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Master of Science in Industrial Engineering and Management Master's Thesis

Nano-scale production of Liquefied Natural Gas (LNG) by Stirling Technology as an improvement of LNG value chain

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Dedicated to…

My father Demetrio and to my grandparents Juana and Isabelino who taught me that no matter where you come from or how little you have, with humility, effort, and faith you can achieve your dreams. They shall forever be in my heart.

Harold Joel Perales Uzcátegui

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Summary in English

The motivation of this work is to explore and increase the knowledge about new opportunities of the Liquefied Natural Gas (LNG) market, specifically introducing a nano scale production, with its description, steps, components, and main constraint. Natural gas is a key fossil component in the transition energy from the present to 2050, is going to be the most demanded energy source, moving out the coal and petroleum, of course, the production, logistics, and transportation are elemental to its trade. A worldwide perspective is presented to understand how demand and supply are affected by different drivers among regions and industry sectors. The nano scale production with the Stirling technology is suggested to be used by different sectors such as facilities that usually vent or burn huge amounts of natural gas, countries that depend on large pipelines grids of natural gas, or emerging small/medium scale productions plants of LNG, Biogas, etc. converting a product that is usually wasted for safety reasons into an added valued at zero cost and, creating a fuel with less CO_2 emissions than the common fuels. The final product (fuel) is suggested to be used for internal transport due different reasons well explained further. A thermodynamic study evaluation is presented to have the limits composition of heavy hydrocarbons at cryogenic conditions in order to avoid freeze out and make feasible the process, finalizing with an economic study of CAPEX and OPEX of the process to prove the financial feasibility.

Summary in Italian

L'obbiettivo di questo lavoro è esplorare e accrescere la conoscenza delle nuove opportunità all'interno del mercato del Gas Naturale Liquefatto (GNL), introducendo specificamente una produzione su nanoscala, con la sua descrizione, i passaggi, i componenti e il vincolo principale. Il gas naturale è un componente fossile chiave nella transizione energetica dal presente al 2050, sarà la fonte di energia più richiesta, sostituendo il carbone e il petrolio entro i prossimi 40 anni, ovviamente, la produzione, la logistica e il trasporto sono fondamentali per il suo commercio. Nella tesi viene presentata una prospettiva mondiale per capire in che modo la domanda e l'offerta sono influenzate da fattori diversi tra regioni e settori industriali. Contemporaneamente viene suggerita la produzione su nanoscala con tecnologia Stirling per essere utilizzata da diversi settori come impianti che solitamente sfiatano o bruciano enormi quantità di gas naturale, paesi che dipendono da griglie di gasdotti di grandi dimensioni, o impianti di produzioni emergenti su piccola / media scala di GNL, Biogas, ecc., convertendo un prodotto che solitamente viene sprecato per ragioni di sicurezza in un valore aggiunto a costo zero e creando un combustibile con minori emissioni di CO_2 rispetto ai comuni combustibili. Si suggerisce di utilizzare il prodotto finale (carburante) per il trasporto interno per diversi motivi ben spiegati. Infine viene presentato uno studio di valutazione termodinamico per avere i limiti di composizione degli idrocarburi pesanti in condizioni criogeniche al fine di evitare il congelamento e rendere fattibile il processo, finalizzato con uno studio economico di CAPEX e OPEX del processo per dimostrare la fattibilità economica.

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NOMENCLATURE

bcm/yr	Billion cubic meter per year
CAPEX	Capital Expenditure
CH_4	Methane
COVID-19	Corona virus Disease 2019
CO_2	Carbon Dioxide
GDP	Gross Domestic Produc
Gm^3/yr	Cubic Gigameter per year
HHC	Heavy Hydrocarbons
Hg	Mercury
H_2O	Water
H_2S	Hydrogen Sulfide
Hz	Hertz
Kw	Kilowatts
LNG	Liquefied Natural Gas
MTPA	Million tons per year
Mt/yr	Mega-ton per year
OPEX	Operational Expenditure
ppm	Part per million
ppmv	Part per million by volume
rmsd	root mean square deviation
$\mu g/Nm^3$	Micro gram per normal metric cubic

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1. Introduction

1.1 Scope

This Master Thesis was written as the final work of the Master Degree in Industrial Engineering and Management within the Bilateral agreement of Double degree between the Central University of Venezuela and the Polytechnic University of Turin with the scope of complement the background of Chemical engineering, analyzing and giving key drivers to make a process and product feasible into the Natural Gas market.

1.2 Objective

The main objective for this thesis is to present an overview and an alternative to improve the liquefied Natural Gas value chain, with the nano-scale production, presenting a LNG worldwide market context, a thermodynamic study composition in order to make feasible the production and finally an economic feasibility.

1.3 Background

The large scale of Gas production and liquefaction is already standardized within the Oil & Gas industry, nowadays key factors are redefining the business such as de-carbonization in the transport and manufacturing sector, also the mentioned sector has been dominated by countries rich in this raw utility. Since 2018 Global Natural gas is increasing its demand by roughly 4%/yr., the highest increment since 2010 [1]. The industry is switching off from Large scale production to small scale production and transportation, in order to supply small markets and end-users. The energy transition and the reduction of CO_2 emissions are already ongoing, this causes the necessity to improve technology, as for example countries which aren't rich in natural gas such Italy, France and Spain are improving and investing in this small scale and by the other hand countries rich in oil & gas are burning tons of natural gas in its refineries, which is a source that can be highly used and converted into and added value.

1.4 Limitations

The use of LNG as a potential source LNG as a potential source of energy for several industries is limited by the lack of information regarding all the advantages it provides. The mitigation of environmental pollution and reduction of CO_2, NO_2 emissions due to its properties, are not well known. This lack of information stunt the development and improvement even though for countries and regions rich in oil & Gas. Its liquefaction process is highly constrained by different factors, being the most limiting its Gas compositions whose freeze out during the process is not so predictable according to the normal thermodynamic equations of state and finally, a CAPEX and OPEX are high overestimated since cryogenic conditions are involved in the process.

2. Theoretical Framework

Since there are many types of fuels, hydrocarbons fossils are the most commons due to their capacity to generate heat during their combustion. Hydrocarbon combustions means a reaction where a hydrocarbon reacts with oxygen to produce carbon dioxide, water, and heat. The energy necessary to break the bonds in the hydrocarbon molecules is significantly less than the energy released in the formation of the bonds in the CO_2 and H_2O molecules [2].

The general reaction is described below,

$$C_xH_y + N(O_2) \leftarrow\!\rightarrow x\,(CO_2) + \frac{y}{2}(H_2O)$$

x refers to the number of carbon atoms

y refers to the number of hydrogen atoms

N refers to the number of oxygen atoms

The main features to be considered on fuels are their efficiency which its directly correlated to the thermal power or Low heating value per kilogram and the amount of CO_2 produced per combustion, measures that will be defined and compared further.

Lower heating Value (LHV) kWh/kg			
Hydrogen (g)	33.3	Kerosene (l)	11.94
Pure Methane (g)	13.9	LNG (l)	13.50
Butane (l)	12.59	LPG (l)	12.64
Diesel (l)	11.83	Marine Gas oil (l)	11.89
Ethane (l)	13.28	Methanol (l)	11.89

Ethanol (l)	7.42	Propane (l)	12.88
Gasoline (l)	12.6	Petroleum Naphtha (l)	12.47
Gas oil (l)	11.89	Petroleum Coke (s)	8.19

Table 1 Fuels Net heating values [3]

In the Table 1 Fuels Net heating values it can be appreciated a list of commons fuels and their LHV (term detailed explained further). The main parameter to have an approach of efficiency in terms of capacity to generate heat, now its importance also depends on how less CO_2 can be emitted.

A comparative Table with the amount of CO_2 emissions per every 293.1 kwh production on different fuels is represented below,

Fuel	***Kg of CO_2 emissions***
Anthracite Coal	104
Lignite Coal	97.9
Subbituminous Coal	97.4
Bituminous Coal	93.5
Diesel	73.2
Gasoline	71.5
Propane	63.2
Natural Gas	53.2

Table 2 Emission of CO_2 per energy production by different fuels [2]

As is evidenced the natural gas provides the lowest amount of CO_2 emissions between several fossil fuels, this represent an economic added value if that amount is equivalent to cash or money saved on decarbonization process.

2.1 Liquefied Natural Gas

LNG is a natural gas which is refrigerated from its gas phase until its liquid phase under very low temperatures at roughly -162 ◦C and at 1 bar (atmospheric pressure). LNG is composed by different organic components in its majority by methane (CH_4) between 84% and 99% depends on its type or reservoir source and usually other organic components like butane, propane, dioxide carbon (CO_2), sulfur of hydrogen (H_2S), nitrogen (N_2) and water (H_2O) [4].

There are 6 types of natural gas which affects directly in its composition.

- Associated gas: Gas in contact with oil into the reservoir
- Non associated gas: Gas in reservoir without contact with oil
- Sweet gas: gas with free content of sulfured components
- Bitter gas: gas with high concentration of sulfured components (more than 4 ppm)
- Dry Gas: Gas with more content of Methane and less contents of others weight hydrocarbon
- Wet Gas: Gas with high concentration content of weights hydrocarbons

In the Table 3 there are illustrated the average range of hydrocarbon and nitrogen compositions

CH_4	83.6 – 99.7 mole %
C_2H_6	0 – 12.1 mole %
C_3H_8	0 – 3.6 mole %
C_4H_{10}	0 – 1.5 mole %
N_2	0 – 1.7 mole %

Table 3 Range of LNG components [5]

The natural gas is upgraded according form its well composition and classify in LNG, NGL (Natural gas liquid) and LGP (Liquid petroleum gas).

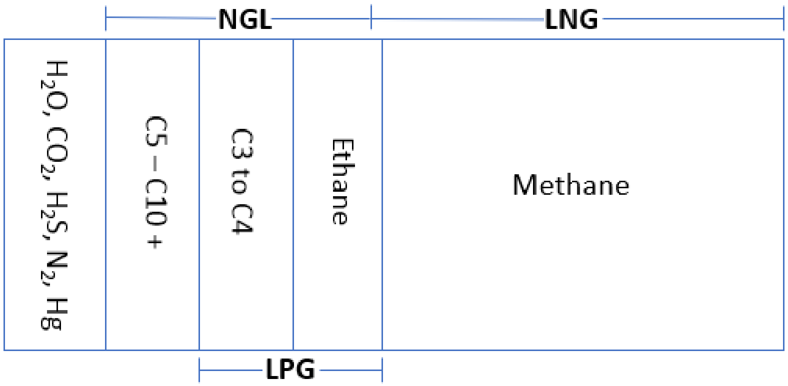


Figure 1 Typical Natural Gas composition [6]

The Figure 1 Typical Natural Gas composition describe of natural is classified according its composition, NGL compounded with mixture of hydrocarbon from C3 (propane), C4 (butane), C5 (pentane) until Decane C10 and, LPG with composition from C2 until C4.

LNG's some physical features are its colorless, odorless, and low density; around 430 kg/m^3 and 470 kg/m^3 (0.45 regarding water), also is noncorrosive [4]. Its volume is 1/600 in comparison to its gas state, which is one of its major characteristics, easy to transportation and storage into vessels.

Herewith below there are the main concepts and definitions regarding the thermodynamic of natural gas, some of them are implicit in the simulators used and explained in the further chapters.

a. Methane number influence

The methane composition rate has an impact on the process of treatment and especially in the efficiency of fuel, this is called "knock resistance of the fuel". A fuel knock resistance that is badly low for the engine affects its efficiency performance and causes engine knock, increases pollutant emissions, number of failures, and reduce its lifetime.

The knock resistance of LNG is characterized by the methane number, which is analogous to the octane number for gasoline. There are several methods for calculating an approximate of the number of methane depending on the mathematical model, which varies from polynomial methods till equation relations, using the quotient between the number of hydrogen and carbon, besides the evaluation of other components like oxygen, nitrogen, etc. Some of those methods are AVL, MWM, CARB, GRI, Cummins, Waukesha knock index, Wärtsilä and PKI MN. [7]

b. Higher heating value

The higher heating value or gross heating value is the energy evolved on burning s standard volume of gas when the total combustion gases are cooled to the reference temperature and the water of combustion condensed. The condensing water releases its latent heat which theoretically available for heating something, this represents the maximum possible heat available. [8]

c. Lower heating value

The lower heating value or net heating value is a lower number based on the assumption that water in the combustion gases remains in a vapor state, this is the usual circumstance is most heating equipment. [8]

d. Wobbe Index

Is a measure that was developed to characterize the similarity of gas mixtures based on the heat release form combustion. Specifically, correlates the heat release from combustion with the heating value density of the gas, is most used in the gas turbine industry for fuel gas specification and gas turbine performance guarantee. It is also one of the specifications for gas interchangeability required for pipeline distribution. The index is calculated by dividing the higher heating value of the gas by the square root of the gas density or MW (molecular weight) relative to air. [9]

2.1.1 Phase equilibria

Phase equilibria are the application of the principles of thermodynamics to the study of equilibrium relations in or among phases, conforming to homogeneous and heterogeneous phase equilibria, correspondingly. [10]

2.1.2 Thermodynamic Equilibrium

The freezing phenomena occur through conditions variations that affect the state of a single component, even more, a mix of them, liquid or vapor state, in that wat is important to understand the variables and thermodynamic equations that drive and can predict that phenomena. The phase equilibrium criteria are developed from the principle of conservation of energy and the 2nd law of thermodynamics.

2.1.3 Gibbs phase rule

Is an equation applied to determine the state of the system, it is defined by the phase rule written below,

$$F + P = C + 2$$

$$F = number\ of\ degrees\ of\ freedom\ which\ a\ system\ possesses$$

$$P = Number\ of\ phases\ in\ the\ system$$

$$C = Number\ of\ components\ or\ chemical\ compounds\ in\ the\ system$$

The degrees of freedom refer to the variables necessary to fix the phase state of the system. One or more of the following variables are commonly used: pressure, temperature, volume, and total or partial composition of one or more phases present. [8]

2.1.4 Compressibility Factor

The compressibility factor *Z*, is defined as the ratio of the actual volume to the volume predicted by the ideal gas law at a given temperature and pressure [11].

$$Z = \frac{v}{(\frac{RT}{P})} = \frac{Pv}{RT}$$

$$Where\ Z = \frac{Actual\ volume}{Volume\ predicted\ by\ the\ ideal\ gas\ law.}$$

$$R\ is\ the\ gas\ constant, T\ is\ temperature\ and\ P\ is\ pressure.$$

2.1.5 Fugacity Coefficient

Fugacity is the term that measures the deviation from ideal gas behavior in terms of chemical potential or the molar Gibbs free energy (G) of a real gas [12].

The fugacity can be obtained by different methods, which are,

- Compressibility Factor
- Properties Tables
- Viral Equation of State
- Equation of State

2.1.6 Peng-Robinson equation of state

The PR equation expresses fluid properties in relations of the critical properties and the acentric factor of each species involved can be applied for a pure gas or mixture of gases. [13]

$$P = \frac{RT}{Vm - b} - \frac{a\alpha}{(Vm)^2 + 2bVm - b^2}$$

$$a = \frac{0.45724R^2Tc^2}{Pc}$$

$$b = \frac{0.07780RTc}{Pc}$$

$$\alpha = (1 + (0.37464 + 1.54226\omega^2)(1 - Tr^2))^2$$

$$Tr = \frac{T}{Tc}$$

$$Where\ \omega\ is\ the\ acentric\ factor\ for\ the\ species, Pc\ is\ critical\ pressure\ and$$

$$Tc\ is\ a\ critical\ temperature$$

2.1.7 Critical Properties

The conditions of equilibrium for coexisting vapor and liquid phases of a pure substance are defined on a pressure-temperature diagram by the vapor pressure curve. This curve starts at the triple point, where vapor, liquid, and solid phases are in equilibrium, and ends at the critical point. [14]

2.1.8 Vapor Pressure

Is the pressure at which the vapor phase of a substance is in equilibrium with the liquid phase of that substance at a specified temperature. [14]

2.1.9 Eutectic Point

The point on a phase diagram where the maximum number of allowable phases are in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. [15]

2.1.9.2 Boil off gas (BOG)

Is the continuous evaporation or boiling gas from the liquefied natural gas that causes a rise of pressure inside the tank or storage increasing the temperature an affecting the quality of the LNG during the storage and transportation.

2.2 Historical Process production of LNG

The LNG industry is characterized by its large-scale production or economies of scale, due to the need of satisfy operation costs established on large size reservoirs.

Two main processes characterized the industry, liquefaction, and regasification since both are directly integrated, liquefaction to facilitate the transportation and supply chain and regasification to deliver the final product as a utility, the value, and supply chain process will be detailed explained further.

The LNG has its beginnings in The United States in 1912 when it was constructed the prototype plant in West Virginia and started its operation in 1917. The first liquefied operation facility was in Ohio, in 1941, also its storage into tanks under precise pressure conditions. The first transportation of a large bulk of LNG took place from Lake Charles, Louisiana, to Canvey Island, United Kingdom, then from 1971 and on were built four terminals in the States in Georgia, Louisiana, Maryland, and Massachusetts. The first offshore terminal began its operation in the Gulf of Mexico, starting the process of gasification for distribution through grid pipelines. [16]

Liquefaction plants frequently are designed with several units (trains) in parallel in order to produce large volumes of products, between 0.5 MTPA and 8 MTPA. The first step is the pretreatment process, which consists of cleaning the gas of impurities like acids, traces of non-hydrocarbon gases, and water. Secondly, heavy hydrocarbons are refrigerated at extremely low temperatures in order to remove them and prevent damage to the equipment. The gas remained (composed by methane) is refrigerated by a specific process, reducing its volume six hundred times ready for its storage. [16].

Baseload plants consist of one or multiple trains, they are designed for variable flow of production, capable to store large amounts of volumes and delivered depends on demand peaks. The train concept has been developed to run into market demand, as well as its parameter designs, on the other hand, there are small reservoirs that nowadays are an attractive option to exploit due to different concepts design of process, with variables CAPEX and OPEX, satisfying different markets segment.

A large design process is made by a rigorous accurate condition, equipment that requires engineering details in inputs conditions, operation, and outputs. Larger train size tends to decrease the unit cost production, making it more competitive in the marketplace.

In the Figure 2 Block Diagram of a LNG production plant it can be appreciated a typical process of LNG production (configuration may vary, depending on the raw gas composition, product specification, local legislation, environmental issues, and limits emissions).

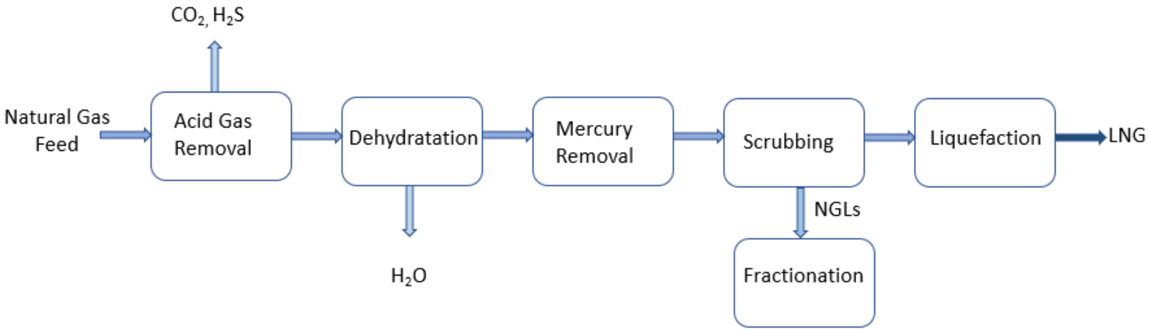


Figure 2 Block Diagram of a LNG production plant [17]

The Figure 2 Block Diagram of a LNG production plant represents a typical LNG process production, the gas coming from upstream shall be mechanical pre-treated. The gas must be treated in order to remove the H_2S and CO_2 to reach the specific standard conditions which are a maximum of 4 ppm and vapor pressure specification of 0.55 bar to 0.88 bar. The condensate hydrotreating unit removes sulfur compounds from the condensate let in the product free of sulfur. [4].

The gas treatment is one of the most critical section of the process, in this unit H_2S and CO_2, H_2O and mercury are removed let them on minimal quantities, fulfilling the gas liquefaction unit requirements (4 ppm of H_2S and 50 ppm of CO_2 as a minimum, 30 ppmv of S, 0.1 ppmv of water and mercury 0.01 µg/Nm^3) [4]. There are three separations processes for the gas treatment, chemical absorption, and physical absorption, and the mix of those two depending on the input gas composition and the product specifications, for instance, amines solvents, membrane treatment, etc.

2.3 Methane liquefaction technologies

During the last years, there have been developed different types of liquefaction, depending on the necessity or requirements, nonetheless, is the same overall technology for the treatment, purify and cool down the methane for liquefaction. The process technology and arrangement of equipment depends on the amount of delivery gas requirement and the conditions of the parameters.

Natural gas liquefaction process can be grouped into two main categories [18]

- Small to mid-scale LNG which relies on single pure refrigerants
- Large-scale LNG which relies on mixed refrigerants

For large-scale LNG, there are several variations of the mixed refrigerant (MR) technologies including:

- Propane pre-cool (C3MR), single mixed refrigerant
- Dual mixed refrigerant (DMR)
- Parallel mixed refrigerant
- Mixed Fluid Cascade Process (MFCP)
- C3 MR with a nitrogen refrigeration cycle (AP-X) process.

Since those processes are characterized by considerable high CAPEX and OPEX, also depending on continuous process production and plants highly restricted regarding mobility or deinstallation, a nano-scale production by Stirling cryogenic technology will be analyzed to optimize those limitations in the further chapters.

3. Market Context of LNG

Several companies and firms develop annual outlooks report analysis regarding energy demand and supply by country, regions, and worldwide but not only by region also by the industrial sector since transport, manufacturing, building, etc. The energy demand depends on several economic factors such as productivity, Gross domestic product (GDP), technology cost and learning curves, and demographic drivers like population and, government policies. Three companies forecast are presented emphasizing the demand and supply LNG and natural gas in order to give an approach to how it is influencing and growing progressively.

3.1. TOTAL outlook

There are two factors to take into account making an energy forecast demand, key drivers, and key outcomes. Key drivers are represented by three major factors, which are gross domestic products (GDP), population grown and access to energy, additionally regulation & policies (governments) and development of new technologies, those factors attached with key outcomes like energy demand growth, energy-saving and sustainability could determine then energy behavior industry among the time. Thus from a vast range of research and the actual behavior of the energy industry is possible to predict which source of energy is going to be more demanded in a certain amount of time [19].

The Gross domestic product is the measure of aggregate output in a national economy accounts or better explained is the value of the final goods and services produced in the economy during a given period [20]. Regarding the energy topic, this driver makes sensible the energy demand and supply, also directly linked to population growth.

There are two scenarios presented by TOTAL.

1) Momentum

The energy demand is based on announced policies and regulations in order to regulate emissions, 50% of sales on electro voltaic energy (EV) and 32% of total fleet by 2040, adopting state of art technologies, which means the highest level of development of technologies and energy intensity falls of 2.2% per year [19]. In a sum up momentum scenario explores in deep non-renewables energy like oil and natural gas and power demand in detail.

2) Rupture

The rupture scenario is characterized for being more impact on some results for instance mass electricity storage, an enormous switch to renewable power generation, faster electrification in all sectors and steeper reduction of energy intensity, ending with the same energy demand level in 2040 as in 2015. In a brief rupture scenario represent the breakout of non-renewable energy and anticipating the technological breakthroughs and strong shift in public policies [19].

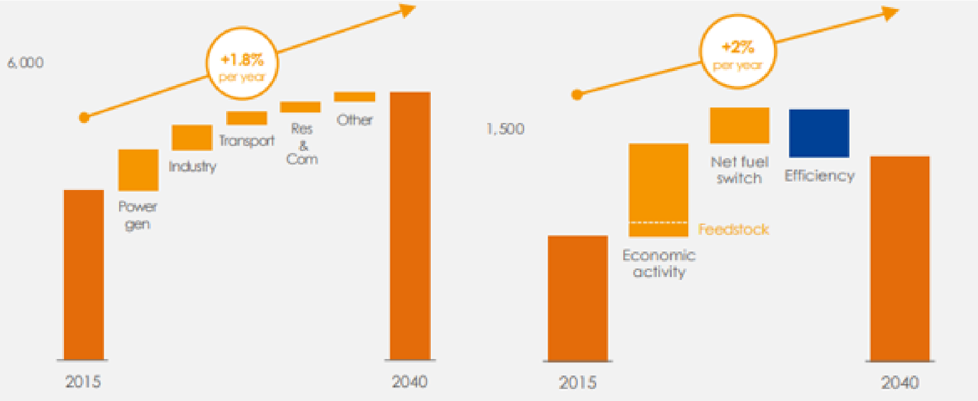


Figure 3 a) Global natural demand gas and b) natural demand gas by industry in bcm/yr [19]

In the Figure 3 there are represented two graphs: a) the global demand of natural gas and b) the demand by sector. In 2015 the global natural gas demand waslyoughky 3,400 Bcm/yr, is notable how by the year 2040 it will be 6,000 bcm/yr, representing an increase of roughly 40%. The power generation, industry and transport are the sectors with more gross demand, this increase represents nearly 1.8% per year, by the other hand, the increase by industry represents a total increase of 1,500 btw distributed as a 2% per year. The economic activity, the net fuel switch, and the efficiency in the main factors. The switch from coal & oil is driven by emission regulations for example the Paris agreement and the program blue sky of China, and the availabilities and affordability of enormous resources of natural gas.

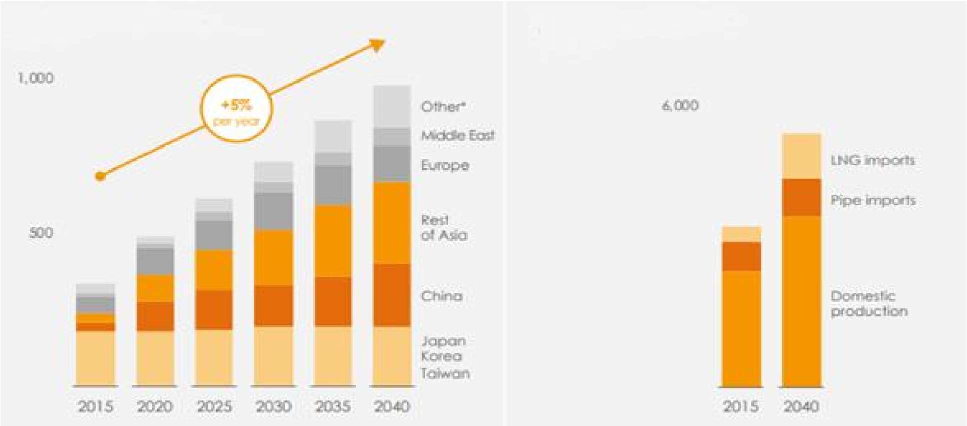


Figure 4 A) Global LNG demand and B) Global gas balance [19]

In Figure 4 A) Global LNG demand and B) Global gas balance are represented the global LNG demand and the global gas balance. The gross growth is represented by Asian countries like China, rest of Asia yet Japan, Korea, and Taiwan will have a constant demand. On the other hand, approximately 25% of the demand is represented by Europe, The Middle East, and others. The consumption will be between 500 and 1,000 bcm/yr with an annual growth of 5%.

The second graph Is represented the global gas balance, showing how is distributed system of gas, by the year 2040 it will be a consumption of 6,000 bcm/yr with a notable increase in LNG imports, contrary to the pipe imports which remains more or less constant.

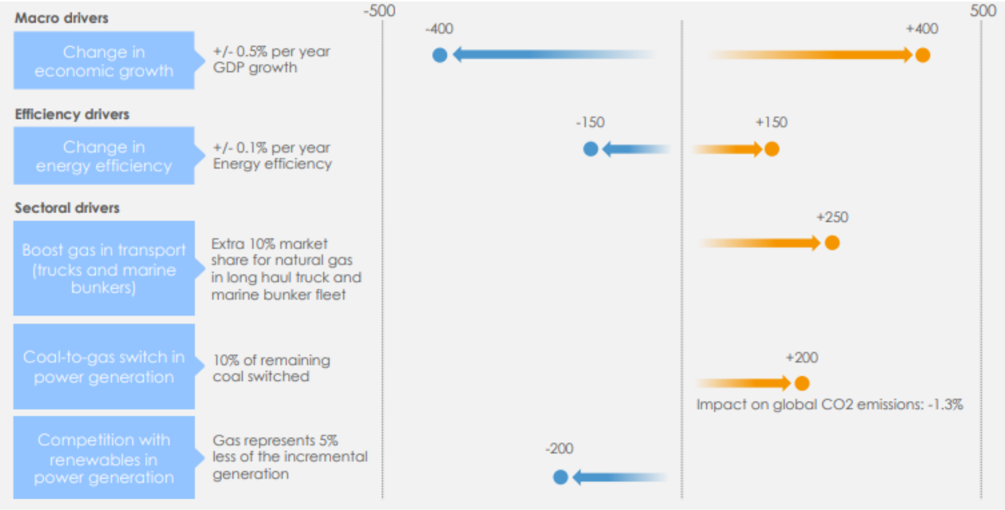


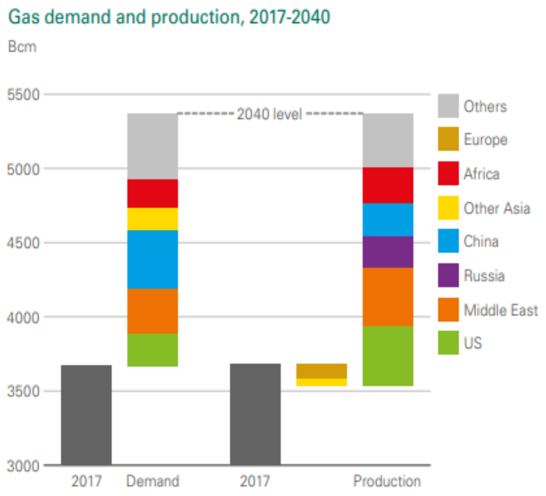
Figure 5 Natural gas demand sensitives [19]

Figure 5 there are represented the main drivers by the year 2040, The change in economic growth and the in energy efficiency have the same probability of increase or decrease, being +/- 0.5% of GDP and +/- 0.1% per year energy efficiency contrary of the sectorial drivers which represent 10% both increase for gas transportation by trucks and marine bunkers and switch energy from coal to gas and 5% less of the generation power because of the competition with renewables energies.

3.2 BP Energy Outlook 2019

The energy outlook considers different factors that drive the global energy transition from 2017 to 2040. The main macro factor is the constant increase of GDP, attached to the population growth of one-third of the actual-world population, which is traduced in 9 billion approximately.

The fast-growing GDP as a consequence of the developing economies, China, India, and the rest of Asia, are pushing out more demand of energy. Thus transportation, industrial, and power consumption are the main demanders for energy. In the evolving scenario carbon emission continuous to rise [21].



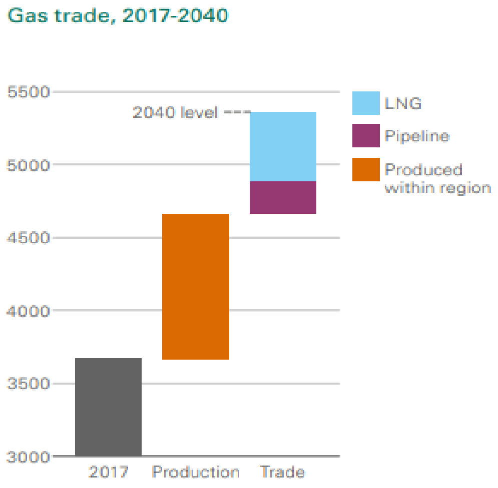


Figure 6 Gas demand and production, 2017-2040 [21]

Figure 7 Production trade of gas 2017-2040

As it showed in the Figure 6 the global demand and production by the year 2040 it's around 5400 bcm which represents an increase of approximately 46% which means 2% per year. It is notable how for the demand countries like US, Middle East, and China are the most demanders representing more than 50% let in regions like Europe, Africa and the rest of Latin America with a minority percentage, contrary for the production China and the rest of Asia show a decrease in production, that could mean the development of new technologies integrated with renewable energy, for the other The hand US and the Middle East will increase notable their production which has sense since they are strong competitors in the oil & gas industry.

In the Figure 7 is represented one of the most important factors for the gas production which is its transportation, as it can be appreciated 1,000 bcm roughly 18% its transported by pipeline or LNG, as a result of the future constantly demand, its notable how the LNG transportation is going to be more demanded than pipeline, therefore, saving cost and improving logistic operation for companies.

Summing up, natural gas is rising powerfully because of the strong energy demand and supported by the large reservoirs of gas available throughout the world, mitigating the transportation problems with LNG supply.

It is remarkable how gas demand is common to spread into the regions, driven by the constant's changes of development, a fast-growing population, and more emissions regulations.

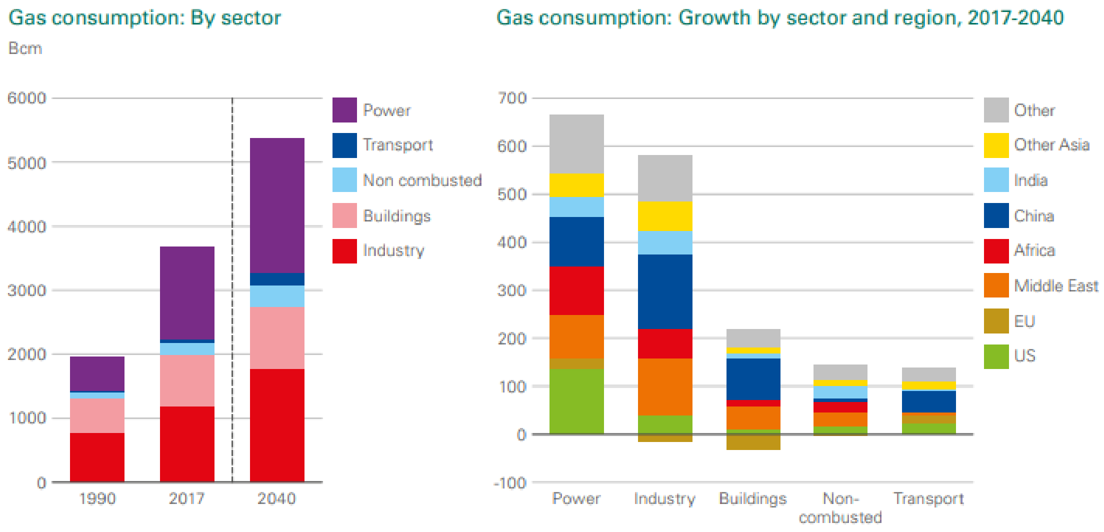


Figure 8 Gas consumption by sector and Gas consumption by country and region from 2017-2040 [21]

In the Figure 8 there are represented the global demand by sector consumption and region, by sector consumption is visible how the growth remains constant along time being power and industry the most consumers of gas, buildings in the third place, being transport and non-combusted the lowest, at the year 2040 power will require more energy because same reasons explained before with a 2,000 bcm of the demand representing approximately 37%, similarly to the demand of the industry with 1,800 bcm, buildings represent roughly 1,000 bcm which is around 18%.

The increased industrial demand is a consequence by developing economies which will demand large amounts of energy in order to keep producing product and services like china or only commodities goods like The Middle East and Africa, yet, for the power industry countries like US, Middle East, Africa, and China will have related demand. For the rest of the sectors is notable how China will keep its presence as a high demander followed by the Middle East, other countries, and The United States.

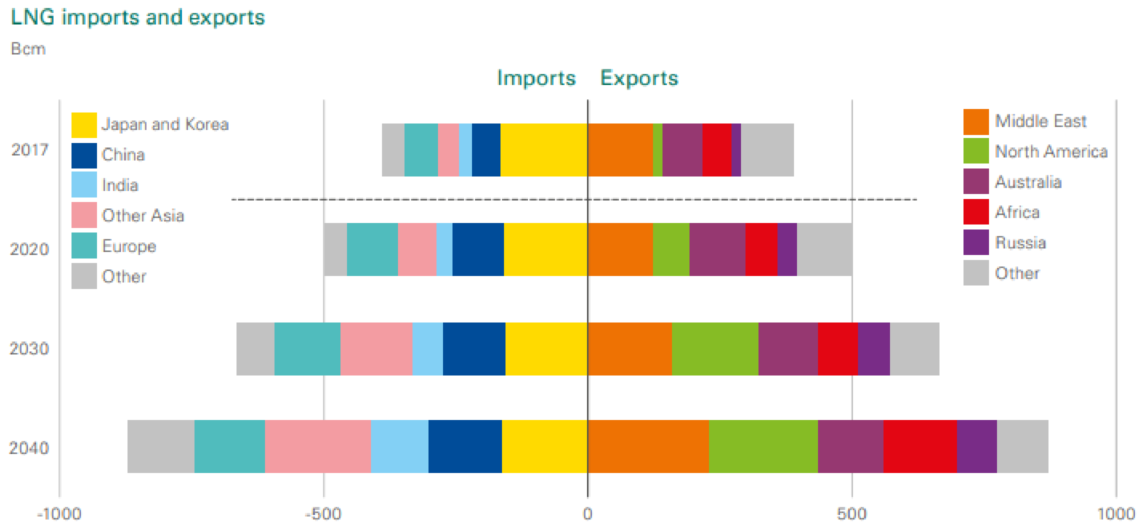


Figure 9 LNG imports and exports, 2017-2040. [21]

The Figure 9 is represented by the Imports and exports of LNG by countries and region, Asia represents more than 50% of the imports, the importers are dived by Japan and Korea with a constant demand along the time, this is because their lack of natural resources to produce energy and the growing emission regulations of non-renewables and nuclear energy, LNG becomes more attractive, by the other hand China and the rest of Asia have a constant increase of demand being both strong emerging economies, in the same way, but with less demand India, Europe remains as a balancing market because of the competition between LNG and pipelines grid. [21]

From the exports side, North America is leading the exports thanks to its shale gas and advanced liquefaction technology, followed by the Middle East thanks to its enormous oil and gas industry and capabilities to take advantage of them, then Africa and Russia.

3.3 DNV.GL Outlook 2019

The main drivers studied by DNV.GL's forecast depends on macroeconomics, technology, and global policies. DNV.GL used a more generalized consideration, dividing the world into the following regions:

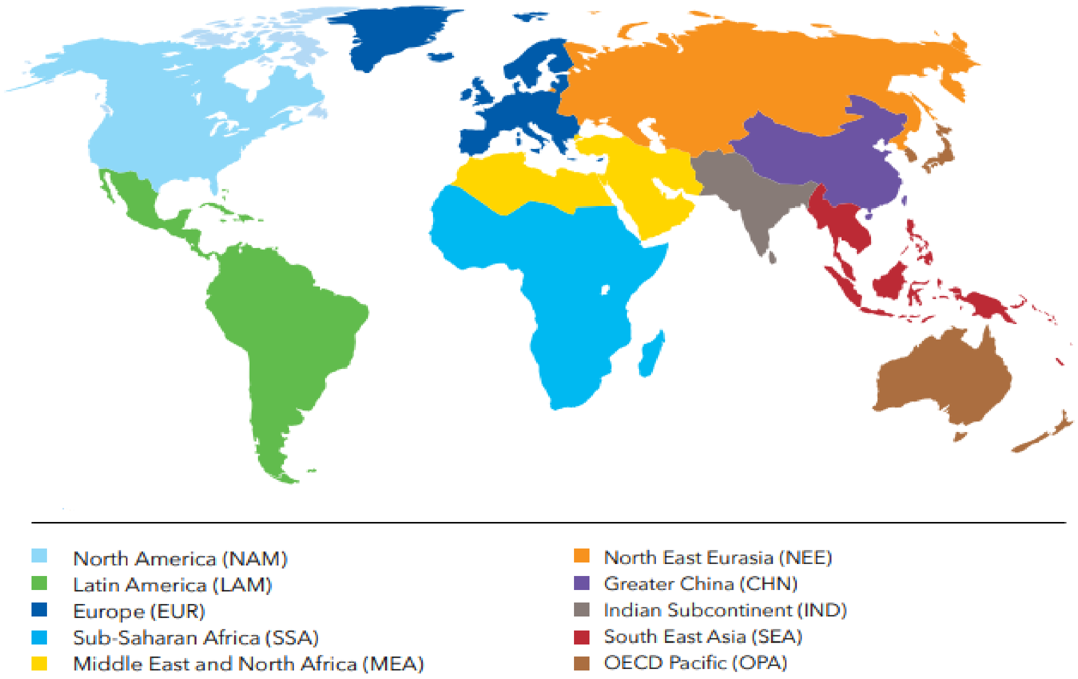


Figure 10 regions among the world [22]

Energy is directly related to people, on a macro scale; growth population, energy needs, consumption is continuing upward, depending on the region, and how developed it is, urbanization and production of assets. The Gross domestic product (GDP) is one of the most key drivers used in the DNV.GL's outlook is defined as the value of the final goods and services produced in the economy during a given period [23] likewise as a measure of the standard of living in a country and from the production point of view is a good measure for labor productivity [22].

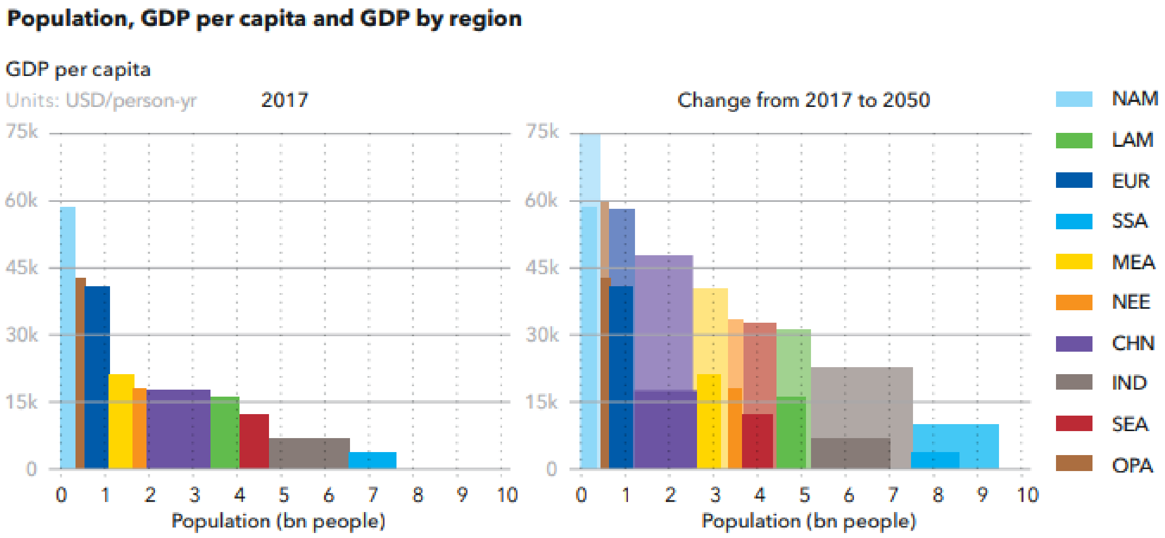


Figure 11 Population, GDP per capita and GDP by region [22]

In the Figure 11 Population, GDP per capita and GDP by region the world population rate by 2017 with a total of roughly 7.6 billion of people, India and China leading the amount of population with more than 2.5 billion, Latin-American with less than 1 billion, North America, OECD pacific and Europe, nearly 1.1 billion and with the highest GDP rate with more than 35k USD/person-year. By the year 2050, there is expected a population of approximately 9.2 billion which means an increase of around 2 billion people, with an increase in the GDP minimum of 10k except for south-Sahara Africa. Those projections are important to take into account at the moment to consider the energy demand expected in the next 30 years.

Government policies have a fundamental role in how fast technologies could be implemented in order to increase productivity, supply the energy demand, and manage the number of emissions. Policies are driven by political groups, economic interests and at the same time attached at cycle elections.

DNV.GL considers policies characterizes by drivers and barriers that maintenance the ongoing society like balance energy-security, preservation of jobs, industrial productivity. Four key areas are controlled by governments, which are: Climate risks, Air pollution, smooth transition, and programs like sustainable development goals (SDGs) and nationally determined contributions (NDCs) [22].

Governments influence three main capacities [22]

1. Stimulating technology development
2. Shaping and Creating demand
3. Fixing market distortions

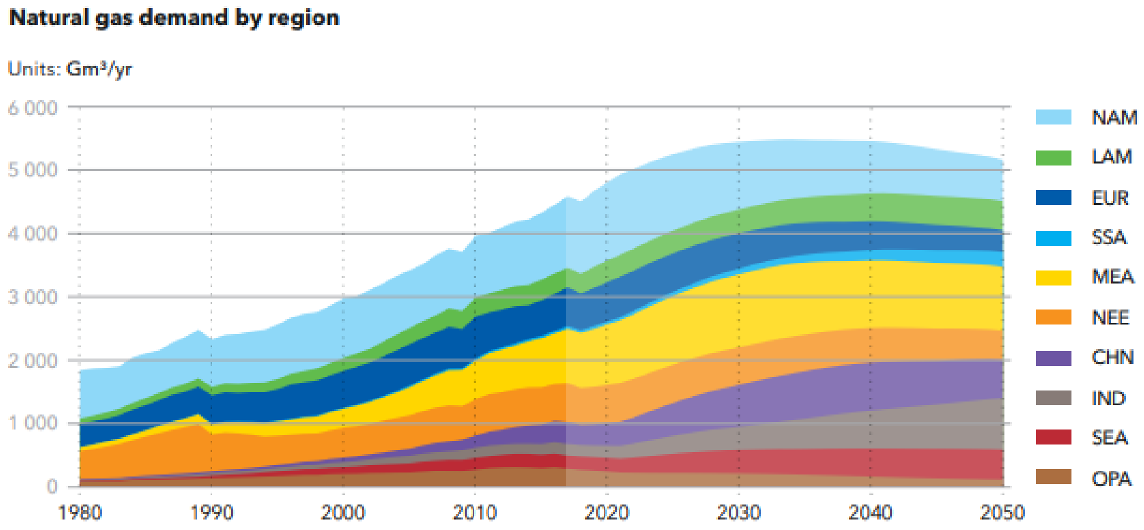


Figure 12 Natural Gas demand by region [22]

Figure 12 Natural Gas demand by region represents the natural gas demand since 1980 until 2050, being the focus in the rate time of interest 2017-2040, is notable how there is a small decrease between 2017 and 2018 and it will be an increase from 2018 with roughly 4,500 gm^3/yr until 2040 with 5400 gm^3/yr representing an increase of 20 %, notice it that the increase is more representative between 2017-2030 with nearly a 1.54 % per year, despite between 2030 and 2040 the behavior is moderately constant. North America, The Middle East, and North Africa, China, and India will lead the demand, followed by Europe, Latin America, Northeast Eurasia, and South East Asia which represent a slight increase in the demand.

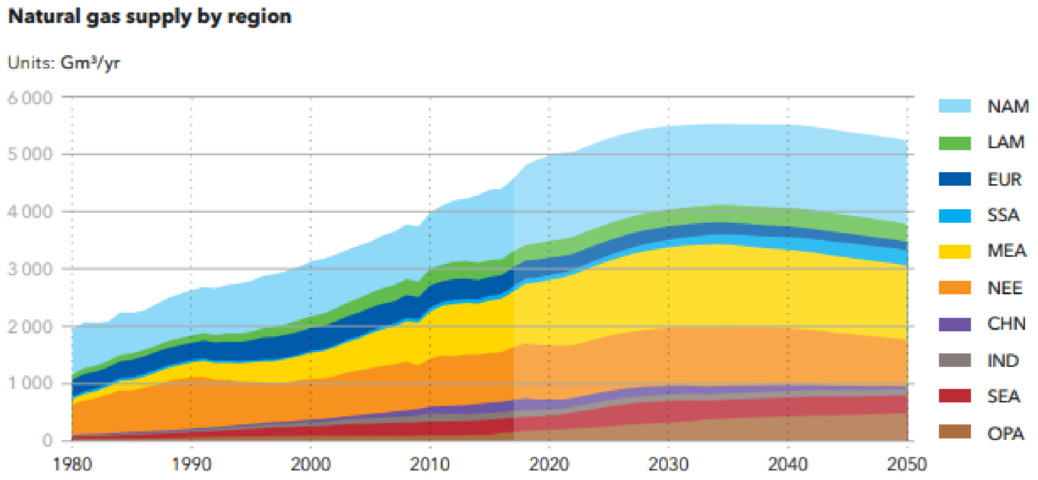


Figure 13 Natural gas supply [22]

Figure 13 Natural gas supply is represented by the amount of gas supply by region, again the rate time of interest is between 2017 and 2040. It can be notice how from 2017 and 2021 there is a considerable increase from nearly 4,600 Gm^3/yr to 5,000 Gm^3/yr, from 2021 till 2023 it will be constant, most probably because government policies changes as mentioned before, from 2023 till 2030 there is a constant increasing till 5,500 Gm^3/yr then go on will be constant with a small decrease.

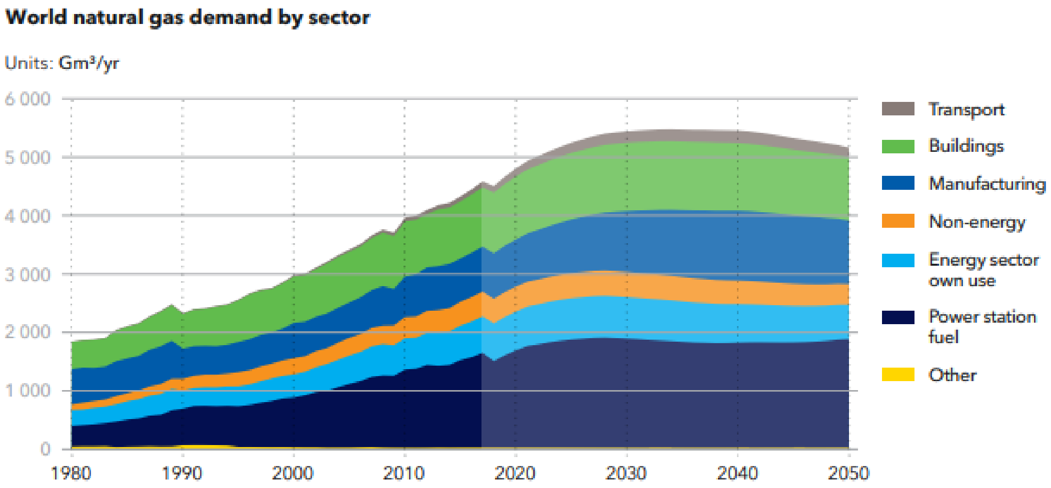


Figure 14 World Natural gas Demand by sector [22]

Figure 14 World Natural gas Demand by sector represents the demands trends by sector worldwide, since the year 1990 the demand has continuous growth and, is expected to keep growing until the year 2030, two notable declines are visible, one at the year 2008, related to the economic crisis and the second one before the 2020 year. The building sector, power fuel supply, and manufacturing represent the majors natural gas consumers, overall power fuel station with the higher demand, and the transport sector caused by.

There are two notables falls, one before the year 2010 and the second one before 2020, the first one is related to the economic world crisis, is characterized by the price decline of oil & Gas price, the second one after the year 2017.

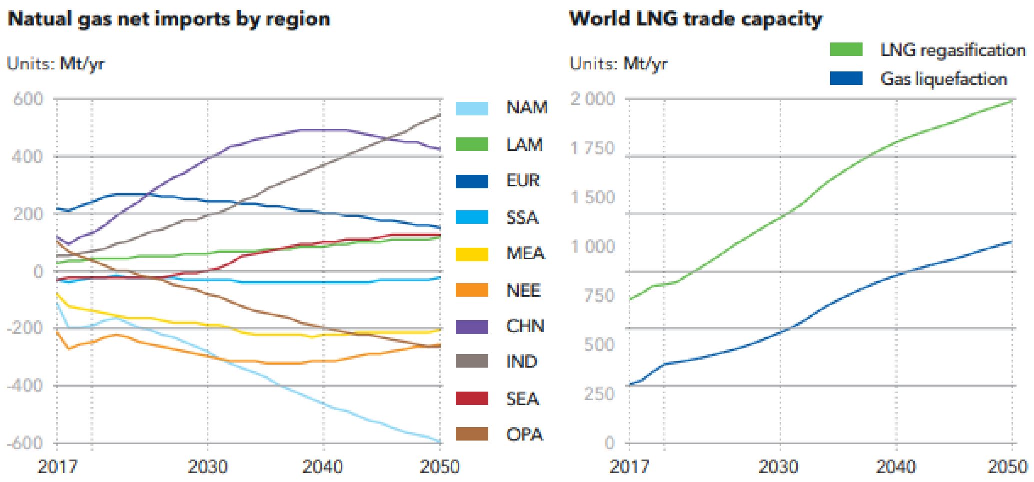


Figure 15 Natural Gas net imports and World LNG trade capacity [22]

Two important graphs are showed above, natural gas net imports by region and world LNG trade capacity, in the first one, three regions are described by their high, constant and low imports, NAM (North America) since 2017 until 2050 shows a decreasing of – 600 Mt/yr of natural gas imports, as mentioned before, NAM is improving in its self-supply of natural gas, not only in production but also in transportation and distribution. SSA (Sub- Saharan Africa) shows a constant net imports through all the timeline, which means has a solid economy and manage in their natural resources. IND (India) shows continuous growth due to its developing economy, with a net import value of 600 Mt/yr. Other regions are characterized by small growths, like Latin-American or small decreases like MEA (The Middle East and North Africa). Some other results not so constant like China, which in it accelerates developing demands huge quantities, and between 2030 and 2040 begins to decrease the net imports.

4. LNG demand and the Market context in Italy

New energy demands have been emerging and with them new challenges, after the worldwide economic crisis of 2008 it was a drop in gas demand in Europe. The transport sector is key in Europe, improve its efficiency, innovation and, efficiency cutting of the dependency on fossil fuels has been one of the main objectives. Improve the logistics, internal Europe trade-off, and the improvement of the economy are the main concerns mitigation at the same time the climate change. Italy had an energetic dependency of roughly 76.9% by 2013 [24], in consequence, as the main objective, the reduction of energetic dependency, reduction of CO_2 emissions, and the improvement of the air quality introducing the use of LNG is a priority.

In addition, the European Union promotes the use of not polluting fuels (direction DAFI), promoting particularly the use of LNG for the transport sector. Reducing the dependency on gasoline, diese,l and mitigating the pollution (at least 60% by 2050 regarding 1990).

In according with the demand and fulfillment the energy needs, the Italian government set off the Strategic National Plan (Quadro Strategico Nazionale) in section C (Supply of natural gas for transport and other uses), specifically the maritime transport of LNG and internal transport for the road transport and other uses. Those plans and strategies are made in order to incentive the LNG in a new market context and make Italy less dependent on Natural gas grids. The mitigation of energy dependence is highly related to geopolitical risks or future tensions between countries or regions. In section 5.13 is mentioned that storage and regasification plants under 50 ton of capacity are well accepted as a source for supply energy in the industrial sector, over 50 tons the plants are already considered as hazardous due the accumulation risks and/or any possible situation with inflammable gases.

In 2018 the Italian government proposed to the European commission a National Plan for the Energy and Environment (Piano Nazionale per l’Energia e il Clima PNIEC) as was the statement in council 2016/0375 about the governance of energy union focused on the essential role of the LNG regarding the energy transition.

Figure 16 LNG Activities in Italy [25]

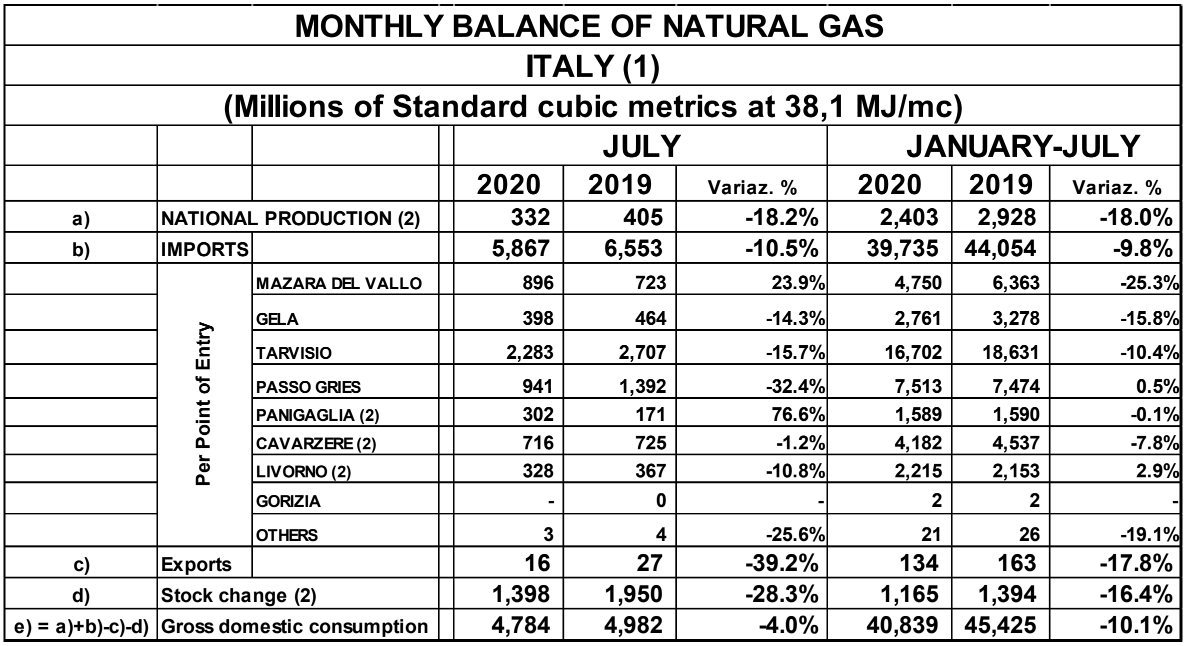
LNG plants Activities in Italy

In operation | Under construction | Planned | hold

⊛	Biogas Liquefaction Plant
● ●	Large Scale LNG import Terminal (without small scale services)
◉	Large Scale LNG import Terminal (with small scale services)
🟥 🟧	Small Scale LNG terminal
◉	Natural Gas liquefaction Plant
●	LNG filling Stations

Table 4 LNG activities figures description

According to the Figure 16 LNG Activities in Italy is notable how the LNG market developing in Italy, with 68 LNG filling stations is the highest number in Europe, and an increasing number of liquefaction plants of liquefied biomethane, furthermore how there are key locations of import terminals to supply the regions less industrialize such south Italy like Sicily, sardine.



MONTHLY BALANCE OF NATURAL GAS

ITALY (1)

(Millions of Standard cubic metrics at 38,1 MJ/mc)

			JULY			JANUARY-JULY		
			2020	2019	Variaz. %	2020	2019	Variaz. %
a)	NATIONAL PRODUCTION (2)		332	405	-18.2%	2,403	2,928	-18.0%
b)	IMPORTS		5,867	6,553	-10.5%	39,735	44,054	-9.8%
	Per Point of Entry	MAZARA DEL VALLO	896	723	23.9%	4,750	6,363	-25.3%
		GELA	398	464	-14.3%	2,761	3,278	-15.8%
		TARVISIO	2,283	2,707	-15.7%	16,702	18,631	-10.4%
		PASSO GRIES	941	1,392	-32.4%	7,513	7,474	0.5%
		PANIGAGLIA (2)	302	171	76.6%	1,589	1,590	-0.1%
		CAVARZERE (2)	716	725	-1.2%	4,182	4,537	-7.8%
		LIVORNO (2)	328	367	-10.8%	2,215	2,153	2.9%
		GORIZIA	-	0	-	2	2	-
		OTHERS	3	4	-25.6%	21	26	-19.1%
c)	Exports		16	27	-39.2%	134	163	-17.8%
d)	Stock change (2)		1,398	1,950	-28.3%	1,165	1,394	-16.4%
e) = a)+b)-c)-d)	Gross domestic consumption		4,784	4,982	-4.0%	40,839	45,425	-10.1%

Table 5 Natural Gas balance 2020-2019 [26]

(1) Preliminary results net of transits

(2) Includes consumption and losses

In Table 5 Natural Gas balance 2020-2019 are represented the amount of volume by millions of cubic metric of natural gas traded by import and export in the main terminals of Italy. Is notable how production was highly affected among the January-July period, with a negative variation of -18.0% of production and roughly -10% from imports. All the terminals except "Passo Gries" reported falls during 2020, this due to the COVID-19 crisis. Regarding the terminal Ports, the highest negative variation was "Mazara del Vallo" with -25.0% followed by "Gela" with -15.8%.

MONTHLY BALANCE OF NATURAL GAS

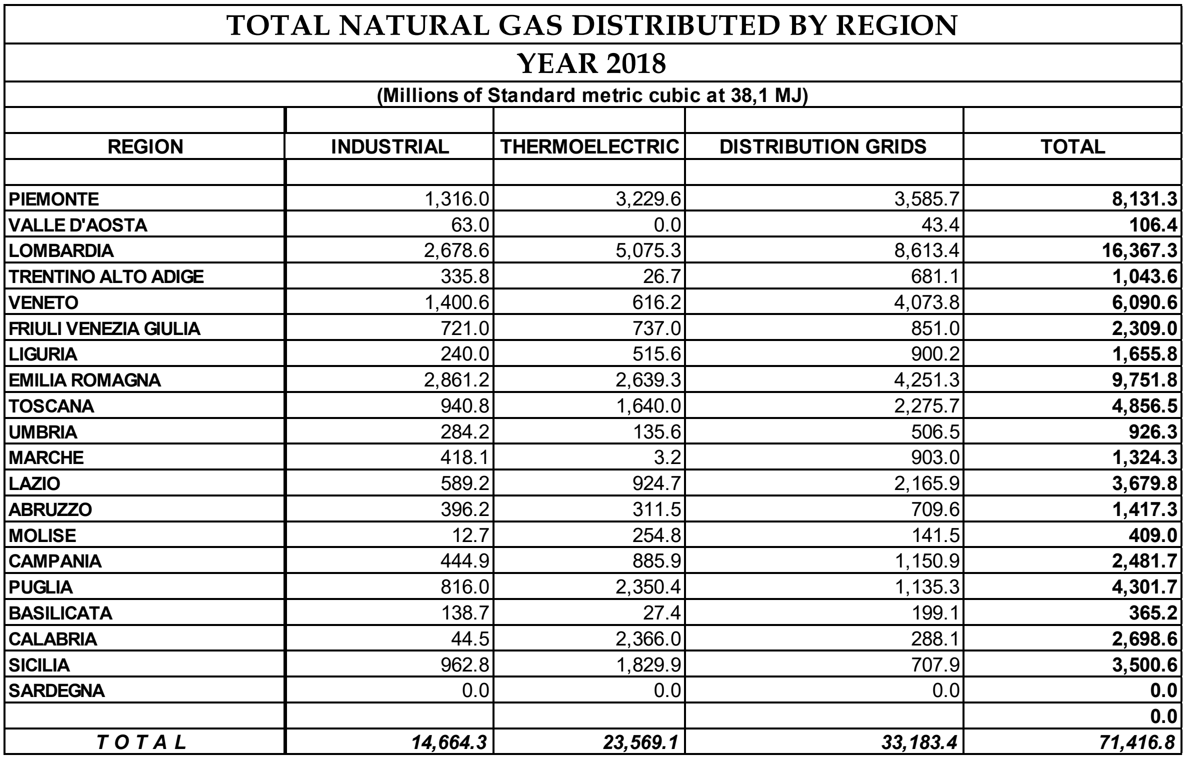
ITALY (1)

(Millions of Standards cubic metrics at 38,1 MJ/mc)

			JULY			JANUARY-JULY		
			2018	2017	Variaz. %	2018	2017	Variaz. %
a)	NATIONAL PRODUCTION (2)		433	413	4.9%	3,197	3,124	2.3%
b)	IMPORTS		5,932	5,967	-0.6%	41,281	41,576	-0.7%
	Per Point of Entry	MAZARA DEL VALLO	1,113	1,167	-4.6%	10,400	11,246	-7.5%
		GELA	387	390	-0.8%	2,159	2,715	-20.5%
		TARVISIO	2,962	2,337	26.7%	18,759	17,506	7.2%
		PASSO GRIES	803	1,116	-28.1%	5,458	5,006	9.0%
		PANIGAGLIA (2)	85	127	-32.8%	468	294	59.3%
		CAVARZERE (2)	573	652	-12.2%	3,804	4,024	-5.5%
		LIVORNO (2)	0	167	-100.0%	149	697	-78.7%
		GORIZIA	0	-	-	21	2	774.2%
		OTHERS	9	11	-16.4%	63	84	-24.9%
c)	Exports		16	20	-20.0%	188	150	25.4%
d)	Stock Change (2)		1,896	1,795	5.6%	1,053	573	83.8%
e) = a)+b)-c)-d)	Gross Domestic consumption		4,452	4,565	-2.5%	43,237	43,977	-1.7%

Table 6 Natural Gas Balance 2018-2017

According to the Table 6 Natural Gas Balance 2018-2017 it can appreciate significant differences between the variations regarding the national production and imports from January to July. National production reported a positive variation of 2.3% instead of imports with a slight negative variation of -0.7%. even though for every single terminal port there are significant numbers, for instance, the “Gorizia” Port with an increase of 774.2%.



TOTAL NATURAL GAS DISTRIBUTED BY REGION

YEAR 2018

(Millions of Standard metric cubic at 38,1 MJ)

REGION	INDUSTRIAL	THERMOELECTRIC	DISTRIBUTION GRIDS	TOTAL
PIEMONTE	1,316.0	3,229.6	3,585.7	**8,131.3**
VALLE D'AOSTA	63.0	0.0	43.4	**106.4**
LOMBARDIA	2,678.6	5,075.3	8,613.4	**16,367.3**
TRENTINO ALTO ADIGE	335.8	26.7	681.1	**1,043.6**
VENETO	1,400.6	616.2	4,073.8	**6,090.6**
FRIULI VENEZIA GIULIA	721.0	737.0	851.0	**2,309.0**
LIGURIA	240.0	515.6	900.2	**1,655.8**
EMILIA ROMAGNA	2,861.2	2,639.3	4,251.3	**9,751.8**
TOSCANA	940.8	1,640.0	2,275.7	**4,856.5**
UMBRIA	284.2	135.6	506.5	**926.3**
MARCHE	418.1	3.2	903.0	**1,324.3**
LAZIO	589.2	924.7	2,165.9	**3,679.8**
ABRUZZO	396.2	311.5	709.6	**1,417.3**
MOLISE	12.7	254.8	141.5	**409.0**
CAMPANIA	444.9	885.9	1,150.9	**2,481.7**
PUGLIA	816.0	2,350.4	1,135.3	**4,301.7**
BASILICATA	138.7	27.4	199.1	**365.2**
CALABRIA	44.5	2,366.0	288.1	**2,698.6**
SICILIA	962.8	1,829.9	707.9	**3,500.6**
SARDEGNA	0.0	0.0	0.0	**0.0**
				0.0
T O T A L	***14,664.3***	***23,569.1***	***33,183.4***	***71,416.8***

Table 7 Total Natural Gas distribution by Region [26]

In the Table 7 Total Natural Gas distribution by Region is possible to observe the consumption measured by the volume distributed by regions. The three major regions with more industrial consumption are Emilia Romagna, Lombardia, and Piemonte, that demand has sense according to the energy outlooks explained in chapter 3.0. Energy demand is highly affected by factors suck GDP and population growth, this can be evidenced not only by the demand in the industrial sector but also for the thermoelectric demand and distribution demand. Regarding supply grids, volume flow (demand) is more distributed through regions since there are not only industrial sectors but also households' zones in regions such as Lazio, Toscana, Puglia, and Calabria. Another important fact is the lack of information regarding the Sardegna gas consumption since the island does not have access to this source of energy, it could be evidenced (by 2018) in Figure 16 LNG Activities in Italy how there already three (3) plants in the planning phase and one LNG plant in the last phase of construction "Oristano Storage plant" with the scope to unload LNG to ship and trucks and be loaded by bunkering ship.

4.1 LNG vs Diesel prices and Propane price

In the following graphs, there are two comparisons between different fuels which are LNG, propane, and diesel even though if the prices are referenced in US dollars since the tracking have been used in the US which has more use of LNG from the past years and the tracking prices have been following in more detail, the main idea is used as a driver of a contrast of price to understand their variation through the months and years, given a highlight of the how balance is the economy in industry, and for 2020 to forward more key drivers such as economic unbalance (COVID-19 effect), decarbonization environmental regulation, etc., that will affect the prices as mentioned previously.

LNG prices vs Diesel prices

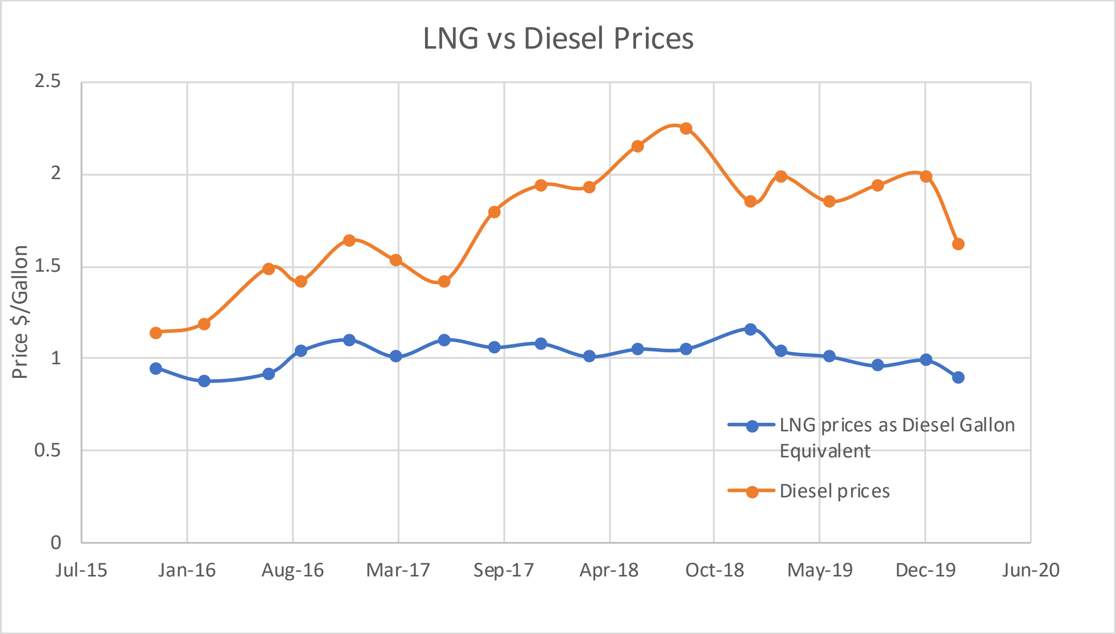


Figure 17 LNG prices vs diesel prices [27]

Is possible to observe in Figure 17 LNG prices vs diesel prices the trend prices per gallon of LNG and diesel in the United States, which is a good reference regarding its high demand of fuel, the first thing to be noted is the differences prices being the LNG 50% and even 100% lower than diesel price, the second feature to be noted is the projection and stability, being the diesel less stable and with behavior more variable regarding LNG.

LNG prices vs Propane prices

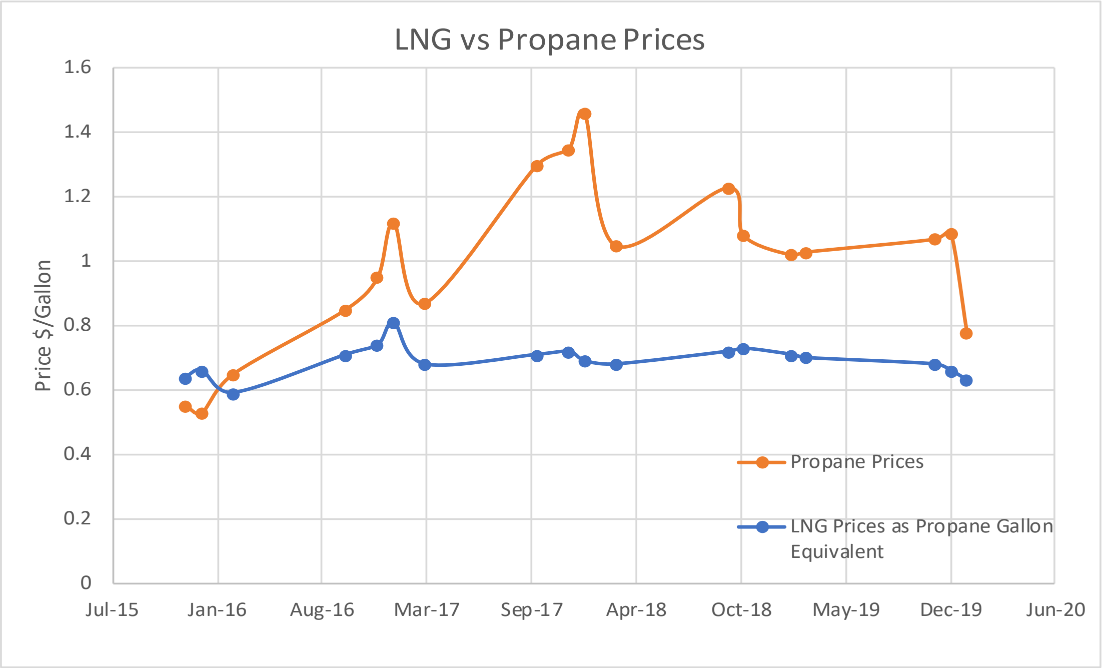


Figure 18 LNG prices vs Propane prices [27]

Is possible to note in Figure 18 LNG prices vs Propane prices how is the price fluctuation between the two fuels, the propane price shows a particular non-stable trend, between the year 2015 and the end of 2016 had a notable rise from 0.4 $/gallon until 1.1 $/gallon, from that point and on the range price is remained in steed variation between 0.9 $/gallon and 1.4 $/gallon. On the other hand, the LNG price had a constant price in the range between 0.6 $/gallon and 0.8 $/gallon.

A Key added value not mentioned so far, is the emissions of CO_2 by fuels, as mentioned in Chapter 3 Government policies is important on how an utility could be implemented in a country or specific region, but not only that but also in the government investment. Decarbonization policies are strongly advancing in every industrial sector and, more restrictions on fuels with high CO_2 emissions more will be the demand on fuels with low emissions.

5. Prices impact by COVID-19

Energy use is deeply linked to economic activity. Since March of 2020, the COVID-19 pandemic has affected economic activities around the world due to lockdowns and temporary stop of industries, quantifying that impact on decarbonization is already a fact. Before the pandemic was an estimated global energy demand of 456 exajoules (EJ) by 2050 now there is a reduction of 8% [28]. This is illustrated in Figure 19 World final energy demand - with and without COVID-19 .

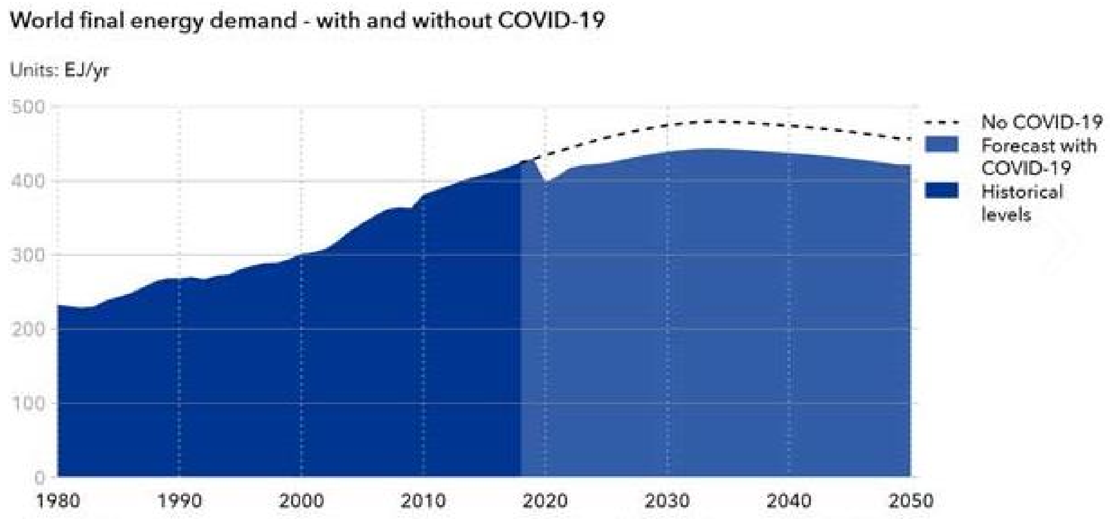


Figure 19 World final energy demand - with and without COVID-19 [28]

Regarding Natural gas and LNG, the combination of very high storage inventories and strong LNG deliveries has led to gas prices that are competitive with carbon generation through much of summer 2020 and at times below the delivered operating costs of US LNG to Europe, nonetheless, the potential reduction of global gas demand by COVID-19 will not unbalance the gas market in Europe because the surplus of LNG cargoes arriving and, if that surplus rise, lower prices will trend to trigger lower US LNG exports. The reduction of US's gas production as a result of lower oil production may cause an increase for European Gas prices set by the delivered Cost of US LNG. There is a forecast that gas prices will average € 8.8/MWh over summer 2020, with a monthly average low of € 8.5/MWh in June 2020.

By the other hand, in the Asian market, China has been highly disrupted normal business operations and created travel bans and trade complications with many countries, particularly affecting the

Chinese gas demand and LNG imports, but the magnitude of the impact will depend on how long it takes to get COVID-19 under control and resume full business trade activities.

6. The Scale of liquefaction

Since the LNG industry started as an industry with an economy of scale production, and so on it has been reducing the scale of production to supply specific demands, there is not a proper or defined definition for different scales of production, only an approximation from large scale to the nanoscale. This segmentation is important in the industry to define the applicable norms and regulations to design and operate those facilities, as possible risk and hazardous. The following table gives an approximation and definition for a range of production.

Large, Medium, and small scales of LNG capacity plants

LNG Scale	LNG storage capacities Storage	Operation
Large	>100,000m^3	A large-scale LNG operation typically includes production trains with single capacities between 1 and 6 MTPA (million metric tons per annum), which can include numerous trains. Receiving terminals or LNG storage facilities typically with a range of capacity of 120,000 m^3 or larger.
Medium	10,000 to 100,000 m^3	Medium-scale liquefaction is not so common, owing to the challenge with high specific production costs. Medium size LNG logistic terminals use to be supplied by small-scale carriers, from 1,000 m^3 to up to around 40,000 m^3.
Small	< 10,000 m^3	Small-scale is becoming popular due to the liquefaction of biogas and other small bags of stranded gas. A small-scale LNG logistics chain is characterized for LNG distribution to local users, such as highway truck transportation with sizes of 20 m^3 to up to a set of pressurized with capacities up to thousands m^3.
		Micro scale is more commonly defined by regasification plants with cryogenic tanks with a capacity of less than 300 m3. Regasification

Micro	100 m^3 - 300 m^3	plants are composed of three components, pump system, vaporizers, and pressure conditioner. Usually are designed to feed and satisfy a specific industrial or domestic demand.
Nano	< 10 m^3	Nano-scale capacity is not feasible for storage due to thermodynamic factors regarding the LNG, the small capacity of a hypothetical cryogenic tank will increase the boil-off effect, which accumulates pressure inside the tank. Liquefaction uses is more feasible to supply an immediate need.

Table 8 Scale of LNG developments and facilities [29]

Regards to the Table 8 Scale of LNG developments and facilities the storage capacity was selected as the main criteria, referencing liquefaction capacity as well.

7. Value Chain and Supply Chain

For Natural Gas sources to final consumers the LNG value chain adopts different shapes and be intended in diverse ways, depending on the necessities for the diversity of end-users. The value chain can be compounded by two products: LNG and NG consumers.

The conventional value chain is described as a conventional Large scale ambient pressure LNG when natural gas is extracted from a gas well, it is sent to an onshore production plant, after liquefaction, its stored, transported, and regasified [30].

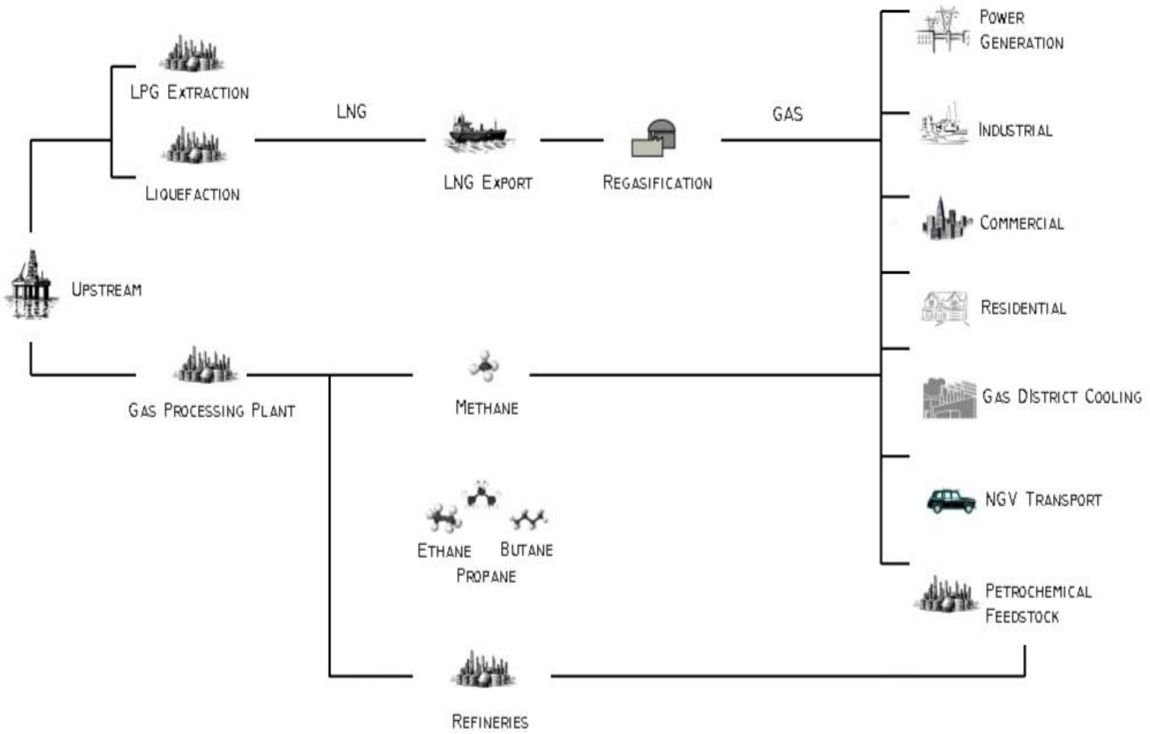


Figure 20 Natural Gas Value Chain [31]

Due to the several chemicals, physical, and thermodynamic features of natural gas, its treatment, transportation, and distribution have been objective of continuous improvement and innovation among the time. The LNG value chain is compounded by different steps, each one of them represented by detailed engineering since exploration and well until the market distribution. The typical final users are characterized to be the industrial sector, domestic/residential, and transport, depend on which phase they need the gas if liquefied or gas state, the chain includes these key steps as liquefaction or regasification, sequential or vice versa. The need of LNG resides in two factors: the first one is to optimize its transportation, as mentioned before its volume advantage from NG to its liquid state is reduced by 600 times, and the second one is to provide NG to transport users. Concerning the reduced volume is important to comment on how the storage is completely integrated into the transportation also as static tanks, located in strategic points to optimize the final delivery.

Many details must be considered in each stage of the value chain owed to its high engineering detail, even though one main rule applies: The more interfaces, liquefaction plants, regasification facilities, and distribution links the more likely it will be to have LNG accidental or operational releases. Small leakages, gas ignition, and overpressures are undesired hazardous issues and undesired methane emissions. Environmental impact represents nowadays the main restriction and rules regulation, higher the interfaces between the faces higher the potential risks and accidental releases.

The LNG value chain is possible to be ramified due to its flexibility of being produced, stored, and transported into several scales, such as large, medium, and small scales, even lowest steps than small which will be discussed further. The natural gas network distribution or imported grid are can be easily decomposed into different supply routes, the Figure 21 Logistic and Transport of LNG showed below illustrates an example of some possible supplies routes, the main steps considered are: Supply, transport, Production, Local storage, and Bunkering.

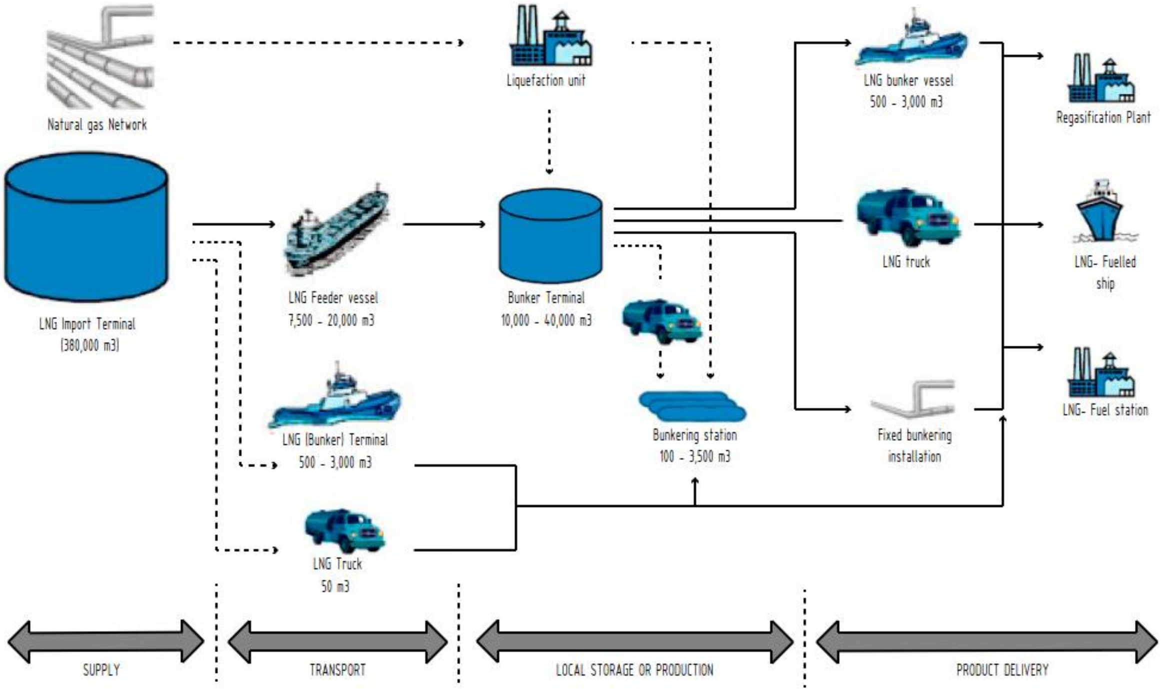


Figure 21 Logistic and Transport of LNG [29]

The figure represented a particular LNG and NG value chain, is possible to observe how the logistic process can be repetitive or cyclic, basically starts in the storage/supply step, following by transport, then local storage, transport, and final users, this process could be repetitive as much the distance of the final delivery and how efficient could be the process of loading and unloading the LNG.

The LNG supply chain is strongly affected by factors related to transportation, marine (offshore), and land (onshore), the source, the gas properties, and the environmental impact, which is highly linked to local regulations. Important criteria that satisfy the above-mentioned factors are the LNG methane number, the LNG spot rate, the distance of the export terminal, the shipping cost, the fuel consumption of the transport medium, environmental indicator, and Energy Efficiency Operational Indicator. [32]

7.1 Elements affecting the LNG Value Chain

The following elements are considered as a determinant in the shape and requirements for an LNG value chain:

- The consumer features: key characteristics as its location, end uses of NG, demand quantity.
- Gas availability requirement: quantity available depends directly on the source or reservoir
- Supplier: Location and distance from the consumer will impact on costs
- Receiving terminals: need it for large scale barge, also location type and sizes to consider
- Boil-off-gas Handling: main issues for storage and transportation
- Distance for LNG distribution (impact directly in distribution/transport mode for LNG) – The longer the distance for LNG distribution the higher should be the investment in insulation, intermediate storage, liquefaction, and refrigeration.
- Logistic and detailed engineering for Ship-to-Ship, Ship-to-Truck, Truck-to-tank and vice versa for each one.
- Distance from end consumers and LNG import terminals will be determinant for the market opportunity of small scales bunkering and plants

8. Process and Technology

8.1 The Stirling technology

In simple words the functioning way of the Stirling is with a fixed amount of gas inside the engine, the gas is then moved back and forth from the hot side to the cold side, turning into a cycle. When the gas is on the hot side, the heated phenomenon creates and expansion, when it is on the cold side creates contracts. The Stirling has a generator that works as a heat exchanger and can save some heat from one cycle for use it to the next cycle. A deeper explanation is written below.

The Stirling cycle is a representation of how the Stirling principle works. Firstly, it is approximate and idealized. There are two basic configurations of the closed-cycled hot-air engine, in both cases, the hot and cold are separate thermally by the generator (a mass of permeable material), and the generator extracts and stores most of the gas' heat as it passes from the hot to the cold space and most of this stored heat is recouped by the regenerated gas, as it returns from the cold to the hot space.

If the generator is placed in parallel with one of the pistons, the latter merely displaces the gas between the hot and cold spaces. All the work of compression is done by the power piston and all the produced by the expansion of the gas is done on this piston. The phase difference between the displacer and power piston is such that the volume of the expansion space *Vc* (hot in an engine) leads that of the compression space *Vc* (Cold in the case of an engine) [33].

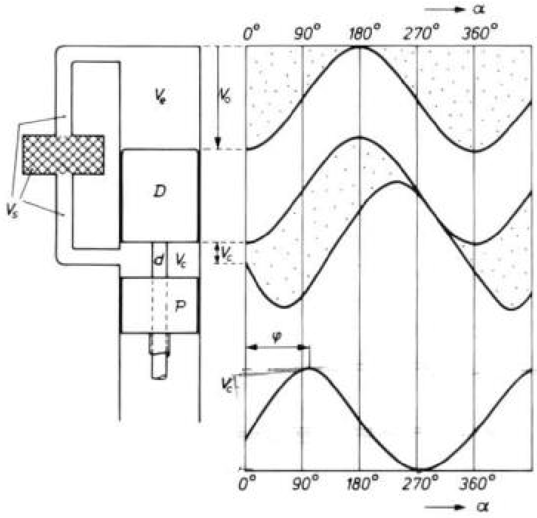


Figure 22 The Stirling Cycle. Pistons placed in parallel. [33]

- *Ve*: Volume of expansion space
- *Vo*: Maximum volume of *Ve* (2x amplitude)
- *Vc*: Volume of compression space
- *Vs*: dead space (space not swept by piston)
- *Vt*: total volume of gas
- *α*: crank angle, heat transfer angle
- *ω*: angular velocity of the crack

According to Figure 22 The Stirling Cycle. Pistons placed in parallel. Figure 22 The Stirling Cycle. Pistons placed in parallel. above, volumes variations *Vc* and *Ve* are assumed to vary harmonically (sinusoidally) with the angle *α*. The expansion space (hot) leads in phase the compression space (cold) by the angle α. The letter volume Vc (between the displacer and working piston) is re-plotted separately below. All angles are measured from $\alpha=0$, where Ve is maximum (= Vo). The total volume of the engine Vt is the sum $Vc + Ve + Vs$.

The generator also may be placed in series with the two pistons according to Figure 23 The Stirling Cycle. Piston placed in series. The hot pistons lead the cold such that, again, the volume of the expansion space (hot in the engine): both pistons then compress the gas, while it is in the cold end, and the gas expands and does work against is in the hot end.

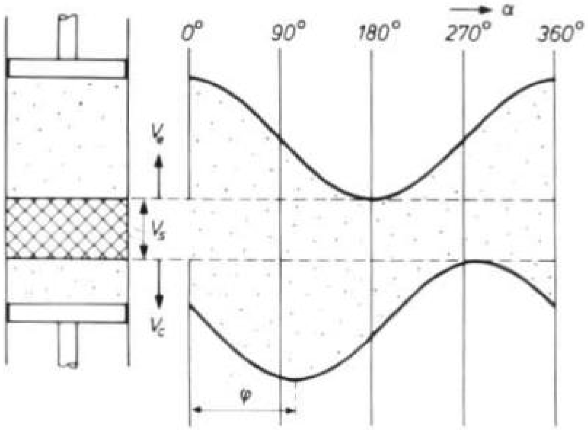


Figure 23 The Stirling Cycle. Piston placed in series. [33]

According to Figure 23 The Stirling Cycle. Piston placed in series. , the movement of the pistons is assumed to be harmonically and the hot space Ve again leads the cold space Vc by the space angle φ. The gas undergoes the same volume and temperature as in the displacer engine. The dead space Vs is showing schematically, it is larger than the free volume in the regenerator owing to the other unwept spaces inside the engine.

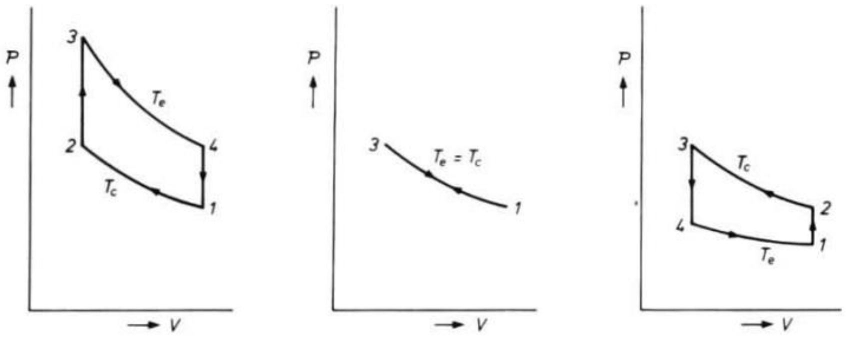


Figure 24 Transition of Stirling engine to a Heat pump, respectively: A, B and C. [33]

The Figure 24 Transition of Stirling engine to a Heat pump, respectively: A, B and C. is a brief thermodynamic explanation about the cycle works, a) in the engine the gas is compressed at the lower temperature *Tc* (1-2), transferred (2-3) to the hot space at *Te*, then expanded at the constant temperature *Te* (3-4) and finally transferred back (4-1) to the cold space at temperature *Tc*. (b) If the heating is removed, the temperature *Te* drops until it reaches *Tc*. If the machine keeps running owing to its (disregarding frictional and other losses). c) If the Machine is kept running by external mechanical power, the temperature *Te* of the expansion space will drop below that of the compressor space; heat is now pumped up from the lower temperature *Te* to the higher temperature *Tc* (heat pump or refrigerator). [33]

A deeper analysis of this process is presented with the following scheme:

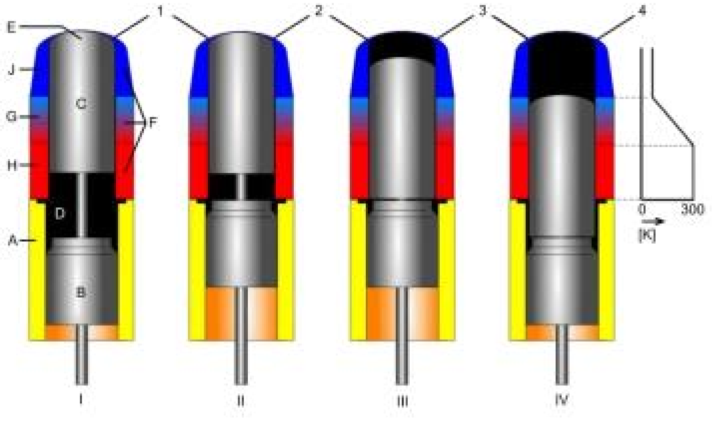


Figure 25 The Four stages of the Stirling cooling cycle. [34]

The gas compressed, in this case Helium, is at room temperature in space D. Going to position II, this gas is compressed by piston B increasing the gas temperature to about 80 °C (see Figure 25 The Four stages of the Stirling cooling cycle.).

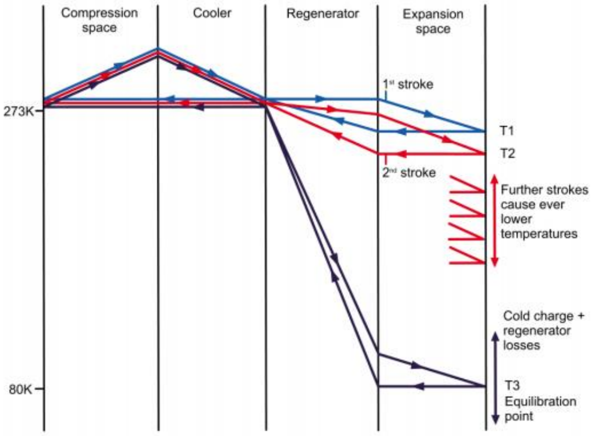


Figure 26 Temperature gradient in a single stage cycle. [34]

When the displacer C moves down from position II to III. The gas is moved from space D to space E, making it first through the cooler H where the compression heat is dissolute into the cooling water, reducing the gas temperature to about 15°C (Figure 26 Temperature gradient in a single stage cycle. column 2). Following the helium flows through regenerator G. Using the cold which was kept in the regenerator by the former cycle, the helium gas is cooled to nearly the final liquefaction temperature when arriving in space E (column 3). The final and main action is the displacer and piston moving down to position IV, expanding the helium gas. This expansion creates the actual cooling power in the cold heat exchanger J (column 3), cooling the customer process. [34]

For a new cycle to start, the displacer moves up to position I, moving the helium to space D again. The regenerator is cooled by the passing helium, storing cold to be used in the next cycle. The helium is reheated to nearly room temperature, so the initial situation of the cycle has now been restored for the cycle to repeat. This cycle is typically repeated at 25 Hz, providing a continuous extraction of heat.

When staring warm, the cryo-generator will initially first cool down itself, building up a cold buffer in the regenerator (column 3). This cool-down requires about 10 minutes only, allowing a fast start-up of the total process.

8.2 Process Integration

The Nano-scale process integration is characterized for not depends on the economy of scale and just for supply a determinate specific need; in this work, it suggested the use of LNG as a fuel to supply internal transportation. The nano scale production is proposed due to its simplicity, that’s mean since there are safety and hazardous regulations for productions or storage for a determined amount of capacity, for instance the European norm EN 13645 there are the safety regulations for storage plants from 5 tons up to 200 tons of capacity. The main hazardous situation is the accumulation of gas, in a determined point, tank, pipelines, etc.

In the specific case of LNG there is Boil off Gas (BOG), can occur in the storage due a small variation of pressure or temperature, also a change of phase during the flowing of the LNG among a pipelines if that would be the case. The nano scale production and proper storage will bring for the industry the following advantages:

1. Convert a usually waste product into fuel
2. Generate profits from a zero-cost raw material
3. Reduce the emissions into the environment
4. Reduce the emission of fuel used for transportation
5. Reduce the consume of usual fuels such diesel or gasoline
6. Add a circular economy as a nano process
7. Reduce cost for logistic or location of the Skid plant
8. Save cost of environmental damage

The Nano-scale NG liquefaction process is characterized by its simplicity. As mentioned before its range of final product is between 200 kg and 1.5 ton per day, the process shall be connected directly to the natural gas source, depends on the source which could be a natural gas reservoir, pipeline, biogas or effluent gases from another large scale process. There are reasons for implement micro and nano-scale production, in Oil & Gas industry, there are numerous facilities which have flare and vent system in continuous operation, tons of natural gas are vented or burned into the environment. The nano-scale production is a solution for incentivizing the circular economy and get profits from a zero-cost raw material. To convert into fuel a normal wasted product. Besides the previous reason, also there are large grids of natural gas pipelines, implementing such nano-scale production into the grids is a possible solution to extend and ramify the scope of gas distribution.

The process is compounded by three key elements:

Three main steps compound the process, which are

1. **Gas treatment equipment**
2. **Liquefaction**
3. **Storage**

The Diagram block process is described below.

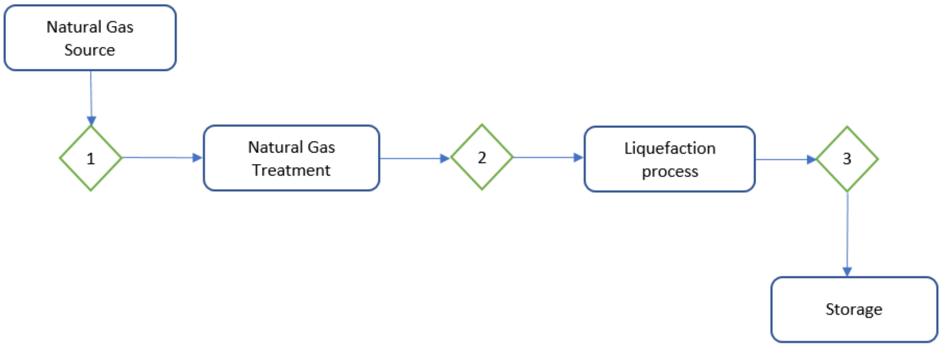


Figure 27 Block Diagram nano-scale liquefaction process [35]

In the following figure is represented the nano value chain proposed regarding the block process diagram at Figure 27 Block Diagram nano-scale liquefaction process.

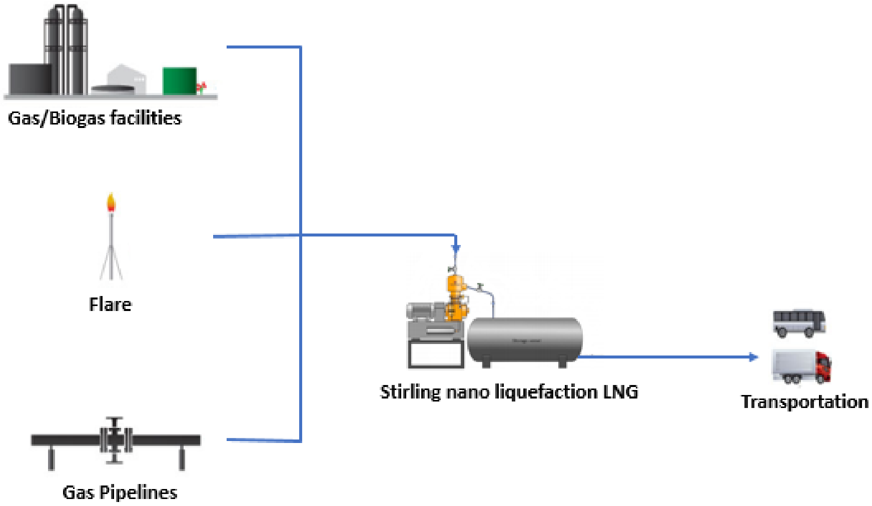


Figure 28 Value chain of nano production of LNG [35]

The gas sources have been segmented by three types,

1. Effluent gas from flare or vent
2. Natural pipelines grids
3. Natural Gas/ Biomethane plants

To understand more practically its use approach, introducing a Skid integrated with the gas liquefaction machine ad its storage since for all the gas process/production is mandatory buffer tanks, drains, and flair systems in which the gas in normal or emergency operation is continuously vented or burned, after its treatment is highly profitable is used as utility, nowadays norms and regulation are restricting more those type of emergency those operations, re-using it shall contribute with circular economy and can generate extra capital income with an environmental added-value.

As explained before the logistic is key in the value and supply chain, in consequence a compact Skid with the Stirling, short pipes and small capacity tanks, shall be easy for transportation if that would be the case.

8.3 Natural gas treatment

The Natural gas as a final product will need to be adjusted to the final consumer depends on its requirements, those requirements may vary depend on the final use, the requirements includes:

- High Heating value
- Low Heating value
- Wobbe Index
- Water Dew point
- Hydrocarbon Dew Point
- Nitrogen Content
- CO_2 Content
- H_2S Content

The range of values of some of these components are determinant in the process as a risk management, in order to avoid any damage in the liquefaction module or the final consumer.

The typical gas specifications before liquefaction are presented in the following table:

CO_2	50-100 ppm
H_2O	0.1-0.5 ppm
HHC	1-10 ppm

Hg	0.1 µg/Nm^3
H_2S	4 ppm

Table 9 Typical Natural gas composition before liquefaction [36]

Some equipment are mentioned in order to filter and puree the natural gas before the liquefaction process, is important to clarify that it will depend on the gas composition.

8.4 Stirling liquefaction

One Stirling machine can produce a minimum of 250 kg/day (185 gal/day), roughly 90 tons per year, several options are depending on the capacity required in which a set of Stirling can be an arrangement in order to increase the nominal capacity 4 times more.

The main driver of the Stirling is gas pressure, less the gas pressure more is the input power required, the following graph shows the normal performance of the machine.

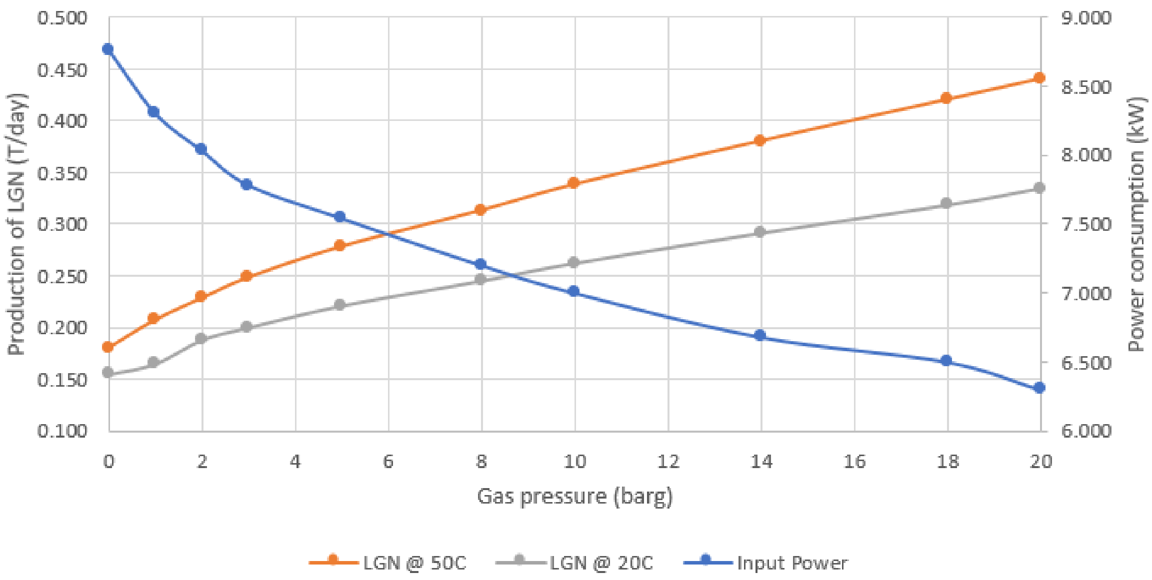


Figure 29 Rate Production and Power consumption vs Gas pressure of nano scale Stirling machine [34]

As is showed in the Figure 29 Rate Production and Power consumption vs Gas pressure of nano scale Stirling machine the temperature of the natural gas affects directly the liquefaction process, in simple words, with a gas of low temperature the machine will do less work and improve its efficiency. It is notable how with inlet gas of -50 °C the production is over 0.4 ton per day, instead of with gas at 20 °C in which the production 0.32 ton per day, a difference of 25 %.

The Stirling machine operates by electrical motor with a range of 8.9 Kw at gas pressure of 0 barg to 6.4 Kw with a gas pressure of 20 arg.

The size is another advantage due to it reduce production capacity, the Stirling's sizes are compounded by; height 1688 mm x Length 1020 mm x 616 mm and weight 550 kg. Relatively small sizes make the process easy to assembly and disassembly, transportation and location depend on the necessity.

8.5 Storage system

Cryogenic enclosures are fairly simple to operate. The most important operating requirement is to keep the atmosphere within the enclosure within the proper operating bounds by ensuring proper purge gas pressure, flow and, composition. [37]

The connection between the Stirling machine and the cryogenic tank is one of the simplest approaches, the Stirling shall be located with a superior high distance above the vessel in order to send out the liquefied natural gas by gravity. Other arrangements are considered, as a buffer vessel.

Storage vessel capacity shall be designed depending on the demand of natural gas, for this work is proposed one tank of 2 m^3 which is equivalent to 1 ton of LNG, the capacity of one Stirling machine per day.

The whole system can be arranged in a skid, to facilitate the mobility and its re-location on different sources of gas, nonetheless precaution shall be evaluated but not as a storage plant due to its nano-capacity for immediate use, even though some pre-operation must be done such as:

- Inerting operation of lines and tank
- Leak test (warm)
- Cooling down
- Leak test (Cold)
- Liquid drain and warming up
- Purging

9. Freeze out due the Gas composition

The formation of solids during the cryogenic liquefaction processing of natural gas represents the main risk. Depending on the range composition of the natural gas or the type of gas will drive the risk probability to form those solids. Heavy hydrocarbon solids (HHS), dry ice, hydrates, water ice formations, represents potential damage, Even small traces could block valves, pipes and cause potential damage to the process, shut down the process and in consequence loss of LNG production and revenue.

Just an example, in large scale production of LNG the consequences of a shut-down are greatest, removal of the blockage and the subsequent plant re-start will require that the main cryogenic heat exchanger be taken through a 300 K temperature cycles, taken several days or a week. For this reason, accurate knowledge of, and procedure to predict the solubility of impurities in LNG is highly important. [38]

Regarding the low temperature of natural gas liquefaction, it's the main parameter that limits the process, due the high critical temperature of the components in the feed stream, some of them with more risk than other and different behaviors under certain conditions, BTEX, CO_2, and water are some of them, each one with totally different properties.

10. Simulation models

Two simulators programs were used in order to predict the limit composition of the heavy hydrocarbons. The scope selected to analyze the heavy hydrocarbons were the BTEX (Benzene, toluene, ethylbenzene, and xylene) and Cyclohexane due to their low triple point, and physical properties. Nonetheless, a brief analysis of composition containing traces of CO_2 and water is presented.

The methodology used to simulate the liquid-phased equilibrium of natural gas was a binary composition of 95 % mol of Methane as a solvent and 5% as a solute component, at cryogenic pressure 1 bar and temperature (-163 °C) conditions.

For calculating the equilibrium conditions of a fluid mixture, the flash procedure is used to determine numerous mixture properties at phase equilibrium such as molar phase composition, the molar amount in each phase, phase densities, molar enthalpies.

The equation of state used is the Peng-Robinson, the reason is the EOS Peng-Robinson is a modification of the Redlich-Kwong equation, redefining the temperature. The EOS of Peng-Robinson has several advantages concerning describing binary and multi-component systems, being precise with the correlation between temperature, pressure, and phase compositions.

10.1 HYSYS

Hysys is a chemical process simulator used to mathematically model chemical processes, making it easy to convert steady-state process model into a dynamic process simulation model to study time-dependent oil & gas processes, including gas processing and petroleum refining [39].

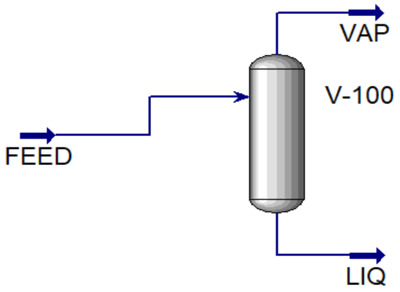


Figure 30 Flash Destilation process [35]

10.2 ThermoFAST

ThermoFAST is a thermodynamic property calculator for LNG and natural gas with the ability to perform vapor-liquid-solid equilibrium calculations, predict conditions at which solid formation can occur in complex, multi-component systems and generate full phase envelopes [40]. Being more specific ThermoFAST can locate solid transition region temperatures or maximum solid concentrations for the selected mixture number, it works with an algorithm that searches at constant pressure for the highest temperature at which solids appear.

In figure presented below, is briefly explained the iteration method in which the software arrives at an approximation of specific concentration values, even in the order of E-10 mol at critical conditions of pressure and temperature. As mentioned before the traditional software are not still well equipped with EOS for real gases and solid states, since is a topic well developed in the private sector, the experimental data and results is not easy to reach.

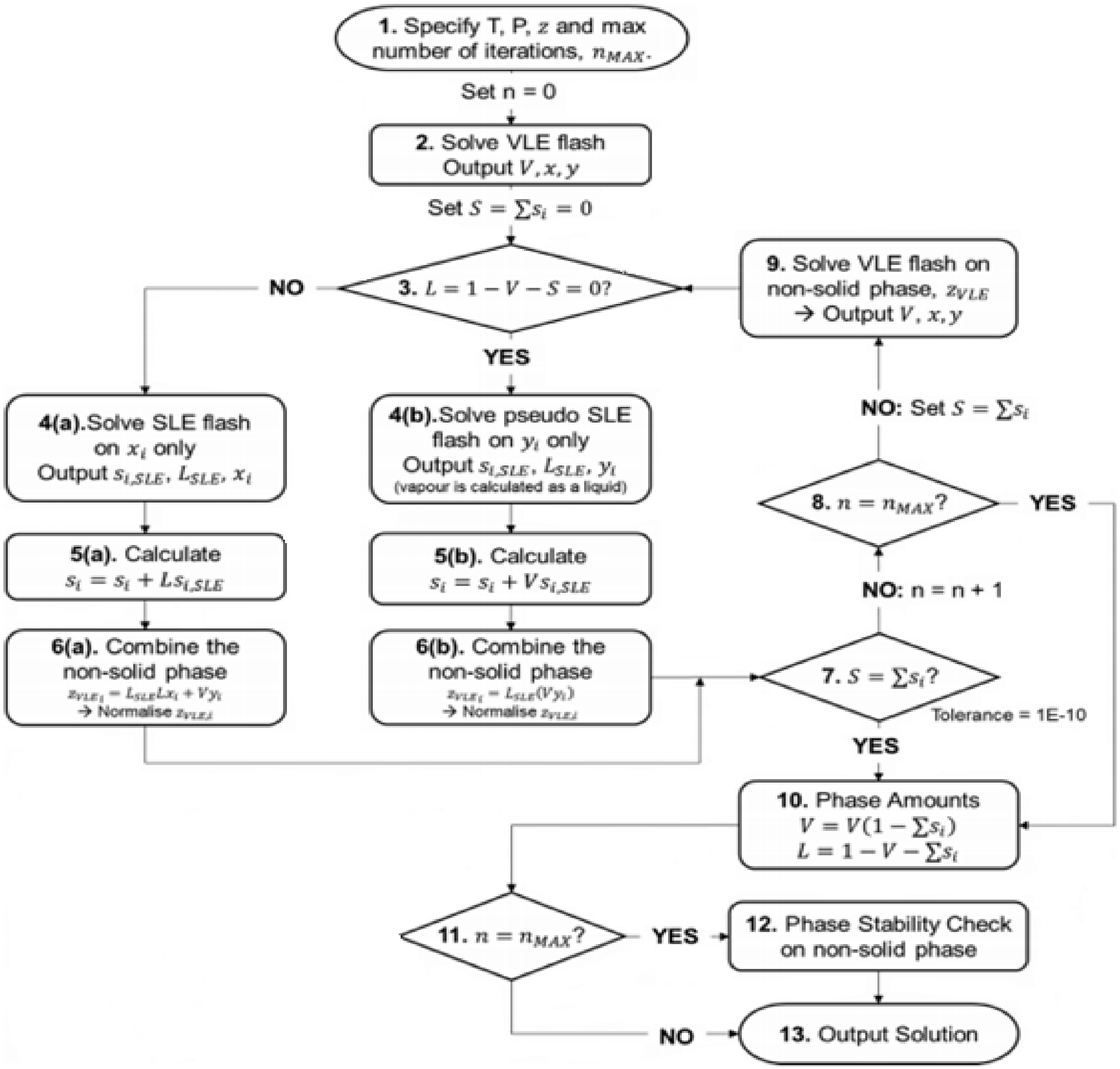


Figure 31 ThermoFast Algorithm [41].

Figure 31 ThermoFast Algorithm works with a substitution method, the T is temperature, P is pressure, z is general composition, I represents a particular single component, f is fugacity, s is the solid composition, x is a liquid composition, y is vapor composition, ϕL is the partial fugacity in the liquid phase, V is the overall vapor mole fraction, L is the overall liquid mole fraction, n the number of iterations, nmax the maximum number of iterations, and the SLE refers to any variable determined from the SLE flash algorithm within multiphase equilibrium calculation.

11. Results

11.1 Hysys Results

After several simulations results of solidification predictions were not achieved, due to the limitation of the software with uses of EOS with solid equilibrium, nevertheless due to its high accuracy to graph and determinate formations of hydrates and CO_2 (dry ice), regarding to their potential risk for the process and assets, results of those formations were presented.

11.1.1 Methane 95% benzene 5%

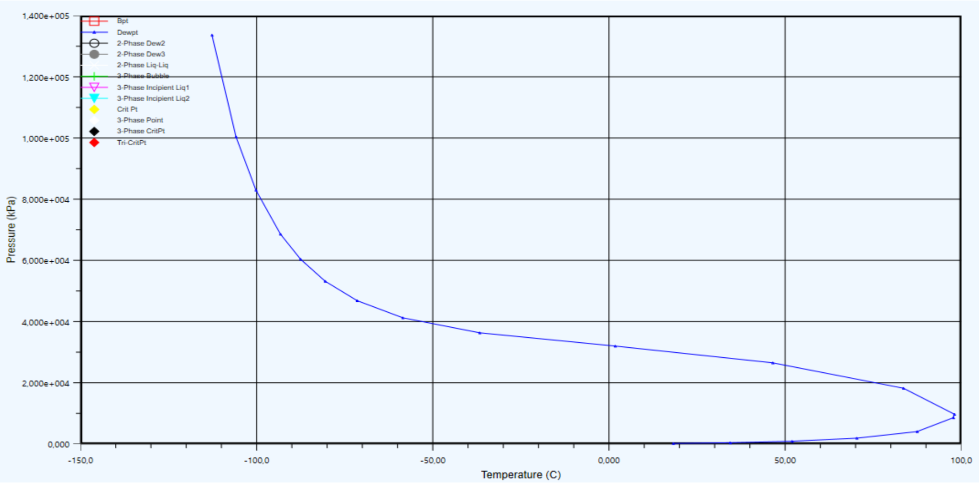


Figure 32 Methane-Benzene Phase Diagram (Hysys) [35]

Figure 32 Methane-Benzene Phase Diagram (Hysys) is possible to observe the equilibrium graph of the solution Ch4 and Benzene, the blue line represents the dew point of the benzene, as it as expected the graph doesn't give relevant information regarding the behavior of benzene at 5% in cryogenic conditions (1 bar, -163 °C) since the software is limited to use the EOS at normal conditions an also limited to calculated equilibrium state for solid phase.

11.1.2 Methane 95% Carbon Dioxide 5%

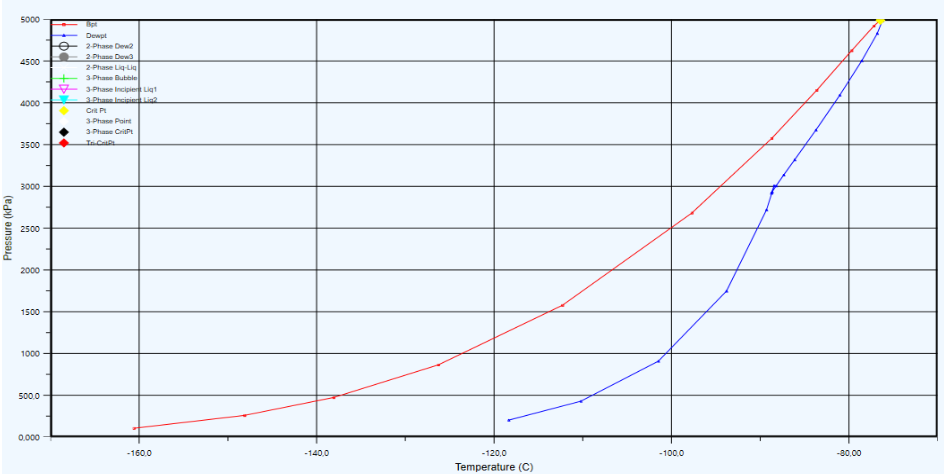


Figure 33 Methane-Carbon Dioxide Phase Diagram (Hysys) [35]

Figure 33 Methane-Carbon Dioxide Phase Diagram (Hysys) represents the equilibrium diagram of a solution 95% methane and 5 % of CO_2 at cryogenic conditions, from 0 to 5,000 kPa (50 bar) and -180 °C to -60 °C, the blue line represents dew points of CO_2 and the red line represents the Bubble point of CO_2, given a result of a critical point at -98.19 °C and roughly 50 bar meaning that at those conditions the CO_2 in the methane solution will start to freeze out.

11.2 ThermoFast Results

11.2.1 Eutectic point diagram of 95% Methane 5% benzene

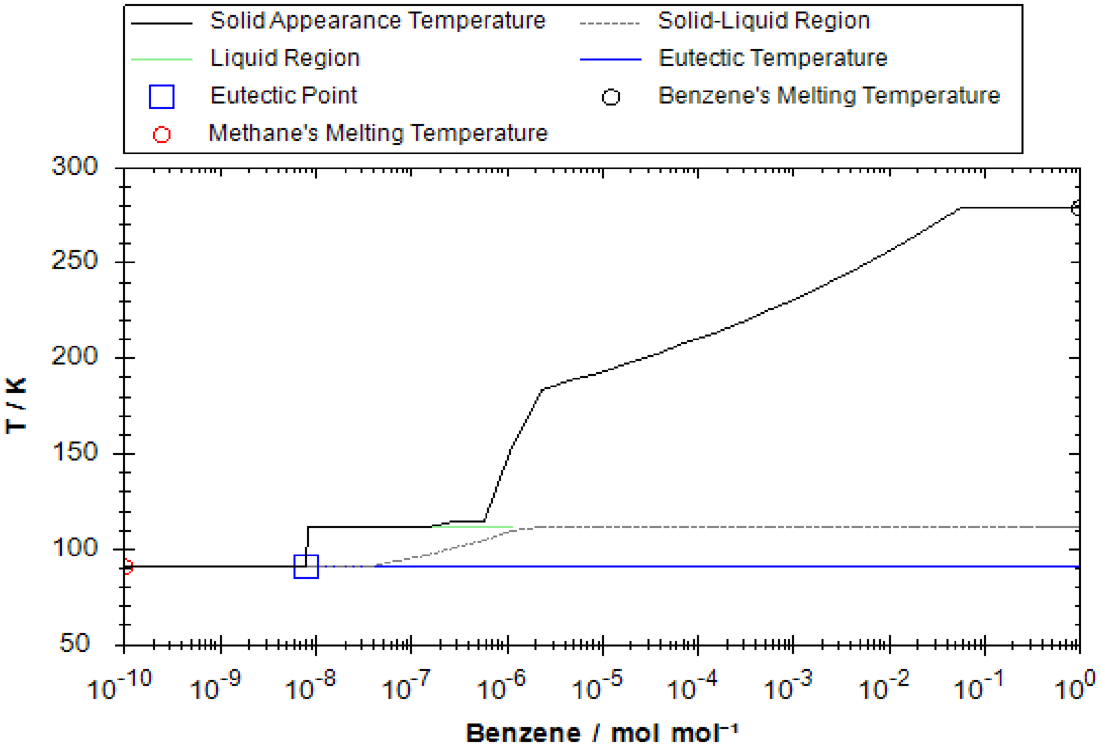


Figure 34 Methane-Benzene phase diagram

In the Figure 34 Methane-Benzene phase diagram, is possible to observe the critical points for the binary solution at critical conditions, limits are defined from the methane's melting point as the solvent to the Benzenes' melting point, the eutectic point for the solution results at 90.675 K and 8.20E-09 mol of benzene, that's means for this low concentration there is a transition of liquid state to SLE. The scalable values of benzene equilibrium transition are shown in the Table 3 Benzene's Equilibrium phases, in which is possible to observe in parallel with the graph how sensitive is small variations of concentration, for instance between 8.30E-09 mol of Benzene and 2.90E-07 mol the temperature remains constant with a slight increase from 111.506 K to 113.686 K followed by a steep increase until roughly 2.32E-06 at 183.271 K, then a constant increase until 280 K (7 °C) with the considerable range from 1E-1 and 1 mol. There are two characteristics lines in the graph, the first one the liquid region, colored by green, and the solid-liquid region defined by the dotted line, both define the limit between the phases from 1E-7 mol of benzene to 1 mol as a limit temperature of 110 K.

Melting T / K	Melting Phase Transition	Freeze-Out Component	Benzene Composition mol mol⁻¹	Methane (Overall) / mol mol⁻¹
90.675	Liquid to SLE	Benzene	8.20E-09	1
111.506	Vapour to SVE	Benzene	8.30E-09	1
113.689	Vapour to SVE	Benzene	2.90E-07	1
153.099	Vapour to SVE	Benzene	1.16E-06	0.999999
183.271	Vapour to SVE	Benzene	2.32E-06	0.999998

Table 10 Benzene's limit points

In the Table 10 Benzene's limit points, are represented the four critical switching points of the melting temperature of benzene, noticed how for a variation from 8.2E-9 to 8.30E-09 mol there is an increase of 18% from 90.675 K to 111.506 K, then with a significant increase between point 2 and point 3 (decrease of two magnitude order) there is a small increase of 1.95%, from that point and on, variations are very sensitive. The critical operation point for the process is point 3 with 2.90E-07 at 113.689 K.

11.2.2 Eutectic point diagram of 95% Methane 5% Ethylbenzene

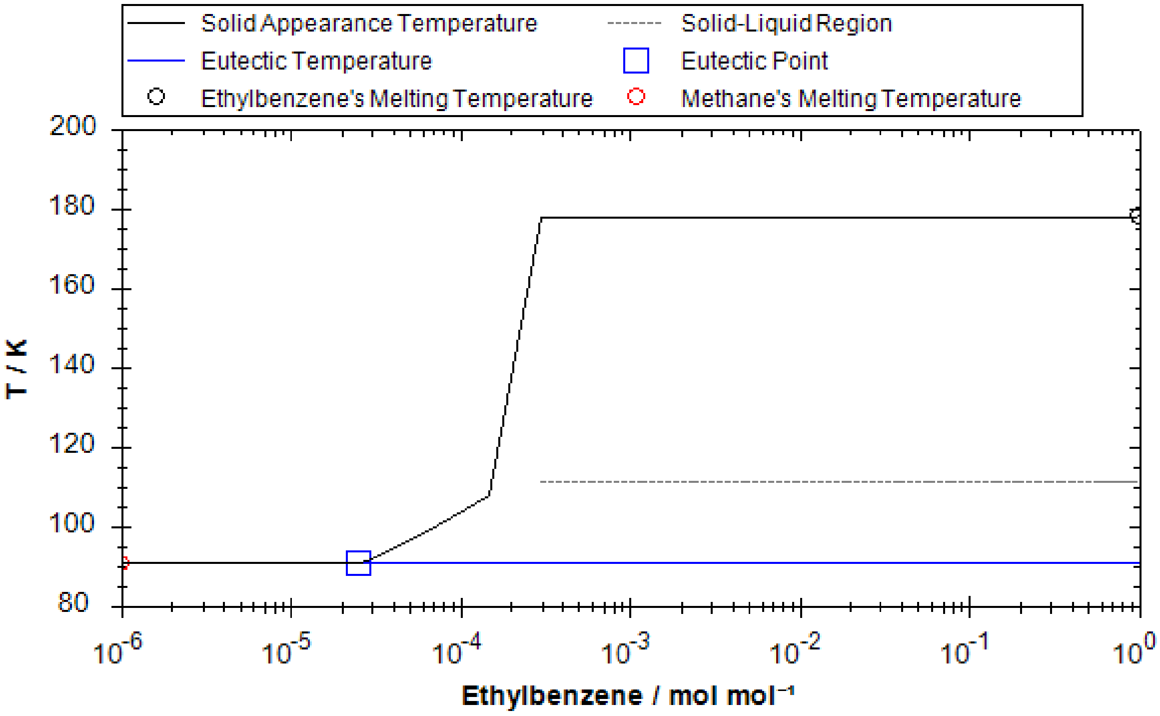


Figure 35 Methane-Ethylbenzene phase diagram

The Figure 35 Methane-Ethylbenzene phase diagram shows similar results for the eutectic point, as well as the Benzene eutectic point, this is at 90.647 K but with a lower concentration of ethylbenzene

2.49E-05 mol of Ethylbenzene, it is possible to observe the lower range concentration of ethylbenzene regarding the methane and how from 90.647 k there is a moderate rise, very sensitive to the concentration, being between 2.19E-0.5 and 1E-04 mol, then a dramatic increase until 177.813 K where it reaches its highest point and the final melting point. Another characteristic of this diagram is the two predominant phases are liquid and SLE, this means all the area below the borderline between 90.647 K and 177.746 K is in continuous interaction between solid and liquid. Another characteristic in the diagram is the solid-liquid line at 111.466 K a concentration between 2.9E-03 and 1 mol this means another area in which the phase at those conditions can change from liquid to solid if therebetween that concentration range and less than 111.446 K. The limit condition for the Stirling machine operation shall be as mentioned before between 90.674K and 107.813 K not less and avoiding having less than 1.85E-5 and 1.48E-4 mol of solvent to not freeze out.

Melting T / K	Melting Phase Transition	Freeze-Out Component	Ethylbenzene Composition mol mol^{-1}	Methane (Overall) / mol mol^{-1}
90.674	Liquid to SLE	Ethylbenzene	2.49E-05	0.999975
91.569	Liquid to SLE	Ethylbenzene	2.78E-05	0.999972
94.018	Liquid to SLE	Ethylbenzene	3.71E-05	0.999963
100.457	Liquid to SLE	Ethylbenzene	7.42E-05	0.999926
107.813	Liquid to SLE	Ethylbenzene	0.000148	0.999852
177.746	VLE to SVE (SLVE)	Ethylbenzene	0.000297	0.999703
178.2	Liquid to solid	Ethylbenzene	1	0

Table 11 Ethylbenzene's limit points

Table 11 Ethylbenzene's limit points shows the limit boundaries already mentioned in the Figure 35 Methane-Ethylbenzene phase diagram, it's important to notice how the composition range is under the maximum limit allowed by the machine which is 1 ppm roughly 1E-6 mol. Thereafter, according to all the limit points, a concentration of ethylbenzene is in the order of 1E-05 which means under that shall be wide delimited by the temperature and pressure.

11.2.3 Eutectic point Diagram of 95% Methane 5% Toluene

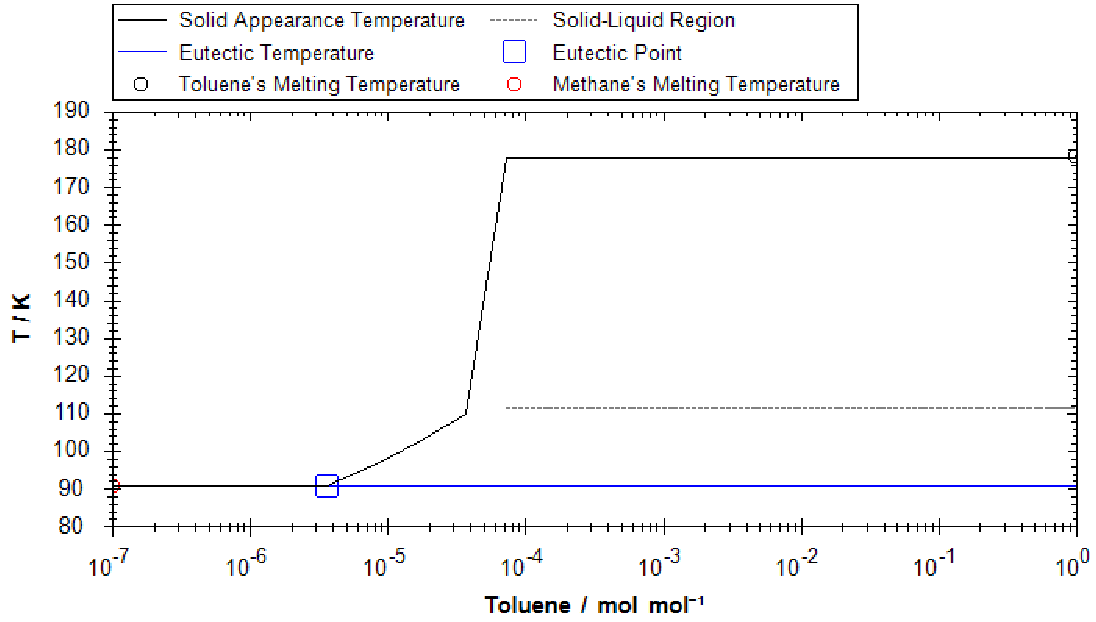


Figure 36 Methane-Toluene Phase Diagram

The Figure 36 Methane-Toluene Phase Diagram as it can seem is very similar to the Figure 35 Methane-Ethylbenzene phase diagram this due to the similar properties of ethylbenzene and toluene, even in the range of temperature and the same eutectic point 90.674 K. The borderline is also the limit between the two phases, liquid, and SLE.

Melting T / K	Melting Phase Transition	Freeze-Out Component	Toluene Composition mol mol^{-1}	Methane (Overall) / mol mol^{-1}
90.674	Liquid to SLE	Toluene	3.66E-06	0.999996
97.494	Liquid to SLE	Toluene	9.28E-06	0.999991
103.281	Liquid to SLE	Toluene	1.86E-05	0.999981
109.788	Liquid to SLE	Toluene	3.71E-05	0.999963
177.807	VLE to SVE (SLVE)	Toluene	7.42E-05	0.999926
178.149	Liquid to solid	Toluene	1	0

Table 12 Methane-Toluene limit points

Table 12 Methane-Toluene limit points as mentioned above, temperatures are similarly regarded to ethylbenzene, with the difference the range of concentration is more narrowed between 3.66E-06 and 7.42E-05 mol. That means the limit operation point is 1.86E-05 at 103.281K.

11.2.4 Eutectic point Diagram of 95% Methane 5% m-Xylene

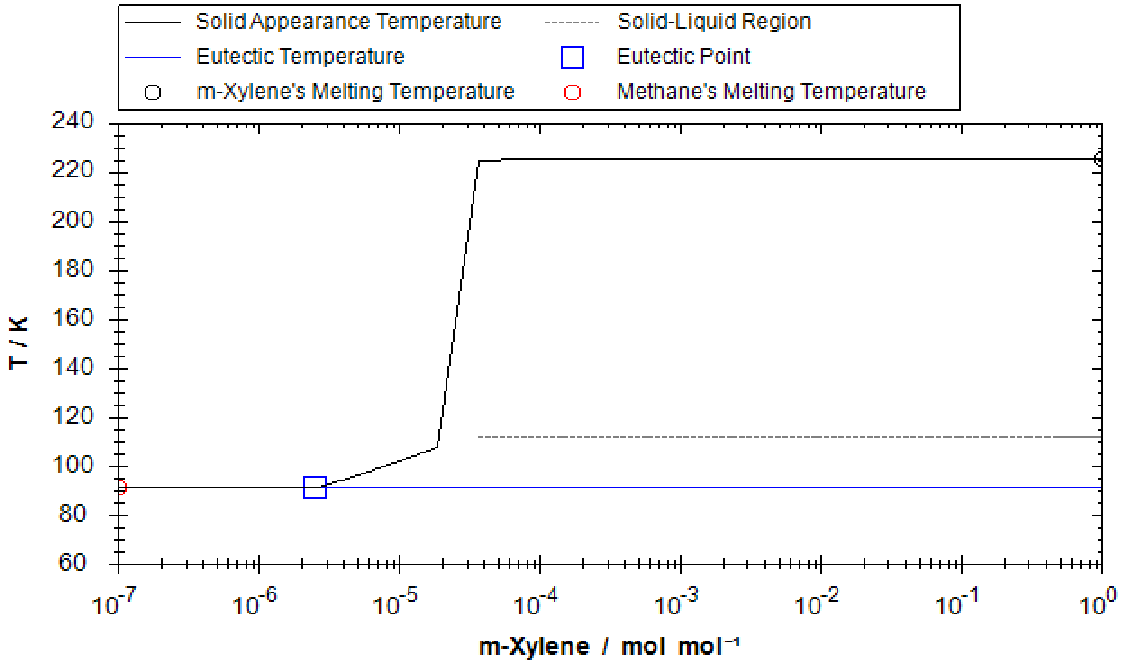


Figure 37 Methane-m-Xylene phase Diagram

Figure 37 Methane-m-Xylene phase Diagram shows a eutectic point at 90.675 K, similar points are presented in the Ethylbenzene and toluene phase diagram, this due to the related physical characteristics and molecular structure, there are three phases interaction in this diagram, which is Liquid, solid, and SLE, the highest temperature reached at 224.53 K, this slight difference is a proof on how can vary the temperature just with a different carbon position on the molecule, and how difficult is to predict accurate variables. Even though it is a good approximation to precise the limit temperature operation base on the composition, starting from the maximum limit of 1 ppm or 1E-06 mol, in this specific case the maximum limit is reached at 1.86E-05 at 107.231K.

Melting T / K	Melting Phase Transition	Freeze-Out Component	m-Xylene Composition mol mol^{-1}	Methane (Overall) / mol mol^{-1}
90.675	Liquid to SLE	m-Xylene	2.52E-06	0.999997
95.142	Liquid to SLE	m-Xylene	4.64E-06	0.999995
100.81	Liquid to SLE	m-Xylene	9.28E-06	0.999991
107.231	Liquid to SLE	m-Xylene	1.86E-05	0.999981
224.53	Vapour to SVE	m-Xylene	3.71E-05	0.999963
225.199	Liquid to Solid	m-xylene	1	0

Table 13 Methane-m-Xylene Limit points

Table 13 Methane-m-Xylene Limit points shows the boundaries points, temperature, and concentrations, those points as mentioned before are similar to the toluene and ethylbenzene points, only with slights differences. Regarding the maximum concentration limit allowed by the Stirling machine, at 1 atm the limit point of m-xylene is 107.231 K with a concentration of 1.86E-05, this means an operation above those limits could cause the freeze-out of m-xylene.

11.2.5 Eutectic point Diagram of 95% Methane 5% Cyclohexane

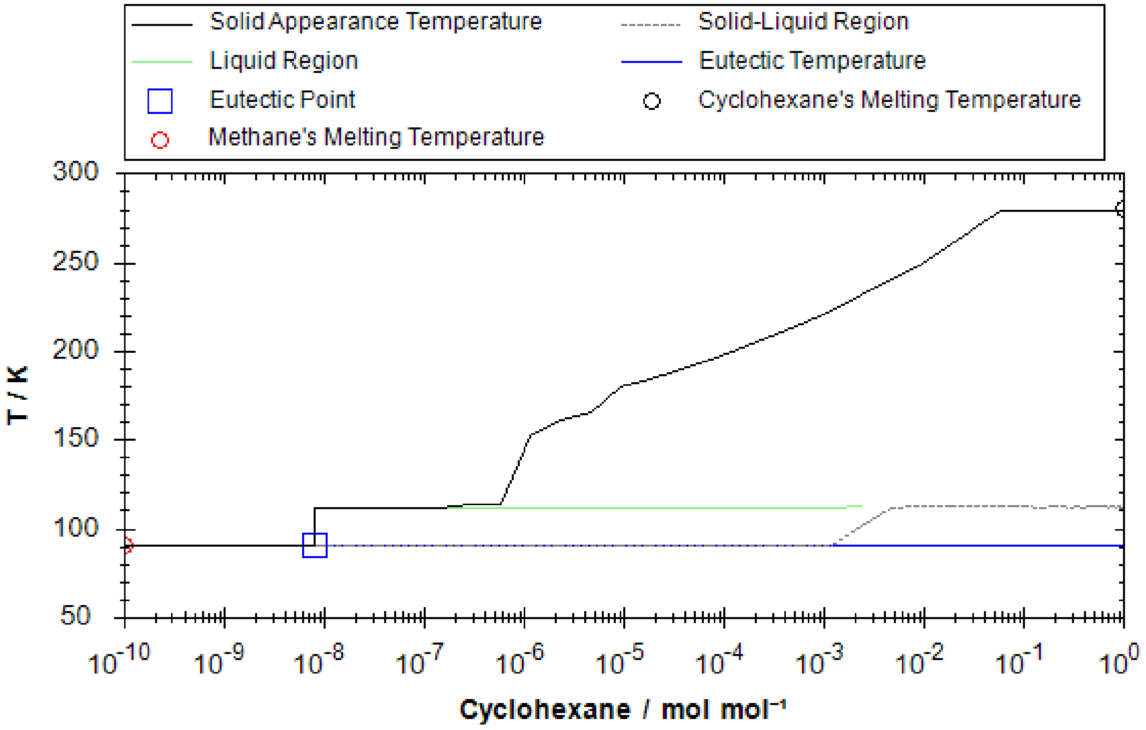


Figure 38 Methane-Cyclohexane Phase Diagram

Figure 38 Methane-Cyclohexane Phase Diagram shows the eutectic point at 90.675 K and a concentration of 8E-09 mol, from this temperature until 111.506 K the cyclohexane doesn't have a variation of concentration with a transition phase from liquid to SLE, then from 111.506 K until 13.269 K there is a modest variation of concentration of 5.91 E-7 mol, being this temperature under de minimum value allowed for normal operation conditions, after that, there is a constant increment of melting point line appearing from 152.265 K until 278.737 K with a considerable variation of concentration arriving at values of 0.059 mol and changing phases from vapor to SVE.

Melting T / K	Melting Phase Transition	Freeze-Out Component	n-Hexane Composition mol mol⁻¹	Methane (Overall) / mol mol⁻¹
90.675	Liquid to SLE	Cyclohexane	8E-09	0.999999992
111.506	Vapour to SVE	Cyclohexane	8E-09	0.999999992
113.269	Vapour to SVE	Cyclohexane	2.9E-07	0.99999971
152.265	Vapour to SVE	Cyclohexane	1.1589E-06	0.99999884411
184.165	Vapour to SVE	Cyclohexane	1.85548E-05	0.9999814452
201.568	Vapour to SVE	Cyclohexane	0.0001484376	0.9998515624
249.534	Vapour to SVE	Cyclohexane	0.0095	0.9905
271.932	Vapour to SVE	Cyclohexane	0.039	0.961
278.737	VLE to SVE (SLVE)	Cyclohexane	0.979	0.021
279.356	Liquid to SLE (Liquid Retrograde)	Cyclohexane	0.999	0.001
279.598	Liquid to Solid	Cyclohexane	1	0

Table 14 Methane-Cyclohexane limit points

Apart from section lines increments and constant section critical at the melting point line, is notable also a phase liquid region, which is between might be between 111.406 K and 111.953 K and mol concentration between 8E-09 and 0.002375 mol of cyclohexane, this means not only a risky vapor to SVE could be formed also pure liquid, then another phase transition it appreciates, a line from 90.674 K to 111.41 K and concentration from 8E-09 mol to 0.999 mol of Cyclohexane.

Table 14 Methane-Cyclohexane limit points represents the key points along the melting point curve, five phases are visible during the variation of temperature and concentration, solid, liquid, vapor, SVE, SLE, SLVE. Those phases characterized the component as risky for the liquefaction process. Between 113.269 K and 111.506 K, the concentration of Cyclohexane is below the maximum concentration allowed which is 1E-06 mol, and the boundary point is at 184.165 K due to its concentration value of 1.855E-05.

11.2.6 Eutectic point Diagram of 95% Methane 5% Carbon Dioxide

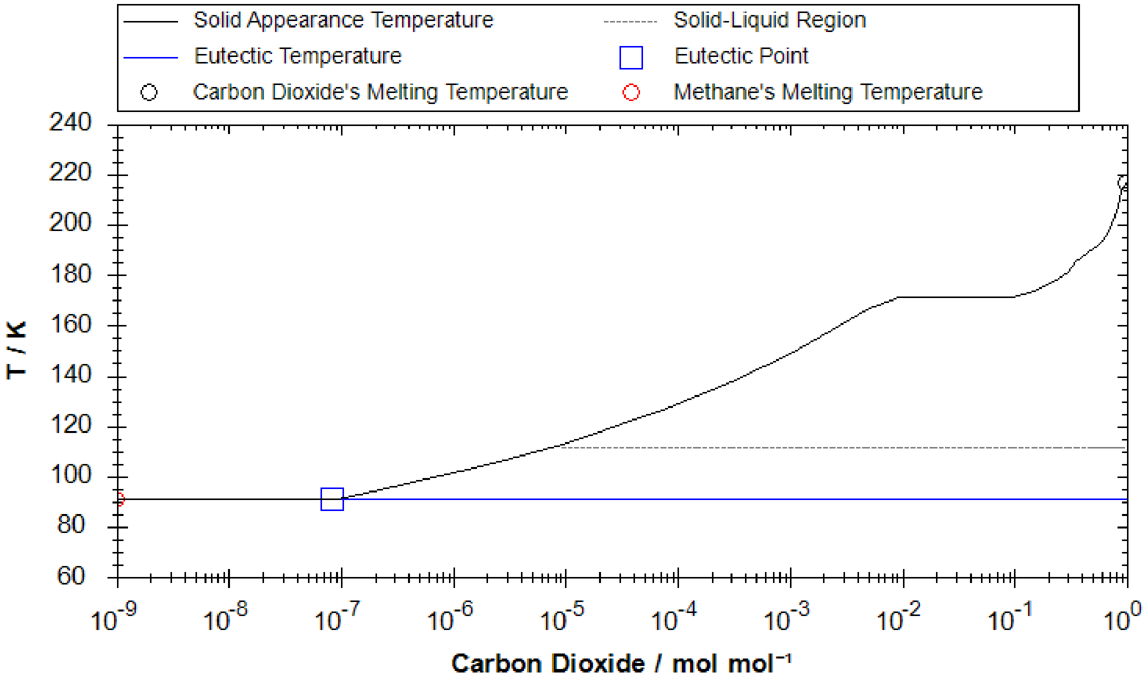


Figure 39 Methane- Carbon Dioxide Phase Diagram

Figure 39 Methane- Carbon Dioxide Phase Diagram the first notable feature of CO_2 behavior is the steed increasement form the eutectic point from 90.675 K at 8.22E-8 mol until 171.231 K at 0.0095 mol, experimenting four state phases; liquid, vapor, SLE, and SVE, after that at 171.231 K the curve remains constant only varying composition from 0.0095 mol to 0.149 mol which is a considerable variation of concentration, then there is a continuous rise until the final melting point at pure CO_2 at 216.569 K. The limit allowance of CO_2 at 1 bar gas pressure is roughly 148 ppm (1.48E-04 mol).

Melting T / K	Melting Phase Transition	Freeze-Out Component	Carbon Dioxide Composition mol mol⁻¹	Methane (Overall) / mol mol⁻¹
90.675	Liquid to SLE	Carbon Dioxide	8.22E-08	1
98.717	Liquid to SLE	Carbon Dioxide	5.80E-07	0.999999
112.955	Vapour to SVE	Carbon Dioxide	9.28E-06	0.999991
131.907	Vapour to SVE	Carbon Dioxide	1.48E-04	0.999852

157.939	Vapour to SVE	Carbon Dioxide	0.002375	0.997625
171.231	Vapour to SVE	Carbon Dioxide	0.0095	0.9905
180.948	Vapour to SVE	Carbon Dioxide	0.299	0.701
200.587	Vapour to SVE	Carbon Dioxide	0.749	0.251
216.569	Vapour to Solid	Carbon Dioxide	1	0

Table 15 Methane-Carbon Dioxide limit points

Table 15 Methane-Carbon Dioxide limit points represents the main boundaries points where there are state phases changes, CO_2 experiments different properties from hydrocarbons, even more, aromatic hydrocarbons, even so, is a high-risk component regarding its trend to freeze-out, as mentioned before the maximum allowance of CO_2 is around 1.48E-4 mol at 1 barg, but regarding the results, the limit concentration at 112.955 K is 9.28E-06, higher concentrations at the operating temperature the component will freeze-out.

11.3 Relationship between pressure and temperature regarding the risk of freeze out

In this section the melting point of three components are evaluated in base on the pressure and the temperature, as mentioned previously, the variation of composition is determinant for the phase change of the component at constant pressure, in this case, the solid appearance regarding the variation of temperature and pressure.

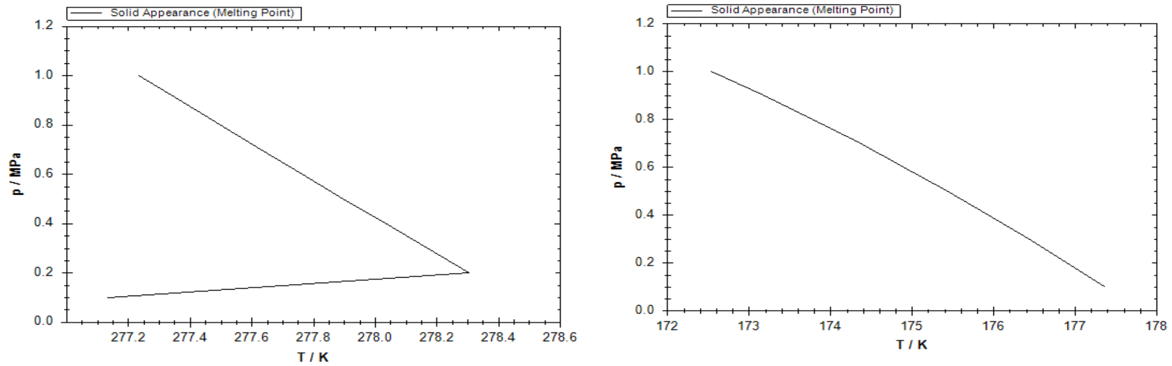


Figure 40 a) Methane-Benzene b) Methane-n-Hexane Temperature vs Pressure

Figure 35 a) shows a particular behavior, there is a constant rise from 277.13 until 278.03, this range presents a variation of temperature of 3 bar and temperature of 0.9 k, being the freeze-out more sensitive to any possible temperature change, after that, the curve shows an inversely proportional behavior, the melting point remains at the same range of temperature but with a variation of 6 bar, being from 0.4 bar to 1 bar, that means the melting point could vary according to a small change of temperature only if remains under 0.4 bar if the pressure is more than that 0.4 bar the melting point appears at lower temperatures

Figure 35 b) shows the melting point curve of the n-Hexane 5% mol in a solution of 95% mol f methane, is possible to observe how at the difference from the benzene the n-Hexane presents only has an inversely proportional behavior, from 177.36 K until 172.53 K and a variation of pressure of 10 bar, being twice than the temperature, is notable how the phase change is more sensitive at temperatures changes than pressure as well as benzene.

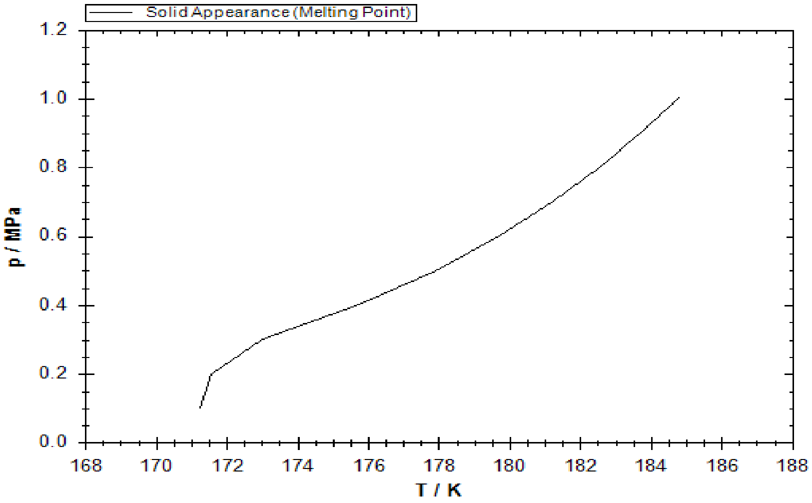


Figure 41 Methane- Carbon Dioxide Temperature vs Pressure

Figure 41 Methane- Carbon Dioxide Temperature vs Pressure represents the melting point of CO_2 with a composition of 5% mol and 95% of methane, the first thing to notice is at the difference from hydrocarbons components CO_2 presents a continuous proportional rise from 171.23 K until 173.00 K and a delta of 0.2 bar, being more sensitive to pressure in this temperature range, from 173.00 K and 184.79 K presents a behavior more linear with a considerable delta of 11.79 K and a delta pressure of 7 bar.

11.4 Analysis of Gas composition Sample provided by the company

A gas composition analysis from a pipeline was provided by the company in order to have more accurate data in the analysis, the sample is compounded by 94% of Methane and 6% of other components, better detailed in appendix table A.1 , some considerations are made

1. Water is not considered due to its high melting point
2. Mixture #1 CO_2 is considered
3. Mixture #2 CO_2 is not considered

As mentioned before the interactions between different components affects the solubility and some properties of each one by separate, a full simulation of mixture 1 and mixture 2 is analyze to get an approach of components more propensity to freeze out in the process of liquefaction

11.4.1 Mixture #1 Composition with CO_2

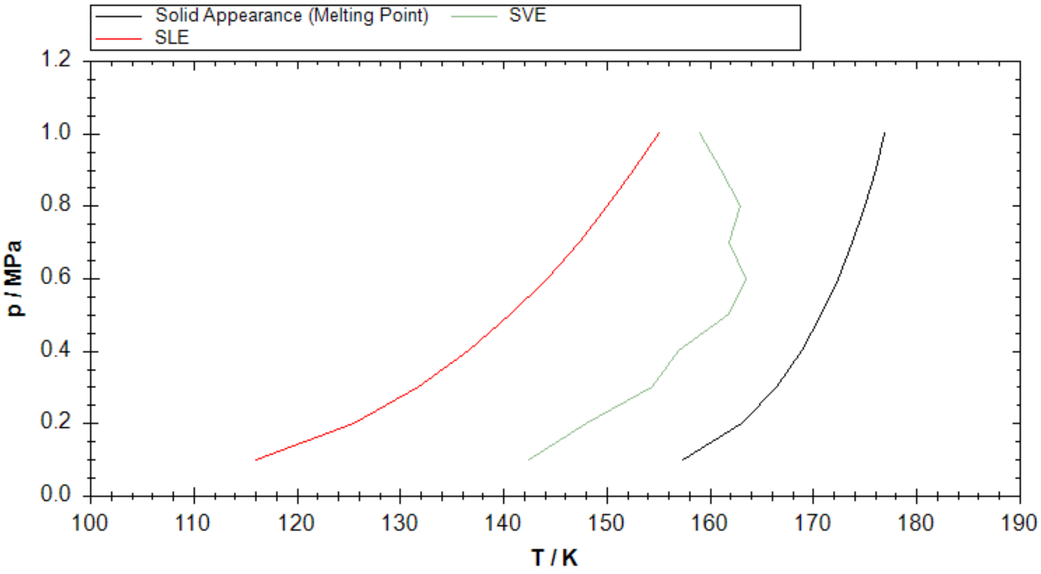


Figure 42 Mixture #1 with CO_2 Temperature vs Pressure

Figure 42 Mixture #1 with CO2 Temperature vs Pressure represents the solid formation in three different phases, solid SVE and SLE, the SLE is the more propensity of all, is between 116.6 K and 155.07 K, is characterized by a continuous rise (a polynomial behavior) and increase as increase the pressure, at the lowest temperature 116.06 K the solid appearance is composed by; CO_2, Benzene, n-Decane, and p-Xylene, being those components the most propensity to solidify at those temperatures, then at temperature 125.45 K and 2 bar, there are only three components, which are; CO_2, Benzene and n-Decane. The same components are repeated at 131.78 K and 3 bars. From 136.67 K and 4 bars, there is only appearance SLE of CO_2 and n-Decane. After that from 140.72 K, 0.5 CO_2, and 155.07 K, 1 bar there is only the presence of CO_2, positioning as the component more propensity to freeze out. Moving on at the second line SVE is formed from a range of temperature slightly higher than SLE, from 142.45 K and 158.97 and from 1 bar to 10 bar, in this interaction of phases the particularity is that there is only the presence of CO_2, only by the except of the first point at 142.45 K and 1 bar there is Benzene. The las curve is the pure solid appearance (Melting point), this curve is characterized by only the appearance of CO_2 from a range of temperature from 157.45 K and 176.97 K up to 10 bar, noticed how values of temperatures are higher, this means much attention shall be taken into the extraction process of CO_2 in order to avoid freeze out.

11.4.2 Mixture #2 Composition without CO_2

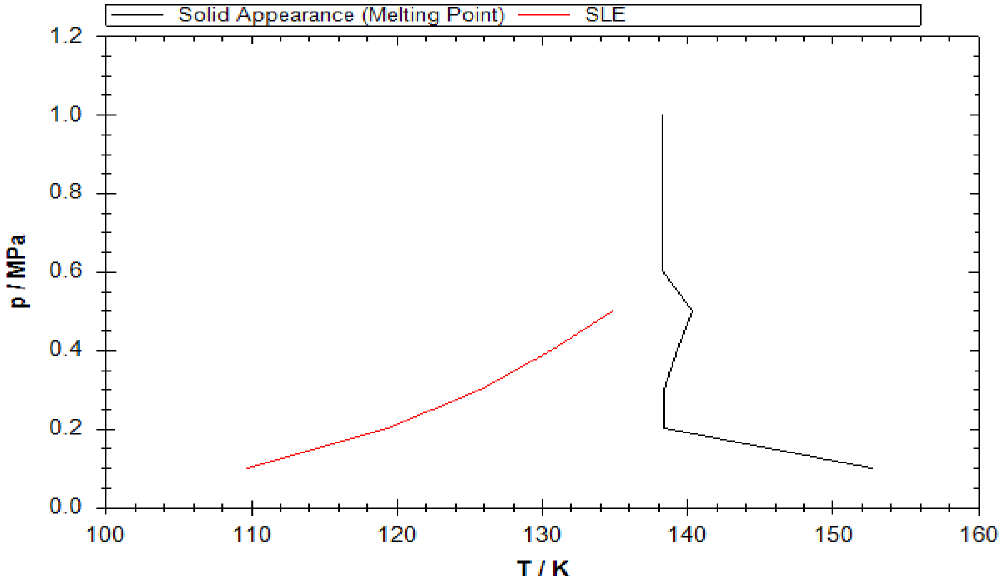


Figure 43 mixture #2 without CO_2 Temperature vs Pressure

Figure 43 mixture #2 without CO2 Temperature vs Pressure represents the solid formation only for two phases, solid and SLE, as mentioned before this gas composition is evaluated without consideration of CO_2, in order to study and analyze phases changes involved at different temperatures and pressure conditions for heavy hydrocarbon in particular. The first particularity to be noticed is the trend of the solid appearance line, how from 0 bar and 5 bar there is a benzene solid formation starting at 152.76 K then with slight variations from 138.43 K to 140.4 K, noticed the decreasing relation regarding the pressure as mentioned before, ongoing the line solid formation from 0.6 bar to 1 bar and variations of 0.01 K there is a solid formation of n-Decane. The second line describes the appearance of SLE, being a rising line from 109.75 K and 134.81 and from 1 bar to 5 bar, the components with solid formation are at the lowest temperature Benzene, n-Octane, n-Decane, and p-Xylene and from 3 bar until 5 bar only solid appearance of Benzene and n-Decane, noticed components are characterized for being aromatic or with high molecular weight, featured that make them the propensity to freeze out.

12. Article support on ThermoFAST Accuracy and results

Below is presented a brief analysis done by [38] regarding the accuracy of the ThermoFAST simulations. The scientific article englobes several data concerning the solidification (freeze out) of heavy hydrocarbons during the liquefaction process of natural gas. The main traditional models that predict the freeze-out are validated by the Gas processes Association even though there are issues to define the equation of state for solids formation. Results and graphs comparison has been made, providing positive predictions for the simulator software.

A standard tool to predict temperatures at which heavy hydrocarbons solids will form is the Kohn and Luks Solids Solubility Program (KLSSP) from GPA (Gas processes Association), KLSSP has converted an industry-standard tool for forecasting solid-fluid equilibria (SFE) in cryogenic processes. The KLSSP suffers from restrictions including fixed ranges of temperature, mixture composition no dependence on pressure and a limited set of possible freeze out-out components [41]. The ThermoFAST model is able to simulate and bring results with an average root-mean-squared temperature deviation of 1.7 K.

For binaries solutions, the KLSSP model presents a root-mean-square temperature deviation of 19.1 K across an extended rage of conditions, although its minimum rms temperature deviation is 5.6 K over its limited range of stated validity. The rapid flash algorithm´s implemented within ThermoFAST allows the exploration and extend the boundaries of possible binaries and multicomponent mixtures with variations of pressure and temperature.

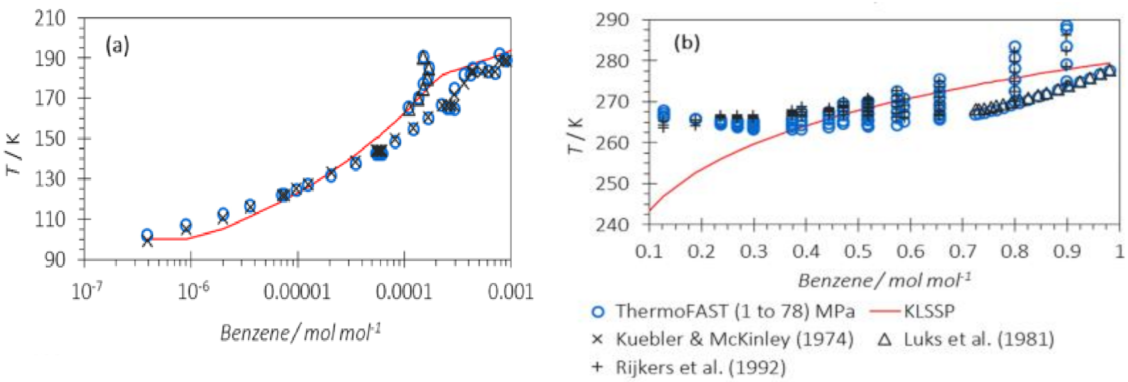


Figure 44 Solid-fluid equilibrium diagram Methane + Benzene comparing ThermoFAST and KLSSP predictions against experimental data [42], [43], [44].

The Figure 44 Solid-fluid equilibrium diagram Methane + Benzene comparing ThermoFAST and KLSSP predictions against experimental data , , .is possible to observe image a) low and b) high concentration of benzene, both represent trending lines of temperatures depending on benzene concentration in a methane solution.

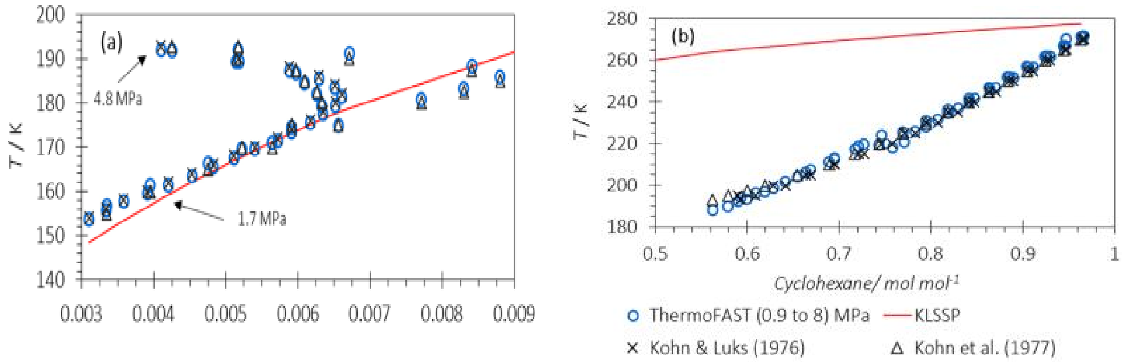


Figure 45 Solid-fluid equilibrium diagram for methane + cyclohexane comparing ThermoFAST and KLSSP predictions against experimental data [45] [46]

Figure 45 Solid-fluid equilibrium diagram for methane + cyclohexane comparing ThermoFAST and KLSSP predictions against experimental data represents the solid-fluid equilibrium for a solution of methane-cyclohexane figure a) at low concentrations of cyclohexane and figure b) high concentration of cyclohexane, it's possible to observe in figure a) how the KLSSP prediction does not vary as increase the pressure and in the figure b) differs notably regarding ThermoFAST and Kohn & Luks predictions. In contrast, ThermoFAST is capable r has an accuracy of rmsd of only 2 K at larges changes of pressure and cyclohexane concentration.

13. Economic evaluation by CAPEX and OPEX

Cash flow was used to study at which year cumulative net cash flow is positive and consequently the investment is recovered, due to the simplicity of the process, even more, the use of the Stirling machine, startup shall be at time zero, and start to produce, some considerations are taken:

- No maintenance cost during the first 5 years
- 1 m^3 gas – 11 kWh
- 1 kg gas – 1.411m^3 gas
- 1 m^3 gas – 1.025 euros
- 1 k – 1000 euros
- 1 operational year – 335 days
- 150 kg gas/day production

Stirling LNG production Cash Flow					
Year	2020	2021	2022	2023	2024
Capital expenditure (k €)	300				
Energy consumption per year (Kwh/yr)	71556	71556	71556	71556	71556
Energy Consump to Gas consumption m^3	6505.09	6505.099	6505.09	6505.09	6505.09
Gas consumption (k €/yr)	6.67	6.67	6.67	6.67	6.67
Total outgoing cash flow (k €)	306.66	6.67	6.67	6.67	6.67
Gas liquefied/year (Ton)	50250	50250	50250	50250	50250
Natural Gas/year (m^3)	70,90	70,90	70,90	70,90	70,90
Natural Gas (k €/yr)	72.68	72.68	72.68	72.68	72.68
Net cash flow (k €/yr)	-233.99	66.01	66.01	66.01	66.01
Cumulative cash flow (k €/yr)	-233.99	-167.98	-101.98	-35.97	30.04

Table 16 Cumulative net Cash flow

Regarding Table 16 Cumulative net Cash flow is possible to observe comparative values of inflow and outflow gas, converted to monetary value, is notable how at the first three years the cumulative cash flow is negative, but from the year 2024 and on, there are positive values which are traduced as fuel for internal use, the main impact is at the first year (2020) regarding the capital investment, which is normal in any acquisition. Incomes are depending on the quantity liquefied, is this one as the lowest per day (150 kg), there is the possibility to arrange the equipment in parallel to increase the total amount of LNG as a fuel depending on the internal demand.

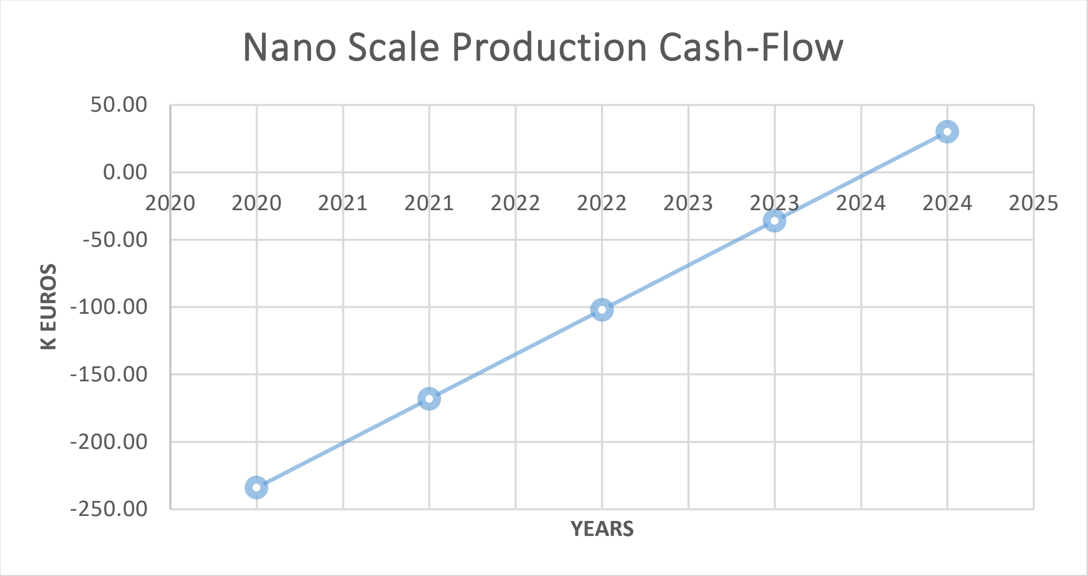


Figure 46 Nano scale production Cash-flow

The cash flow evaluated previously is represented by a linear curve. The linear curve has a constant rising since the production process shall be continuous with same amounts of energy consumption and liquefaction capacity. A hypothesis case in order to understand the profitable uses of LNG from cost zero of raw material (Gas) is compare it with the acquisition with Diesel fuel.

The average price of Diesel fuel is roughly 1.30 euros per liter (just an example) is used to simulate the acquisition of 1 ton of diesel for 335 labour days. For one labour year the expenses are nearly 512,352 euros, in five years are about 2,561,760 million of euros plus 30% more emissions than natural gas.

13.1. Comparison with other liquefaction technologies

As explained before, the liquefaction process of natural gas it is has been characterized by its large scale, but since the demand has been increasing and in consequence the supply chain has been expanding a market has emerged. New technologies have been rising to fill out different segments of markets regarding the LNG.

Three technologies (Stirling included) are compared in the following table, to analyze their scope and capacity, since the TBF (Turbo-Brayton) cover a minimum production capacity of 4.8 ton per day, the Stirling System to be compared is made by four (4) Stirling machine in parallel. The TBF and the LIN (Liquid nitrogen) are brief described below, The TBF its machine compounded by a centrifugal compressor and expanders, turbine, heat exchanger and a chiller with the capacity to adjust at different scale of liquefaction, with a specific refrigeration between 25 K and 200 K adapted to customer's applications.

The LIN process is an arrangement that could be used the liquid nitrogen as a refrigerant, the process can be,

1. Close cycle
2. Open Cycle (Production of N_2)

The close cycle is characterized by the storage of liquid nitrogen, following by heat exchanger to liquefy the gas in this case methane, also includes system of compressors and coolers to reliquefy the nitrogen and re-used into the system.

Liquefaction technologies

Manufacturer	**Stirling Cryogenics**	**Stirling Cryogenics**	**Air liquid**	**Air liquid**	**LIN System (5 units)**
Model/Technology	**Stirling x4**	**Stirlingx1**	**Turbo-Brayton TBF-175**	**TBF-350**	**Cycle Heat Exchanger**
Capacity (ton/day)	4 ton	1 ton	4.8 ton	12 ton	5 ton
Size, assuming the equipment is in parallel (m)	1.75x3x1.7	+ 1.75x0.75x1.22	9.5x1.7x3m	11x 1.7x 3m	7x29x3 (storage included 2,000 l) + 4 m2 of heat exchanger
Weight (ton)	Abt. 2.5 ton	Abt. 0.6 ton	15 ton	17 ton	26 ton

Power requirement (kW)/day	Abt. 50 kW	11 kW	195 kW	390 kW	180 kW (chiller included)
Cooling water temperature (°C)	Normal 15 °C	Normal 15°C	Max 36 °C	Max 36 °C	Normal 15°
Approximate Heat loss (kW)	1.93 kW	0.48 kW	3.3 kW	3.3 kW	5 kW
Flow rate/Power Input / Cooling power (0 bar -111 K)	-	1 tpd/ 35.4 kW/ 0.62 kW	20% flow rate / 28% power input	-	2-ton LIN/ BOG ton
Noise level	-	-	< 100 dB	< 100 dB	74 dB
Time rate maintenance	Every 4 years and >6000 operating hours (small parts)	Every 4 years and >6000 operating hours (small parts)	Every 5 years	Every 5 years	Filters every 6,000 op hours
Price (euros)	**1.2 M**	**300 k**	**2.1 M**	**2.8 M**	**2.5 M**

Figure 47 Liquefaction technologies comparison [34] [47]

As it can be appreciated in Figure 47 Liquefaction technologies comparison there are similar factors such capacity, once again depends on the scope of the equipment, as showed previously price is highly affected by the capacity, and the power consumption.

In that sense is in evidence there is a gap for micro a nano-scale production. Since the economic feasibility is directly dependent on the capital expense and operating expense (continuous liquefaction of gas). If for any reason, there is a decrease in the production capacity, the cash flow will be negative. Other important issues are the dimension and weight of technology. The supply chain and logistics play a key role in the feasibility of the process, in that way, relocation of the liquefaction skid will provide an important advantage.

14. Conclusions

1. According to the Energy Outlook of Total, BP and DNV.GL, from 2018 to 2050, the demand for natural gas will increase by roughly 20% and LNG by nearly 30%.
2. The LNG value chain and Supply chain in Europe are in continuous improvement due to the rising of natural gas and incentives and government policies.
3. According to the thermodynamics simulation results due to ThermoFast software, the minimum concentration values to avoid the formation of solids (Freezeout) are 0.29 ppm Benzene, 148 ppm Ethylbenzene, 37.1 ppm Toluene, 18.6 ppm Xylene, 0.29 ppm Cyclohexane, 9.28 ppm Carbon dioxide.
4. Analyzing the solubility of a real sample of natural gas (considering CO2) contributes to the benzene solid formation, increasing its freezeout temperature 113 K to 116 K (-160 °C to -157°C).
5. Analyzing the solubility of a real sample of natural gas (not considering CO2) contributes to the benzene solid formation, increasing its freezeout temperature from 113 K to 157 K (-160 °C to -116°C), caused by heavy hydrocarbons effects.
6. The economic evaluation with Capex and Opex producing 1 ton of LNG per day (1 machine) results in positive cash flow at year number 5, from that year only profits shall be expected.
7. According to the tracking prices of LNG, the prices have been stable from 2015 until 2020, which is a good incentive for its use and investment.

15. For Future work

1. It is highly recommended to analyze a study case with a specific facility or refinery with a flair or vent system to determine the process feasibility regarding the gas composition and the economic feasibility.
2. It is highly recommended to analyze a study case with a specific pipeline grid to determine the whole feasibility and the possible contribution to the supply chain and distribution to remotes areas or users.
3. Noted the difficulty regarding the few equations of states for solid formation predictions on heavy hydrocarbons, it is recommended to study deeply component by component solubility in methane solution.
4. It is exceedingly recommended to simulate several times, multicomponent solutions of natural gas to understand and predict the effects of heavy hydrocarbons on solid formation.
5. Inquire the possible insertion of the nano-scale production skid, as complementary equipment for support liquefaction process in small and medium-scale plants of LNG or regasification.
6. Considering the improvement of decarbonization technologies and their increasing implementation, incentive by government policies, its highly recommended study the economic impact of the amount of CO2 emissions reduction using Natural gas as fuel.
7. Considering the increase of Biomethane plants and Bio-LNG plants, specifically in north Italy. Study the feasibility to insert the nano-scale LNG production in that market niche.
8. Study the social impact that LNG supply chain and small/micro/nano-scale distribution might have in communities without direct access to natural gas.

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17. Appendix

Table A.1 Solid formations of Table A.1 considering water

Solid Phase Diagram								
Solid Appearance T / K	Solid Appearance p / MPa	Solid at Melting Point	SLVE T / K	SLVE p / MPa	SLVE Solid	SLE T / K	SLE p / MPa	SLE Solid
229.45	0.1	Water	208.07	0.1	Water	116.06	0.1	Carbon Dioxide, Water, Benzene, n-Decane, p-Xylene
235.22	0.2	Water	216.03	0.2	Water	125.48	0.2	Carbon Dioxide, Water, Benzene, n-Decane
238.71	0.3	Water	221.02	0.3	Water	131.78	0.3	Carbon Dioxide, Water, Benzene, n-Decane
241.23	0.4	Water	224.8	0.4	Water	136.67	0.4	Carbon Dioxide, Water, n-Decane
243.22	0.5	Water	227.03	0.5	Water	140.72	0.5	Carbon Dioxide, Water
244.85	0.6	Water	228.82	0.6	Water	144.23	0.6	Carbon Dioxide, Water
246.24	0.7	Water	230.31	0.7	Water	147.34	0.7	Carbon Dioxide, Water
247.45	0.8	Water	231.57	0.8	Water	150.13	0.8	Carbon Dioxide, Water
248.52	0.9	Water	232.64	0.9	Water	152.7	0.9	Carbon Dioxide, Water
249.48	1	Water	233.57	1	Water	155.07	1	Carbon Dioxide, Water
250.35	1.1	Water	234.39	1.1	Water	157.3	1.1	Carbon Dioxide, Water
251.14	1.2	Water	235.1	1.2	Water	154.61	1.2	Carbon Dioxide, Water
251.88	1.3	Water	235.72	1.3	Water	155.43	1.3	Carbon Dioxide, Water
252.55	1.4	Water	236.27	1.4	Water	157.28	1.4	Carbon Dioxide, Water
253.18	1.5	Water	236.75	1.5	Water	159.04	1.5	Carbon Dioxide, Water

Table A.2 Natural Gas sample composition (with consideration #1 and #2) provided by Hysytech s.r.l.

Natural Gas Sample Composition		
Mixture Number	Mixture #1 CO2 considered	Mixture #2 CO2 not considered
Methane	0.9073668	0.9324233
Ethane	0.0535355	0.0535355
Propane	0.003986	0.003986
isoButane	0.001157	0.001157
n-Butane	0.000583	0.000583
Carbon Dioxide	0.025	0
Nitrogen	0.0075	0.0075
Water	5.65E-05	0
isoPentane	0.000248	0.000248
n-Pentane	0.000145	0.000145
n-Hexane	0.0001	0.0001
Hydrogen Sulfide	4.60E-06	4.60E-06
Benzene	4.32E-05	4.32E-05
m-Xylene	1.50E-06	1.50E-06
Toluene	9.80E-06	9.80E-06
Ethylbenzene	4.00E-07	4.00E-07
n-Octane	2.40E-06	2.40E-06
n-Decane	9.00E-07	9.00E-07
Cyclohexane	0.0001	0.0001
Neopentane	0.000145	0.000145
o-Xylene	4.00E-07	4.00E-07
p-Xylene	1.50E-06	1.50E-06
n-Nonane	3.00E-07	3.00E-07
n-Heptane	1.22E-05	1.22E-05
Total	1	1

Table A.3 Solid Formation with 95% Methane 5% Benzene

Solid Phase Diagram				
Melting T / K	Melting Phase Transition	Freeze-Out Component	Benzene Composition mol mol^{-1}	Methane (Overall) / mol mol^{-1}
90.675	Liquid to Solid	Methane	0	1
90.675	Liquid to Solid	Methane	1.00E-10	1
90.675	Liquid to SLE	Methane	4.60E-09	0.999999995
90.675	Liquid to SLE	Methane	6.90E-09	0.999999993
90.675	Liquid to SLE	Methane	8.00E-09	0.999999992
90.675	Liquid to SLE	Methane	8.20E-09	0.999999992
90.675	Liquid to SLE	Benzene	8.20E-09	0.999999992
111.506	Vapour to SVE	Benzene	8.30E-09	0.999999992
111.506	Vapour to SVE	Benzene	8.60E-09	0.999999991
111.506	Vapour to SVE	Benzene	9.20E-09	0.999999991
111.525	Vapour to SVE	Benzene	1.82E-08	0.999999982
111.56	Vapour to SVE	Benzene	3.63E-08	0.999999964
111.579	Vapour to SVE	Benzene	7.26E-08	0.999999927
111.579	Vapour to SVE	Benzene	1.45E-07	0.999999855
113.689	Vapour to SVE	Benzene	2.90E-07	0.99999971
113.689	Vapour to SVE	Benzene	5.80E-07	0.99999942
153.099	Vapour to SVE	Benzene	1.16E-06	0.99999884
183.271	Vapour to SVE	Benzene	2.32E-06	0.999997681
187.561	Vapour to SVE	Benzene	4.64E-06	0.999995361
192.073	Vapour to SVE	Benzene	9.28E-06	0.999990723
196.824	Vapour to SVE	Benzene	1.86E-05	0.999981445
201.834	Vapour to SVE	Benzene	3.71E-05	0.999962891
207.127	Vapour to SVE	Benzene	7.42E-05	0.999925781
212.727	Vapour to SVE	Benzene	0.000148438	0.999851562
218.664	Vapour to SVE	Benzene	0.000296875	0.999703125
224.973	Vapour to SVE	Benzene	0.00059375	0.99940625
231.688	Vapour to SVE	Benzene	0.0011875	0.9988125
238.855	Vapour to SVE	Benzene	0.002375	0.997625
246.522	Vapour to SVE	Benzene	0.00475	0.99525
254.747	Vapour to SVE	Benzene	0.0095	0.9905
263.596	Vapour to SVE	Benzene	0.019	0.981
263.596	Vapour to SVE	Benzene	0.019	0.981
273.515	Vapour to SVE	Benzene	0.039	0.961
278.441	VLE to SVE (SLVE)	Benzene	0.059	0.941
278.441	VLE to SVE (SLVE)	Benzene	0.079	0.921
278.441	VLE to SVE (SLVE)	Benzene	0.099	0.901
278.441	VLE to SVE (SLVE)	Benzene	0.149	0.851
278.441	VLE to SVE (SLVE)	Benzene	0.199	0.801
278.441	VLE to SVE (SLVE)	Benzene	0.249	0.751
278.441	VLE to SVE (SLVE)	Benzene	0.299	0.701
278.441	VLE to SVE (SLVE)	Benzene	0.349	0.651
278.441	VLE to SVE (SLVE)	Benzene	0.399	0.601
278.441	VLE to SVE (SLVE)	Benzene	0.449	0.551
278.441	VLE to SVE (SLVE)	Benzene	0.499	0.501
278.441	VLE to SVE (SLVE)	Benzene	0.549	0.451
278.441	VLE to SVE (SLVE)	Benzene	0.599	0.401
278.441	VLE to SVE (SLVE)	Benzene	0.649	0.351
278.441	VLE to SVE (SLVE)	Benzene	0.699	0.301
278.441	VLE to SVE (SLVE)	Benzene	0.749	0.251
278.441	VLE to SVE (SLVE)	Benzene	0.799	0.201
278.441	VLE to SVE (SLVE)	Benzene	0.849	0.151
278.441	VLE to SVE (SLVE)	Benzene	0.899	0.101
278.441	VLE to SVE (SLVE)	Benzene	0.919	0.081
278.441	VLE to SVE (SLVE)	Benzene	0.939	0.061
278.441	VLE to SVE (SLVE)	Benzene	0.959	0.041
278.441	VLE to SVE (SLVE)	Benzene	0.979	0.021
278.535	Liquid to SLE (Liquid Retrograde)	Benzene	0.999	0.001
278.599	Liquid to Solid	Benzene	1	0

Table A.3 Solid Formation with 95% Methane 5% n-Hexane

Solid Phase Diagram				
Melting T / K	Melting Phase Transition	Freeze-Out Component	n-Hexane Composition mol mol^{-1}	Methane (Overall) / mol mol^{-1}
90.675	Liquid to Solid	Methane	0	1
90.675	Liquid to Solid	Methane	1.00E-10	1
90.675	Liquid to SLE	Methane	4.60E-09	0.999999995
90.675	Liquid to SLE	Methane	6.90E-09	0.999999993
90.675	Liquid to SLE	Methane	7.50E-09	0.999999993
90.675	Liquid to SLE	n-Hexane	7.70E-09	0.999999992
111.506	Vapour to SVE	n-Hexane	7.80E-09	0.999999992
111.506	Vapour to SVE	n-Hexane	7.90E-09	0.999999992
111.506	Vapour to SVE	n-Hexane	8.00E-09	0.999999992
111.506	Vapour to SVE	n-Hexane	9.20E-09	0.999999991
111.509	Vapour to SVE	n-Hexane	1.82E-08	0.999999982
111.509	Vapour to SVE	n-Hexane	3.63E-08	0.999999964
111.509	Vapour to SVE	n-Hexane	7.26E-08	0.999999927
111.509	Vapour to SVE	n-Hexane	1.45E-07	0.999999855
113.595	Vapour to SVE	n-Hexane	2.90E-07	0.99999971
113.595	Vapour to SVE	n-Hexane	5.80E-07	0.99999942
151.07	Vapour to SVE	n-Hexane	1.16E-06	0.99999884
161.083	Vapour to SVE	n-Hexane	2.32E-06	0.999997681
167.088	Vapour to SVE	n-Hexane	4.64E-06	0.999995361
174.226	Vapour to SVE	n-Hexane	9.28E-06	0.999990723
177.83	Vapour to SVE	n-Hexane	1.86E-05	0.999981445
177.364	VLE to SVE (SLVE)	n-Hexane	3.71E-05	0.999962891
177.364	VLE to SVE (SLVE)	n-Hexane	7.42E-05	0.999925781
177.364	VLE to SVE (SLVE)	n-Hexane	0.000148438	0.999851562
177.364	VLE to SVE (SLVE)	n-Hexane	0.000296875	0.999703125
177.364	VLE to SVE (SLVE)	n-Hexane	0.00059375	0.99940625
177.364	VLE to SVE (SLVE)	n-Hexane	0.0011875	0.9988125
177.364	VLE to SVE (SLVE)	n-Hexane	0.002375	0.997625
177.364	VLE to SVE (SLVE)	n-Hexane	0.00475	0.99525
177.364	VLE to SVE (SLVE)	n-Hexane	0.0095	0.9905
177.364	VLE to SVE (SLVE)	n-Hexane	0.019	0.981
177.364	VLE to SVE (SLVE)	n-Hexane	0.019	0.981
177.364	VLE to SVE (SLVE)	n-Hexane	0.039	0.961
177.364	VLE to SVE (SLVE)	n-Hexane	0.059	0.941
177.364	VLE to SVE (SLVE)	n-Hexane	0.079	0.921
177.364	VLE to SVE (SLVE)	n-Hexane	0.099	0.901
177.364	VLE to SVE (SLVE)	n-Hexane	0.149	0.851
177.364	VLE to SVE (SLVE)	n-Hexane	0.199	0.801
177.364	VLE to SVE (SLVE)	n-Hexane	0.249	0.751
177.364	VLE to SVE (SLVE)	n-Hexane	0.299	0.701
177.364	VLE to SVE (SLVE)	n-Hexane	0.349	0.651
177.364	VLE to SVE (SLVE)	n-Hexane	0.399	0.601
177.364	VLE to SVE (SLVE)	n-Hexane	0.449	0.551
177.364	VLE to SVE (SLVE)	n-Hexane	0.499	0.501
177.364	VLE to SVE (SLVE)	n-Hexane	0.549	0.451
177.364	VLE to SVE (SLVE)	n-Hexane	0.599	0.401
177.364	VLE to SVE (SLVE)	n-Hexane	0.649	0.351
177.364	VLE to SVE (SLVE)	n-Hexane	0.699	0.301
177.364	VLE to SVE (SLVE)	n-Hexane	0.749	0.251
177.364	VLE to SVE (SLVE)	n-Hexane	0.799	0.201
177.364	VLE to SVE (SLVE)	n-Hexane	0.849	0.151
177.364	VLE to SVE (SLVE)	n-Hexane	0.899	0.101
177.364	VLE to SVE (SLVE)	n-Hexane	0.919	0.081
177.364	VLE to SVE (SLVE)	n-Hexane	0.939	0.061
177.364	VLE to SVE (SLVE)	n-Hexane	0.959	0.041
177.405	Liquid to SLE (Liquid Retrograde)	n-Hexane	0.979	0.021
177.81	Liquid to SLE (Liquid Retrograde)	n-Hexane	0.999	0.001
177.83	Liquid to Solid	n-Hexane	1	0