Liquefied Natural Gas

General Knowledge
Natural gas exists in nature under pressure in rock reservoirs in the Earth’s crust, either in conjunction with and dissolved in heavier hydrocarbons and water or by itself.

It is produced from the reservoir similarly to or in conjunction with crude oil.

Natural gas has been formed by the degradation of organic matter accumulated in the past millions of years. Two main mechanisms (biogenic and thermogenic) are responsible for this degradation.
Natural gas produced from geological formations comes in a wide array of compositions. The varieties of gas compositions can be broadly categorized into three distinct groups:

- **Nonassociated gas** – it occurs in conventional gas fields
- **Associated gas** – it occurs in conventional oil fields
Unconventional gas – it occurs outside of the former two. Most common types of unconventional gas are:

- **tight gas** - natural gas produced from reservoir rocks with such low permeability that massive hydraulic fracturing is necessary to produce the well at economic rates;
- **coalbed methane** - methane adsorbed into the solid matrix of the coal;
- **natural gas from geopressurized aquifers**;
- **gas hydrates** – methane clathrate is a solid clathrate compound in which a large amount of methane is trapped within a crystal structure of water, forming a solid similar to ice;
- **deep gas**
The origin

Gas hydrate on seabed

Methane clathrate burning (inset: clathrate structure)
Natural gas is a complex mixture of hydrocarbon and non-hydrocarbon constituents and exists as a gas under atmospheric conditions.

Raw natural gas typically consists primarily of methane (CH$_4$), the shortest and lightest hydrocarbon molecule. It also contains varying amounts of:

- Heavier gaseous hydrocarbons: ethane (C$_2$H$_6$), propane (C$_3$H$_8$), normal butane (n-C$_4$H$_{10}$), iso-butane (i-C$_4$H$_{10}$), pentanes and even higher molecular weight hydrocarbons.
- Acid gases: carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S) and mercaptans such as methanethiol (CH$_3$SH) and ethanethiol (C$_2$H$_5$SH).
- Other gases: nitrogen (N$_2$) and helium(He).
- Water: water vapor and liquid.
- Liquid hydrocarbons: crude oil and/or gas condensates.
- Mercury: only trace amounts
## Typical composition of Natural Gas

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>70-90</td>
</tr>
<tr>
<td>Ethane</td>
<td>C$_2$H$_6$</td>
<td>0-20</td>
</tr>
<tr>
<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>0-20</td>
</tr>
<tr>
<td>Butane</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0-20</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO$_2$</td>
<td>0-8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>0-0.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N$_2$</td>
<td>0-5</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>H$_2$S</td>
<td>0-5</td>
</tr>
<tr>
<td>Other gases</td>
<td>A, He, Ne, Xe</td>
<td>Trace</td>
</tr>
</tbody>
</table>
Phase transition is the transformation of thermodynamic system from one phase (commonly referred to as "state of matter") to another.

Enthalpy is a measure of the total energy of a thermodynamic system. It includes the internal energy, which is the energy required to create a system, and the amount of energy required to make room for it by displacing its environment and establishing its volume and pressure.

The enthalpy is the preferred expression of system energy changes in many chemical, biological, and physical measurements, because it simplifies certain descriptions of energy transfer. Enthalpy change accounts for energy transferred to the environment at constant pressure through expansion or heating.
Phase transition

GAS

sublimation

vaporization

condensation

deposition

LIQUID

freezing

fusion

SOLID

enthalpy of system
Enthalpy of fusion

- Enthalpy of fusion is the change in enthalpy resulting from heating a given quantity of a substance to change its state from a solid to a liquid. The temperature at which this occurs is the melting point.

- The 'enthalpy' of fusion is a latent heat, because during melting the introduction of heat cannot be observed as a temperature change, as the temperature remains constant during the process.
Often called heat of vaporization or heat of evaporation, is the energy required to transform a given quantity of a substance from a liquid into a gas at a given pressure.

The heat of vaporization diminishes with increasing temperature and it vanishes completely at the critical temperature because above the critical temperature the liquid and vapor phases no longer co-exist.
Enthalpy of sublimation, defined as the enthalpy change required to completely change the state of one mole of substance between solid and gaseous states.
Phase transition of water

Temperature

Heat

Solid

Fusion or freezing

Liquid

Vaporization or condensation

Vapor

Latent heat (constant at all pressures)

Temperature is fixed

Latent heat (varies with pressure)

Temperature varies with pressure

Part-financed by the European Union (European Regional Development Fund)
Gas Rules

- Gas has three quantities:
  - Volume
  - Temperature
  - Pressure

- Three major Gas rules govern the behaviour of gases:
  - Boyle’s Law
  - Charles’ Law
  - Gay-Lussac’s Law
The absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies if the temperature and amount of gas remain unchanged within a closed system.

Boyle’s Law

![Diagram illustrating Boyle’s Law](image-url)
The volume of a given mass of an ideal gas is directly proportional to its temperature on the absolute temperature scale if pressure and the amount of gas remain constant; that is, the volume of the gas increases or decreases by the same factor as its temperature.
Gay-Lussac's Law (a.k.a. Amontons’ Law)

- The pressure of a gas of fixed mass and fixed volume is directly proportional to the gas' absolute temperature.
Pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.

The vapor pressure of any substance increases non-linearly with temperature according to the Clausius–Clapeyron relation. The atmospheric pressure boiling point of a liquid (also known as the normal boiling point) is the temperature at which the vapor pressure equals the ambient atmospheric pressure.
The LNG Trade Chain

- Exploration and production of Natural Gas
- Treatment and Liquefaction process
- Shipping
- Storage and Regasification
According to the Statistical Review of World Energy 2013 by BP, for year 2012 there is over 187 trillion cubic meters of proved Natural Gas reserves.

Biggest consumption is located in Europe & Eurasia and North America.

Production is often located long way from current markets.

Leading countries in terms of production and selling Natural Gas to markets worldwide are:

- Qatar
- Indonesia
- Malaysia
- Australia
- Nigeria
- Trinidad & Tobago
- Algeria
- Russian Federation
Raw natural gas after transmission through the field-gathering network must be processed before it can be moved into long-distance pipeline systems for use by consumers.

The objective of gas processing is to separate:

- Natural gas
- Condensate
- Noncondensable
- Acid gases
- Water
Simplified treatment process

Raw Gas → Phase Separation
- Solids
- Water
- Condensate to Stabilization Unit

→ Gas Treating

→ Inlet Gas Compression

→ Dehydration
- Water

→ Recovery of Natural Gas Liquids
- NGL to Fractionation

→ Final compression

→ Gas to pipeline, Reinjection, Flare
Four liquefaction processes can be distinguished:

- C3MR or ACPI (designed by Air Products & Chemicals)
- Cascade (designed by ConocoPhillips)
- Shell DMR
- Linde
This method is based on propane pre-cooled mixed refrigerant.

There are two main refrigerant cycles.

- The precooling cycle which uses a pure component propane.
- The liquefaction and sub-cooling cycle using a Mixed Refrigerant (MR) made up of nitrogen, methane, ethane and propane.

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.

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.
DMR – Dual Mixed Refrigerant is very similar to C3MR

- The difference is in utilization of a second pre-cooling refrigerant component.
- Use of two 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.
The raw gas is first treated to remove typical contaminants. Next, the treated gas is chilled, cooled and condensed to -162 °C in succession using propane, ethylene and methane. Last stage is pumping LNG to storage tanks and awaiting shipment.
PHILLIPS OPTIMIZED CASCADE LNG PROCESS

Inlet raw gas -> Inlet meter -> Amine treater -> Propane chiller -> Scrubber -> Dehydrator -> Dry gas filter

Amine treater -> Propane chiller

Gas turbine -> Methane compressor -> Gas turbine

Ethylene compressor -> Propane compressor

Air fin heat exchanger

Heat exchanger, flash tanks, and pressure letdown valves

LNG -> Tank vapor blower -> Storage tanks and loading pumps

Ship vapor blower

Transfer pump

Vapors from shop when loading -> To ship loading facility

from: http://lnglicensing.conocophillips.com
Natural gas is considered “dry” when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed.

When other hydrocarbons are present, the natural gas is “wet”.

The composition of natural gas varies depending on the field, formation, or reservoir from which it is extracted.
Water vapor is a common impurity and it can cause:

- Increased corrosion when present in liquid form and accompanied by H₂S gas.
- Creation of solid hydrates with hydrocarbons, which in turn may lead to plugging valves and pipelines.

H₂S and CO₂:

- Both gases are corrosive in the presence of water.
- H₂S is toxic when burned, it creates SO₂ and SO₃.
- CO₂ lowers heating value of gas.

Liquid hydrocarbons:

- The heavier hydrocarbons have higher boiling temperature and when cooled beyond that point will phase to liquid. It is a serious problem for pipelines to handle a two-phase flow (gas and liquid simultaneously).