°C . As LNG tanks have undergone vigorous testing and studies, the knowledge of them can be transferred to the new LUWS tanks. LUWS will however, contain a large portion of solids, e.g. 10-20%, and it will have to be taken into account when designing the vessel.

Solid CO_2 , or dry ice, will have a density of around $1,562 \text{ kg/dm}^3$ [19]. Because natural gas will have a density similar to liquid methane, which again is $0,422 \text{ kg/dm}^3$, the dry ice might settle at the bottom of the tank quite quickly [19]. If H_2S is not removed either, this will form a solid fraction with a density of about $1,1 \text{ kg/dm}^3$. As the H_2S fraction is small this will be negligible compared to the other solids. In addition there will be approximately 6 mole% HHC's in the gas mix that will form solids at -160°C resulting in yet more species of solids. The solids might not cause problems as long as they are mixed with the liquids, forming a slurry, but as soon as they divide into layers they can make the loading and unloading complex. If they are left immovable over a period of time the layers made up of small solid particles may form larger solid layers, making solids suspension in the liquid less feasible. If practical, a circulation system that inhibits the solids to cluster could be installed in the tanks. However, the large differences in density for the liquid and solid fraction, in addition to having over 10 mole% solids can make this an ineffective and costly measure. If the phase separation is unwanted is also an issue as solids removal options are evaluated at the receiving site.

Usually the presence of water and CO_2 will pose a threat to corrosion in a steel tank [20]. The free water will react with the carbon forming carbonic acid, or H_2CO_3 , which again corrodes

the steel forming corrosion products like FeCO_3 among others [20] . In the one option of LUWS without pre-processing dehydration, there will be both CO_2 and water present, but both the substances will be in solid phase preventing the reactions to take place. However, there are times in the LUWS process where the temperatures are above the hydrate formation limits. This can be when loading/unloading the shipping vessel or when the gas is evaporated.

5.2.4 Transportation

In theory, the LUWS product can be shipped in ordinary LNG tanks with only minor design modifications. There are however major differences that might cause problems in the utilization. The new tanks would have to withstand solids in contact with the container walls during transportation. In difference to the storage tanks at the production site, the content of the containers used under transportation will be moving and exposed to sloshing. The solids in the containers will then consequentially touch and scrape the walls exposing the wall materials to a possible erosion problem. Measures that could be taken include reinforcing of the walls or a more resistant building material.

A LNG shipment that has a duration of 20 days or so will have a substantial amount of boil-off gas as heat leaks into the containers. This amount is usually around 5% of the cargo [4]. Since it is the liquid components that will vaporize first during transportation and since this liquid is similar to conventional LNG, the boil-off gas should not be very different from what the industry is used to today. A standard small re-liquefaction unit could therefore be installed on a LUWS vessel.

Usually, the boil-off gas will result in ageing of the gas when the more volatile components vaporize. This will increase the Gross Calorific Value (GCV) during the transportation time and one must take measures to ensure the requirements at arrival still are satisfied. This will not be a problem for the LUWS concept since this will need post processing at the receiving point in any case and adjustments may be done then.

5.2.5 Receiving facilities

If the product is a fine slurry with free floating solids in suspension, the use of ordinary pumps may be possible. But arriving at the delivery site, the product species may be in separated layers, thus inhibiting the use of conventional unloading systems. A typical distribution of components in the shipping tanks could look like the one in Figure 27, if the layers are allowed to settle.

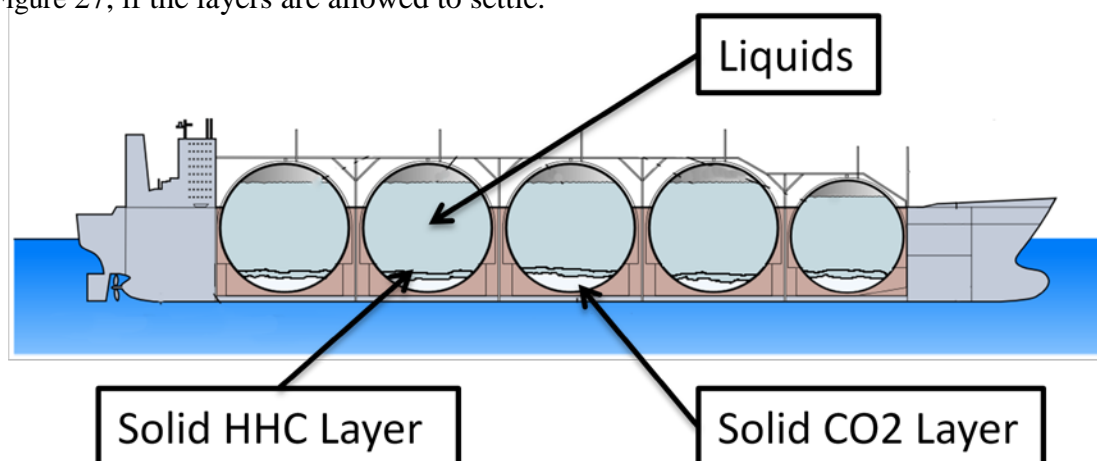


Figure 27: LUWS Settling

Cryogenic separation of CO₂

As the solids accumulate at the bottom of the storage tank, the liquid light-end hydrocarbons can be extracted with a cryogenic pump. The pump must tolerate some degree of solid as the liquid may have debris floating around in it. When there are mostly solids left in the tank a heat source should be utilized to increase the temperature in the tank thus melting the heavy hydrocarbons like Figure 28 shows. The maximum temperature should be kept well below the freezing point of carbon dioxide and in this way avoid this being vaporized. As CO₂ has a normal boiling point below the freezing point, the only CO₂ leaving the tank will be in gas phase and could be sent to the pipeline sales gas for heating value reduction.

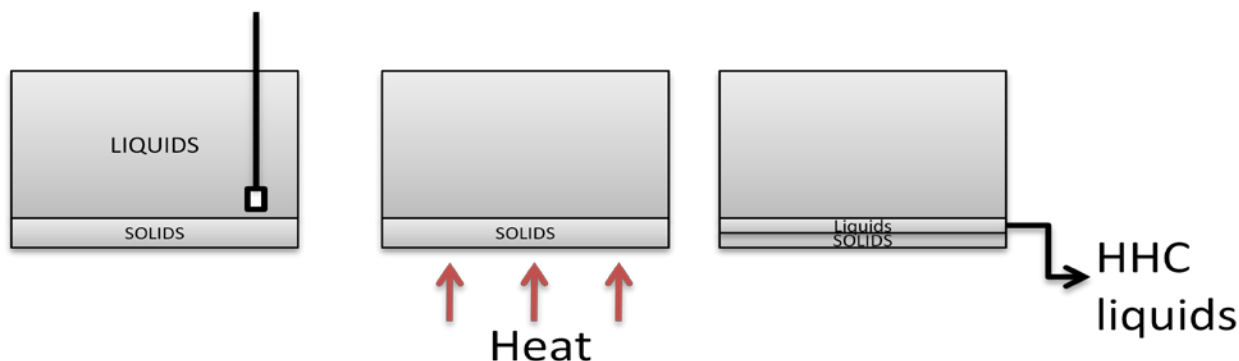


Figure 28: Mechanical Solids Separation

Reaching the target temperature, the solids will contain a large concentration of CO₂ and smaller of heavy hydrocarbons from C₈+ and aromatics. These will need to be separated by other means or shipped back to the liquefaction plant for re-gasified re-injection.

5.2.6 Other pre-processing units

Mercury may become a problem for the LUWS concept if not removed. As mentioned, mercury will react with aluminum in the heat exchangers, forming mercury amalgams. A possible approach will be to have a different build material for the heat exchangers and avoid the problem or a simple Hg removal unit will have to be installed. Means would typically include activated charcoal-sulfur bed systems.

5.2.7 Post processing and CO₂ disposal

As there is no treatment of the gas before liquefaction, all the necessary processing will have to be done at the receiving site. LPG's and NGL's should be extracted and the CO₂ fraction lowered to comply with the sales specifications.

The gas at the receiving end of the chain will contain all the carbon dioxide from the well stream when it is vaporized. The maximum CO₂ content in the end product can only be 2,5% in compliance with the pipeline specifications, so all the excess gas must be disposed of. Since the receiving terminal usually is far away from any reservoir, the carbon dioxide cannot be re-injected at site and must therefore be transported for disposal elsewhere. Building a pipeline exclusively for this purpose would be costly and would be an unrealistic measure for reducing the CO₂ emissions.

One possible solution would be to transport the CO₂ back to the production site with the same ship it came in on since this is practically empty on the return trip. A proposed value chain for a CO₂ return-shipment for conventional LNG has been proposed by Aspelund and Gundersen and much of the same principles may be utilized for LUWS [21]. The CO₂ cold when heated may be used for pre-cooling of the well stream. A simplified value chain is shown in Figure 29 where the solids are returned with the shipping vessel for reinjection.

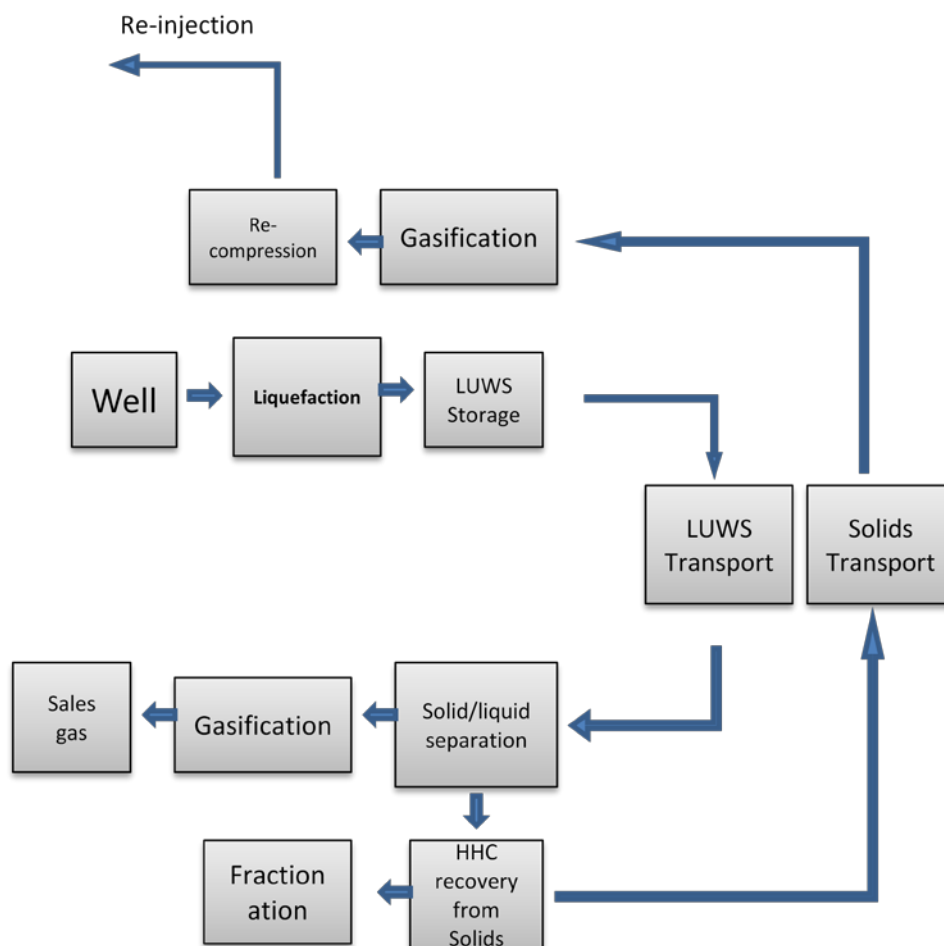


Figure 29: Solids Return Transport Diagram

As the phases can already easily be separated at the production site mechanically, it might be favorable to remove the CO₂ there instead of transporting it first. This will save around 2,5% of the cargo space and avoid having solid CO₂ in the tanks on the return trip. However, this would need to be evaluated for the site specific cases.

5.2.8 Slurry behavior in Storage

The freeze out components will together with the lighter liquid fractions make up a slurry with some solid particles in possible suspension. The slurry can either be of a settling or a non-settling type [22]. A non-settling type will consist of solid particles floating practically uniformly in the liquid or it could settle so slowly that for transportation purposes could be regarded as non-settling. This type can have a Newtonian flow behavior and may be pumped in a laminar fashion. The settling type will consist of larger solid particles at lower

concentrations and will after a while settle above or below the liquid, depending on the densities. The solids will in this case not affect the viscosities of the liquids as the layers are separated. Settling slurries may be pumped, or influenced by a jet stream, to form a turbulent flow in which the solids may appear non-settling.

How the slurry behaves will largely be dependent on the solid particle size and densities of both the liquid and solids. Predicting the particle size may be difficult as it is dependent on numerous variables [23]. For LUWS, this will include how the solids are formed in the liquefaction cycle by either expansion cooling or heat exchangers. Particles will most likely be different in the different solutions selected.

Some parameters affecting the solid particle sizes in a storage tank are [23]:

Attrition

Attrition is the mechanism where the solids in moving slurry become smaller either due to breakage or abrasion. Breakage is when the crystals are broken up into smaller crystals due to collisions with the walls or other obstacles it may run into. Abrasion is when small fragments from larger crystals are removed. Breakage will need much higher collision energy than abrasion.

Agglomeration

When two smaller crystals form a larger one, we have agglomeration. The speed at which this happens is again dependant on crystal size, slurry distribution and temperature. CO₂ in LUWS may have a lower agglomeration speed due to the low stickiness of the solids at -160°C.

Ostwald ripening

When stored for relatively long periods of time, solids may experience what is known as Ostwald ripening. This is when large solid crystals grow in size taking mass from smaller crystals. This will happen as the molecules on a surface are energetically less stable than in the interior [23]. Large particles with a low surface to volume ratio will therefore increase in size while the smaller ones decrease. This effect might not be of big concern for LUWS as the liquid can have a short storage time.

Due to the major temperature differences in the liquid and the ambient, around 185°C, there will be a potentially large amount of heat entering the vessel in the same way as for LNG. During transportation, some of the light hydrocarbons and nitrogen, will vaporize due to this heat flux and will manipulate the movement of the solid particles in the tanks. If this effect is large enough, a circulation system may not be needed and the solids not settle at the bottom of the tanks.

5.2.9 Possible LUWS approaches

As the main obstacle for the LUWS concept is the freeze out during liquefaction, a thought solution for this is proposed. Instead of utilizing a heat exchanger or an expansion process as the cooling means, a simple bubble column reactor without trays could suffice. The unprocessed gas stream would be injected into the column where it mixes with LNG at around -160°C . The gas should be distributed through a fine mesh to spread the gas flow over the whole column. This would ensure the gas bubbles to become sufficiently small as shown in Figure 30. The gas will here be cooled down well below the freeze out temperature for the freezable components which will form solids making a slurry. The column size should be designed in such a way that the freezable component will have time to be cooled and form solids. The injected gas stream will have a slightly elevated pressure, e.g. 2 bars, while the produces LUWS will be at 1 atm.

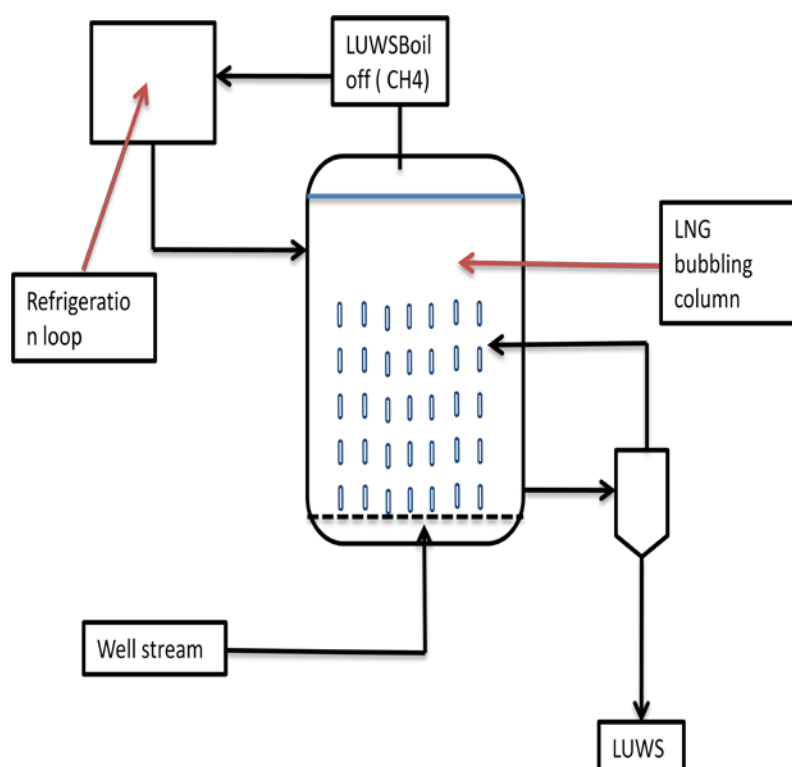


Figure 30: Possible LUWS Solution

As the solids form, heat from the well stream gas will vaporize part of the LNG in the tank which will leave the column at the top. As this boil off gas is almost pure methane, this can be re-liquefied in a conventional LNG process with no modifications of the heat exchangers and sent back to the column. LUWS will be drawn off for shipment at the bottom of the column and will contain both a part solids and a larger part LNG. If too much liquid is drawn off, some of this should be sent back into the column. Many units in parallel would be necessary for a large production rate and the columns may be impractically high for giving the gas time to be cooled. In this method, all the cooling is provided at -160°C which means the temperature lift is unnecessary high which again will lead to a badly performing process, energy wise. A possibility would be to have a different cooling medium than LNG, e.g. one with a vaporization temperature close to the freeze out temperatures, and separate this from the lean gas in a second processing unit. It is also of high importance that the injected gas does not come into contact with the column walls, as this would lead to solid deposits here.

A simple PRO/II simulation has been done as shown in Figure 31. This shows that the energy consumption will be greatly increased compared to the other processes with a specific energy consumption of around 0,87 kWh/kg or 6,55% of the higher heating value. This is not acceptable for large optimized liquefaction plants, but for the smallest reservoirs with a remote location the alternative of a full scale preprocessing may just as well be as costly. This method would also open for the possibility of leaving the water in the feed leaving only the liquefaction process and the column arrangement. The large amount of CO₂ produced from the power plant could be re-injected into the well, or separated and injected into the column for transport in the LUWS. The conditions and assumptions for the simulation are given in chapter 6.1.

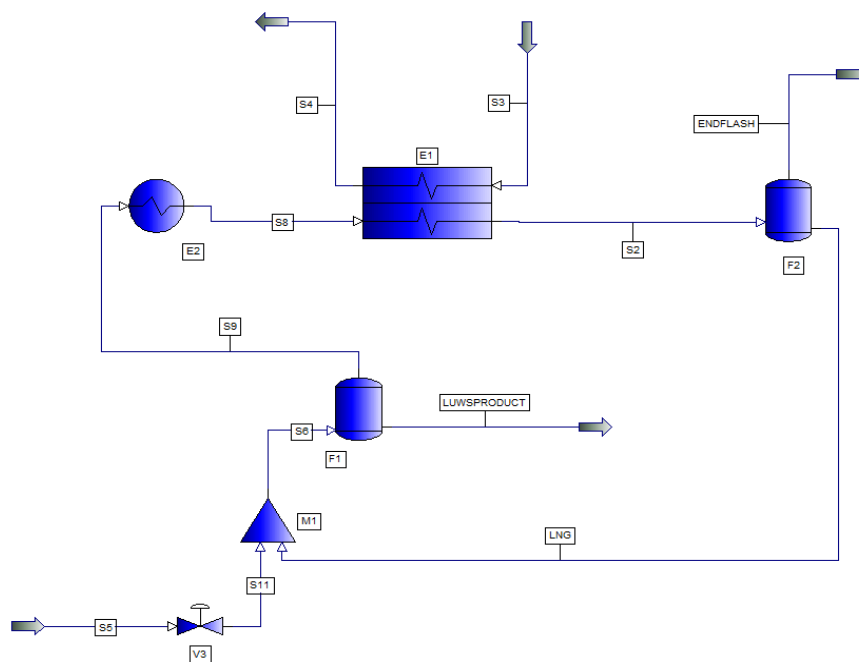


Figure 31: Solution: Flow Diagram of possible LUWS

5.3 Value chain for HLG/PLNG/LHG

Both HLG, PLNG and to some extent LHG, will be treated under the same chapter as these are all fairly similar in construction and the boundaries of how they differ can be unclear. The names used for the concepts in this chapter depend on the patents or origin, but the topics covered are interchangeable. A general value chain for HLG or similar, will not be entirely different from a conventional LNG chain and will under most circumstances include all the same parts.

The main value chain steps will however comprise of different systems and requirements depending on the well stream specifications and the location of the gas field. A detailed block diagram of the whole process is illustrated in Figure 32 below where one can follow the processing steps from the well stream to the delivery to a pipeline with the required specifications. Again the green colored boxes represent a simplified or improved part while the red indicates a possible complication or uncertainty. In this section we will go through the different steps and evaluate solutions for processes and equipment.

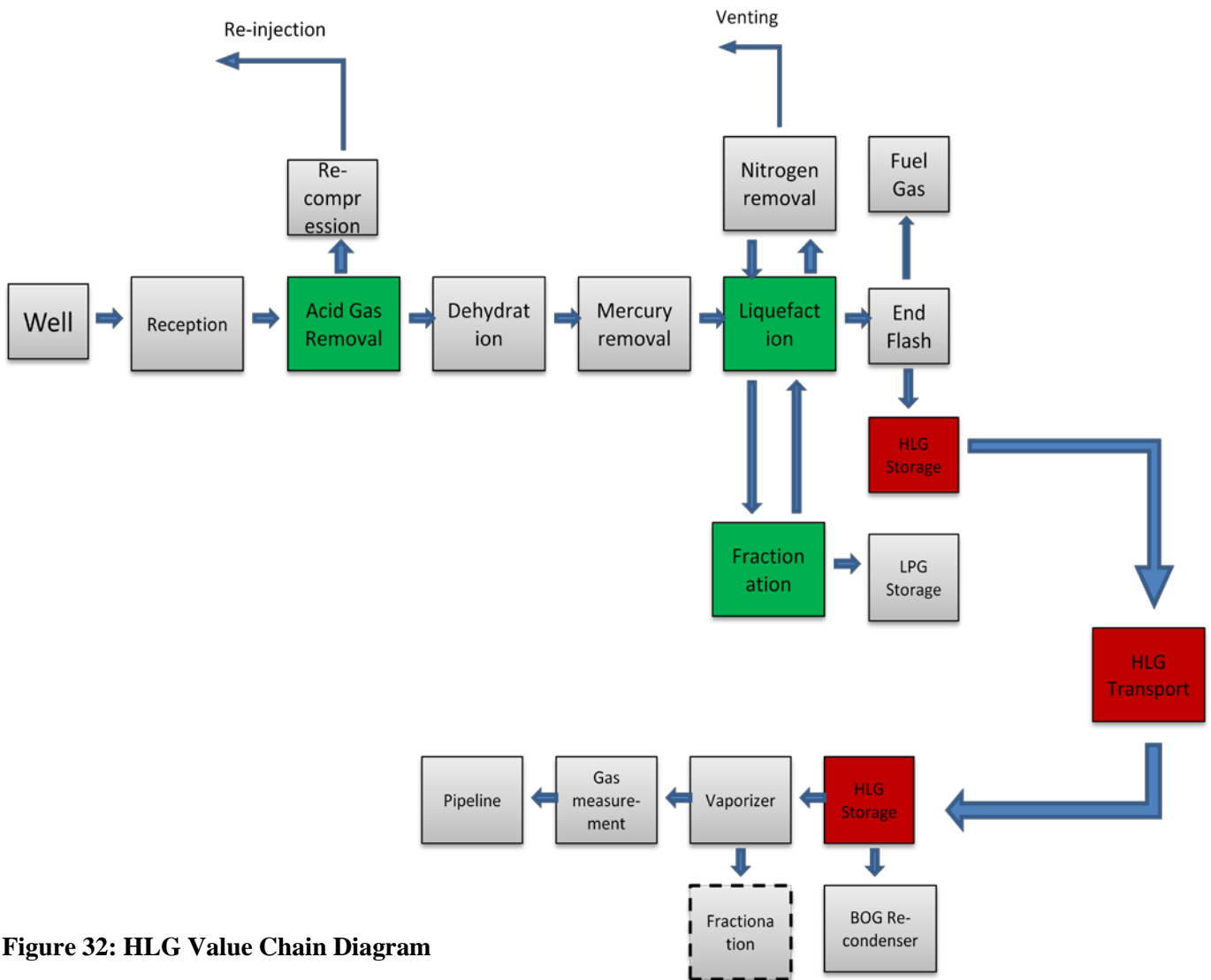


Figure 32: HLG Value Chain Diagram

5.3.1 CO₂ removal requirements

A major advantage of producing and shipping LNG at elevated pressure is the increased solubility of CO₂ in the liquid product which reduces the concentration limit for solid formation risk. The concentration limit the HLG will be able to solve will strongly be affected by the pressure and the resulting temperature. This will increase with rising pressure and especially when increasing the temperature to -130°C or about 7 bars from 1 bar. At the typical proposed pressure for HLG, a CO₂ concentration of around 2% can be tolerated without formation of solids [11]. In the circumstance of processing a CO₂-lean gas reservoir below this limit, the acid gas treatment requirements may altogether be eliminated, resulting in vast reduction in heat requirements for the liquefaction plant.

For many gas fields in operation, the CO₂ content is relatively low e.g. < 2%, but with depleting resources the accepted content for initiating development is bound to increase. Because of this, a HLG liquefaction plant will in most cases have to have some form of CO₂ removal process to reduce the concentration below the preset limit.

In any case, the extent of the removal will be less profound and this opens for installing other removal processes than the ones usually employed in existing plants. This could be any process able of reducing the concentration to the specific level which most of the commercially available processes are.

Selecting the correct gas sweetening means should be carefully considered and some of the main variables are:

- Feed gas concentration of impurities
- Hydrocarbon composition
- Operating conditions
- Capital and operating costs
- Sweet gas CO₂ concentration requirements

For HLG, these conditions may be very different from conventional LNG resulting in other terms for selection. For instance, the HHC part of the gas will be much higher which will have an effect on some of the absorption processes especially. If the used absorption solvent has a strong affinity to HHC's the loss of these will constitute a great waste in the produced value of the feed and will have to be recovered resulting in a higher energy need and space requirement.

Usually, the CO₂-removal process is based on a water soluble absorption process making the gas saturated with water. This results in the dehydration necessarily being placed subsequent to this. Because of the decreased requirements for CO₂-removal and the options in selecting removing processes, the dehydration may in some cases be placed prior to this for a HLG plant extending the options for integration.

Membrane CO₂ removal

Another possibility would be to install a membrane CO₂ removal unit instead of a regenerative process. A membrane removal unit works by having a semi-permeable and thin barrier that selectively lets some compounds through while others not [24]. In variation to a solvent removal process, membranes have a different effect on their size with respect to the thoroughness of the removal. While the size of the first is directly linked to the amount of CO₂ removed from the gas, the latter will be dependent on the percentage of the CO₂ removed. A reduction from 10% - 5% will therefore require a just as large system as a reduction from 20% - 10% [24]. With a starting value of 5% and a HLG specification of 2% the total removed percentage will therefore be 60%. The membrane system will eliminate the thermal power needs as it only needs a pressure gradient to operate.

A membrane system will also need some pre-treatment due to some gas specification restrictions. The membrane cannot handle liquids as these will lead to swelling in addition to HHC's over C15 can coat the membrane surface. These will have to be removed prior to the treatment. As the membrane decreases the pressure of the gas, it will cool down in the same way as a traditional valve due to the Joule-Thomson effect. This will cause some of the content to condensate so the pre-treatment stage will have to include a dew point control system. This will set the dew point well below the lowest temperature through the membrane. An example of a membrane system is shown in Figure 33.

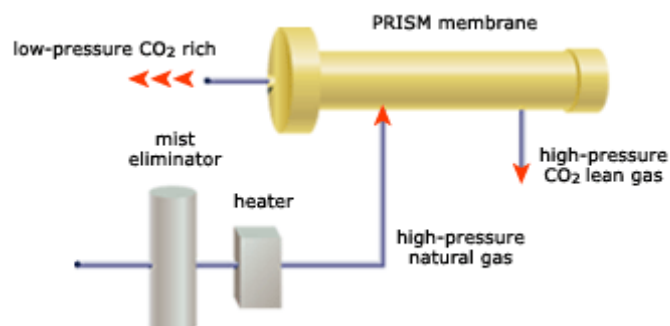


Figure 33: Membrane Separator [46].

The advantages of membrane systems are

- Lower capital costs
- Lower space requirements
- Lower operating costs and energy demand
- Low complexity

5.3.2 Dehydration

Even though the increased temperature will allow slightly higher water content before liquefaction, the requirements will still be restricted by the limit where gas hydrates will form. A molecular sieve adsorption process is therefore also required for HLG pre-processing in the same way as for conventional LNG. The water content limit is discussed later together with the process simulations.

5.3.3 Reduced HHC scrubber requirements

Independent of the gas field, production of LNG will always require removal of HHC's before liquefaction due to higher freezing points of these than the product storage temperature. Higher temperatures will allow a greater amount of aromatic and heavy hydrocarbons to maintain in the product without freezing. Again, depending on the well stream composition, the fractionation system to separate these may not be needed for some cases of HLG and especially for the high pressure LHG. Where some smaller amount of heavy hydrocarbons needs to be removed, a supersonic separator technology like the Twister could be utilized to set the preferred HC dew point.

5.3.4 Power requirements

A higher product temperature will result in lower power consumption for liquefaction. Because removing heat at cryogenic temperatures require an increasingly large amount of power per removed kilowatt, the most expensive cooling can be avoided by setting the condensation temperature at a higher level. The higher the pressure is set, the lower the power consumption will be resulting in a smaller amount of gas used for power production and a larger amount of produced HLG delivered to the customer. The largest savings will be in the lowest temperature areas so an increase from -160°C to -120°C will constitute a substantial amount of the total power requirements. The exact work requirements are discussed in the simulation chapter. The reduced work is the foremost reason for considering the HLG/PLNG solution and has the potential of making the gas delivery more competitive for where a full scale LNG plant is unprofitable.

Usually the heat recovered from the power producing gas turbines is not lost but is utilized in the regenerative processes of water and CO_2 removal. For HLG these heat requirements can be reduced quite significantly with possibly eliminating the acid gas treatment process. The heat produced would also be reduced due to the lower compressor work in the liquefaction stage and so less heat would be wasted.

In the case where the CO_2 -content in the field gas is below the permitted level the largest thermal power consumer is lost. One can in this case evaluate if running the liquefaction compressors on electrical power from the grid instead of gas turbines is suitable. This might help reduce the total CO_2 emissions which in turn can save costs for the operators. Because one in this case will have no recovered heat source, you will be forced to produce the needed

heat supply with a boiler or similar to feed the regenerator in the molecular sieve process during dehydration.

5.3.5 Loading systems

As the product liquid is pressurized, the loading systems from the production site to the shipping tanks have to be specially designed. A system for loading and unloading PLNG has been proposed and patented by ExxonMobil in *US Patent No. 6,237,347 B1 of May 29, 2001*. “Method for loading pressurized liquefied natural gas into containers.”

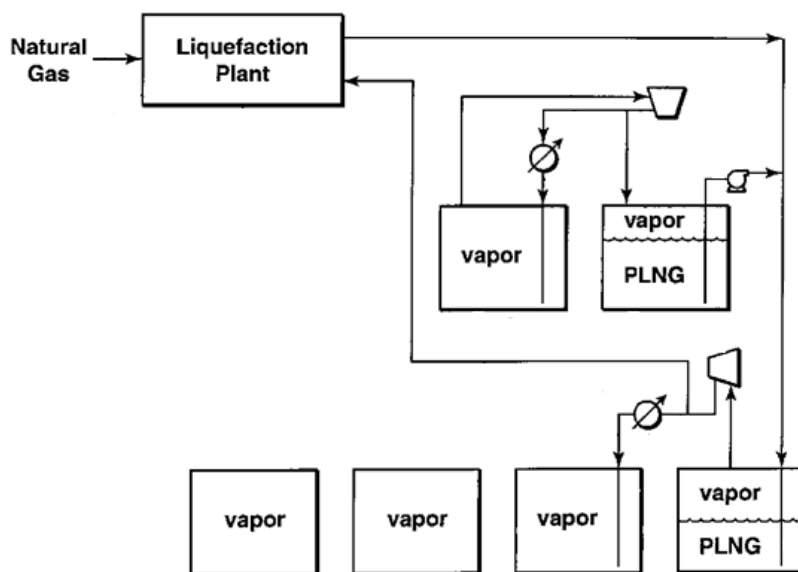


Figure 34: PLNG Unloading

The system consists of multiple storage compartments where the liquid is stored as shown in figure 34. When unloading the tanks, a methane rich gas is compressed and injected into the compartments, pressuring out the liquid. When loading, the gas is displaced by the entering liquid and sent to the liquefaction facilities. The empty return shipment will contain some compressed gas reducing the total delivered amount.

5.3.6 Storage tanks and Transportation

Conventional LNG ships can of course not be utilized in HLG/PLNG transportation so design and construction of a high pressure containment system will also be required for this concept. Because of the low temperatures, special concern should be taken when selecting the material for the vessels due to brittleness at low temperatures. Using ordinary cryogenic carbon steels will be very costly and will make the total weight of the ship unacceptably high as the thickness of the tank walls need to be increased. Development of new steel or other material types would be necessary. In US Patent no. 6,085,528, such a steel is described, claiming to withstand temperatures of between -62°C and -123°C at pressures between 10,35 bar and

75,90 bar [25]. This HSLT steel has a Nickel content of around 9 wt%, giving it properties to withstand the harsh conditions. The amount of Nickel would depend on the operating conditions and should be kept at a minimum for limiting the expenses associated with the costly material. A 17m tall prototype of the container constructed with this new steel has been built for ExxonMobil by Kawasaki Heavy Industries and is shown in Figure 35.



Figure 35: PLNG Vessel Prototype [11]

Alternatively, a glass fiber composite reinforced vessel might contribute to limit the weight and lower the production costs. Several designs for such a vessel are presented in US patent no. 7,147,124 [26]. In this patent an inner self supporting liner will contain the cryogenic liquid and would be made of a material able to handle the low temperatures. This could be any suitable material, but aluminum or a cryogenic steel type is proposed used [26]. This liner would be impermeable, preventing the liquid in coming in contact with other parts of the container. Around the liner a load bearing vessel made of a composite material is laid capable of withstanding the high pressure. In this way the inner layer would not need to support the high stress. This vessel is proposed made of carbon, glass, Kevlar or other suitable materials. The advantages of this proposed containment vessels are many over the HSLT steel mentioned above. In addition to being less heavy, the production process for the vessel is simpler and the insulation requirements are reduced. The form of the vessel can either be a large semi-spherical container or many smaller cylindrical. Both schematics of the proposed design forms in the patent are shown in Figure 36 and Figure 37.

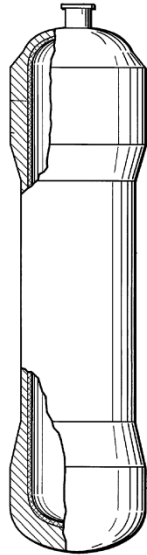


Figure 37: Cylindrical Composite

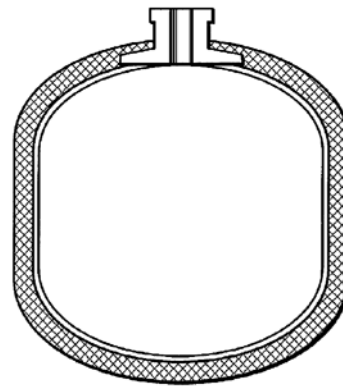


Figure 36: Spherical Composite

The cost of shipment for HLG will undoubtedly be much higher than transport at atmospheric pressures in the development stages and will make out a large portion of the increased expenses. The key to commercialization of HLG lies in making of an economically reasonable system which can be mass produced reducing the cost for each unit.

5.3.7 Receiving facilities

The consumers of gas rely on a steady supply and not only when the shipments of liquid gas arrive. Due to this, the liquid arriving ashore on delivery will have to be unloaded to storage tanks as a buffer, waiting to be re-gasified. For LNG, this is normally not a problem since the pressure at which it is stored is at approximately atmospheric. For these new concepts however, a specially designed receiving facility will have to be constructed in order to deal with the increased pressure. The complexity of these receiving facilities will be higher than the ones used for LNG today, and will also amount to a larger portion of the total investment costs in the value chain.

Today there are well established receiving facilities for LNG, making shipments and trading routes flexible and easily rearranged. Getting the same flexibility for HLG would be difficult without building high pressure facilities at all the possibly desired destinations. This would also be costly as the worlds LNG market is expanding rapidly and new receiving facilities also will need to be able to handle LNG.

Another possibility would be to have additional transportation ships in the delivery chain, unloading the HLG directly to the re-gasification plant. This will avoid the construction of new receiving facilities and making the delivery chain more dynamic and flexible. Some of the cold energy recovered when heating and expanding the HLG may even be used to produce some amount of LNG at 1 bar for storage in the existing LNG storage tanks. This would however require further processing and removal of CO₂ and HHC's as these would freeze out

at such low temperatures. This could be done in a cryogenic separation process like the CRYEX process where the freezable components are allowed to form solids after being expanded in a liquid state through a valve. In the same way, the existing LNG receiving facilities could be retrofitted with a HLG-terminal and the pressure tanks for storage would not be needed. The flash gas after the expansion could be fed to the sales-gas pipeline directly or be liquefied or compressed for storage.

Such a system is described in US Patent No. 6,560,988 B2 patented in May 13, 2003, and a flow diagram of the invention is shown in Figure 38.

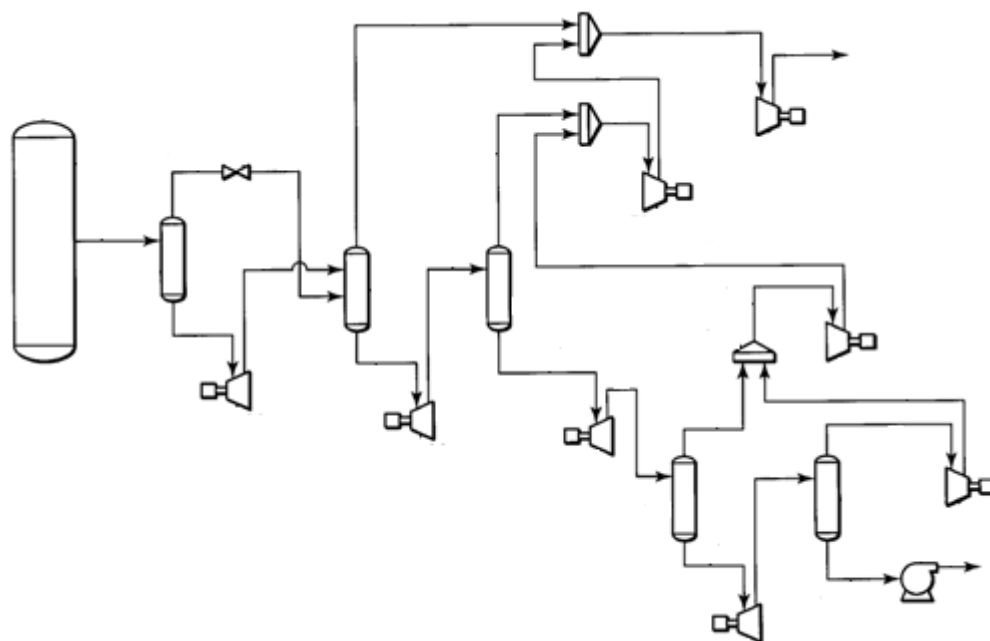


Figure 38: Unloading pressurized Liquefied Gas into LNG storage facilities

As seen in the diagram, the pressurized liquid is led through a series of turbo expanders decreasing the pressure in stages. After each expansion, some vapor will be produced when moving down into the liquid-vapor phase envelope. This gas is flashed off for recompression and distribution in pipelines. The turbo expanders will create some mechanical work which may be utilized in the recompression of the vapor. After the last expansion step the temperature will be the same as for conventional LNG but at atmospheric pressures, making storage in LNG tanks possible. The produced amount of LNG compared to the shipping load is around 51% giving the possibility of storing half of the shipment onshore for a longer period of time [27]. This will liberate the shipping vessels from expensive port time reducing the required number of vessels. The patent however, does not mention the complications of changing solubility of CO₂ and HHC's in the liquid at the different pressures. These components will run the risk of freeze out when the temperature and pressure is decreased.

5.3.8 Post processing

Depending on the selected process and the resulting pre-processing at the liquefaction site, the liquid product may need conditioning before the sale specifications are satisfied.

Due to the wide range of accepted heating values, staying within these limits is not the greatest concern. However, removal of heavy hydrocarbons will be necessary for reducing the HC dew point to -2°C or lower as required by EASEE [28].

The maximum CO_2 content in the sales gas is 2,5% and acid gas removal may be needed. The need for reduction of the CO_2 -content at the receiving site is not necessary for the cases of HLG where the gas is sweetened below the 2,5% limit at the liquefaction site. For the lowest HLG pressures, this limit will need to be subceded to prevent freeze out, avoiding this problem altogether. When operating at temperatures allowing more than the pipeline limitations, it could be advantageous to remove more CO_2 than needed to avoid the need for post removal and transport. This would limit the gas sweetening units in the value chain to only one place. Eliminating the need for a heat source at the receiving site is advantageous as there is not as much waste heat from power production here compared to the liquefaction plant. Some utility heat may also be required to operate the regenerative processes if installed.

5.3.9 End User Alternatives

The natural gas produced with the lowest level of pre-processing will need a large unit for post-processing which will question the economical feasibility. This will only be the case if the gas is to be delivered at pipe gas specifications, but some alternative end user may be more suitable. For instance, having a large power plant running on the delivered gas from a LUWS or a LHG concept, may altogether eliminate the need for post processing and the resulting value chain is considerably simplified. Other end users may be large petrochemical industries where methanol, ammonium, hydrogen etc is produced. The amount of delivered gas from a liquefaction plant may however exceed the needed gas amount for these alternative end users substantially.

The largest power production today from a single natural gas power station is the Kawagoe power station in Japan with a total of 4802 MW production [29]. A reasonably sized well stream for LNG production is around 2,1 million tons per year, or around 60 kg/s. With a heating value of roughly 50 MJ/kg the total produced power would be 1500 MW as Table 2 shows.

	Heating Value MJ/kg	Turbine Efficiency	Combined cycle Efficiency	Mass Flow MM Tons/ year	Mass Flow Kg/s	Power Produced MW
Power Plant	50	35%	50%	2,1	60	1500

Table 2: Power production end user

The plant efficiency used is of combined cycle and is well below the maximum achieved for a similar plant [30].

As we can see from the table, the resulting electrical power is in the obtainable region for a natural gas power plant. Nevertheless, as the gas is delivered in a liquid state, and for some concepts stored under pressure, the fuel storage and supply becomes more complex than coming from a pipeline. A conversion from pressurized to non-pressurized liquid would be needed or pressure containers onshore would have to be built. Alternatively, the shipping vessel could deliver gas directly to the plant while in dock as discussed earlier.

NGL & LPG recovery

Extracting heavier hydrocarbons at the receiving site is one of the means to adjust the gas properties. In addition, the heavier components such as propane, has a higher market price than LNG and should if possible be sold separately. Other means of adjusting the properties are mixing with other gas streams or injecting an inert gas, typically nitrogen. As nitrogen injection is expensive, HHC removal is preferred when mixing streams are unavailable [5]. For the new concepts, a larger amount of HHC's will need to be extracted. For LHG, which has practically all its LPG/NGL solved, this amount will make out around 20-25 percent of the total liquid delivered as the calculations in chapter 8 shows. This would require a much larger infrastructure for handling and transporting the different products.

6 Process simulations

For evaluating the energy requirements and the degree of influence by the variables, some non-extensive energy and material balances have been established for the new liquefaction processes and receiving sites. The process layouts can be seen in the appendix.

The acid gas removal, dehydration and other pre-processing stages have not been simulated in this thesis due to their complexity and the widespread study of these in previous papers. Instead, some estimates have been done to get comparable data for energy needs and gas properties. The calculations are done for five different types of transportation liquids. These are all liquids at the dew point temperature with varying transportation pressures:

- Conventional LNG
- LUWS concept with solids

- HLG concept at 12 bars pressure
- HLG concept at 20 bars pressure

- LHG concept at 50 bars pressure

The LHG concept was originally thought to produce a liquid with a much higher HHC fraction than in the selected well stream gas. As we have set a specific gas composition for all cases, this will be lower, resulting in a lower dew point temperature than proposed in the LHG patent.

6.1 Assumptions

Cooling requirements

The cooling requirement for LNG production can either come from an expansion process or through a refrigeration process with heat exchangers removing the heat from the feed gas. In the simulations, the cooling loops are not simulated fully but instead approximated with a set exergy efficiency. The duty of the heat exchanger cooling is taken directly as the enthalpy difference at the inlet and outlets of the heat exchanger.

Minimum theoretical work for liquefaction

The ideal minimum work can be expressed as an infinite number of Carnot cycles each removing an indefinitely small amount of heat from each temperature level. W_{\min} can therefore be expressed in the equation below. This correlation can however be very difficult to find for a mixed gas composition.

$$W_{\min} = \int \delta q \left(1 - \frac{T_0}{T} \right)$$

For a stream at a given starting condition, the theoretical amount of energy needed for liquefaction can be found by evaluating the thermo-mechanical exergy changes before and after the cooling. This is given by exergy change equation below and is only dependent on the starting and ending conditions as well as the temperature T_0 , where the heat is delivered. In the simulations this equation is used with T_0 set as sea water cooling at 15°C for all concepts.

$$\Delta e = (h_2 - h_1) - T_0(s_2 - s_1)$$

Because below around -130°C thermal cooling is more valuable than mechanical energy, one should expect a substantial reduction in the minimum work for a HLG process with the end product temperature above this level.

Approximation of actual work requirements

Obtaining reasonable results for the liquefaction processes, based on establishing full and energy and material balances will require a lot of work. This is especially true if one wants to optimize the processes to obtain energy requirements in the range of operating LNG plants. As the objective of this thesis is not to look into different cooling processes, an approximation between the required cooling and the work for heat removal will be used.

The specific power consumption of the Snøhvit LNG plant is 0,23 kWh/kg giving it an exergy efficiency slightly under 50% [31]. The exergy efficiency of 50% will be used for all processes in the simple energy and material balances. It is important to remember that this efficiency will decrease for the simpler processes e.g. the PRICO process used for smaller reservoirs or on FPSO's in addition to not being necessarily constant for all temperature levels.

Liquefaction pressure

The pressure where the liquefaction is done will greatly affect the needed power for the process. This can be shown in Appendix 7, where the minimum work for different pressures is shown. The higher the liquefaction pressure the lower the energy requirement. This is especially true for a pressure right above 1 bar and less so when having high enough pressure to stay clear of the gas-liquid phase envelope, around 60 bars. All liquefaction is done at this pressure level for all the concepts before being depressurized to the storage pressure. Conserving the feed pressure throughout the pre-processing stage would be a big advantage but is not always easily done as many acid gas removal processes require a relatively low pressure, e.g. in amine strippers.

End flash gas fraction

The feed stream will contain some nitrogen that will have a lower saturation temperature than the other components. Having the whole fraction of nitrogen remaining in the product will not only demand a lower end temperature, but also decrease the heating value and increase the transportation volumes. Some gas will therefore be flashed off after expansion. This nitrogen rich methane gas could be used as fuel gas or a nitrogen removal system could be installed sending the methane fraction back for liquefaction. When considering all the different power

consumers in the process a typical LNG plant will need between 5 and 10 percent of the feed gas for power production [4].

For the concept examples, a minimal amount of flash gas will be produced. The flash gas will be used for power generation in a gas turbine with a presumed constant energy efficiency of 35 percent of the gross heating value. Due to solubility differences of nitrogen under different pressures in addition to the flash gas amount, it is not equal in all the cases but will consist of around 75% methane and 25% nitrogen. For HLG and LHG more nitrogen could have been solved in the product stream without flashing off gas. In these cases, the necessary fuel could have been taken from the well stream or from the gas before liquefaction.

In all the cases a JT-valve is utilized for pressure reduction. An expander would in optimized cycles be used to right above the bubble point as these give a higher temperature fall and can produce some work. These are for simplicity however, left out in the simulations.

Gas Composition

Real well stream gas compositions will consist of a huge number of different components but for simplicity an approximation is given at which the calculations have been done and is shown in Appendix 3: Gas composition. The results can therefore not be transferred directly to other compositions without adjustments. This is especially true for the LHG concept which heavily depends on the heavier hydrocarbon content for lowering its dew point. The CO₂ fraction can also exceed the 5% assumed in this thesis which again would affect the pre-processing requirements.

Equation of state

For all the calculations, a SRK Equation of State has been used. The simulations have been tested with other equations to verify the results are within a reasonable range.

6.2 Freeze out Temperatures

Carbon Dioxide

As the temperature is increased, the liquid can contain a higher percentage of carbon dioxide. Finding the exact limit temperature for which the freeze out will occur can be complicated when there are other components present in the mixture.

For finding the maximum allowed amount of CO₂ in the end product, a binary Methane-CO₂ system can be used as a basis. This is shown in the Solid-Liquid-Vapor diagram, (SLV) in Figure 39: SLV diagram for Methane-CO₂ [32]. This will not however, describe the accurate limit value at where CO₂ will form solids due to the influence of the other components. The presence of nitrogen will slightly increase the CO₂ freezing temperature while light-end hydrocarbons like ethane and propane will lower the CO₂ freezing temperature [32].

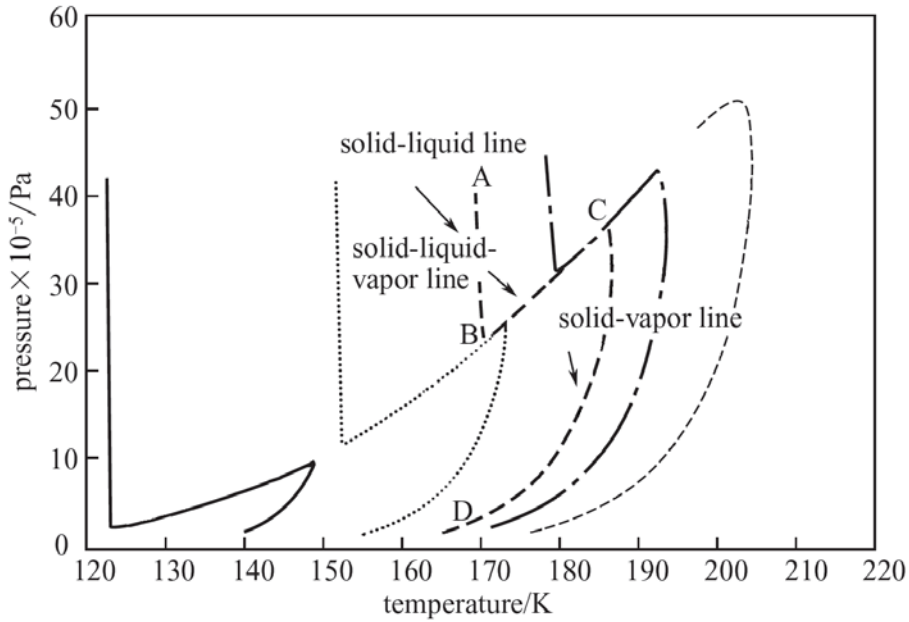


Figure 39: SLV diagram for Methane-CO₂ [32].

The Solid-Liquid line in the diagram is, as we can see in Figure 39, not very dependent on the liquid pressure with the freezing point only slightly decreasing with increased pressure. Due to this, a good approximation of the allowable CO₂ mole-percent can be found with a solubility curve for a CO₂-CH₄ system shown in Figure 40. For typical pressures of HLG the CO₂ mole% will be in the range of 1-2% while a Chevron LHG liquid might be able to contain a percentage as high as 5-6%. The phase diagram Appendix 4 indicates that at 50 bars the CO₂ freeze out temperature is over -60°C and any CO₂ over the solubility limit will then form solids. A gas-solid transition may still occur.

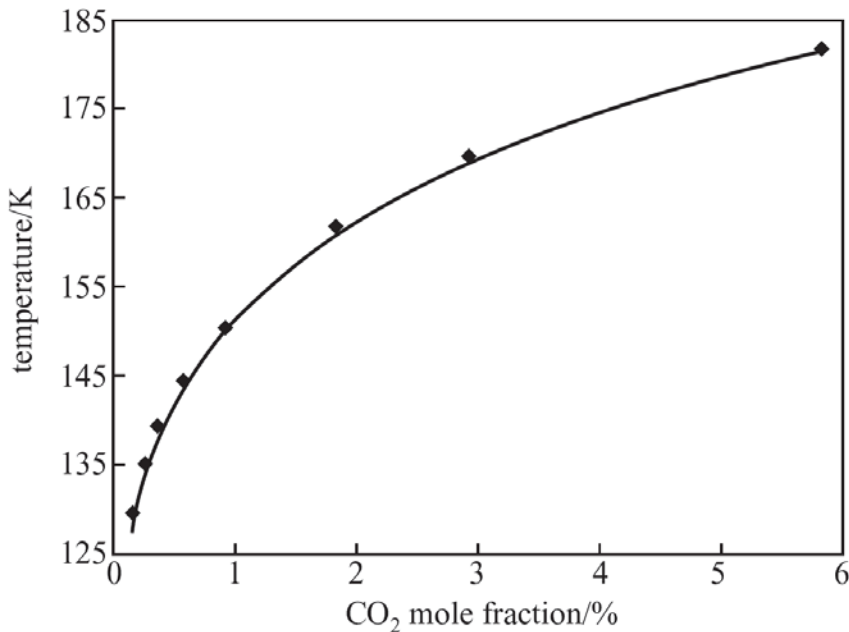


Figure 40: CO₂ solubility in CH₄ [32]

Heavy Hydrocarbons

The heavier hydrocarbons will also form solids for most of the temperatures in the simulation cases. The feed gas specifications in the simulations contain components from Cyclo-Hexane, with a normal freezing point of over 6°C, to hexane with -95,3°C which will all form solids under atmospheric pressures. The mole fraction of these will have to be reduced in a hydrocarbon scrubber to satisfy the freeze out concentration limits if over the solubility.

In order to find the maximum allowable mole fractions for the various temperature and pressure states, a non-equilibrium simulation program called NeqSim has been used [33]. This predicts the freeze out temperatures for the mixture based on SRK EOS for the liquid phase, and a solid fugacity model for the solid phase. See the appendix for equations and further explanation. The solids are assumed formed only in sub-cooled liquid so a further evaluation of potential frosting in gas phase should be done for a more extensive prediction.

The program has been used to find the boundary cases for three different systems of LNG under pressure with resulting temperatures. These are HLG at 12 bars, HLG at 20 bars and a LHG case at 50 bars. The results are shown in Appendix 10. The LHG case does not form solids even without any pre-processing of the specified well stream composition at the set conditions.

Post processing and recompression

All the compressors in the calculations are assumed to have a polytropic efficiency of 80% while the efficiency of the pumps is set to 80%. Inter-cooling of the compressors is not taken into account, but should be integrated with the vaporization heat exchanger. Hydrocarbon dew point control is done by setting the cricondenthem to -2°C by flashing the gas during vaporization.

6.3 An approximation of the Amine treatment energy needed

There is a large heating demand associated with an amine process for removing acid gas. Due to the corrosive effects of high concentration of amines, the maximum allowed weight fraction (WF) is between 0,20-0,55 depending on the type used. For this simple approximation Mono-ethanolamine, or MEA, is used as this is cheaper than MDEA and less corrosive than DEA [18]. MEA will typically have a WF of around 20% and an acid gas loading of 0,33 mol acid gas/mol MEA [18]. The approximate heat duty for the amine re-boiler is set to 300 kJ/L amine and the amount of amines can roughly be found by the equation:

$$Q_{MEA} = \frac{CO_2 \cdot \frac{M_{MEA}}{M_{CO_2}}}{(AG \cdot WF)}$$

$$Q_{MEA} = MEA \text{ kg} / s$$

$$CO_2 = \text{mol } CO_2 / s$$

$$M_{MEA} = g / \text{mol}$$

$$M_{CO_2} = g / \text{mol}$$

$$AG = \text{Acid gas loading}$$

$$WF = \text{Weight fraction}$$

Assuming a linear energy requirement independent of the acid gas concentration of the feed gas, the heat requirement can be calculated to 6200 kW per kg CO₂ removed. In comparison, although using MDEA, Melkøya LNG at 4,3 Mtpa needs 69 MW of hot oil at 190°C equal to around 5400 kW/kg removed CO₂ [34].

Because the heat requirements for a certain amount of CO₂ rich amine with a particular load is given, the heat needed for regeneration is directly linked to the removed CO₂. This means that a system decreasing the acid gas content from 6 to 3% will require approximately the same amount of energy as a system from 3 – 0%.

The amine-stripper condenser will require cooling but this is usually obtained through air or seawater heat exchange as the required temperature is only around 55-60°C [18]. The energy consumption for this then only comes from the cooling water pump.

6.4 Results and discussion

6.4.1 Concept results

Even though the results obtained through the simulations and calculations are simplified, they will give us some comparable data for evaluating them based on the same assumptions as will be presented in this chapter.

The theoretical work for a liquefaction process based on the given gas specifications given are shown in Figure 41 and is calculated based on exergy change. The graph shows rapidly decreasing energy consumption for the low range pressure increase up to 6 bars. An increase between 1 and 6 bars gives a power reduction of over 30%. This is as expected as the most expensive cooling is in the lowest temperature regions and the dew point temperature is a function of pressure. The work requirement is then decreasing more linearly down to the highest regions of the HLG pressure range below 0,06 kWh/kg.

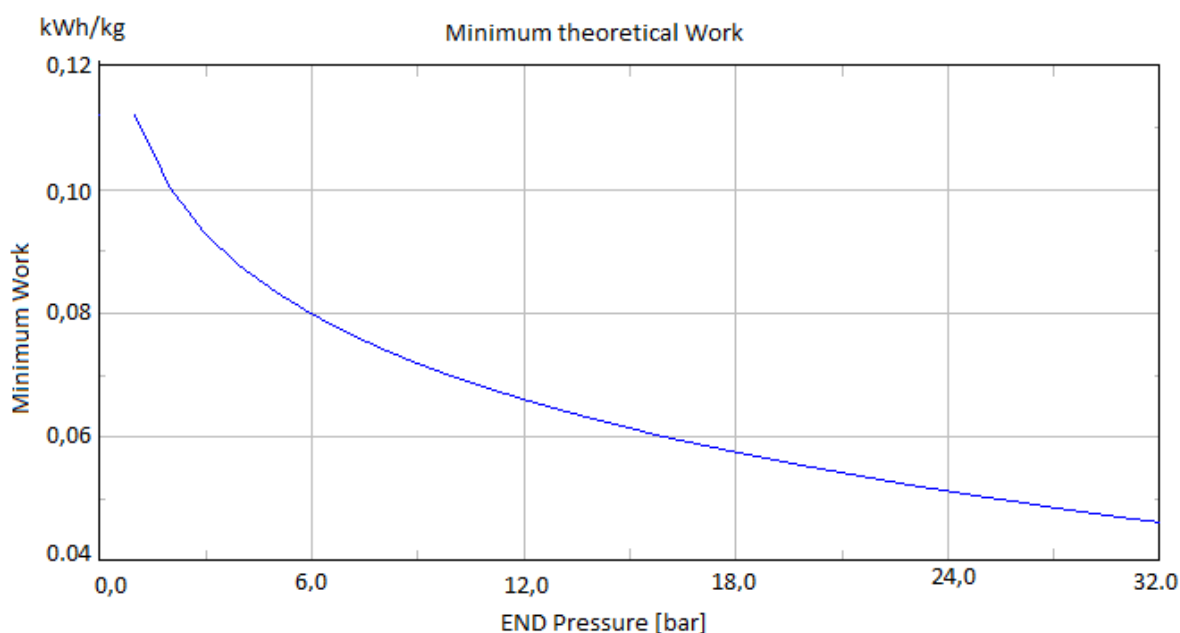


Figure 41: Minimum Theoretical Work

Process	Energy Consumption [kWh/kg]	Energy % of LNG	% of HHV	HC dew point [°C]	WI [kWh/m ³]	Temperature [°C]	Pressure [Bar]
LNG	0,2300	100	1,536	-2	15,26	-162,42	1,1
LUWS	0,1803	78,39	1,371	130	15,37	-161,66	1,1
HLG 12	0,1309	56,91	0,920	20	14,77	-121,17	12
HLG 20	0,1003	43,61	0,729	45	14,63	-107,27	20
LHG	0,0570	24,78	0,438	130	15,13	-77,97	50

Table 3: Simulation results I

The results of energy requirements and some liquid properties for the liquefaction processes based on the previously mentioned assumptions are shown in Table 3 and Table 4.

As expected, the energy consumption decreases with increased pressure with LNG consuming 0,23 kWh/kg of produced liquid and HLG12 and HLG20 0,1309 and 0,1003 respectively. The LNG energy consumption is identical for Melkøya LNG due to the exergy efficiency taken from this plant, but this also verifies the models and assumptions used.

The LHG concept has very low energy consumption with only 0,057 kWh/kg. LNG needs over 404 percent more than this which gives the LHG concept a large advantage. The low consumption is due to two factors:

- Higher dew point temperature because of the pressure
- Higher content of components with a high dew point temperature

As all the CO₂ and HHC's liquefy or solidify at high temperatures, the concepts containing some or all these components in the liquid will have abnormally low power consumption. This will be especially true for the LHG and LUWS concepts where none of these components are extracted. The percentage of the heating value used for liquefaction will also be influenced by this as LPG is drawn off for individual sale in the other three concepts. This is the reason why the percentage of the heating value used for liquefaction of LNG, is only 350% higher than that of LHG. The LUWS concept has a specific work requirement which is lower than that of LNG. This is misleading as liquids are drawn off from conventional LNG before cooling, resulting in a smaller amount of produced cryogenic liquid. In this case, a more correct comparison can be made in the calculated example presented in chapter 6.4.2.

The LPG/NGL fraction drawn off at the liquefaction plant will vary with the largest possible amounts solved in the liquid product. The higher the solubility is, the lower the LPG fraction becomes. However, this amount could be increased if this is practical to the downstream processing facility's availability and costs. The amount is in these examples set to an approximate minimum, assuming the removal is more costly at the liquefaction site.

The HC dew point for LNG will not be entirely correct as the maximum HHC amount in the gas should be 1-10 ppm to avoid freeze out. As we do not simulate the scrubber in the pre-processing, this amount is left in the liquid but would in a real case increase the LPG fraction and decrease the amount of delivered pipe gas.

Process	HHV MJ/kg	Density Kg/m ³	Density Percent of LNG	LPG I fraction of well stream	End flash frac.*	Amine regeneration kWh/kg LNG
LNG	53,91	461,6	100	0,260	0,0591	795
LUWS	47,36	576,8	125	0	0,0604	0
HLG 12	51,22	418,6	90,7	0,238	0,0316	563
HLG 20	49,51	406,9	88,2	0,193	0,0248	356
LHG	46,81	417,0	90,3	0	0,0163	0

*Fraction of mass flow through the heat exchangers

Table 4: Simulation Results II

The liquid densities will also be influenced by the different factors giving a span of 170 kg/m³ between 576,8 for LUWS and 406,9 for HLG20. This difference will have a large impact on the size or the number of transportation vessels needed for the same volume of transported gas. The transport volume for LHG will have to be 41,7% larger than for LUWS while the two HLG concept will need 10,3% and 13,7% larger volume than LNG. An overview of the needed transport volumes is shown in Figure 42 which indicates that all the pressurized concepts have around the same need for extra shipping volumes per weight.

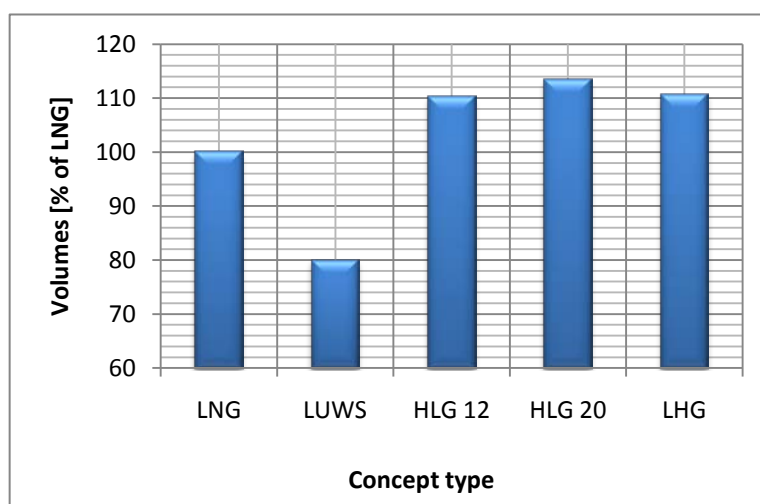


Figure 42: Density Chart

The total mass of transported product will of course be the same for all concepts except for the removed CO₂ and the flash gas used for fuel. LPG produced on the liquefaction site will require a LPG transportation vessel from here, while the concepts where this is included in the liquefaction stream, does not. Whether it is best suited to remove the high end liquids at the producing or receiving site will need to be evaluated specifically for each development based on cost, availability and sales markets.

The last column in Table 4: Simulation Results II shows the regeneration heat for the amines in the CO₂ removal process. This is as expected highest for LNG where all the acid gases are removed and nonexistent for LHG and LUWS. This only represents the regeneration heat at the liquefaction site and it is important to take into account the removal at the receiving site as well when considering the whole value chain. This is better represented in the example in chapter 6.4.2.

The liquid product compositions for the concepts are shown in Table 5: Liquids Composition.

Composition [mole %]	LNG	LUWS	HLG 12 bars/-121°C	HLG 20bars/-107°C	LHG 50 bars/-78°C
CO2	0,0000000*	5,3191416	1,4285300	2,695933	5,049991
Methane	90,6853214	80,2175696	88,1478902	85,80425	79,82015
Ethane	5,4373723	5,3211878	5,2649753	5,275842	5,063532
Propane	1,7824487	2,1286006	1,7957381	1,947102	2,030505
I-Butane	0,6690971	1,0643007	0,7155577	0,866179	1,015923
I-Pentane	0,3367910	1,0643007	0,4211510	0,644057	1,016356
Hexane	0,0886523	0,5321504	0,1658628	0,351701	1,016469
Heptane	0,0110768	0,5321504	0,0359488	0,093204	0,508251
Octane	0,0020720	0,5321504	0,0146955	0,044734	0,508257
Nonane	0,0003314	0,5321504	0,0059663	0,020692	0,508259
Decane	0,0000446	0,5321504	0,0022923	0,008946	0,50826
Benzene	0,0348156	0,5321504	0,0684914	0,150482	0,508235
CH	0,0308994	0,6276966	0,0645207	0,143539	0,508235
N2	0,9210798	1,0643007	1,8683683	1,95332	1,937576

*Value based on total CO₂-removal.

Table 5: Liquids Composition

Again, we can see that the C₅+ components are present in the LNG composition. The total amount of these make out 0,5 mole% when in reality with a scrubber installed in the pre-processing, this would be around 0,01 mole% (100ppm). As the difference is quite small and specially for the heaviest compounds, we choose to ignore the effects this has on the gas.

The CO₂ content for LNG should be 50-100ppm and not non-existent as here, but is not present in the feed gas for simplifications. All the other concepts will need acid gas treatment except for HLG at 12 bars which has 1,43 mole% CO₂ which is well below the requirements. As the HLG20 has only slightly more CO₂ than the pipe gas specifications, it would be reasonable to remove some more of it at the liquefaction plant to avoid having two separate removal processes at both the liquefaction and vaporization sites.

The LUWS and LHG composition will be almost the same as these are both unprocessed well streams. There will however be a slight difference as the energy needed for liquefaction will be higher for the LUWS concept. The nitrogen content in LUWS will be around half of that for LHG due to this, because the flash gas consists of around 25% N₂. The ethane will also be quite stable at just over 5 mole%. This will not be drawn off as liquid nor will it be part of the end flash fraction.

As we can see from EASEE's gas pipeline specifications in the appendix, the hydrocarbon dew point needs to be -2°C or lower between 1-70 bara. This is not satisfied for any of the

four new liquefied gas products and dew point control will therefore have to be part of the post processing at the receiving site. This is in the simulations obtained by removing liquids during the heating in the evaporator.

The Wobbe-Index requirements are according to EASEE, to be between 13,60 and 15,81 kWh/m³. This is a very wide range of acceptable values and none of the products will deliver gas outside these even without any post processing. However, since the gas will need to be processed to comply with other specifications, the index will be influenced by the removal of CO₂ and heavy hydrocarbons among others.

Composition %	HLG 12 bars/-121°C	Limit		HLG 20bars/-107°C	Limit
CO ₂	1,4285300	1,48717		2,695933	2,84697
Methane	88,1478902	84,4877		85,80425	82,7123
Ethane	5,2649753	5,28047		5,275842	5,16952
Propane	1,7957381	2,11218		1,947102	2,0678
I-Butane	0,7155577	1,0561		0,866179	1,0339
I-Pentane	0,4211510	1,0561		0,644057	1,0339
Hexane	0,1658628	1,0561		0,351701	1,0339
Heptane	0,0359488	0,528047		0,093204	0,516952
Octane	0,0146955	0,127118		0,044734	0,360942
Nonane	0,0059663	0,345105		0,020692	0,516952
Decane	0,0022923	0,0128439		0,008946	0,0444435
Benzene	0,0684914	0,0330198		0,150482	0,0776918
CH	0,0645207	0,305844		0,143539	0,516952
N ₂	1,8683683	2,11218		1,95332	2,0678

Table 6: Freezable components Concentrations

In Table 6: Freezable components Concentrations, the two HLG concepts and their freezable component concentration compared to the limits calculated in NeqSim are shown. The concentrations and freeze out limits will vary with the concentration of all the components in the liquid and has a complex coherence. The limits are therefore not absolute and a safety margin should be established. A good insight is however obtained showing which components to specially take precaution against.

The yellow colored rows in Table 6 make up the freezable components in the temperature ranges in which we operate. For all the products, the freezable components are below the maximum allowed limits with the exception of benzene. Benzene will form solids in both the HLG cases and will therefore need to be removed in a pre-processing unit. This could be a selective benzene removal unit or the hydrocarbon dew point may be lowered. In addition the

CO₂ in HLG12 is too close to the freeze out limit to handle any fluctuations and some more should be removed in the amine process.

6.4.2 Calculated example

As an example of a typical liquefaction plant, a 2,1 million tons well stream per year example is calculated. The results are shown in Table 7 and Table 8.

Concept	Pipe gas sale	Pipe gas sale	LPG amount I	LPG amount II	Liquefaction power	Power % of LNG	Re-compression power
	Kg/sec	m ³ /sec	Kg/sec	Kg/sec	MW	%	MW
LNG	37,9600	47,26	14,2247	0	31,428	100,0	1,566
LUWS	40,6530	48,54	0	14,313	37,284	118,63	13,615
HLG 12	40,6152	49,34	13,3539	0,911	19,570	62,27	6,516
HLG 20	42,0269	50,20	11,1172	3,158	16,381	52,12	6,590
LHG	41,7185	51,59	0	15,405	12,236	38,93	9,382

Table 7: Example Calculations I

Concept	End flash for fuel	CO ₂ Removed on site	Amine regeneration heat	CO ₂ Removal required*	Amine regeneration heat	Pipe gas HC dew point
	Kg/Sec	Kg/s	MW	Kg/s	MW	°C
LNG	2,5067	5,6815	35,2	0	0,0	-2,0
LUWS	2,9401	0	0,0	2,463	15,27	-2,03
HLG 12	1,2844	4,2043	26,1	0	0,0	-2,07
HLG 20	1,0271	2,8408	17,6	0,199	1,2	-2,02
LHG	0,7351	0	0,0	2,510	15,56	-2,06

*Removal at receiving site

Table 8: Example Calculations II

The well stream flow without acid gas removal is equal to 60,368 kg/sec. As the different concepts have different requirements for CO₂ content and the amine processes are not simulated in this thesis, the CO₂ concentrations are set for each case and the flow rate decreased corrected accordingly.

The LHG concept is by far the least energy demanding concept in addition to being the simplest for this gas composition. For a reasonably sized production rate as in this example, the power requirement for liquefaction is only just over 12 MW. This is very low, reducing the need for a large power producing unit considerably. In addition, the acid gas removal process is unnecessary before liquefaction and LPG/NGL is shipped solved in the LHG product. This high LPG/NGL fraction will also have a negative effect on the power consumption for LHG as more liquid is cooled down than for LNG. From Table 7: Example Calculations I, we see the liquefaction power for LHG is 39% compared to LNG. This could

be reduced additionally if liquids are drawn off at ambient temperatures before liquefaction and stored and shipped in a separate vessel than the LHG product. This would then also reduce the amount of CO₂ possible solved in the product liquid and a removal process should be installed. The work requirement is still well below all the other concepts. For LUWS, an increase of 18,6% is observed due to the larger amount of gas needed to be cooled to the storage temperature.

The amine regeneration heat will only be half that of LNG for the LUWS and LHG concept as these have a 2,5 mole% of CO₂ left in the sales gas. The need for this regeneration heat will however be at the receiving site where there might not be a surplus of heat for power production. The best alternative may be to remove just enough CO₂ for the sales gas to have the maximum allowed specifications of 2,5 mole% before liquefaction. This could be done for HLG20, LHG and LUWS. There will also then not be any abundant removed CO₂ at the receiving site which needs to be disposed of as all the CO₂ is sold as pipe-gas. If the heat is to be produced from combustion of some the gas the amount would be around 0,5 kg/s LHG with a thermal efficiency of 70%. This heat could of course be produced in connection with producing power for the recompression.

All the concepts will have a total LPG/NGL production of around 14,3 kg/s except LHG which has 15,4 kg/s extraction at the receiving site. This elevated amount is due to the high concentration of C5+ which must be removed to satisfy the 2°C HC dew point. LHG will have both a higher percentage of HHC and nitrogen resulting in a lower methane concentration. Both HLG20 and LHG will deliver around the same mass flow of pipe gas at 42 kg/s while the other two has equally 40,6 kg/s. The low 38 kg/s for LNG is due to the total removal of CO₂ from the pipe-gas, but this could be adjusted to increase the gas value adding to this flow rate. The mole-percent nitrogen will be just under 2 for the pressurized concepts while for LNG and LUWS approximately 1.

The power needed for recompression is based on recompression of evaporated liquid, as well as pumping work of the liquid. The end pump pressure is set to a pressure such that extraction of liquids needed for hydrocarbon dew point control is possible. The vapor is recompressed using a compressor with an efficiency of 80%. There do exist some NGL and LPG recovery processes that allow the pressure increase to be done by a pump, utilizing the cold in the liquid streams [5]. This could reduce the power requirement by as much as 90%, but are in these concepts not simulated. As hydrocarbon extraction can be done more energy efficient, the power needed for recompression should not be weighted too heavily in the comparison.

6.5 Pressure vessel calculations

Comparable weight estimates have been calculated for all the concepts to find the containment vessel weights for both steel and composite material.

Yield strength is the stress limit where the steel will start to deform plastically and therefore will change shape permanently. As the containers will have a wall thickness of less than one tenth of the diameter, the simplified equations for the maximum stresses can be found from a net force balance and are [35]:

$$\sum F_y = 0$$

$$\sigma_A A - p A_e = 0 = \sigma_A \pi (r_0^2 - r^2) - p \pi r^2$$

With $r_0 = r + t$, this becomes:

$$\sigma_A = \frac{p \pi r^2}{\pi ([r+t]^2 - r^2)} = \frac{p \pi r^2}{\pi (r^2 + 2rt + t^2 - r^2)} = \frac{p r}{2t + t^2/r}$$

Since t^2 will be much smaller than t due to the size of t , this expression can be simplified to:

$$\text{Axial Stress: } \sigma_A = \frac{Pd}{4t}$$

The hoop stress is found in a similar manner to form equation:

$$\text{Hoop Stress: } \sigma_H = \frac{Pd}{2t}$$

The ambient pressure containers for LNG and LUWS are of Moss type while the pressurized vessels have a cylindrical shape. For the spherical LNG tanks there is only axial stress and the maximum stress can be twice that of a cylindrical vessel. As there is a technical limit to the maximum thickness of the plates, this is set to a constant 150mm for the pressure vessels. The diameter of the vessels is calculated from this criterion and at a set height of 40m. The area of the ends of the cylinder is set to two half spheres with the same diameter.

$$d = \frac{\sigma_{max} \cdot t \cdot 2}{p}$$

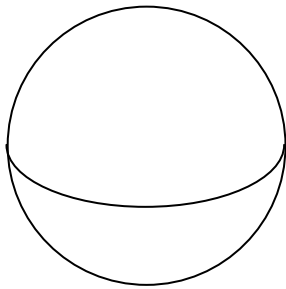
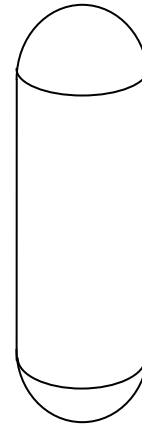
Simplified steel mass calculation: Surface Area x Thickness x Density:

Cylinder:

$$m = (2\pi r h + 4\pi r^2) \cdot t \cdot \rho$$

Sphere:

$$m = 4\pi r^2 \cdot t \cdot \rho$$


Figure 43: Moss type

Figure 44: Cylindrical Pressure Vessel

The same Cr-Ni Austenitic Stainless Steel 304 is assumed used for all the containers as this covers the whole temperature range for all the concepts [36].

From Appendix 8 we find the yield stress for the 9% Nickel steel to be 215 MPa. With a factor of safety of 4, the allowable stress limit is:

$$\sigma_{Allow} = \frac{\sigma_y}{\eta} = \frac{215MPa}{4} = 53.75MPa$$

The factor of safety should be quite high as the weakest areas of the vessels can be found in the welding seams, allowing a much lower stress. The resulting dimensions and weights for the four concepts are shown in Table 9 below.

		LNG	HLG 12	HLG 20	LHG
Safety factor		4	4	4	4
Yield	[Mpa]	215	215	215	215
Total volume	[m ³]	150000	150000	150000	150000
Steel density	[kg/m ³]	8000	8000	8000	8000
Pressure	[Mpa]	0,3	1,2	2	5
Thickness	[mm]	124,30	150	150	150
Diameter	[m]	44,54	13,44	8,06	3,23
Height	[m]	-	40	40	40
TYPE		Sphere	Cylinder	Cylinder	Cylinder
Volume per tank	[m ³]	37500	5672,7	2042,2	326,7
No of tanks		4	26	73	459
Steel volume per tank	[m ³]	774,65	338,38	182,61	65,69
Mass per tank	[tons]	6197,2	2707,0	1460,9	525,5
Steel volume total	[m ³]	3098,6	8947,7	13412,8	30157,0
Steel weight total	[tons]	24789	71581	107302	241256

Table 9: Steel Vessel Calculations

As we see from the simple calculations, the total weight of the shipping containment system is increasing rapidly with the elevated pressure. To compare the results, the weight of an operating LNG tanker is around 55000 tons in total, plus the weight of the cargo [37]. This agrees with the total steel weight in Table 9 with the tanks weighing 24789 tons in total. The LUWS tanks will have a similar weight as the LNG tanks as these are both at 1 bar. The proposed PLNG tank in the concept description by ExxonMobil has a dimension of 10m in diameter and a height of 46m [11].

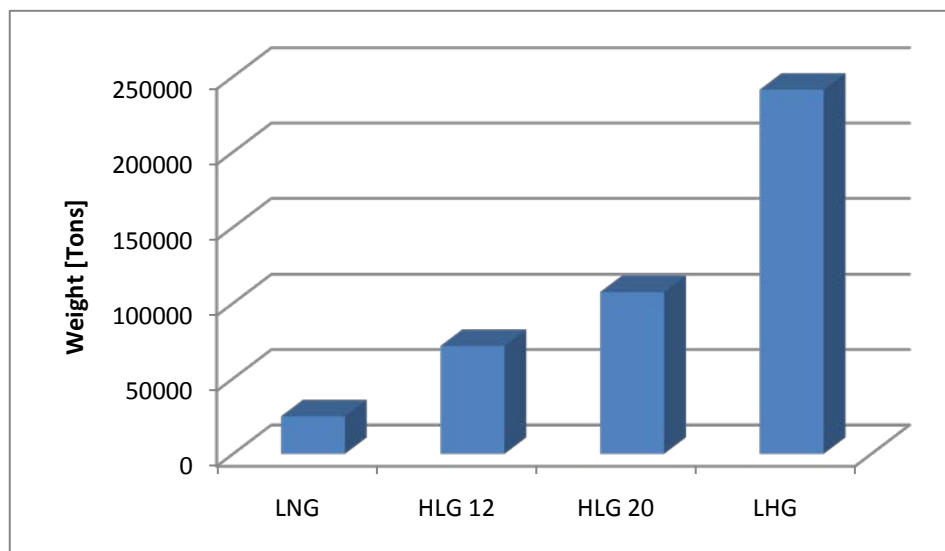


Figure 45: Total Steel Vessel Weight

HLG12 and to some extent HLG20, might both have a tolerable total weight of shipping vessel even though far heavier than conventional LNG carriers with three and four times the weight respectively. The diameters of the cylinder containers decrease very fast, thus increasing the number of containers to give the same volume cargo space. One solution could be to decrease the tonnage and increase the number of ships. At 241000 tons, the LHG vessels constructed of steel will be too heavy to be on a reasonably sized ship and this design will have to be abandoned. The total steel weight per kilogram of LHG liquid is almost 3,86kg compared to 0,36kg for LNG as shown in Table 10. This means a substantial amount of steel will have to be transported as deadweight increasing the capital and operating expenses. Instead, an optional build material should be considered as the temperature in LHG is only -78°C .

The calculations are done with a constant freight volume equal 150000m^3 , but as the densities and heating values of the liquids are dissimilar, the delivered pipe gas and net calorific value for the shipments will be different. A comparable measure is the transported energy per ton of vessel weight, but one should also keep in mind that in this value lays both the heating value and the density differences. The transported energy per ton of vessel is 12,44 times higher for LHG than for LNG, with a lower HHV of LHG contributing to this.

	Pressure Vessels Weight	Cargo capacity	Density Liquid	Full trans. vessels	HHV	Energy per vessel weight	Kg steel/kg cargo
	Tons	m ³	Kg/m ³	Kg/m ³	MJ/kg	MJ/ton	Kg/Kg
LNG	24789	150000	461,6	165,3	53,91	150,6	0,35802
LUWS	24789	150000	576,8	165,3	47,36	165,3	0,28651
HLG 12	71581	150000	418,6	477,2	51,22	44,9	1,14001
HLG 20	107302	150000	406,9	715,3	49,51	28,2	1,75804
LHG	241256	150000	417,0	1608,4	46,81	12,1	3,85701

Table 10: Containment Vessel Comparison

Glass fiber reinforced pressure vessel

For the heavier pressure vessels, a composite material relieving the steel from the hoop stress would make the total weight become acceptable as mentioned previously. A metal inner liner will then contain the liquid while a composite overwrap will absorb all the stress. The liner should have a construction and thickness to minimize the resulting weight, but tolerate a fluctuation in pressure.

As the tanks will only need to withstand pressure forces from the tank, it is assumed that all loads are taken up by the fibers only and that the resin in the composite is only there to keep the fibers in place and distribute the forces evenly. Typical tensile strength of a fiber reinforced plastic, or FRP, is between 550-1700 MPa depending on the ratio of fibers to resin [38]. Because the pressure vessels will need limited compressive strengths, a high fiber fraction can be utilized giving a tensile strength in the upper levels of this. In addition, the FRP at low temperatures will gain strength and become less brittle than at room temperature which is an obvious advantage for these vessels [38]. The resin however becomes brittle and must be chosen with care. A moderate 1000 MPa tensile strength is assumed and with a factor of safety of 4, the thickness of the spherical FRP is calculated.

A conservative estimate for the specific weight is set at 2,5 tons/m³ with generic E-glass Fiber having a density of 2,54-5,6 tons/m³ [36]. With the same tanks and volumes as the steel design and with the same tonnage, the specifications of the FRP vessels are shown in Table 11. The steel liners are set to withstand a pressure of 3 bars regardless of the concept pressures, resulting in different liner thicknesses due to the different shape and sized of the pressure vessels. The result is a decreasing thickness of the liner from over 9mm in the HLG12 tanks to 2,25mm in the 50bar LHG concept.

		HLG 12	HLG 20	LHG
Factor of safety		4	4	4
Yield Mpa	[Mpa]	1000	1000	1000
Total volume	[m ³]	150000	150000	150000
Frp density	[kg/m ³]	2500	2500	2500
Pressure	[Mpa]	1,2	2	5
Thickness	[mm]	32,25	32,25	32,25
Diameter	[m]	13,44	8,06	3,23
Height	[m]	40	40	40
TYPE		Cylinder	Cylinder	Cylinder
Volume per tank m3	[m ³]	5672,7	2042,2	326,7
No of tanks		26	73	459
FRP volume per tank	[m ³]	72,75	39,26	14,12
Mass per tank	[tons]	181,9	98,2	35,3
FRP volume total	[m ³]	1923,8	2883,8	6483,8
FRP weight total	[tons]	4809	7209	16209
Steel liner thickness	[mm]	9,375	5,625	2,25
Steel liner weight	[tons]	4474	4024	3619
Total weight	[tons]	9283	11233	19828

Table 11: Fiber Reinforces Plastic Calculations

While the steel tanks in the highest range of pressures gave an intolerable amount of steel and resulting weight, the FRP tanks show great potential for reducing the ship size and weight. As we compare Table 9: Steel Vessel Calculations and Table 11, it becomes clear that it might be possible to construct a LHG ship carrying the same amount of liquid as a conventional LNG carrier with around the same weight using fiber reinforced plastics.

6.6 Water content limits

In the presence of free water, light hydrocarbons, and in some cases other gases like CO₂ will form gas hydrates under the right conditions. At high pressures e.g. 200 bars, the hydrate formation temperature limit can be as high as 25°C while in a typical HLG pressure range, 10-50 bars with the typical limit is between -40°C and -30°C [39]. As we can see from Figure 46, LNG at -160°C will unquestionably form hydrates at any pressure above ambient and must therefore contain no more water than that solved in the liquid hydrocarbons. The new concepts will both differ in temperature and pressure and the requirements for dehydration will change. The conditions however, will not be inside the safe zone of the hydrate formation curve so no free water can be present in any of the compositions.

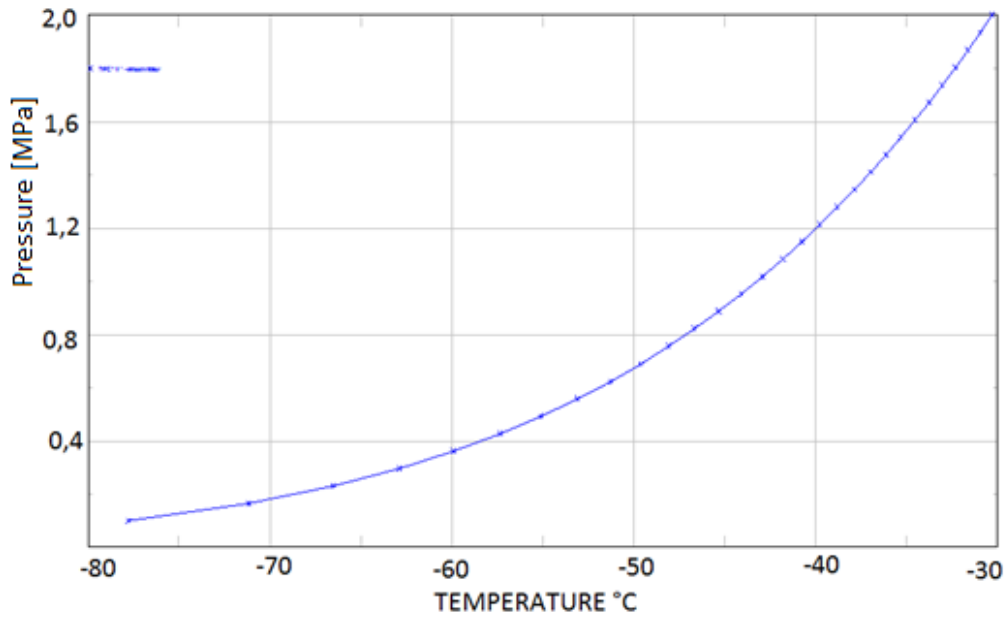


Figure 46: Hydrate Formation Curve

For any condition, hydrate formation is very complex and both kinetics and phase equilibrium contribute to the solid formation. Due to the kinetics, the formation of solids will not occur even though the water content is higher than the equilibrium concentration. With increased liquid temperature, the water removal limit may be increased. However, with increased pressure, the phase equilibrium for water-hydrate is influenced and less water can be present in the liquid as shown in Figure 47. The effect is particularly large when going from atmospheric to about 50 bars. The consequence of this will be a requirement of thorough dehydration for all the pressurized concepts if hydrate is to be avoided. This should be done in a molecular sieve adsorption process. For the LUWS concept, a small hydrate formation rate may be permitted. In any case, the delivered pipe gas will need to have a water dew point of -8°C or lower to comply with the EASEE’s harmonized gas specifications.

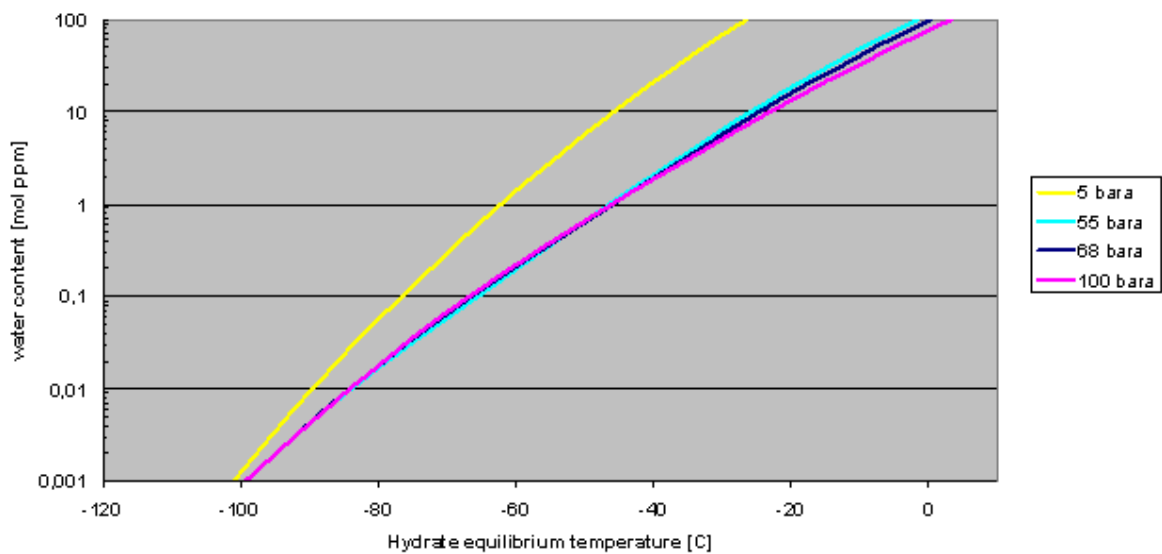
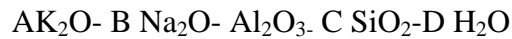


Figure 47: Water Content at hydrate equilibrium (E.Solbraa)

Molecular Sieve Dehydration

Molecular sieves, or mol-sieves, have been utilized for dehydration and other gas purification processes for many years and are well proven. The mol-sieves are crystalline hydrated metal aluminosilicates and are synthetically manufactured [40]. This crystalline has an enormous amount of cavities which were formed during the production, giving them an extremely large surface area and resulting pore volumes. It is in these cavities water or other substances will be adsorbed. When heated, these cavities will be emptied without damaging the structure. A typical chemical composition of the sieves is;



Where A, B, C and D are constants.

The molecular sieves may be classified by the size of the cavities and can be specified in the form X A, where X is a numerical value of the opening and A stands for the unit Ångström. The size of the cavities can be controlled by altering the fraction of substances in the crystalline giving different mol sieves for adsorption of different substances. The most common is 4A which is used for dehydration of air while the larger 5A can adsorb larger molecules like H₂S and CO₂. The smaller 3A will exclude most molecules other than water [40]. The theoretical equilibrium water capacity of the sieves is around 20-25%, depending on the sieve type. The regeneration temperature is between 200 – 350°C depending on the wanted speed of regeneration.

The silicates are usually placed in fixed packed beds where the gas stream is lead through and adsorbs the water. Gas pre-treatment for LNG production is usually done by a number of molecular sieve beds in parallel. These are arranged in a way that some may be regenerated while others are operative, giving a continuous process.

For some of the concepts of unprocessed liquefied gas, the whole well stream is intended liquefied without removal of any liquids, except water. However, as the molecular sieves needed for dehydration will be severely reduced by high boiling hydrocarbons, all the free liquids will need to be separated thoroughly in advance. The dew point of the entering gas should also be lower than the minimum internal temperature through the adsorber. This temperature may decrease as a result of the pressure drop over the adsorption beds. Even so, special attention should be taken when considering a system without a hydrocarbon stripper prior to the mol sieve process. Olefins and aromatics etc can enter the system as aerosols if not filtered properly and may polymerize inside the pores of the molecular sieves. When this occurs, the polymer molecules are too big to leave the pores during regeneration resulting in degradation of the performance [41]. Removal of aromatics and other heavy molecules from the cavities can be achieved by burn-off where the mol sieves are heated to high temperatures and injected with a small amount of oxygen.

6.7 Comparison of Concepts

There will be negative and positives sides to the different concepts depending on the various assumptions. As an overview of the most important aspects, tables of pros and cons are shown in Table 12 and Table 13.

There will be many good reasons for selecting conventional LNG as the preferred transportation method over the new, unconventional ones. The most obvious reason being the uncertainty of the other concepts as these have not been fully tested in a commercial way. Even for the largest oil companies in the world with solid finances, being the first to make use of some of these concepts would involve a risk that might not be worth the savings if successful. Choosing a method that turns out to be non-functional or problematic would inflict a heavy financial loss. Once a concept is proven and is successfully and economically delivering gas, the risk will be greatly reduced. This again will result in other companies wanting to utilize the same technology.

	Pros	Cons
Conventional LNG	Well proven technology	High equipment count
	Established receiving facilities	Extensive pre-treatment
	High flexibility in market	High power consumption for liquefaction
	Low pressure transport	High complexity for high performance
		High boil-off rate Low temperature
LUWS	Low equipment count at liquefaction site	Freeze out problems
	Low pressure transport	Low technical verification
	Transportation in conventional LNG ships possible	Low flexibility in market
	Possibility of mechanical separating methods at receiving site	Need for mechanical separation of solids or melting at receiving
	Possibly low complexity	High power consumption for liquefaction
	Very little pre-processing	Unproven commercialization

Table 12: Pros and Cons; LNG LUWS

Conventional LNG is a well proven and a safe option to choose but has high power consumption for liquefaction due to its low storage temperature. All the pressurized concepts will decrease this considerably. LUWS does not offer a lower power consumption in reality, as the whole well stream needs to be cooled to around -160°C, whereas LNG will have a LPG/NGL fraction removed before the cooling loop. From the calculated example in Table 7, this extra amount of liquid results in an increase in the net power need of around 18% compared to LNG. The only savings of energy demand for LUWS will be in the form of a decreased heat requirement for the regeneration processes and the fractionation of heavy hydrocarbons. As the energy consumption goes up for this concept, there will be more heat available from the power production even though the need for it is decreased. The only savings then will be in the form of a reduced number of equipment at the liquefaction site. For reducing the power consumption, the LPG could be stored and shipped in separate vessels.

With the increased focus on CO₂ capture and storage, the LUWS concept would be suitable for small reservoirs and where CO₂ re-injection is impossible. Having CO₂ solids in the transported product will avoid a second transportation method for this from the production site. The CO₂ would have to be separated at the receiving site and shipped for disposal.

	Pros	Cons
HLG	Low power consumption for liquefaction	High pressure storage
	Increased tolerance for CO₂	Lower flexibility in market
	Decreased Scrubber requirements	Unproven Commercialization
	Potentially less expensive ships	Heavier transportation vessels
	Possibility of steel pressure vessels	Pre-processing needed.
LHG	Very low power consumption for liquefaction	Very high storage pressure
	Option of not extracting LPG/NGL at production site	Need for alternative building material for storage vessels
	Possibility of no acid gas removal at production site	Safety issues associated with high pressure
	High transportation temperature	Unproven Commercialization
	Potentially less expensive ships	Lower flexibility in market

Table 13: Pros and Cons; HLG, PLNG, LHG

In addition to the increased energy needs, LUWS has a number of difficulties connected to the controlled freeze out of CO₂ and HHC's which none of the other concepts have. The extent of these difficulties is not yet fully been investigated, giving the LUWS concept a high uncertainty. The testing of this, both in small and big scale, will need to be successful before this concept can be considered a genuine option. If successful, it could prove to be competitive for smaller reservoirs where high specific power consumption is traded off in exchange of a simple process. For large optimized liquefaction plants the power consumption will have a larger impact on the value chain and a LUWS option will be less attractive.

LUWS would probably be able to utilize a transportation vessel designed for LNG but with specially fitted pumps and jetties for handling solids. This would make it less expensive to implement as soon as the technical difficulties with freeze out are solved. The other concepts would require building of new, specially designed tanker. This may be more expensive for the first vessels produced due to the design costs, but with larger number produced the cost might drop and turn out to be less expensive than LNG tankers. The reduction in cost the smaller pressure vessels can be manufactured separately from the hull decreasing the total delivery time for a ship order. Yet another possibility for small scale production is to retrofit an existing shipping vessel e.g. a dry bulk ship, to transport the relatively small containers for the pressurized liquid in smaller quantities.

The buildup of the value chain for LUWS will be similar to the one for LHG in many ways. They both will have their gas purification processes downstream at the receiving site with only dehydration and other minimal pre-processing before liquefaction. This is only true in the cases where a relatively CO₂ and HHC-lean gas is to be liquefied. According to the solubility diagram for CO₂, the 50 bar LHG should be able to contain at least 6 mole% of it. If the amount of contaminants exceed the amount the liquid can dissolve, a removal unit will be required. This can consist of a dew point control device like the Twister, and a CO₂ removal membrane. All the removed components will need to be re-injected or shipped by other means and will complicate the value chain. LHG will also need pressure vessels constructed of a light-weight material as steel would be too heavy. Some uncertainty regarding the cost, building methods and the fatigue life of these will also be a factor to consider. LUWS will have a power requirement for liquefaction of over three times that of LHG, giving large incentives for selecting LHG in preference to LUWS. Choosing LHG would also reduce the space needed for power production with around one third which would make it suitable for installation on a floating vessel in remote areas.

Today, there are a large number of receiving facilities for LNG in operation. The market is relatively flexible and producers can deliver the gas where they get the best price. For all the new concepts, a rebuild or extension of the receiving facilities is necessary as the delivered gas is not fulfilling the pipe-gas requirements. Retrofitting one receiving terminal may not be too expensive, but changing all is. Therefore, the new concepts will lose some of its flexibility in the gas market compared to LNG. The result of this will be entering long-term contracts for delivery to a specific site in the same way as pipe gas contracts.

All the concepts as presented in this thesis will need some conditioning at the receiving site. However, adjusting the amount of pre-processing so the post-processing is minimized is an option. Reducing the CO₂ content below 2,5 mole% and setting the hydrocarbon dew point below -2°C could eliminate the need for post-processing. The biggest saving will then be the power consumption for liquefaction, but still a large reduction of the pre-processing stages occurs. For the HLG12 presented here, just a slight increase in CO₂ removal and a lower hydrocarbon dew point at liquefaction would be sufficient for the gas to be sold directly as

pipe gas. This sweetening should be done by a membrane to decrease the complexity and both the capital and operating expenses. If other components are exceeding the limits for pipe gas e.g. O₂ and H₂S, some minor processing units may still be needed, but could be easily dealt with.

Using components from conventional LNG, or components from this with minor alterations, will reduce the cost for research and development. All the non freeze-out concepts should be able to use ordinary LNG heat exchangers as these usually have an operating pressure of around 60 bars. Mercury removal will be necessary however, as the aluminum will corrode when in contact with it. The heavier hydrocarbons that might deposit on the heat exchanger walls will need to be removed prior to liquefaction, but may not constitute a problem for all gas reservoirs. The LUWS concept will need a totally different design with larger tubing for solid formation. For the high pressure concepts, new fittings downstream of liquefaction will be needed in addition to a loading system to storage tanks and between this and the transportation vessel. Due to this similarity with LNG in the liquefaction, LHG and HLG could be tested and implemented at a reduced cost compared to LUWS giving another incentive for selecting one of these.

The total weight of the pressurized vessels will be greatly increased compared to LNG if constructed of steel. For LHG, the total weight of just the pressure vessels will be over 200 000 tons given a factor of safety of 4. The resulting ship would need to be 5-8 times the size of a conventional LNG tanker to bear the weight of both the pressure vessels and the cargo. For this heavy pressure, an alternative building material is necessary to limit the weight below an acceptable level. Prototypes for a fiber reinforced plastic pressure vessel of considerable size must be built and tested before the LHG concept could be an option. These would need to withstand low temperatures and comply with safety regulations. For the lower pressures in HLG, steel containment could prove viable, but still with an increase in weight and size compared to LNG.

Recently developed as well as unconventional equipment and processing systems may aid in the implementation of the new concepts. Because they do not need as thorough pre-treatment as LNG, all open for alternative CO₂ and HHC removal. Separating technologies like the Twister and 3S show potential for simplifying the dew point control as well as possibilities of simplifying CO₂ extraction in the future with further development. The CRYEX system fits perfectly with the potential pressure reduction at the receiving site for HLG/LHG, separating the CO₂ as a solid. In this way, parts of all the pressurized concepts can be stored at atmospheric pressures in existing LNG storage facilities.

A high level comparison chart of the new concepts together with CNG and LNG is shown in Table 14: Comparison of Concepts. The complex and negative red squares for LNG in the early stages of the value chain represent the thorough pre-processing and energy demanding liquefaction. These are changed to much more satisfying ones for all the new concepts. The exception is the energy demand for LUWS. Further down the value chain where conventional LNG is competitive and well established, the new concepts show noticeably less positive properties. The pressurized containment vessels make up a key barrier to making the new concepts more attractive. If these are provided, the comparison chart becomes more in favor of these and especially LHG. Shipped directly to a power plant for combustion with minimal post processing, this concepts becomes extremely attractive with only elements of uncertainty and technology qualification left as possible show stoppers.

	Pre-processing	Liquefaction Equipment count	Energy requirement	Containment Vessels	Receiving facility	Post processing	Complexity	Uncertainty	Technology Qualification
LNG	Red	Red	Red	Green	Green	Green	Red	Green	Green
HLG	Yellow	Green	Green	Yellow	Red	Yellow	Yellow	Yellow	Yellow
LHG	Green	Green	Green	Red	Yellow	Red	Yellow	Green	Yellow
LUWS	Green	Green	Red	Green	Red	Yellow	Red	Green	Red
CNG	Green	White	Green	Red	Yellow	Green	Green	Yellow	Green

Table 14: Comparison of Concepts

6.8 Further work

Deciding to modify the value chains for gas transportation worldwide is not a decision to handle leniently. In the case of the presented concepts, a huge amount of investments must be done before a well working and profitable delivery chain can be realized. In addition, the risks involved in some of the concepts may become too high for most companies to participate.

Pressure vessel material

For the high pressure concepts HLG and LHG, the main technical difficulty is the weight of the containment vessels if they are to be made of ordinary Nickel steel. The option of a composite material should be looked into further and evaluated thoroughly under cryogenic temperatures.

Economical analysis of HLG/PLNG/LHG

An economical analysis should be carried out for the concepts of increased pressure. As the technical differences from LNG would require new production techniques for the needed equipment and storage, the first units would be very expensive. A number of liquefaction plants and transportation vessels must be produced before the concept would be economically

profitable. Finding this limit when comparing to other alternatives for profitability, is a major undertaking with huge uncertainty, but should be looked into.

Optimal Pressure Selection

The optimal pressure for the HLG and LHG concepts would depend greatly on the gas reservoir which is to be developed due to the increased solubility of contaminants in the gas. Therefore, a case study with an existing potential reservoir with specific data for this site should be explored. The delivered liquid hydrocarbons could be used for a thought power plant where this is suitable. The number of transporting vessels, HLG and LPG, should be found in addition to the potential cost of these compared to LNG. Avoiding almost all the contaminants removal at the production site will save a lot of space and simplify the potential FPSO on which the process is installed. If the increased building costs and complexity of high pressures will justify the lower equipment count for this specific reservoir should be discussed.

Solid particles in suspension

An evaluation of the particle sizes and how they will behave in a specific gas composition over a shipping period of 20 days should be done. As this behavior is highly complex, a test rig may be needed for observation. The solid particles should be generated in both a heat exchanger and through expansive cooling to get the correct solid particle sizes. The test should be done in a similar composition as gas from a potential reservoir.

7 Conclusion

Alternative value chains to LNG based on natural gas in liquid form, have been proposed and patented by many parties over the last decades. The most studied are Liquefied Unprocessed Well Stream (LUWS) Aker solutions Heavy Liquid Gas (HLG), ExxonMobil's Pressurized Liquefied Natural Gas (PLNG) and Chevron's Liquefied Heavy Gas (LHG).

The work required for liquefaction is reduced for all the new concepts except LUWS, where an increase of 18,6% is observed. This increase is due to the larger amount of gas cooled to storage temperature. The two simulated HLG concepts at 12 and 20 bars consumed 62 and 52 percent respectively compared to conventional LNG. The 50 bar LHG concept would only need 39 percent, but this could be lowered if liquids were drawn off and stored and shipped separately. This would however make the value chain more complex, but could be a possible option depending on the cost of the shipping vessels.

Dehydration is required for all the concepts as hydrate formation during cool down would cause severe problems. CO₂ removal can be reduced significantly reducing the thermal energy need and complexity of the liquefaction plants. For LUWS and LHG, all the CO₂ may remain in the gas with freeze-out in LUWS, while dissolved in LHG. The two HLG concepts would require some acid gas treatment with a maximum limit of 1,4 and 2,7 mole% respectively. As the thoroughness of acid gas removal is considerably reduced, alternative removal processes such as membranes may be utilized.

New pressure vessel designs are needed to transport cryogenic liquids in large quantities. Steel would make the shipping vessel too heavy for LHG, but a fiber reinforced plastic with a metal liner shows potential in reducing this. If successfully built at an acceptable cost, LHG or a high pressure HLG is likely to be a favorable option compared to LNG in terms of complexity and energy requirements.

As a transition and as a trial study, an end consumer such as a power plant is suggested for the concepts with high concentrations of CO₂ and HHC's. In this way, post processing may be excluded giving a simple and energy efficient value chain. Due to the lowest work requirement and possibly no acid gas removal, the 50 bar LHG concept should be used. The main obstacle for implementing this is the pressure vessels which must be built in a light material.

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9 Appendix

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Appendix A – Gas Properties

Stream Name Stream Description		WELL
Phase		Vapor
Temperature Pressure	C BAR	90.000 200.000
Flowrate	KG-MOL/HR	1.000
Composition		
CO2		0.050
METHANE		0.800
ETHANE		0.050
PROPANE		0.020
IBUTANE		0.010
IPENTANE		0.010
HEXANE		0.010
HEPTANE		0.005
OCTANE		0.005
NONANE		0.005
DECANE		0.005
BENZENE		0.005
CH		0.005
N2		0.020

Appendix 3: Gas composition

Stream Name Stream Description		S1 WELL
Phase		Mixed
Temperature Pressure	C BAR	90,000 200,000
Flowrate	KG-MOL/SEC	5,969
Composition		
CO2		0,000
METHANE		0,842
ETHANE		0,053
PROPANE		0,021
IBUTANE		0,011
HEXANE		0,011
HEPTANE		0,005
OCTANE		0,005
NONANE		0,005
DECANE		0,005
BENZENE		0,005
CH		0,005
N2		0,021
IPENTANE		0,011

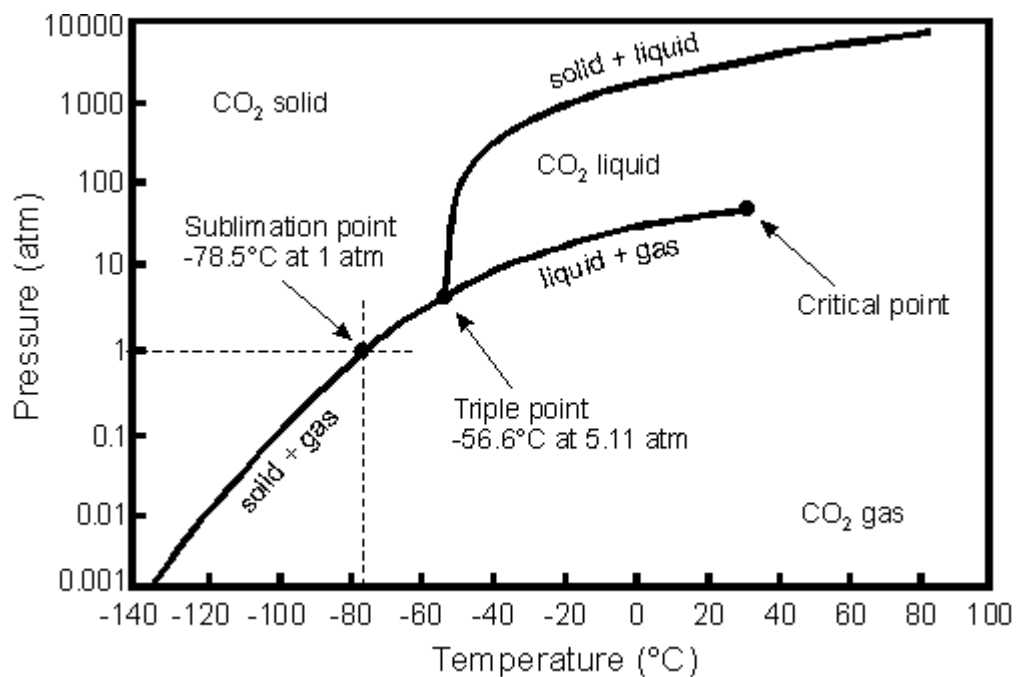
 Appendix 2: Gas composition after CO₂ Removal

Parameter	Unit	Min	Max	Recommended implementation date
WI	kWh/m ³	[13.60]	15.81	1/10/2010
d	m ³ /m ³	0.555	0.700	1/10/2010
Total S	mg/m ³	-	30	1/10/2006
H ₂ S + COS (as S)	mg/m ³	-	5	1/10/2006
RSH (as S)	mg/m ³	-	6	1/10/2006
O ₂	mol %	-	0.001*	1/10/2010
CO ₂	mol %	-	2.5	1/10/2006
H ₂ O DP	°C at 70 bar (a)	-	- 8	See note**
HC DP	°C at 1- 70 bar (a)	-	- 2	1/10/2006

* Limit is <0.001 mol%, daily average. However, cross border point daily average levels up to 0.01 mol% will be accepted if these are the result of the prudent operation of UGS's, existing in 2006, which use oxygen for desulphurisation purposes. (Based on the full CBP Wobbe range).

**At certain cross border points, less stringent values are used than defined in this CBP. For these cross border points, these values can be maintained and the relevant producers, shippers and transporters should examine together how the CBP value can be met in the long run. At all other cross border points, this value can be adopted by 1st October 2006.

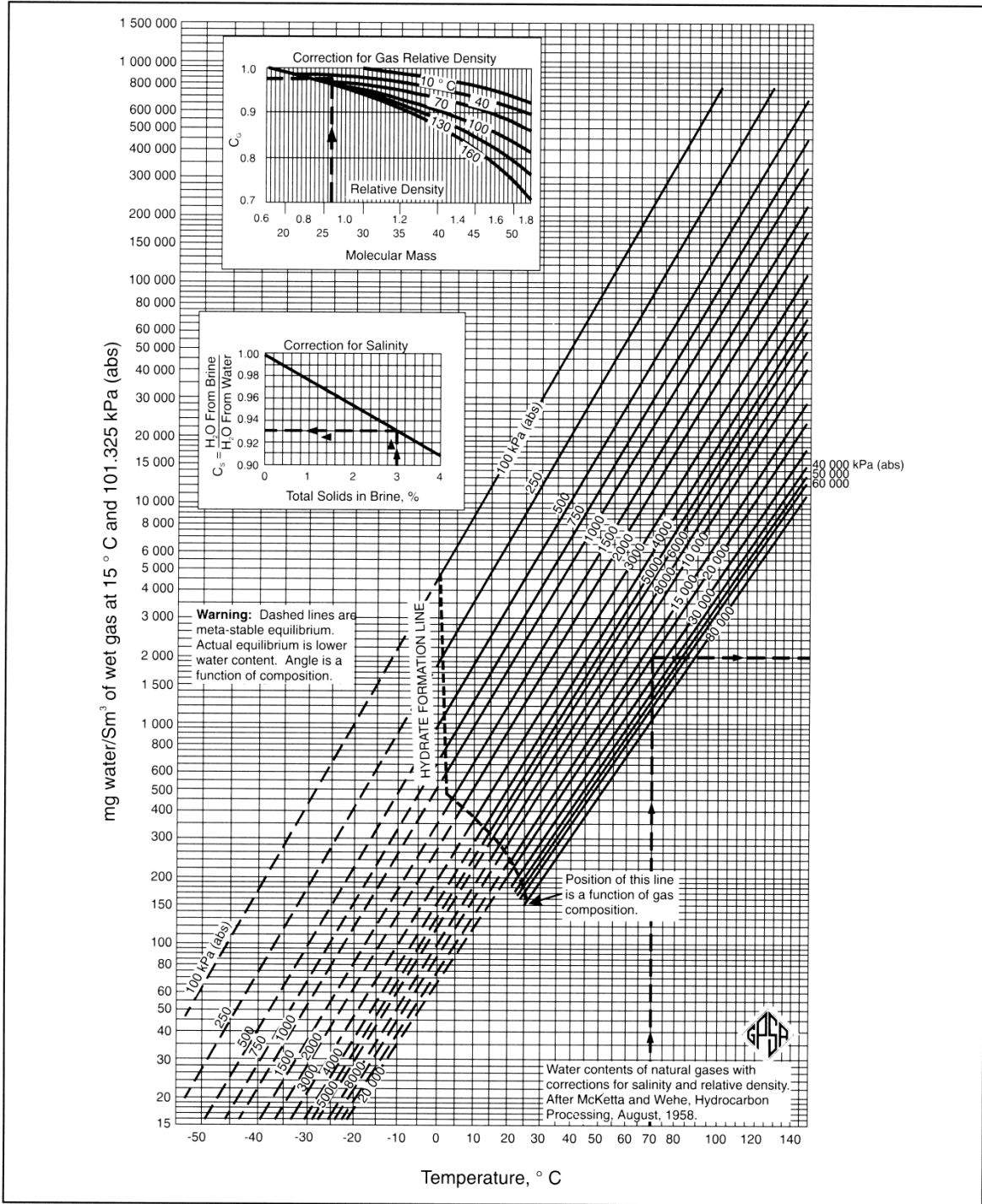
Appendix 1: EASEE Harmonized pipeline specifications for natural gas



Appendix 4: CO₂ Phase diagram (Prof. Shakhshiri 2008)

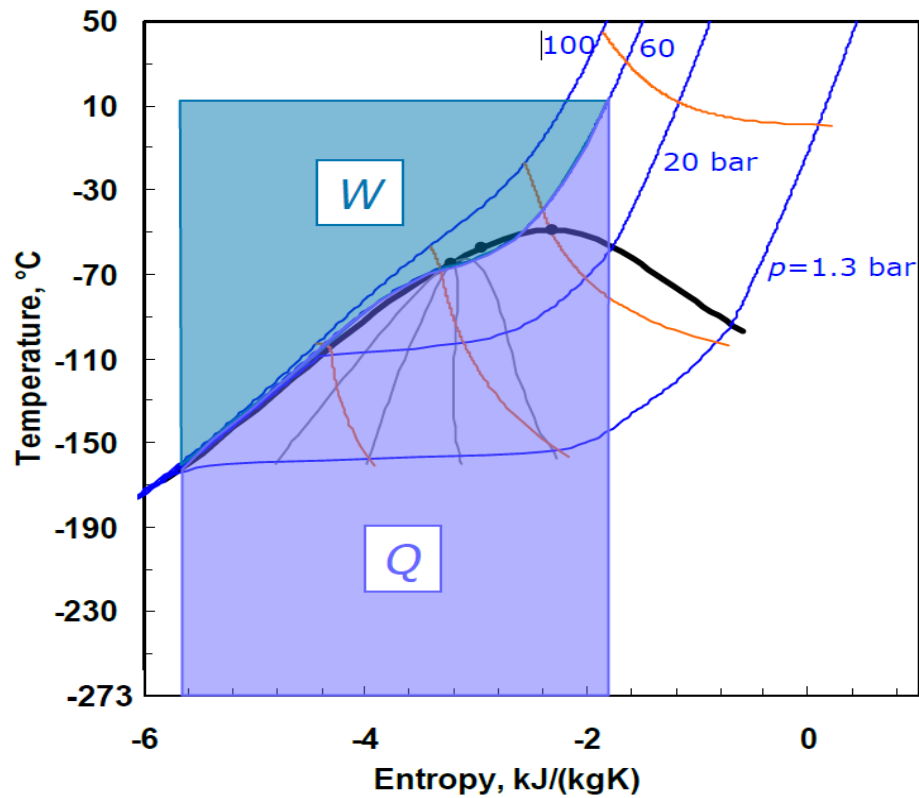
	T _c °C	P _c bar	NB °C	NF °C
Cyclo hexane			81	7
Benzene			80	6
Decane			174,2	-29,7
Nonane			150,8	-51
CO ₂	-31,05	73,8	-78,45	-56,4
Octane			126	-56,8
H ₂ S	100	89,37	-60,35	-85,55
Heptane			98	-91
Hexane			69	-95
Ibutane	134,9	36,48	-11,7	-159,55
Ipentane			28	-160
Methane	-82,55	49,2	-161,3	-182,45
Ethane	-32,25	48,8	-88,5	-183,25
Propane	-96,65	42,25	-41,9	-187,65
N ₂	-147	33,999	-195,9	-210

Appendix 5: Chemical compound Properties [42].



Appendix 6: Water content of Natural Gas (GPSA)

Appendix B: Miscellaneous



Appendix 7: TS diagram for liquefaction

Cr-Ni Austenitic Stainless Steel	304	
Density	8,00	g/cc
Hardness, Brinell	123	
Hardness, Knoop	138	
Hardness, Rockwell B	70	
Hardness, Vickers	129	
Tensile Strength, Ultimate	505	Mpa
Tensile Strength, Yield	215	Mpa
Elongation at Break	70,0	%
Modulus of Elasticity	193-200	Gpa
Poissons Ratio	0,29	
Charpy Impact	325	J
Shear Modulus	86,0	GPa
Carbon	<=0,080	%
Chromium	18,0-20,0	%
Nickel	8,0-10,5	%

Appendix 8: Cr-Ni Steel Properties [36]

Appendix 9: NeqSim Equations [33].

Liquid phase: SRK EOS

SRK EOS is one of the most often used cubic equations of state, which is:

$$p = \frac{NRT}{V-b} + \frac{a}{V(V+b)} \quad (1)$$

p is the pressure, N is the total amount of the component, R is the gas constant, T is the temperature of the system, V is the volume of the system, the parameters a and b are determined by critical temperature T_c , critical pressure P_c and acentric factor ω .

The Van der Waals 1-fluid mixing rule is used for the mixture, which is:

$$N = \sum_i n_i \quad (2)$$

$$a = \sum_{ij} \sqrt{a_i a_j} (1 - k_{ij}) n_i n_j \quad (3)$$

$$b = \sum_i b_i n_i \quad (4)$$

where i and j denote for component i and j in the mixture, n is the number of moles of each component, and k_{ij} is the binary interaction parameter.

Solid Phase: Solid fugacity model based on assumed sub-cooled liquid

The solid phase appears in the mixture is assumed to contain only pure hexane. The solid fugacity is expressed as:

$$f_i^{solid} = f_i^{liquid} \exp\left(-\left(\frac{\Delta H - T_i^{melt} \Delta C_p}{R}\right)\left(\frac{1}{T} - \frac{1}{T_i^{melt}}\right) + \frac{\Delta C_p}{R} \ln\left(\frac{T}{T_i^{melt}}\right) - \frac{(p - p_{atm})\Delta V}{RT}\right) \quad (6)$$

f_i^{solid} is the fugacity of pure solid component i , f_i^{liquid} is the fugacity of the same component as a pure liquid at the same pressure p and temperature T (calculated from the fluid phase model), ΔH , ΔC_p and ΔV are the changes in molar enthalpy, molar heat capacity and molar volume respectively on fusion at the melting point, T_i^{melt} is the normal melting point temperature of component i , and p_{atm} is the atmospheric pressure.

Regeneration heat in the sweetening process:

LNG:

Weight percent CO2 after LPG extraction: 0,1282

Regeneration heat= 0,1282*6200 kW/kg CO2= 795 kW/kg produced LNG

HLG12:

0,09076 kg CO2 removed for every kg produced HLG12

Regeneration heat= 0,09076*6200 kW/kg CO2= 563 kW/kg produced HLG12

HLG20

0,0574 kg CO2 removed for every kg produced HLG20

Regeneration heat= 0,0574*6200 kW/kg CO2= 356 kW/kg produced HLG20

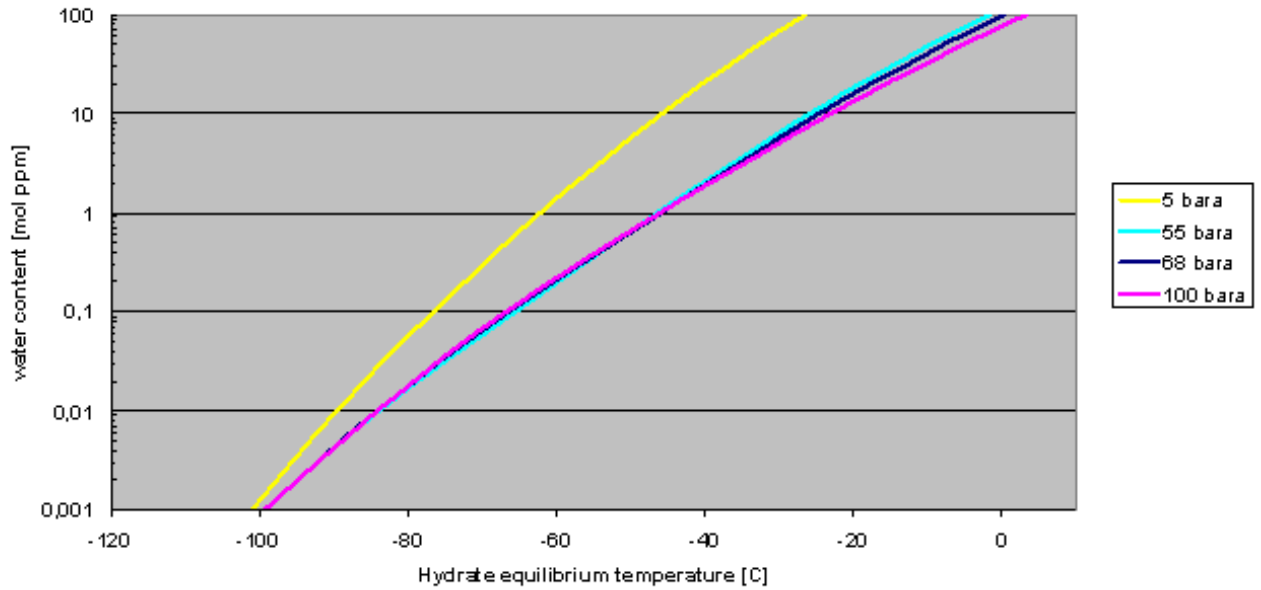
Appendix C: Simulation Results

HLG	12 bar	minus 125 oC
		Phase Fraction
	Solid-CO2	0,0359182
	Solid-n-Octane	0,003796333
	Solid-n-Nonane	0,00173224
	Solid-n_decane	0,004878383
	Solid-benzene	0,004687332
	Solid-c-Hexane	0,002114393
	liquid	0,946873119
		Liquid mole concentration
	CO2	0,0148717
	methane	0,844877
	ethane	0,0528047
	propane	0,0211218
	i-butane	0,010561
	i-pentane	0,010561
	n-hexane	0,010561
	n-heptane	0,00528047
	n-octane	0,00127118
	n-nonane	0,00345105
	nC10	0,000128439
	benzene	0,000330198
	c-hexane	0,00305844
	nitrogen	0,0211218

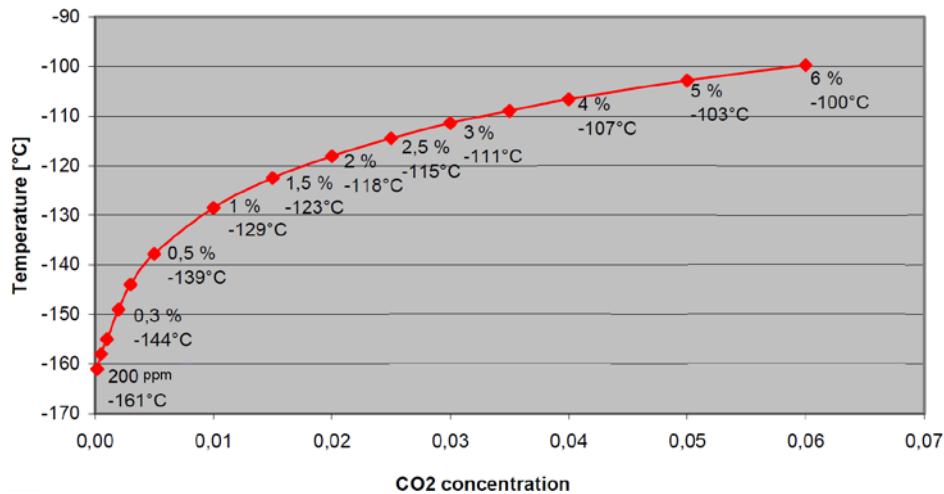
Appendix 10: NeqSim Results HLG12

HLG	20 bar	minus 115 oC
		Phase Fraction
	Solid-CO2	0,0224639
	Solid-n-Octane	0,001508954
	Solid-n-Decane	0,004570138
	Solid-n_benzene	0,00424856
	liquid	0,967208449
		Liquid Mole Fraction
	CO2	0,0284697
	methane	0,827123
	ethane	0,0516952
	propane	0,020678
	i-butane	0,010339
	i-pentane	0,010339
	n-hexane	0,010339
	n-heptane	0,00516952
	n-octane	0,00360942
	n-nonane	0,00516952
	nC10	0,000444435
	benzene	0,000776918
	c-hexane	0,00516952
	nitrogen	0,020678

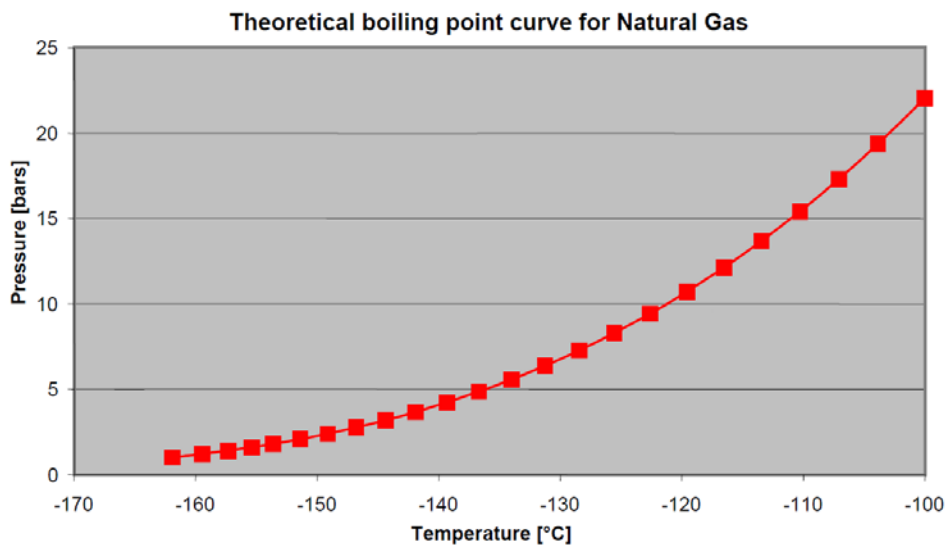
Appendix 11: NeqSim Results HLG20



Appendix 14: Hydrate Equilibrium curves (E. Solbraa)



Appendix 12: CO₂ Solubility in CH₄ (Aker Kværner)



Appendix 13: Theoretical Boiling Point of NG (Aker Kværner)

