LNG is natural gas in its liquid state with high energy density, which makes it useful for storage and transportation over long distances from the gas fields to the consumers. LNG is recovered from natural gas in large-scale liquefaction plants. Process automation is a key issue in LNG plants to ensure cost efficient plant operation and high product quality. Process analyzer deliver important data therefore.

Siemens, a leader in process analytical instrumentation, has proven over decades its capability to plan, engineer, manufacture, implement and service analyzer systems for NG liquefaction plants. This Case Study provides an overview of the processes and describes how Siemens with its analyzer and application know-how meets best the process requirements.

**Liquefaction of natural gas to LNG**

Natural Gas (NG) is a vital component of the world’s supply of energy. It is one of the cleanest, safest, and most useful of all energy sources. NG is colorless and odorless in its pure form. While it is formed primarily of methane, it can also include ethane, propane, butane, pentane and certain impurities.

Liquified Natural Gas (LNG) is natural gas in its liquid form. It is an odorless, non-toxic and non-corrosive liquid. Natural gas is converted to LNG by cooling it to about -180 °C, at which point it becomes a liquid. This process reduces its volume by a factor of more than 600. This allows natural gas to be transported economically by sea. At its destination, LNG is stored as a liquid until it is warmed to convert it back to gas, blended to comply with local composition and BTU requirements and then sent through pipelines for distribution to consumers and industries. The first LNG liquefaction unit came into operation in 1964 at Arzew, Algeria.

Typical natural gas includes additional components like sulfur, CO₂, water and heavier hydrocarbons which have to be removed from the natural gas before cooling. If not, some of them would become solid during refrigeration and interrupt the cooling process. Consequently, a LNG liquefaction unit produces also other chemicals like solid sulfur, NGL (Natural Gas Liquids) and LPG (Liquified Petroleum Gas).

Today LNG accounts for about 4% of natural gas consumption worldwide, and is produced in dozens of large-scale liquefaction plants.
LNG supply chain from gas fields to consumers

The LNG supply chain from gas fields to consumers comprises a number of process and logistic (storage and transportation) steps as shown in fig. 1.

NG pre-treatment

The liquefaction process requires all impurities and components that solidify at liquefaction temperatures to be removed from the wellstream prior to liquefaction. When the raw gas reaches the process plant it consists of three phases: natural gas, condensate and water. They are separated and split into three streams in a unit called slug catcher.

The condensate is heated to remove any residual gas. Pure condensate is stabilized by removing lighter hydrocarbons (NGL, Natural Gas Liquids) such as methane, ethane, propane and butane. Condensate is used as an additive in motor fuel production at refineries and as a feed material at petrochemical plants.

The liquid removed from the bottom of the slug catcher is treated to remove solid particles, salts and most of the water. The water is filtered through a biological treatment system before being discharged.

The Natural Gas is further treated by:

- Passing through an absorption column to remove carbon dioxide using the amine method. This is necessary to prevent the CO₂ freezing during liquefaction and cause damages along the process.
- Drying it in dewatering columns to prevent the water turning to ice later in the process.
- Removing very small quantities of mercury that could damage metal equipment in other parts of the process by passing through a separate unit.

Some of the natural gas is diverted from the flow to generate electricity in gas turbines. Exhaust heat from these units is used to warm up the heating medium in the plant.

NGL removal

The product specification for liquefied natural gas (LNG) defines the minimum content of propane, butane and other heavier hydrocarbons the gas is allowed to contain, and its calorific value. To meet these requirements, the heavier components (natural gas liquids, NGL) must be removed through a fractionation process by passing the gas through a fractionation column.

Methane and ethane are taken off from the top of the column and continue into the gas liquefaction process. NGL products such as propane, butanes and other heavier hydrocarbons are removed from the bottom of the column and sent on to the plant for liquefied petroleum gases (LPG).

Liquefaction

The gas continues to the liquefaction part of the plant (”cold box”) for cooling to liquefied natural gas (LNG). This facility consists fundamentally of several heat exchangers. The gas passes through them for pre-cooling to about -50 °C, beginning of liquefaction at about -80 °C and sub-cooling at about -160 °C and finally emerges as a liquid. The gas flows through thin tubes which are constantly bathed in coolant – pure fluids or mixes of nitrogen, methane, ethane and propane. The coolant takes up heat from the gas and evaporates, while the gas is cooled and condenses to liquid.

When it enters the cooling process, the gas may contain too much nitrogen in relation to the specification. This surplus is extracted initially in a nitrogen removal column. The top product of that process is nitrogen and some LNG, which go to a separate two-column removal process. Separated nitrogen is finally released to the air and any LNG returns to the process flow. LNG taken out at the bottom of the nitrogen removal column has a temperature of about -163 °C. It is piped from the cold box to storage tanks.
The liquefaction process reduces the volume of natural gas by a factor of 600 allowing it to be shipped by sea. LNG is typically transported by specialized tanker with insulated walls, and is kept in liquid form by autorefrigeration, a process in which the LNG is kept at its boiling point. Upon arrival at its destination, LNG is generally transferred to specially designed and secured storage tanks and then warmed to its gaseous state in evaporators with different design – a process called regasification. Finally it is transported via pipelines to the end user.

Real processes or plants may deviate from the above description depending on varying technologies and product demands.

Liquefaction technologies

A refrigerant or a mixture of refrigerants is used in most technologies to cool and liquefy the process gas. The natural gas, being a mixture of compounds, liquefies over a wide temperature range. Energy efficient operating conditions can be obtained by minimizing the temperature difference between the cooling process gas and the refrigerant streams. This can be realized by using a mixture of refrigerant to match best the cooling curve of the process gas. Thus, the composition of the refrigerant represents an important process parameter.

The cooling process can be performed along different process routes, e.g.:

Classic cascade cycle

Following carbon dioxide and water removal, the natural gas is cooled down in three cooling cycles, where propane, ethane and methane are used as coolants. The propane from the first cycle is also used to cool ethane from the second cycle, and the ethane from the second cycle to cool the methane in the third cycle. This method is quite energy efficient.

Cascade cycle with mixed coolant

This is a modification of the classic cascade cycle, which uses only one compressor and one coolant made of a mixture of hydrocarbons. Natural gas is first pre-cooled with propane and then further cooled with a hydrocarbon mixture.

This method is slightly more energy intensive than the classic cascade cycle but requires less installations effort and is therefore used more frequently.

<table>
<thead>
<tr>
<th>Natural Gas Liquefaction Technologies (selection)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air Products and Chemical Inc.</strong></td>
</tr>
<tr>
<td>APCI PPMR process</td>
</tr>
<tr>
<td>This propane precooled mixed refrigerant process (PPMR) uses pure propane for pre-cooling, while the liquefaction and subcooling cycle uses a mixed refrigerant made up of nitrogen, methane, ethane and propane.</td>
</tr>
<tr>
<td><strong>Philips optimized cascade process</strong></td>
</tr>
<tr>
<td>In this optimized cascade liquefaction (OCLP) process refrigeration and liquefaction is achieved by using three pure component refrigerants (propane, ethylene and methane) in series.</td>
</tr>
<tr>
<td><strong>Statoil / Linde</strong></td>
</tr>
<tr>
<td>This mixed fluid cascade process (MFCP) uses three mixed (from methane, ethane, propane and nitrogen) refrigerants for precooling, liquefaction and subcooling.</td>
</tr>
<tr>
<td><strong>Shell</strong></td>
</tr>
<tr>
<td>This dual Mixed Refrigerant (DMR) process uses two separate mixed refrigerant cooling cycles. One is for pre-cooling gas to about - 50 °C (PMR cycle), and the other is for final cooling and liquefaction (MR cycle).</td>
</tr>
</tbody>
</table>

Fig. 3: LNG technologies (selection)

Decompression cycle

This version operates similar to installations that produce liquid oxygen and nitrogen using the low-temperature air fractioning method. In this process, a part of the gas is decompressed in a turbo-expander, and then cooled down to a very low temperature. The cooled gas is then used to liquefy the next portion of the gas passing through the installation.

Proprietary processes

The refrigeration and liquefaction section is the key element of a LNG plant. Many proprietary process technologies are available and more under development. All of them are based on the general methods described above but designed in detail by the respective companies, see fig. 3.
**Process Analytics in the LNG supply chain**

**Manifold analysis demands**

The development of new liquefaction technologies, the construction of larger plants and the increasing demand in energy efficiency and product quality has also increased the demand in efficient process analytical techniques.

Manifold measuring points with different analysis tasks are located along the process route from the gas field through the NG production and NG shipping to the NG distribution and consuming section (fig. 5 and 6). Measuring tasks include process control, products quality control and heating value measurement (BTU).

**Need of Gas Chromatography**

Process gas chromatographs are the prevailing type of process analyzers in LNG plants to collect the required information from the process for plant performance optimization and for fast, accurate and reliable determination of the calorific value for fiscal energy measurement. Gas chromatographs are completed by continuous gas analyzers to measure e.g. CO₂.

**Optimal solutions by Siemens**

With the line of three different process gas chromatographs (MAXUM edition II, MicroSAM and SITRANS CV) Siemens Process Analytics is able to offer optimal solutions to any analysis task along the route from one hand. Highest flexibility and analysis performance of MAXUM edition II, the miniature size and micromechanical technology of MicroSAM and the special design of SITRANS CV (calorific value) for calorific measurements are key elements of this outstanding products line of gas chromatographs.

**Analysis systems**

Siemens Process Analytics also supplies turnkey analysis systems for LNG plants as well as for tanker and pipe line control, from planning and engineering to start-up, commissioning and training services.

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**Sampling point**

**Measuring Components**

**Suitable Siemens Analyzers**

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Measuring Components</th>
<th>Suitable Siemens Analyzers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 From gas field</td>
<td>CO₂, H₂S</td>
<td>MAXUM edition II, ULTRAMAT</td>
</tr>
<tr>
<td>2 NG pretreatment</td>
<td>C₁ - C₅</td>
<td>MicroSAM, MAXUM edition II</td>
</tr>
<tr>
<td>3 NGL removal</td>
<td>N₂, C₁ - C₄</td>
<td>MicroSAM, MAXUM edition II</td>
</tr>
<tr>
<td>4 Liquefaction, gaseous</td>
<td>C₁ - C₅, C₁⁺</td>
<td>MicroSAM, MAXUM edition II</td>
</tr>
<tr>
<td>5 Liquefaction, liquid</td>
<td>C₁ - C₅, C₆H₅</td>
<td>MAXUM edition II</td>
</tr>
<tr>
<td>6 From separation</td>
<td>N₂, C₁ - C₅</td>
<td>MicroSAM, MAXUM edition II</td>
</tr>
<tr>
<td>7 LNG storage</td>
<td>C₁ - C₅, C₆⁺, N₂, CO₂</td>
<td>MicroSAM</td>
</tr>
<tr>
<td>8 Export terminal</td>
<td>C₁ - C₅, C₆⁺, N₂, CO₂</td>
<td>SITRANS CV</td>
</tr>
<tr>
<td>9 LNG tank</td>
<td>N₂, CO₂, C₁</td>
<td>SITRANS CV</td>
</tr>
<tr>
<td>10 Import terminal</td>
<td>C₁ - C₅, C₆⁺, N₂, CO₂</td>
<td>SITRANS CV</td>
</tr>
<tr>
<td>11 LNG storage</td>
<td>C₁ - C₅, C₆⁺, N₂, CO₂</td>
<td>SITRANS CV</td>
</tr>
<tr>
<td>12 LNG regasification</td>
<td>C₁ - C₅, C₆⁺, N₂, CO₂</td>
<td>SITRANS CV</td>
</tr>
<tr>
<td>Various</td>
<td>H₂O</td>
<td>Third party analyzer</td>
</tr>
</tbody>
</table>
SITRANS CV, the Calorific Value Chromatograph

Design and application

SITRANS CV (fig. 9) is the consequent advancement of an existing, micromechanical technology based process chromatograph to a high performance calorific value (CV/ BTU) analyzer. It has been specially developed for fast, exact and reliable determination of calorific values of Natural Gas. Because of its rugged and compact design SITRANS CV is suitable for extreme areas of use, e.g. off-shore exploration, or direct mounting on a pipeline. Weighing only 15 kg, the compact analyzer can be installed at any position in the plant (fig. 8). SITRANS CV has been assigned the required certificates for such applications, such as explosion protection EEx d and splashwater protection according to IP65 or NEMA 4X.

Fiscal energy measurement

SITRANS CV provides all information to the natural gas quality and its physical properties such as calorific value and density, which are required for manifold applications in the natural gas industry, especially for fiscal energy measurement. From the measured concentration of gas components, SITRANS CV calculates the superior and inferior calorific values, standard density and Wobbe index according to ISO 6976. The analyzer saves the mean values of all components and the calorimetric values for a period of up to 100 days.

SITRANS CV Highlights

• Fast analysis through innovative micro electromechanical systems (MEMS) technology. For example, when analyzing natural gas, C_1 to C_{+6} with N_2, CO_2 and O_2 measurements are possible in 100 seconds.
• Independence from sample and ambient pressure changes due to unique “live sample injection”. In this manner, the SITRANS CV achieves a repeatability of RSD (Relative standard deviation) of 0.007 % for the superior and inferior calorific values.
• High separation performance through narrow-bore capillary columns which can therefore be optimally combined with MEMS technology and live injection in the SITRANS CV to achieve as high a separating performance as possible.
• Low detection limits through powerful detectors.
• High linearity over the measuring range saves expensive calibration gases. Multi-level calibration is unnecessary with the SITRANS CV because of the high linearity of the calibration function throughout the measuring range. Reliable and accurate (certified by official authorities) measurements can be achieved using a single-point calibration, giving the possibility to abandon expensive calibration gases.
• Easy and safe operation using CV Control. CV Control software is designed to minimize the need for elaborate training of maintenance technicians. The software has been specially developed for measurements requiring verification, with critical parameters password protected.
• Automatic optimization of methods increases availability. SITRANS CV optimizes the column switching commands and retention windows depending on the current retention times.
For more information, please contact:

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