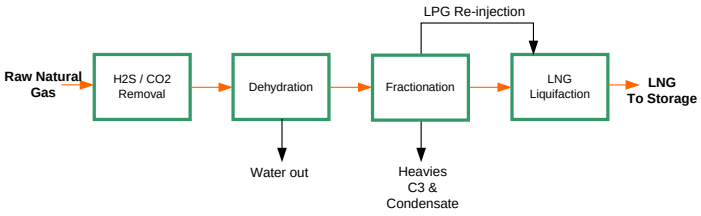
LNG Processing and On Stream Analysis

When natural gas is cooled below -160 °C (-256 °F) at atmospheric pressure it condenses to a liquid and becomes liquefied natural gas (LNG). LNG is stored as a boiling cryogenic liquid at relatively low pressure; the gases that boil off are vented and collected insuring that the liquid temperature remains constant. This paper will discuss a typical LNG process and examine the critical measurements required.

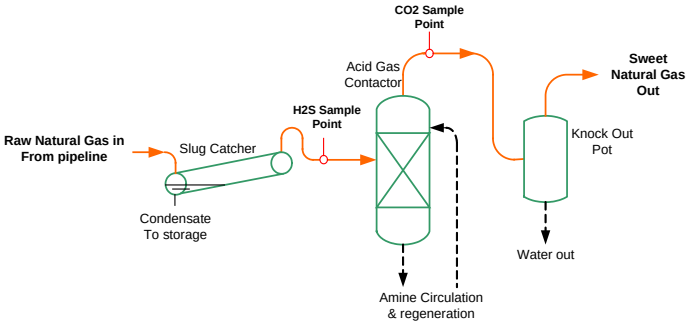
Raw natural gas is transported by pipelines from production facilities, usually offshore, to the LNG Plant site. The offshore production facility collects raw natural gas from the gas fields, removes sand and separates natural gas from condensate. The gas is dried in glycol contactors, and compressed. A quantity of condensate is re-injected for pipeline transport. At the LNG plant the incoming natural gas first enters a slug catcher where the condensate is separated, removed and stored for processing. The raw gas is then sweetened, dehydrated, fractioned, refrigerated and under liquefaction becomes Liquid Natural Gas (LNG).

Typical LNG Plant Flow (APCI C3/MCR)



The raw natural gas is a mixture of a number of components and must be conditioned prior to refrigeration and liquefaction. Impurities may include carbon dioxide, hydrogen sulfide, mercaptans, nitrogen, helium, water and possibly mercury and trimethylarsine. Pentanes, aromatics and heavier components with a high freezing point must also be substantially removed. The heavy components can be recovered as condensate that is stabilized in a separate facility for the production of gasoline or for chemical sales. In this discussion we will use a mid sized plant model based on the Air Products & Chemicals International, Propane / Mixed Component Refrigerant (APCI C3/MCR) process. Raw natural gas composition varies from each field and geographic area so each plant design will be optimized according to the available gas supply and market requirements. Economics and market demand are driving a rapid evolution of technologies that preclude a complete discussion of all existing technologies. The front end, from acid gas removal through dehydration will have common considerations to almost all of the available technologies and plant designs; it is here in the front end of the LNG process that we find the most critical measurement requirements.

Acid Gas Removal

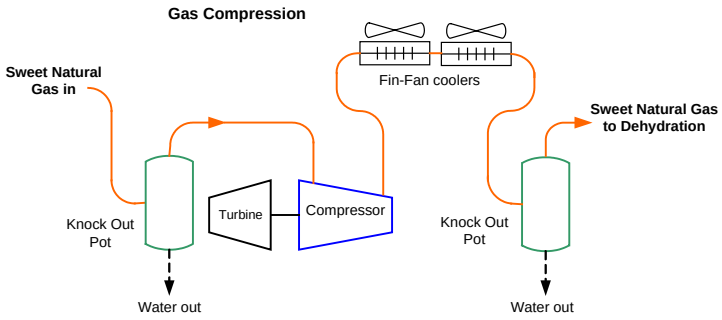


The raw natural gas arrives wet by pipeline, saturated with condensate that is separated in a slug catcher. Recovered condensate is stored for processing in a separate facility. The natural gas is then sweetened, passed through an acid gas contactor where the CO_2, H_2S and other acid gases undergo a neutralization reaction (converted to salts). The acid gas contactor typically uses an amine and water solution (up to 75% water) so the sweetened gas leaves the contactor saturated with water vapor at approximately 54 bar G at the prevailing ambient temperature. It is at this point in the process where we have our first critical analytical measurements. The sweetened natural gas leaving the acid gas contactor must be monitored for CO_2 and H_2S. If H_2S is expected in the natural gas from the pipeline it is likely that it will be monitored at the outlet of the slug catcher. The CO_2 will freeze and block or damage the cryogenic LNG exchanger so this measurement is very critical; sweetened natural gas CO_2 concentrations should not exceed approximately 5 ppmv.

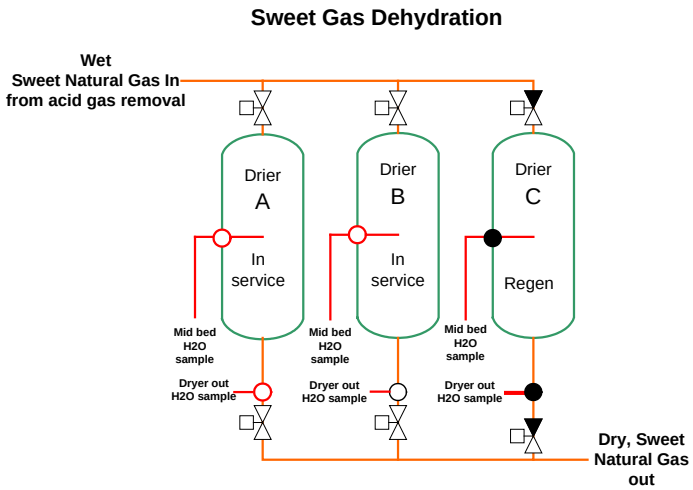
The CO_2 sample point pressure is expected to be approximately 54 bar G, saturated with water vapor and has suspended salts and mist present. This is a wet and dirty sample point! We sample here at the outlet of the contactor, before the knock out pot, to minimize measurement lag time. Process flows are very high! A membrane filter, drop back probe with pressure reduction is called for. The sample is transported at a pressure of approximately 2 bar G reducing the dew point temperature to less than 20 °C.

Heat tracing is required to keep the sample above maximum ambient temperature to minimize diurnal temperature effects. We have a low level (trace) acid gas measurement so EP tube specification would be a minimum requirement. Sample line lengths are normally 50 to 80 meters. Continuous NDIR Gas, CO_2 analyzers are used with flowing reference cells in most cases. Interference is a problem and FTIR methods would be a better choice. Two CO_2 analyzers for each train (take off point) are operated in parallel, in a redundant configuration.

The sweetened natural gas leaves the first knock out pot saturated with water vapor. Process designs vary from one to three knock out pots. Next the gas is compressed and passed through fin / fan coolers prior to dehydration.



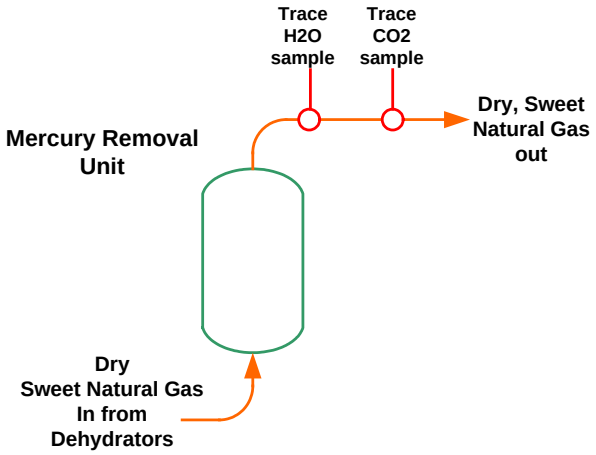
Post compression the wet natural gas must be dried (dehydrated), reducing water vapor content to a level of less than 1.0 ppmv. The middle bed of each drier and its outlet will require trace moisture measurement.



The Trace Moisture sample points are at approximately 54 bar G, the sample is usually transported at process pressure to AlO_3 moisture sensor probes. The sample transport line should be heat traced to maximum ambient temperature + 10 °C to minimize diurnal temperature effects. We have a trace moisture measurement so EP tube specification would be a minimum requirement. Sample line lengths are normally short, less than 10 meters.

It is important to note that two of the three driers are always in service and one is in regeneration. To simplify the drawings I left out the regeneration valve line up. The drier in regeneration has a reverse flow of heated gas (~ 250 °C). Gas at the regeneration temperature would destroy the moisture sensors so the sample take off points must be isolated and a portion of dry gas from one of the in service driers routed to flow through the isolated lines. This prevents atmospheric moisture in leakage from wetting up the sample lines of the drier in regeneration. A wet sample line will require significant time to dry down. We normally use existing drier regeneration control logic signals to switch moisture probes in and out of service and control flow through the isolated lines.

The next process is a mercury removal unit. Natural gas may contain trace levels of mercury vapor that must be removed prior to refrigeration and liquefaction. We normally measure CO_2 and Trace Moisture at the outlet of the mercury removal unit.



It is common to use a different method of moisture measurement as a cross check here. So if we use Aluminum Oxide (AlO_3) sensors to measure moisture at the dehydrators we would use a Vibrating Crystal method to measure moisture at the mercury removal unit outlet at concentrations less than 1 ppmv. The CO_2 measurement methods remain the same. The dehydrators (driers) use 4A (Angstrom) mol sieve as a drying agent. CO_2 can be held up in the drier beds and at some level of saturation break or migrate through so the CO_2 measurement here is also critical, expect maximum concentrations of less than 5 ppmv.

At this point the natural gas is dry, free of acid gases and ready for final processing. But we are measuring trace levels of polar gases so the sample transport lines should be heat traced to maximum ambient

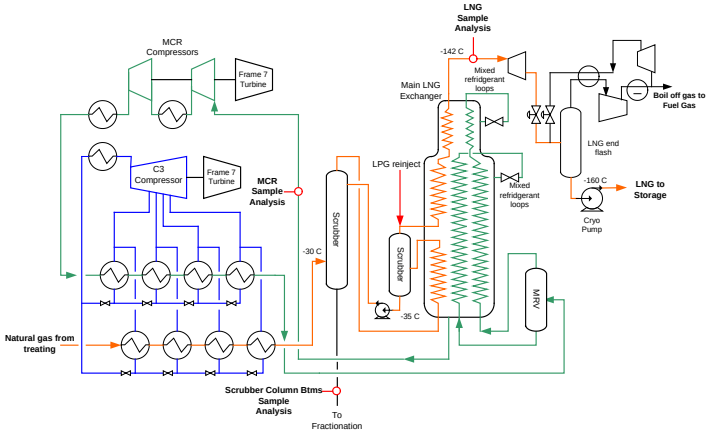
temperature + 10 °C to minimize diurnal temperature effects and EP tube specification would be a minimum requirement. Transport line lengths expected to be from 30 to 50 meters.

We have discussed the front end of the LNG process, sweetening and drying the natural gas is common to a number of different downstream liquefaction techniques. LNG Technology is evolving and at the present time there are a number of process variations available.

We will continue our discussion concentrating on the APCI Process using propane - mixed component refrigeration (C3/MCR). This is still the most common process in use today for mid capacity LNG production. The table below shows a typical raw natural composition post sweetening and drying.

Typical Raw Natural Gas Composition	
Component	**Mol %**
Nitrogen	0.10
Methane	86.00
Ethane	7.50
Propane	3.50
iso-Butane	1.00
n-Butane	1.00
iso-Pentane	0.30
n-Pentane	0.20
n-Hexane plus	0.40
Total	100.00

Typical (simplified) APCI C3/MCR LNG Liquefaction Process



The C3/MCR Liquefaction process flow diagram appears to be more complicated than the actual process. Basically the C3 (propane) cooling stage is a multistage system using expansion valves and exchangers to bring the natural gas temperature down to approximately -30 °C. It also removes heat from the compressed MCR prior to input to the APCI LNG Exchanger. The MCR cycle is a simple expansion – flash (Joule Thompson) cooling system where the cooling coils are cooled by expansion across valves into the cryogenic exchanger. This cools the MCR and it is again expanded across Joule Thompson valves at lower temperatures. The object is to bring the natural gas temperature down to about – 142 °C at a pressure where it is a liquid. The LNG Exchanger is a spiral wound exchanger composed of a number of small diameter tubing bundles, which permit very close temperature approaches between the condensing and boiling streams. The term used is main cryogenic heat exchanger (MCHE). After leaving the MCHE the LNG is flashed in a LNG end flash exchanger at reduced pressure (near storage pressure) to bring the temperature down below approximately -151.4 °C.

There are at least four critical measurements to consider in this final part of the LNG Process.

Mixed component refrigerant (MCR) composition is monitored closely for coolant efficiency. Natural gas has a cooling curve that must be matched by the MCR, so its composition is very critical to the efficiency of the liquefaction process. MCR is usually a mixture of nitrogen, ethane, propane and possibly a small amount of butane. We also look for any increases in methane concentration to detect leaks in the primary LNG exchanger coils. The LNG exchanger has at least 25 miles of coiled aluminum tubing; any leaks or cracks will show up as an increasing methane concentration in the MCR fluid. This is a straight forward vaporized sample and transport solution.

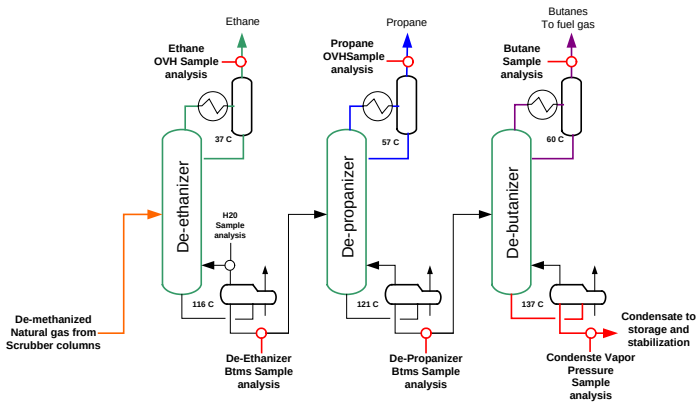
Scrubber column bottoms analysis monitors the efficiency of the columns and provides an input to the heat and material balance calculations for fractionation to operate the process. This is a very difficult sample, the scrubber bottoms are heavy components with a wide boiling point range. We have everything from trace levels of hydrogen and methane to hexanes present. A vaporized sample requires at least 100 °C heat traced lines. A liquid sample would require a chilled sample line to prevent bubble point temperature problems. Sample conditioner vents must be heat traced; condensables in the vent system are common problems.

LPG re-injection composition is monitored to control the composition of the LNG and its heating value before liquefaction and storage. This is a straight forward vaporized sample and transport solution. Finally the LNG to storage is monitored to confirm composition and heating value. A difficult sample take off problem, LNG is at approximately 3.5 bar G and at a temperature of at least -151.4 °C. Any heat gained and LNG will fractionate and flash.

Note: Due to Joule Thompson effects we heat trace at least 5 meters of all low temperature high pressure samples after pressure reduction. Process gas chromatographs are the preferred method of analysis in these applications.

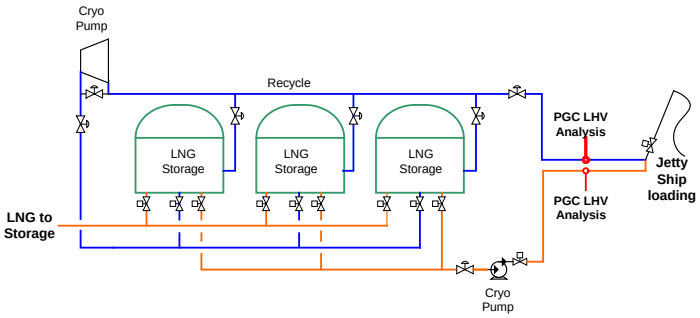
The scrubbers in liquefaction are primarily de-methanizers. The overhead of the scrubber columns are methane and the bottoms provides the primary feed to the fractionation unit. Here we separate the scrubber bottoms to obtain the components for MCR and the propane cycle chillers. Excess components can be used for NGL, LPG and condensate production depending on feed gas composition and market demands.

Typical (simplified) Fractionation unit.



The overhead analysis of the fractionation columns is straight forward; the bottoms are liquids utilizing a vaporizing pressure reduction preconditioning system requiring heat traced sample lines. As we move down the unit to the de-butanizer the bottoms samples become heavier. The bottoms of the de-butanizer are gasoline quality condensate. We use PGC applications for the overheads and bottoms. A KVP or RVP analysis for the condensate to storage is common.

The typical integrated APCI C3/MCR LNG plant will use the recovered heat from exhausts of the Gas Turbines to generate 150 °C hot water and steam. The hot water and steam are used to drive the columns in fractionation and for heating as required. The boil off gas from LNG storage is mixed with components of fractionation to make fuel gas to run the turbines. Almost self contained, the only utility steam boiler required is at start up, once the trains are running it is shut down and never used again.



We have skipped fuel gas analysis requirements, they are straight forward. I have also not discussed the hot water system and the utility water plant. It should be apparent that there are a large number of heat exchangers used in the LNG process. It is a common requirement to measure water in the hydrocarbon liquids on the tube outlet side of a number of exchangers. It is also common to measure volatile hydrocarbons in the hot water system.

Typical LNG Storage and Loading

The parallel loading line has a requirement for a manual sample system for heating value and composition during loading. A pair of process gas chromatographs is applied on each of the parallel loading lines for a record of the heating value over the load period. Note that the loading line is in continuous recycle, LNG always flows in the recycle loop.

One liter of LNG will yield approximately 600 liters of gas at one atmosphere

The APCI C3/MCR process represents 84% of all installed and operating LNG plants world wide as of 2005. For new capacity plants from 2006 through 2012 this process represents about 36% of world production, still the largest share but new technologies are gaining ground. Shell's DMR/PMR, a modification of the C3/MCR, process has approximately 22% of the market today with Cascade, Mixed Cascade and APX sharing the remaining 42% of the global market.

LNG specified heating value of 1,100 BTU per standard cubic foot. LNG liquid density is approximately 467 kg/m3 at -151.4 °C.

LNG tanker ships have high speed steam turbines; the steam is generated from boilers fired with LNG boil off gas. It takes seven to ten days to cool down a new LNG Ship's storage tanks and approximately 11 hours to load. The tankers leave a portion of LNG in their tanks to power the return trip and to keep them cooled down to cryogenic temperatures.

A typical medium sized, three train, LNG plant can load three to four ships each week with a cargo value of approximately US$ 3 million.

The preceding has been a very brief look at the LNG process and its critical analysis requirements. I encourage further reading on LNG Liquefaction and Re-gasification.

Summary of Common Analyzer Points in LNG Liquefaction

Location	Analysis	Transport Tube	Maintain Temperature
Raw Natural Gas from Pipeline	Physical Properties	316L SS	Ambient
After Slug Catcher	H_2S	O'Brien TrueTube FS	Ambient +10ºC
After Acid Gas Contactor	CO_2 (5 ppm) (redundant)	O'Brien TrueTube EP	Ambient +10ºC
Drier Bed (typically in threes)	H_2O	O'Brien TrueTube EP	Ambient +10ºC
Drier Outlet	H_2O (1 ppm)	O'Brien TrueTube EP or EPS	Ambient +10ºC
Mercury Removal Outlet	H_2O (1 ppm)	O'Brien TrueTube EP or EPS	Ambient +10ºC
Mercury Removal Outlet	CO_2 (<5 ppm)	O'Brien TrueTube EP or EPS	Ambient +10ºC
Mixed Component Refrigeration (MCR)	CH_4 (methane) MCR composition	316L SS	Ambient +10ºC
Scrubber Column Bottoms	H, CH_4, hexane	316L SS	100C – Vaporized Sample Chilled – Liquid Sample
LPG Re-Injection	Physical Properties & Btu	316L SS	Ambient +10ºC
LPG to Storage	Physical Properties & Btu	316L SS	Ambient +10ºC
Fractionation Overhead	Ethane, Propane, Butane	316L SS	Ambient +10ºC
Fractionation Bottoms	Light components in a heavy bottoms stream	316L SS	75 to 90ºC from take off preconditioner through vents Ambient +10ºC after vents
Loading	BTU – Composition	316L SS	Ambient +10ºC

Useful references:

1. www.fwc.com/publications/pdf/LNG%20brochure.pdf Good pictures of plants, facilities and ships.
2. www.oxfordprinceton.com/pdf/ieca_presentation.pdf LNG market overview, a comprehensive look
3. Benefits of Integrating NGL Extraction and LNG Liquefaction Technology Copyright – 2005 Conoco-Phillips Company Published in the proceedings of the AIChE 2005 Spring National meeting
4. LNG A guide to Severe Control Valve Applications in the LNG Process CCI Valve, www.ccivalve.com Great overview of the C3/MCR LNG Process
5. LNG Process selection, no easy task Pierre Yves Martin, Jerome Pigourier, Axens, France Hydrocarbon Engineering May 2004
6. Large-capacity LNG Trains, The Shell Parallel Mixed Refrigerant Process Jolinde M Van de Graaf and Barend Pek Business Briefing: Instrumentation & Processing, LNG Review 2005
7. SPE-102160-LNG Onshore LNG Process Selection S. Mokhatab, U. of Wyoming, and MJ Economides, SPE of Houston Society of Petroleum Engineers CR 2006 Detailed paper, very useful

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