Methanol is a clear liquid usually made from natural gas. It is a clean burning fuel, containing almost no sulphur or nitrogenous materials. It is a petrochemical that is used to make countless industrial and consumer products. In the future, methanol could be used as a source of hydrogen for fuel cells. Different concepts are in use to produce methanol looking always for higher plant efficiency and product quality.

All processes require the use of extensive process analyzer systems to monitor both process chain and product quality. Siemens, a leader in process analytics, has proven over decades its capability to plan, engineer, manufacture, implement and service such analyzer systems. This Case Study provides details about the Methanol process and related analyzer tasks.

**Methanol**

**Methanol (CH$_3$OH)** is an important multipurpose base chemical, a simple molecule which can be recovered from many resources, predominantly natural gas. By tradition, methanol is principally used to produce formaldehyde, methyl tertiary butyl ether (MTBE) and acetic acid. To a lesser extend, methanol is used as a general solvent. Today, Methanol is projected to be increasingly used as a fuel, so a comparison to LNG could be made. Like LNG, methanol is manufactured from natural gas, but with higher capital costs per unit of energy. But it is easier and cheaper to transport.

**Natural Gas (NG)** is one of the cleanest, safest, and most useful of all energy sources. NG is colorless, shapeless, and odorless in its pure form. It is combustible, and when burned it emits lower levels of potentially harmful by-products into the air than other fuels. NG is a mixture of hydrocarbon gases. While it is formed primarily of methane, it can also include ethane, propane, butane, pentane and certain impurities.

To produce methanol, Natural gas is heated, desulfurized, mixed with steam, heated further and fed to the synthesis gas production reactor. Synthesis gas is then cooled and compressed to a suitable pressure for methanol synthesis in a cascade of reactors. The crude methanol passes to a methanol distillation section where it is stabilized and treated for transport.

Many different Methanol production technologies exist (Lurgi, Haldor Topsoe, Davy, Uhde e.a.). Whatever technology is applied, the process steps require always to be monitored and controlled continuously. Process analyzers play an important role for that. Up to 100 and more process analyzers, most of them process gas chromatographs, are in use in a typical methanol plant.
Methanol production process

Process chain

The methanol processing chain (Fig. 1) consists of a number of fundamental steps each of which is important to achieve the final goal of producing high quality methanol.

Step 1: Feed purification

Natural gas is compressed and sulphur removed by hydrodesulphurization in the purifier. The desulphurized gas is cooled and flows to the saturator where it contacts with hot water over a bed of packing. The saturated gas contains most of the steam required for later reforming. Additional steam, generated in the boiler, is made up to the gas stream to achieve the required “steam to carbon ratio” for reforming.

Step 2: Feed reforming (Syngas generation)

Syngas (from Synthesis Gas) is composed of hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂), whereas the ration H₂/CO is important in view of the process efficiency using a certain catalyst material. Syngas is produced mainly from natural gas (NG) through a reforming process. Various technologies are used for that, with or without using air or oxygen: Steam Methane Reforming (SMR), Partial Oxidation (POX), Autothermal Reforming (ATR), e.a. After cooling, syngas is compressed to synthesis pressure, which ranges from 40 to 110 bar and helps the conversion reaction to occur.

Step 3: Methanol Synthesis

The synthesis gas is fed to the methanol synthesis converter at about 130°C. The converter is of different design (typically in cascades) depending on the particular technology applied. The compressed gas is preheated to reaction temperatures inside the tubes as it flows through the hot catalyst bed. The hot reacted gas leaves the converter and provides heat to the saturator water circuit and the loop interchanger before finally being cooled. Crude methanol is separated from the uncondensed gases and the gases are recirculated back to the converter via the circulator.

Step 4: Methanol distillation

The crude methanol passes to a methanol distillation section, where it is stabilized and reduced to an economic water content for transport. Purge gas from the methanol synthesis cascade is treated to recover hydrogen for recycling with the tail gas passing to the gas turbine as fuel.

Various technologies

Various methanol synthesis technologies have been developed and are implemented worldwide in methanol plants, for example:

- **Lurgi** uses an autothermal reformer for syngas generation and a two stage synthesis reactor system consisting of a gas-cooled and a water cooled reactor with very favorable temperature profiles over the catalyst bed.
- **Uhde** uses steam reforming for syngas generation and an isothermal tubular reactor with the catalyst contained in vertical tubes providing low by-product formation.
- **Topsoe** uses steam reforming for syngas generation and a straight-tubed boiling water reactor for methanol synthesis. Another technology is based on autothermal reforming followed again by a boiling water synthesis reactor.
- **Davy** uses a two-stage steam reforming followed by a synthesis loop that can operate at pressures between 70 to 100 bar.

![Fig. 1: Generic flowsheet of the methanol process, simplified](image-url)
Feed pretreatment
NG is a mixture consisting primarily of hydrocarbons, but other gases are also present such as nitrogen, carbon dioxide and sulfur compounds. In order to avoid poisoning of the catalyst material in the conversion process, the NG is first purified, mainly from sulfur, in a hydrogenation reactor and a washing system. After purification the feed gas is pretreated (saturated with process condensate and process water and preheated) before being fed to the syngas generation process.

Feed reforming (Syngas generation)
Syngas can be made by various technologies which require mostly steam and air or oxygen. During the feed (NG) reforming process, the hydrocarbon molecules are broken down and stripped of their hydrogen atoms. The carbon atoms together with oxygen, introduced as steam, air or as pure gas, form CO molecules. All reactions, independently of the technology applied, result in a gas consisting of H2, CO and CO2 called Synthesis Gas or Syngas.

Steam-Methane Reforming (SMR)
In steam-methane reforming, the most widely used technology for syngas production, natural gas and steam are mixed and passed over a catalyst located in a firebox. Heat for the reaction is supplied by burning some of the feedstock gas. SMR does not require a separate air or oxygen supply from a oxygen plant.

Partial Oxidation Reforming (POX)
The partial oxidation process is a direct non-catalytic reaction between oxygen and the hydrocarbon gas. It uses no steam and requires no catalyst. It is operated at very high temperatures of about 1400 °C and oxygen is needed.

Autothermal Reforming (ATR)
Unlike POX, autothermal reforming uses a catalyst to reform NG to syngas in the presence of steam and oxygen. The reaction produces high temperatures and no additional heat source is needed (“autothermal”). It produces syngas that is suitable for most conversion processes. But an air separation plant is required.

Process analysis in NG pretreatment and conversion
A great number of process analyzers are used in the NG pretreatment and NG conversion sections. Details regarding analyzers, sampling locations, measured components etc. will differ from plant to plant depending on the existing process technology and plant design. Therefore, Fig. 2 and Table 1 show typical measuring point locations and typical measuring tasks. Real plant conditions may differ from that.

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th>Measuring Components</th>
<th>Suitable Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Saturator Condensate stabilizer</td>
<td>Total S, H2S</td>
<td>MAXUM, MAXUM</td>
</tr>
<tr>
<td>1.2 Hydrogenation/Desulphurization Claus off gas</td>
<td>Total S, H2S, CO2, Mercaptans, O2, SO2</td>
<td>MAXUM, MAXUM, OXYMAT 6, TPA</td>
</tr>
<tr>
<td>1.3 Dehydration/ Mercaptan removal</td>
<td>Total S, COS, H2S, Mercaptans</td>
<td>MAXUM</td>
</tr>
<tr>
<td>1.4 LPG</td>
<td>Total S, COS, H2S, Mercaptans</td>
<td>MAXUM</td>
</tr>
<tr>
<td>1.5 Propane, Butane product</td>
<td>C2-C4, C3-C5+</td>
<td>MAXUM/MicroSAM</td>
</tr>
<tr>
<td>1.6 Treated NG</td>
<td>Sulphur (ppm,ppb)</td>
<td>MAXUM</td>
</tr>
<tr>
<td>1.7/1.8 Various furnaces flue gases and process off gases</td>
<td>O2, SO2, NOx, H2, ...</td>
<td>OXYMAT 6, ULTRAMAT 6, CALOMAT 6</td>
</tr>
<tr>
<td>1.9 Raw Syngas</td>
<td>CH4, CO2</td>
<td>ULTRAMAT 6</td>
</tr>
<tr>
<td>1.10 Syngas</td>
<td>H2, CO, CO2, N2, CH4, COS, H2S, Total S</td>
<td>MAXUM</td>
</tr>
</tbody>
</table>

Table 1: Process analyzer measuring tasks in steam reforming, acc. to Fig. 2
Methanol Synthesis

In the Methanol Synthesis section, compressed synthesis gas is converted into methanol in a synthesis reaction, where carbon oxides and hydrogen react to form methanol and water according to CO + 2H₂ → CH₃OH. This reaction is highly exothermic and the heat must be promptly removed in a one or two stages cooler.

A methanol synthesis reactor system typically comprises main converters, feed/effluent exchanger, saturator water cooled reactor, and a crude cooler. Different reactor designs are in use, generally based on the concept of synthesis gas flowing in the catalyst beds across boiler (cooling) tubes to recover the reaction heat as qualitative steam.

Methanol Distillation

The crude methanol from the synthesis loop contains both water and low levels of by-products, which must be removed by distillation to achieve the required product quality. This is typically performed in a two or three column system. In the topping column, compounds with boiling points lower than methanol are removed for use as fuels. In the refining column, methanol is separated from water and by-products. Product quality finally ranges from fuel grade to to highly pure methanol.

Process analysis in Methanol Synthesis and Distillation

Process analyzers, mainly continuous gas analyzers and process gas chromatographs, are used in the methanol synthesis and distillation section to monitor process function and product quality. Details will differ from plant to plant depending on process technology and plant design.
Steam and Oxygen Supply

Steam and oxygen supply
Utilities are pieces of equipment or plants to provide services such as heat or electricity necessary to fulfill the plants main goal. Methanol plants typically require steam, compressed air, and oxygen.

For steam generation units (boiler), process analyzers are used to optimize the combustion process through measurement of $O_2$ as well as to monitor the flue gas for air polluting components such as $SO_2$, $NO_x$, etc. (according to local regulations) using CEM systems.

Oxygen supply
The production of oxygen is a more complex process. Large-scale oxygen production units use cryogenic air separation processes, which are based on differences in boiling points to separate and purify products. Cryogenic air separation plants are referred to as an Air Separation Unit (ASU) or Oxygen Plant.

Different process configurations are in use, but all of them include the following steps (Fig. 4):
- Filtering and compressing of air
- Removing contaminants, including water vapor and carbon dioxide (which would freeze in the process)
- Cooling the air to very low temperature through heat exchange and refrigeration processes
- Distilling the partially-condensed air to produce desired products
- Warming gaseous products and waste streams in heat exchangers that also cool the incoming air

The units of the ASU that operate at very low temperatures (distillation columns, heat exchangers and cold interconnecting piping sections) must be well insulated to minimize energy consumption. Therefore, these components are located inside insulated “cold boxes”.

Fig. 4 and Table 2 show typical measuring point locations and related measuring tasks in a ASU plant.

### Table 2: Process analyzer measuring tasks in the oxygen production unit

<table>
<thead>
<tr>
<th>Sampling Location Sampling Stream</th>
<th>Measuring Component</th>
<th>Measuring Range</th>
<th>Suitable Siemens Analyzers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Feed to high pressure column</td>
<td>$CO_2$, $THC$, $H_2O$</td>
<td>0 ... 10 ppm 0 ... 10 ppm</td>
<td>ULTRAMAT 6 FIDAMAT 6 TPA</td>
</tr>
<tr>
<td>2 Circle gas nitrogen</td>
<td>$O_2$</td>
<td>0 ... 21 %</td>
<td>OXYMAT 61</td>
</tr>
<tr>
<td>3 Low pressure column, liquid phase</td>
<td>$O_2$, $CO_2$, $THC$</td>
<td>98 ... 100 % 0 ... 10 ppm 0 ... 300 ppm</td>
<td>OXYMAT 6 ULTRAMAT 6 FIDAMAT 6</td>
</tr>
<tr>
<td>4 Feed to low pressure column</td>
<td>$O_2$</td>
<td>0 ... 50 %</td>
<td>OXYMAT 6</td>
</tr>
<tr>
<td>5 Liquid nitrogen</td>
<td>$O_2$, $CO_2$, $H_2O$</td>
<td>0 ... 10 ppm 0 ... 10 ppm</td>
<td>OXYMAT 64 ULTRAMAT 6 TPA</td>
</tr>
<tr>
<td>6 Liquid oxygen</td>
<td>$O_2$, $C_2H_4$, $C_2H_6$, $C_3H_8$</td>
<td>98 ... 100 % low ppm ranges</td>
<td>OXYMAT 61 MAXUM</td>
</tr>
<tr>
<td>7 Gaseous oxygen</td>
<td>$O_2$, $THC$, $CO_2$, $H_2O$</td>
<td>98 ... 100 % Traces Traces</td>
<td>OXYMAT 61 ULTRAMAT 6 FIDAMAT 6 TPA</td>
</tr>
<tr>
<td>8 Gaseous nitrogen</td>
<td>$O_2$, $THC$, $H_2O$</td>
<td>0 ... 10 ppm 0 ... 10 ppm 0 ... 10 ppm</td>
<td>OXYMAT 64 FIDAMAT 6</td>
</tr>
<tr>
<td>9 High purity Argon and Krypton</td>
<td>$H_2$, $O_2$, $N_2$, $CH_4$, $CO$</td>
<td>Ultra traces (ppb)</td>
<td>MAXUM with sensitive detector (PDHID)</td>
</tr>
<tr>
<td>10 Process air feed before main condenser</td>
<td>$CH_4$, $C_2H_6$, $C_2H_4$, $C_3H_8$</td>
<td>low ppm ranges</td>
<td>MAXUM</td>
</tr>
<tr>
<td>11 Process air before molecular sieve</td>
<td>$CO_2$</td>
<td>0 ... 10 ppm</td>
<td>FIDAMAT 6</td>
</tr>
</tbody>
</table>

Fig. 4: Oxygen production through air separation (G: gaseous; L, LI: liquid)
Siemens Process Analytics at a Glance

Product overview

Siemens Process Analytics is a leading provider of process analyzers and process analysis systems. We offer our global customers the best solutions for their applications based on innovative analysis technologies, customized system engineering, sound knowledge of customer applications and professional support. And with Totally Integrated Automation (TIA). Siemens Process Analytics is your qualified partner for efficient solutions that integrate process analyzers into automation systems in the process industry.

From demanding analysis tasks in the chemical, oil and gas and petrochemical industry to combustion control in power plants to emission monitoring at waste incineration plants, the highly accurate and reliable Siemens gas chromatographs and continuous analyzers will always do the job.

Siemens Process Analytics offers a wide and innovative portfolio designed to meet all user requirements for comprehensive products and solutions.

Our Products

The product line of Siemens Process Analytics comprises

- extractive and in-situ continuous gas analyzers (fig. 8-11)
- process gas chromatographs (fig. 12-13)
- sampling systems
- auxiliary equipment

Analyzers and chromatographs are available in different versions for rack or field mounting, explosion protection, corrosion resistant etc.

A flexible networking concept allows interfacing to DCS and maintenance stations via 4-20 mA, PROFIBUS, OPC, Modbus or industrial ethernet.
Product Scope

Siemens Continuous Gas Analyzers and Process Gas Chromatographs

Extractive Continuous Gas Analyzers (CGA)

ULTRAMAT 23
The ULTRAMAT 23 is a cost-effective multicomponent analyzer for the measurement of up to 3 infrared sensitive gases (NDIR principle) plus oxygen (electrochemical cell). The ULTRAMAT 23 is suitable for a wide range of standard applications. Calibration using ambient air eliminates the need of expensive calibration gases.

CALOMAT 6/62
The CALOMAT 6 uses the thermal conductivity detection (TCD) method to measure the concentration of certain process gases, preferably hydrogen. The CALOMAT 62 applies the TCD method as well and is specially designed for use in application with corrosive gases such as chlorine.

OXYMAT 6/61/64
The OXYMAT 6 uses the paramagnetic measuring method and can be used in applications for process control, emission monitoring and quality assurance. Due to its ultrafast response, the OXYMAT 6 is perfect for monitoring safety-relevant plants. The corrosionproof design allows analysis in the presence of highly corrosive gases. The OXYMAT 61 is a low-cost oxygen analyser for standard applications. The OXYMAT 64 is a gas analyzer based on ZrO₂ technology to measure smallest oxygen concentrations in pure gas applications.

FIDAMAT 6
The FIDAMAT 6 measures the total hydrocarbon content in air or even in high boiling gas mixtures. It covers nearly all requirements, from trace hydrocarbon detection in pure gases to measurement of high hydrocarbon concentrations, even in the presence of corrosive gases.

ULTRAMAT 6
The ULTRAMAT 6 uses the NDIR measuring principle and can be used in all applications from emission monitoring to process control even in the presence of highly corrosive gases. ULTRAMAT 6 is able to measure up to 4 infrared sensitive components in a single unit.

ULTRAMAT 6 / OXYMAT 6
Both analyzer benches can be combined in one housing to form a multi-component device for measuring up to two IR components and oxygen.

Process Gas Chromatographs (Process GC)

MAXUM edition II
MAXUM edition II is very well suited to be used in rough industrial environments and performs a wide range of duties in the chemical and petrochemical industries and refineries. MAXUM II features e. g. a flexible, energy saving single or dual oven concept, valveless sampling and column switching, and parallel chromatography using multiple single trains as well as a wide range of detectors such as TCD, FID, FPD, PDHID, PDECD and PDPID.

MicroSAM
MicroSAM is a very compact explosion proof micro process chromatograph. Using silicon-based micromechanical components it combines miniaturization with increased performance at the same time. MicroSAM is easy to use and its rugged and small design allows mounting right at the sampling point. MicroSAM features drastically reduced cycle times, provides valveless sample injection and column switching and saves installation, maintenance, and service costs.

SITRANS CV
SITRANS CV is a micro process gas chromatograph especially designed for reliable, exact and fast analysis of natural gas. The rugged and compact design makes SITRANS CV suitable for extreme areas of use, e.g. off-shore exploration or direct mounting on a pipeline. The special software "CV Control" meets the requirements of the natural gas market, e.g. custody transfer.

In-situ Continuous Gas Analyzers (CGA)

LDS 6
LDS 6 is a high-performance in-situ process gas analyzer. The measurement (through the sensor) occurs directly in the process stream, no extractive sample line is required. The central unit is separated from the sensor by using fiber optics. Measurements are carried out in realtime. This enables a pro-active control of dynamic processes and allows fast, cost-saving corrections.
Analytical solutions are always driven by the customer’s requirements. We offer an integrated design covering all steps from sampling point and sample preparation up to complete analyzer cabinets or for installation in analyzer shelters (fig. 15). This includes also signal processing and communications to the control room and process control system.

We rely on many years of world-wide experience in process automation and engineering and a collection of specialized knowledge in key industries and industrial sectors. We provide Siemens quality from a single source with a function warranty for the entire system.

Read more in chapter “Our services”.

Siemens Process Analytics provides networking solutions to meet the demands of both objectives.
Siemens Process Analytics – Our Services

Siemens Process Analytics is your competent and reliable partner worldwide for Service, Support and Consulting.

Our resources for that are:

• **Expertise**
  As a manufacturer of a broad variety of analyzers, we are very much experienced in engineering and manufacturing of analytical systems and analyzer houses. We are familiar with communication networks, well trained in service and maintenance and familiar with many industrial processes and industries. Thus, Siemens Process Analytics owns a unique blend of overall analytical expertise and experience.

• **Global presence**
  With our strategically located centers of competence in Germany, USA, Singapore, Dubai and Shanghai, we are globally present and acquainted with all respective local and regional requirements, codes and standards. All centers are networked together.

Service portfolio

Our wide portfolio of services is segmented into Consulting, Support and Service. It comprises really all measures, actions and advises that may be required by our clients throughout the entire lifecycle of their plant:

- Site survey
- Installation check
- Functionality tests
- Site acceptance test
- Instruction of plant personnel on site
- Preventive maintenance
- On site repair
- Remote fault clearance
- Spare part stock evaluation
- Spare part management
- Professional training center
- Process optimisation
- Internet-based hotline
- FEED for Process Analytics
- Technical consulting

**Fig. 18 Portfolio of services provided by Siemens Process Analytics**

**FEED for Process Analytics**

Front End Engineering and Design (FEED for PA) is part of the planning and engineering phase of a plant construction or modification project and is done after conceptual business planning and prior to detail design. During the FEED phase, best opportunities exist for costs and time savings for the project, as during this phase most of the entire costs are defined and changes have least impact to the project. Siemens Process Analytics holds a unique blend of expertise in analytical technologies, applications and in providing complete analytical solutions to many industries.

Based on its expertise in analytical technology, application and engineering, Siemens Process Analytics offer a wide scope of FEED services focused on analyzing principles, sampling technologies, application solutions as well as communication system and given standards (all related to analytics) to support our clients in maximizing performance and efficiency of their projects.

Whether you are plant operators or belong to an EPC Contractor you will benefit in various ways from **FEED for Process Analytics** by Siemens:

- Analytics and industry know how available, right from the beginning of the project
- Superior analyzer system performance with high availability
- Established studies, that lead to realistic investment decisions
- Fast and clear design of the analyzer system specifications, drawings and documentation
- Little project management and coordination effort, due to one responsible contact person and less time involvement
- Additional expertise on demand, without having the costs, the effort and the risks of building up the capacities
- Lowest possible Total Costs of Ownership (TCO) along the lifecycle regarding investment costs, consumptions, utilities supply and maintenance
Notes:
For more information, please contact:

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