LIQUEFIED NATURAL GAS AND LIQUEFIED PETROLEUM GAS TECHNOLOGIES

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The increasing demand of LNG and LPG in the market worldwide has forced companies to create and improve separation of its hydrocarbons chains components through the different designs, refrigeration systems and/or structures' adaptations to satisfy the needs.
The available technologies offer a range of options regarding to the requirements: location (onshore – offshore), rate of production, investment. However there processes are company patented but still it is available for third parties licensors.

LIQUEFIED NATURAL GAS (LNG)

Liquefaction process.
LNG processes are generally patented by large engineering, oil and gas companies, but are generally based on a one- two- or three-stage cooling process with pure or mixed refrigerants. The three main process types of LNG process with some examples of process licensors are [2]:

Liquefaction technology licensors by the number of cycles and refrigerants

	REFRIGERANTS		
N ° of cycles	Pure	Pure+Mixed	Mixed
1	-	-	APCI (SMR) Black & Veath (PRICO II) BHP (cLNG)
2	-	Shell (C3-MR) APCI (C3-MR) Shell (PMR)	Shell (DMR) Axens-IFP (Liquefin)
3	Conoco Phillips (POCP)	APCI (AP-X)	Statoil-Linde (MFC)

Most processes use a mixed refrigerant (MR) design. The reason is that the gas has a heat load to temperature (Q/T) curve that, if closely matched by the refrigerant, will improve stability, throughput and efficiency. The curve tends to show three distinct regions, matching the pre-cooling, liquefaction and sub-coiling stages. The refrigerant gas composition will vary based on the individual design, as will the power requirement of each stage, and is often a patented, location-specific combination of one or two main components and several smaller, together with careful selection of the compressed pressure and expanded pressure of the refrigerant, to match the LNG gas stream.

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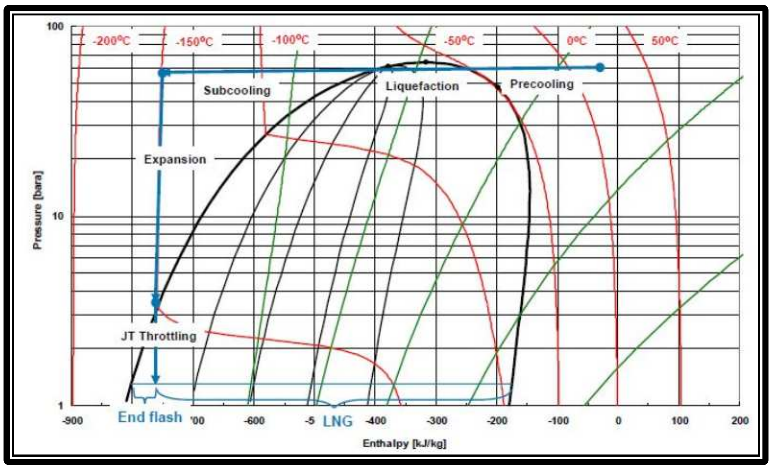
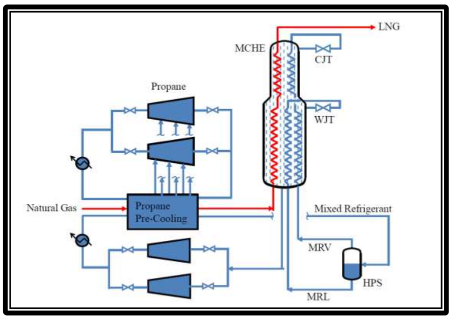


Natural gas path through liquefaction for a typical onshore based LNG production. The composition is C1 89,7%, C2 5,5%, C3 1,8% and N2 2,8% [11]. The natural gas enters with a pressure of 60 bar. As figure 4.7 illustrates is the cooling done below the critical point [7].

C3MR

This method has two main refrigerant cycles. It is based on propane pre-cooled and a mixed refrigerant. The process undergoes as follows [11]:

- The feed gas enters into the system.
- The precooling cycle uses a pure component propane. The pre-cooling cold box also cools the cooling medium for the liquefaction and sub cooling stage.
- The precooling cycle uses propane at three or four pressure levels and can cool the process gas down to (- 40°C). It is also used to cool and partially liquefy the MR.
- After the precooling cycle a centrifugal compressor with the side streams recovers the evaporated C3 streams and compresses the vapour to 15-25 bara to be condensed against water or air and recycled to the propene kettles.
- The liquefaction and sub-cooling cycles use a Mixed Refrigerant (MR) made up of nitrogen, methane, ethane and propane.
- In the MR cycle the partially liquefied refrigerant is separated into vapor and liquid streams. The refrigerant is used to liquefy and sub-cool the process stream from typically -35°C to the temperature range -150 to -160°C.
- The Main Cryogenic heat exchanger (MCHE) consists of two or three tube bundles arranged in a vertical shell, with the process gas and refrigerants entering the tubes at the bottom which then low upward under pressure.
- The overall vaporized MR stream from the bottom of the MCHE is recovered and compressed by the MR compressor to 48 bara. It is cooled and partially liquefied first by water or air and then by propane and recycled to the MCHE.
- Train capacities of up to 4.7 million tonnes/year.



Simplified C3MR flow sheet.

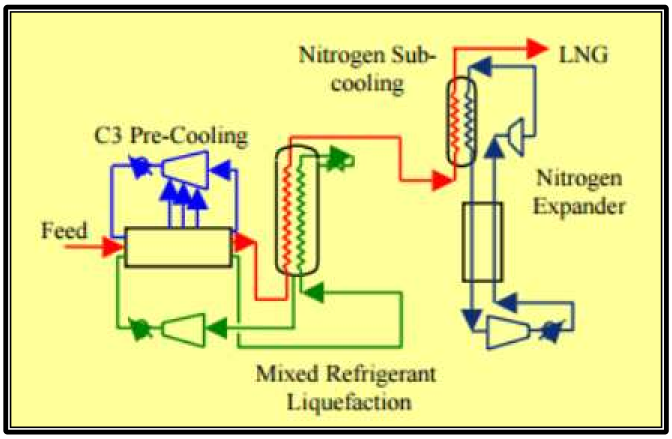
Component	Fraction
Methane (C1)	45.0 %
Ethane (C2)	45.0 %
Propane (C3)	2.0 %
n-Butane (n-C4)	-
Nitrogen (N2)	8.0 %

Mixed Refrigerant (MR) composition

AP-X

The AP-X process is designed to satisfy the great demands of liquefaction plants. It works together with the C3MR unit and is described as follows[12]:

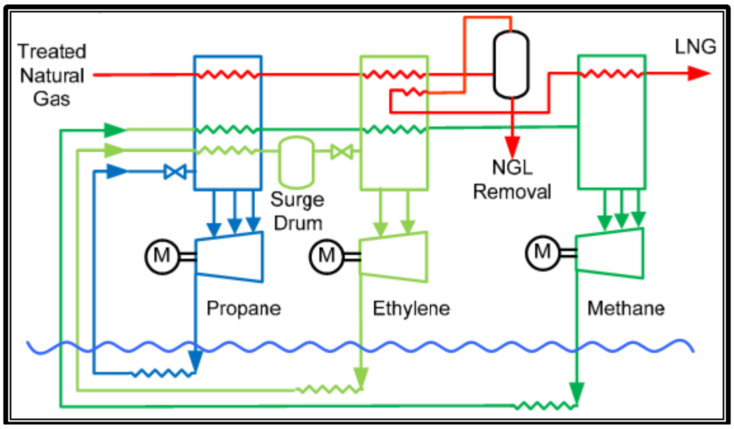
- The feed gas enters into the system
- Propane is used for pre-cooling natural gas, while natural gas is liquefied and partially sub-cooled in the MCHE with a mixed refrigerant, as described above. However, final sub-cooling is not done in the MCHE and the temperature exiting the exchanger is about -115C rather than -150C to -162C.
- Final stage of sub-cooling is done using a nitrogen expander loop.
- Nitrogen is compressed to a high pressure and then cooled to near ambient temperature.
- The high pressure nitrogen is then cooled with low pressure nitrogen returning to the compressor, after which it is expanded to a lower pressure further reducing its temperature.
- The nitrogen provides refrigeration for sub-cooling LNG. Using nitrogen to sub-cool LNG, the percentage of the total refrigeration load on the upstream C3MR section is reduced, allowing for greatly increased capacity in a single train without having to parallel major equipment (e.g. refrigerant compressors and the main exchanger). The Nitrogen's cycle has a 20 bar to 70 bar compressor and an expansion turbine system (instead of a valve) to decrease stream consume.
- Capacity of the AP-XTM train beyond 8 MTA.



Phillips Optimized Cascade Process (POCP)

The ConocoPhillips optimized cascade process was developed around 1970 by Phillips Petroleum Company. It has three cycles with a single refrigerant gas (propane, ethylene and methane) in each and consists on [11]:

- The feed gas enters into the system.
- The pre-cooling stage cools the gas to a temperature of about -30 to -50 ºC in the precooling cold box. The cooling element is generally propane or a mixture of propane and ethane and small quantities of other gases.
- The liquefaction process takes the gas down from -30 ºC to about -100-125 ºC, typically based on a mixture of methane and ethane and other gases. It cools the LNG stream as well as the refrigerant for the final stage.
- Sub-cooling serves to bring the gas to final stable LNG state at around -162 ºC. The refrigerant is usually methane and/or nitrogen. The actual design varies considerably with the different processes. The most critical component is the heat exchanger, also called the cold box, which is designed for optimum cooling efficiency. Designs may use separate cold boxes, or two or three cycles may combine into one complex common heat exchanger.
- Train capacities if 3.3 T/year



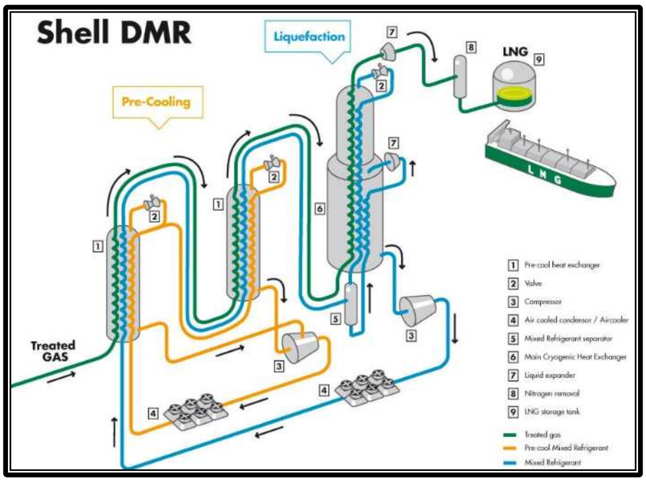
Optimized cascade process.

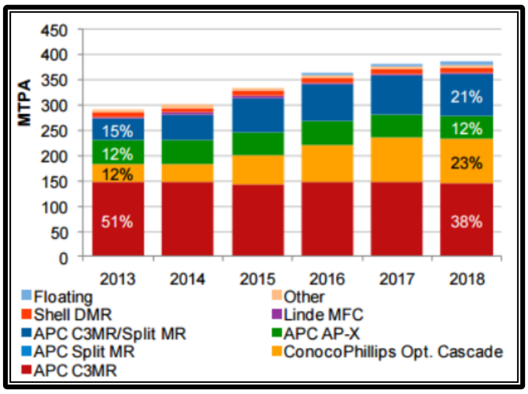
Dual cycle mixed refrigerant (DMR).

The dual cycle mixed refrigerant (DMR), developed by Shell and others, may look simpler but the overall design will be similar in complexity as multi-stage compressors are typically needed.

- Feed gas at 45C and 65 bars.
- The difference is in the utilization of a second pre – cooling refrigerant component typically composed of methane, ethane, propane and butanes.
- The cold MR of a DMR process that is used to liquefy and sub-cool the LNG is typically composed of nitrogen, methane, ethane and propane.
- Use of two different mixed refrigerant cycles allows Full utilization of power in a design with two mechanically driven compressors.

- It allows keeping the compressors at their best efficiency point over a very wide range of ambient temperature variations and changes in feed gas composition.
- The natural gas stream is cooled via two stages. The first stage cools natural gas to -50°C while the second column cools natural gas to LNG at -160°C.





Process cycle efficiency comparison (LNG production per unit power)[9].

Train capacities by process

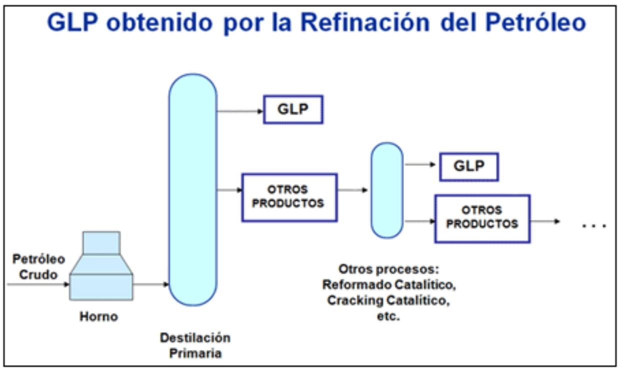
LIQUEFIED PETROLEUM GAS (LPG)

LPG processing

The sources of obtaining this fuel are refineries (petroleum distillation) plants and natural gas processing, which contribute about 25% to 75% of LPG respectively.

LPG in refineries:

For LPG production, the oil is subjected to an operation called distillation, whereby they separate in order, according to their densities and boiling points, the various components: light gasoline, kerosene, butane, propane, diesel oil, fuel -oil and heavy oils. The gases resulting from this distillation from the Group of LPG are butane (40%) and propane (60%), which are distinguished by their chemical composition, pressure, boiling point and its calorific value.



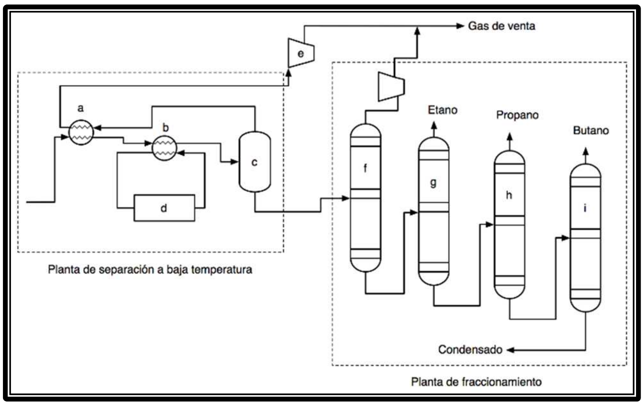
LPG from distillation tower scheme

LPG recovery from a gas stream can be accomplished by a variety of techniques. The most common technique applied in new plants LPG recovery is to cool the gas stream to condense LPG fraction. The recovered liquid is then fractionated to separate the components of LPG.

Low-temperature separation (LTS)

Cooling of a gas stream containing LPG can be achieved by indirect heat transfer with external coolant stream. In a conventional plant for gas conditioning, refrigeration is normally provided by a propane refrigerant circuit closed loop.

- The feed gas and drying the treated plant is contacted first with LPG poor and cold gas leaving the ground (a).
- Then the pre-cooled gas is further cooled by propane refrigeration to condense LPG fraction in the feed gas (b).
- The condensed liquids are then recovered in the separator HP (c) and
- Fed to a fractionation plant later. The cold producer gas exiting separator HP is then used to cool the feed gas.

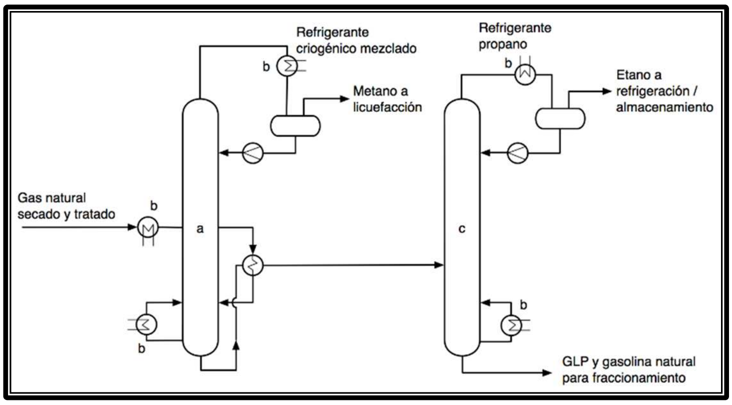


Scheme LPG plant
a) Gas Feed - gas heat exchanger; b) Gas Feed - refrigerant heat exchanger; c) HP separator; d) cooling unit; e) sales gas compressor; f) methaniser; g) Deethanizer; h) depropanizer tower; i) Torre debutanizer[4].

Liquid separator HP are fed to a conventional fractionation plant comprising a demethanizer, a deethanizer, a depropanizer and debutanizer to separate the components of LPG. If there is no extra outputs available ethane, then the demethanizer and deethanizer columns can be combined to a single column. The main advantages of this type of process are its simplicity and low pressure drop.

LPG from natural gas:

Natural gas consists of methane, ethane, propane, butane and heavier hydrocarbons and impurities such as sulfur. This gas is sent to the processing plants. In a first stage the gas stream passes through a Sweetening plant, where sulfur is removed. Subsequently it is introduced into a cryogenic plant in which successive expansions by cooling and two streams are obtained: a gas consisting essentially of methane (residual gas) and a liquid (liquefiable). In the following fractionation process, the liquid phase is separated into different components: ethane, LPG and natural gasoline.



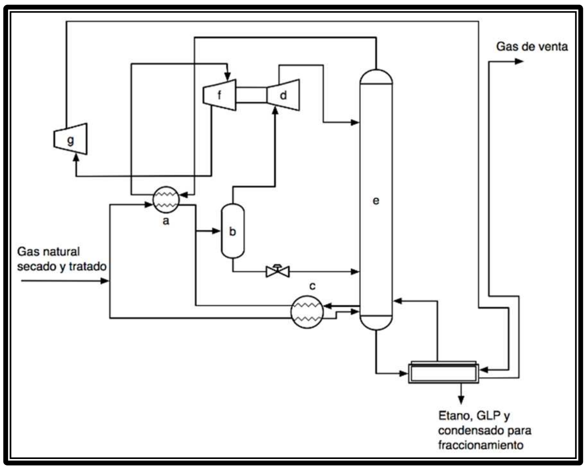
LPG recovery in an LNG plant
a) Distillation; b) heat exchanger; c) demethanizer[4].

In natural gas processing plants due to the production and for the usage of the heavier chains than methane and ethane there are two types of LPG processing plants, describe as follows:

Expansion plant

Expansion plants generate cooling by expansion of the feed gas. The pressure drop across a control valve or an expander can generate a temperature low enough to condense LPG fraction in the feed gas.

- The treated gas is first cooled by indirect heat exchange with cold lean gas that leaves the plant (a).
- All liquids formed during this initial cooling step are then recovered in the separator HP (b) and
- Fed to the lower section of the demethanizer column (e).
- The overhead vapor separator HP expands either through a rotary expander or through a control valve (commonly called a valve Joule - Thomson, d).
- The gas / liquid cold of the expansion is then fed to the top of the demethanizer. The demethanizer separates the lighter components (methane, nitrogen) liquids.
- The overhead vapor is subsequently fed to the gas heat exchanger - feed gas for recovery cooling before being compressed for export as sales gas. The compressor power is minimized by engagement of the first compression stage expander.



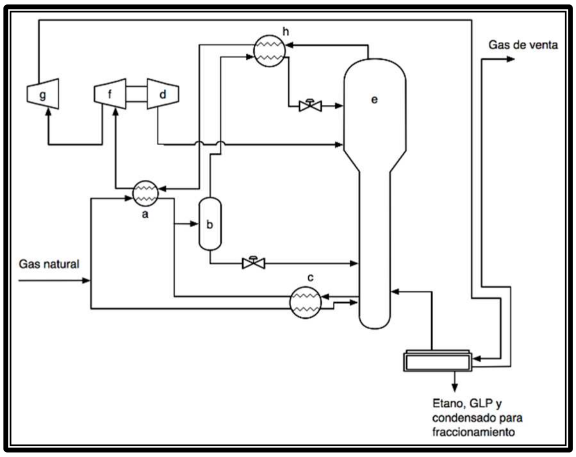
Scheme conventional plant expansion

a) Gas Feed - gas heat exchanger; b) HP separator; c) Caldera demethanizer; d) Turbo expander; e) methaniser; f) First gas compressor sales; g) second sales gas compressor[4].

Super-cooling plant

This process has been improved by adding a rectifying section to the demethanizer column. The purpose of the addition of this section is to reduce the ethane and LPG in the overhead vapor by refluxing with cold liquefied gas supply. Reflux is obtained by taking a small portion of the HP separator gas is liquefied by cooling then against the demethanizer overhead vapor.

Then the cold high pressure fluid is depressurized and fed to the top tray of the demethanizer column. The gas sub-cooled process is capable of recovering over 99% of LPG in the feed gas and is also suitable for the recovery of more than 95% of the ethane in the feed.



Outline of process gas super-cooled.

a) Gas Feed - gas heat exchanger; b) HP separator; c) Caldera demethanizer; d) turboexpander; e) methaniser; f) First gas compressor sales; g) second sales gas compressor; h) reflux exchanger[4].

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