Vinyl chloride monomer (VCM), made from ethylene and chlorine by pyrolysis, is the feedstock for the production of the very common plastic material PVC. Modern VCM plants use integrated processes, combining endothermic and exothermic reactions in an almost energy balanced operation. Plants optimize the product quality, plant safety and cost efficiency by using advanced process control equipment including process analyzers.

Siemens, a leader in process analytical instrumentation, has proven over the decades, its capability to plan, engineer, manufacture, implement and service analyzer systems for VCM plants worldwide.

This Case Study provides an overview of the typical processes and describes how Siemens with its analyzer and application know-how meets best the process requirements.

Vinyl chloride monomer (VCM)

Vinyl chloride monomer (CH₂=CHCl, monomer, in contrast to polymers, PVC) is a colorless, flammable gas, first obtained in 1912 through catalytic hydrochlorination of acetylene. VCM is heavier than air hence can sink to the ground and may, under specific circumstances, form peroxides, initiating explosive polymerization. Under incineration, VCM decomposes producing toxic and corrosive fumes (hydrogen chloride and phosgene).

VCM is used as feedstock in the production of PVC (polyvinyl chloride), one of the world’s most versatile thermoplastics for a wide variety of industrial applications. As a hard plastic, it is used as vinyl siding, magnetic stripe cards, window profiles, pipe, plumbing and conduit fixtures. It can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is used in clothing and upholstery, and to make flexible hoses and tubing, flooring, roofing membranes, and electrical cable insulation. The material is often used for pipelines in the water and sewer industries because of its low-cost.

Since 1940, acetylene as feedstock was replaced stepwise by the inexpensive ethylene. Complete changeover to almost exclusive use of ethylene became possible in 1955, when the large-scale oxychlorination of ethylene to 1,2-dichlorethane became possible. Today, more than 90 % of the global VCM production is based on ethylene.

Modern VCM plants mostly use integrated processes which combine both highly exothermic reactions of ethylene chlorination and oxychlorination with the endothermic cracking process. This results in an almost energy balanced operation.
VCM process in brief

A modern VCM production can be considered as "balanced process" where ethylene, chlorine and oxygen are converted into VCM and water. The three process steps direct chlorination, oxychlorination and EDC cracking are summarized in the "VCM synthesis reaction". For details see text box below.

Based on the "VCM synthesis" principle different production technologies are in use. They differ, for instance, in details of the reactor design, type of catalysts, and reaction temperatures applied.

Many hundreds of VCM plants are in use worldwide with capacities from 30 000 up to 600 000 t/year each. All plants are operated with the aim of a high and constant product quality as well as cost efficiency and safety (corrosive, poisonous and explosive substances are handled). Considerable investments are required in instrumentation and process control to meet these requirements. Process analytics contribute an important part to that.

Process steps

The major steps of a VCM production process (fig. 1) include:

Direct chlorination
Ethylene and chlorine are fed to a reactor where a catalytic reaction (direct chlorination) takes place. 1,2-dichlorethane (EDC) is formed, together with heat, water and HCl-rich waste gas. The EDC is fed to a tank for temporarily storage. The waste gas is fed to the oxychlorination and reused as reacting component.

Oxychlorination
Ethylene, oxygen and hydrogen chloride are fed into a fluidized-bed reactor for the oxychlorination process. Raw EDC is formed, removed by condensation and fed to the EDC distillation unit for purification and heat. Waste gas and effluent are also formed and fed to the HCl recovery and water treatment units.

EDC distillation
To produce pure EDC both the EDC from the oxychlorination and the unconverted EDC from the cracking process (recycle EDC) are purified in the EDC distillation unit. The purified EDC is then fed to the EDC tank for temporarily storage.

EDC cracking (pyrolysis process)
Cracking of the EDC from the temporarily storage tank is performed in a fuel heated cracking furnace at temperatures of 500 ºC and above. Vinyl chloride monomer (VCM) and HCl are formed together with various by-products. Some EDC remains unconverted and is fed back to the EDC distillation unit. HCl is fed back into the oxychlorination unit and reused in the process as well. The VCM is either used as feedstock for direct manufacturing of PVC or stored as a product for sale.

By-product recovery
The by-products formed during VCM production are further treated and recovered in an oxidation process at approx. 1 250 ºC and completely converted into CO₂, water and hydrogen chloride. The process heat is used to generate steam and the HCl is recovered as valuable feed stock and returned into the process.

Emission monitoring
In most countries VCM plants must comply with the statutory regulations and local specifications regarding the limit values of pollutants that are released into the atmosphere. With an optimized operation of the by-product oxidation and recycle process only very low volume flow rates are emitted through the stack. Therefore, very often only discontinuous emission control measurements of some compounds (see fig. 1 and table 1, MP 10) are requested by the authorities. Samples are taken at the stack daily or weekly, and measured in the laboratory.

VCM production process

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct chlorination</td>
<td>C₂H₄+Cl₂ → C₂H₄Cl₂</td>
<td>EDC (1,2-dichlorethane, &quot;DC-EDC&quot;) is formed by a highly exothermal direct chlorination reaction of ethylene and chlorine</td>
</tr>
<tr>
<td>Oxychlorination</td>
<td>C₂H₄+2HCl+½O₂ → C₂H₄Cl₂+H₂O</td>
<td>EDC (1,2-dichlorethane, &quot;Oxy-EDC&quot;) and water is formed by a highly exothermal catalytic reaction of ethylene with hydrogen chloride and oxygen.</td>
</tr>
<tr>
<td>EDC cracking (pyrolysis)</td>
<td>C₂H₄Cl₂ → C₂H₃Cl + HCl</td>
<td>The EDC is cracked at high temperatures in a fuel heated furnace in an endothermic and incomplete reaction. VCM and HCl are formed together with various by-products; some EDC remains unconverted.</td>
</tr>
<tr>
<td>VCM synthesis (balanced process)</td>
<td>2C₂H₄ + Cl₂ + ½O₂ → 2C₂H₃Cl + H₂O</td>
<td>The three process sections as above can be combined into a one complete VCM synthesis process, in which only VCM and water is formed (balanced on hydrogen chloride).</td>
</tr>
</tbody>
</table>
**Analyzer tasks**

Process analytical equipment is an indispensable part of any VCM plant because it provides the control system and the operator with key data about the process and its environment.

**Four major applications**

Analyzer applications can be classified in four groups depending on how the analyzer data are used:

- Closed-loop control for process and product optimization
  This application helps to increase yield, reduce energy consumption, achieve smooth operation, and keep product quality according to the specification
- Quality control and documentation e.g. for ISO compliance
- Plant monitoring and alarms
  This application protects personnel and plant from possible hazard from toxic or explosive substances
- Emission monitoring
  This application helps to keep emission levels in compliance with local environmental regulations.

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**Table 1: Sampling points and measuring details of a VCM production plant, according to fig. 1**

<table>
<thead>
<tr>
<th>Sampling point/sampling stream</th>
<th>Component</th>
<th>Measuring range</th>
<th>Measuring task</th>
<th>Suitable analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Direct chlorination</td>
<td>C₂H₄, O₂</td>
<td>0 ... 3 %</td>
<td>0 ... 10 %</td>
<td>Process control, Safety monitoring</td>
</tr>
<tr>
<td>2 From direct chlorination and EDC distillation</td>
<td>HCl, H₂O, Impurities</td>
<td>0 ... 10 ppm</td>
<td>0 ... 20 ppm</td>
<td>EDC quality</td>
</tr>
<tr>
<td>3 Oxychlorination</td>
<td>O₂, CO, CO₂, C₂H₄, pH, conduct.</td>
<td>0 ... 10 %</td>
<td>0 ... 10 %</td>
<td>Process control, Safety monitoring</td>
</tr>
<tr>
<td>4 EDC distillation</td>
<td>H₂O</td>
<td>0 ... 20 ppm</td>
<td>Process control</td>
<td>Third party analyzer</td>
</tr>
<tr>
<td>5 See line 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 EDC cracking</td>
<td>O₂, H₂O</td>
<td>0 ... 10 %</td>
<td>0 ... 20 ppm</td>
<td>Process control</td>
</tr>
<tr>
<td>7 VCM distillation</td>
<td>H₂O</td>
<td>0 ... 100 ppm</td>
<td>Process control</td>
<td>Third party analyzer</td>
</tr>
<tr>
<td>8 From VCM distillation</td>
<td>Impurities*</td>
<td>ppm range</td>
<td>VCM quality</td>
<td>MAXUM edition II</td>
</tr>
<tr>
<td>9 By-product recovery</td>
<td>O₂, pH, O₂</td>
<td>0 ... 10 %</td>
<td>0 ... 10 %</td>
<td>Process control, Emission and safety monitoring</td>
</tr>
<tr>
<td>10 Plant ambient air and stack</td>
<td>EDC/VCM, various</td>
<td>ppm range</td>
<td>Environmental compliance</td>
<td>MAXUM edition II, FIDAMAT, CEM system (or laboratory devices)</td>
</tr>
</tbody>
</table>

*e.g. methyl chloride, ethyl chloride, vinyl acetylene, butadiene, dichloroethane, dichloroethene
Analyzers and sampling points
Different analyzers are used in VCM plants ranging from simple sensor type monitors to high technology process gas chromatographs. The list typically includes:
- Process gas chromatographs
- Continuous gas analyzers (paramagnetic oxygen analyzers, NDIR analyzers, total hydrocarbon content analyzers)
- Analyzers for moisture and oxygen traces
- Low Explosion Level (LEL) analyzers

Fig. 1 and table 1 show typical sampling points of a VCM plant along with the respective measuring components and suitable analyzers.

Analyzer installation
Analyzers are installed partially in the field close to the sampling location and/or in analyzer houses (shelter). In modern plants the analyzers are interfaced to a plant wide data communication system for direct data transfer from and to the analyzers. The number of analyzers in a VCM plant varies from plant to plant depending on the type of process, specific plant conditions and user requirements.

Oxygen measurements
Continuous monitoring of oxygen in the process gas in both the direct chlorination and oxychlorination plant units (MP 1 and 3 of fig. 1 and table 1) is of exceptional importance. To protect from the danger of heavy explosions, the process must be ensured to run outside the critical ignition levels of the process gas at any time. Therefore, the use of Siemens SIPROCESS GA700 with OXYMAT 7 or OXYMAT 6 gas analyzer (see text box) which provide most and accurate oxygen measuring technology is essential. Because of the high importance, this oxygen measurement is often engineered redundantly with two analyzers at the same sampling point and fail-safe data processing.

The oxygen measurement at sampling point 9 (by-product recovery) has a different meaning. Here, the oxygen content reading is used to optimize the incineration conditions to minimize the remaining emission rate of pollutants. High measuring accuracy is required here as well, but along with corrosion resistance because of the aggressive gas composition. Again, the OXYMAT 6, in its tantalum version, is most suitable for this task.

Measurement of impurities
Gas chromatographs are standard equipment in VCM plants to measure impurities in trace concentrations. They are used to analyze the product stream at MP 2 and 5 (fig. 1) and help very much to ensure compliance with product specification and quality. The Siemens process gas chromatograph MAXUM edition II is very much suited for this task. Another process gas chromatograph application in VCM plants is to monitor ambient air for chemical compounds that may emerge from certain plant units in case of sudden leakages (MP 10, combined with sample point switching).

Measurement of HCl
HCl in the ppm range (MP 2, 5 and 8) is usually determined by conductivity measurements. However, at MP 3 with a concentration range of 0 to 3 %, photometric measurements are preferred. With the in-situ laser spectrometer LDS 6, Siemens offers a very effective solution for this task. LDS 6 is a diode laser-based in-situ gas analyzer for measuring specific gas components directly in a process gas stream. Measurements are carried out free of spectral interferences and in real time, enabling proactive control of dynamic processes.

The OXYMAT operates according to the paramagnetic principle and is designed for high-precision measurements of oxygen concentrations in gases. The pulsating magnetic field creates minute flow pulses detected by the Siemens micro flow sensor and converted into the measuring signal. Thus, the OXYMAT does not comprise any moving parts and the sample gas does not come into contact with the micro flow sensor, which ensures an extremely long life time and high operation stability. A good example for that is the independence from humidity which may be present in the sample gas and could cover the surface of mirrors (with negative impact on the measuring accuracy) that are used with other oxygen measuring principles.