

# Process Analytics in Polyethylene (PE) Plants

## Polyethylene

*Polyethylene (PE)* is a generic name for a family of semicrystalline polymers. PE, as well as polypropylene (PP), belong to the group of polyolefins, that are derived from a group of base chemicals known as olefins. Polyolefins are made by joining together small molecules (monomers) to form long-chain molecules (polymers) with thousands of individual links using a variety of catalysts.

The base monomer for PE is ethylene, which is a gas at room temperature, but when linked together as polymers, it forms tough, flexible plastic materials with a large variety of applications. The linking of molecules is referred to as **polymerization**. There are various commercial technologies used to manufacture polyethylene. Each technology produces unique combinations of polymer characteristics.

Polyolefins (Polyethylene and Polypropylene) are the world's mostly produced and fastest growing polymer family because

- modern polyolefins cost less to produce and process than other plastics or conventional materials
- polyolefins are available in many varieties. They range from rigid materials, which are used for car parts, to soft materials such as flexible fibres. Some are as clear as glass; others are completely opaque. Some, such as microwave food containers, have high heat resistance while others melt easily.

# chemical INDUSTRY

For the **production of polyethylene** a variety of processes is in use depending on what final products are intended to be produced. However, regardless of the process type, all plants require process analytical equipment to collect reliable and accurate information for process control, product quality, plant safety and environmental compliance.

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

This *Case Study* provides an over-view of the processes typically used and describes how Siemens with its analyzer and application know-how meets best the process requirements.

## SIEMENS

# Polyethylene production processes

## Polyethylene

is made in a polymerization reaction by building long molecular chains comprised of ethylene monomers, mostly by using catalysts. The type and nature of the catalysts are of great influence on the polymerization. As catalysts became more efficient, the polyethylene products became purer and more versatile and the production process became simpler and more efficient.

**Polyethylene (PE)** is a family of resins made from the polymerization of ethylene gas. It is produced either in radical polymerization reactions or in catalytic polymerization reactions. Most PE molecules contain „branches“ in their chains which are formed spontaneously in case of radical polymerization or deliberately by copolymerization of ethylene with  $\alpha$ -olefins in case of catalytic polymerization.

PE resins are classified according to their density which partly depends on the type of branching.

- **HDPE**  
High Density PolyEthylene has almost no branching and thus has stronger intermolecular forces. It is produced mainly in slurry and gas-phase polymerization processes. HDPE is a white opaque solid.
- **MDPE**  
Medium Density PolyEthylene has a high degree of resistance to chemicals and is very easy to keep clean.
- **LDPE**  
Low-Density PolyEthylene has random long branching, with branches on branches. It is produced mainly in high-pressure polymerization processes. LDPE is a translucent solid.

## • LLDPE

Linear Low-Density PolyEthylene is a substantially linear polymer, with significant numbers of short branches, produced mainly by copolymerization of ethylene with longer-chain olefins. LLDPE is a translucent solid.

## Production Processes

A large number of production processes exist for PE with some general similarities. But the processes are evolving continuously. So the specifics can be significantly different and the following descriptions and graphic displays should be, therefore, considered exemplarily only with no direct relation to existing plant or process designs.

### Generic polymerization process

Similarities between the processes follow a generic olefin polymerization process scheme as shown in Fig. 1 (from left):

- Feedstock materials and additives must be purified and catalyst material must be prepared. And - in case of a high pressure process - the gas must be compressed in several stages.
- Polymerization takes place either in the **gas phase** (fluidized bed or stirred reactor), the **liquid phase** (slurry or solution), or in a **high pressure** environment. Polymerization is the heart of the processes. On any one unit, only one of the three processes is used. More details will be explained on the next pages.
- Polymer particles are then separated from still existing monomers and diluents, pelletized, dried and dispatched.
- Monomers and diluents are recovered and fed again to the process.

## Gas-Phase Polymerization

In gas-phase polymerization (Fig. 2, left) the ethylene is contacted with solid catalyst material intimately dispersed in an agitated bed of dry polymer powder. Two different methods are used to carry out this reaction

- In the *fluidized-bed process* the monomer flows through a perforated distribution plate at the reactor bottom and rapid gas circulation ensures fluidization and heat removal. Unreacted polymer is separated from the polymer particles at the top of the reactor and recycled. Fluidized-bed plants are able to produce either LLDPE or HDPE and are free of constraints from viscosity (solution process) or solubility (slurry process). A modification uses a second reactor connected in series to perform copolymerization.
- The *stirred-bed process* uses a horizontal or vertical reactor with compartments, in which the bed of polymer particles is agitated by mixing blades.

The gas-phase polymerization technology is economical and flexible and can accommodate a large variety of catalysts. It is by far the most common process in modern ethylene production plants.

Some processes are listed in Table 1.

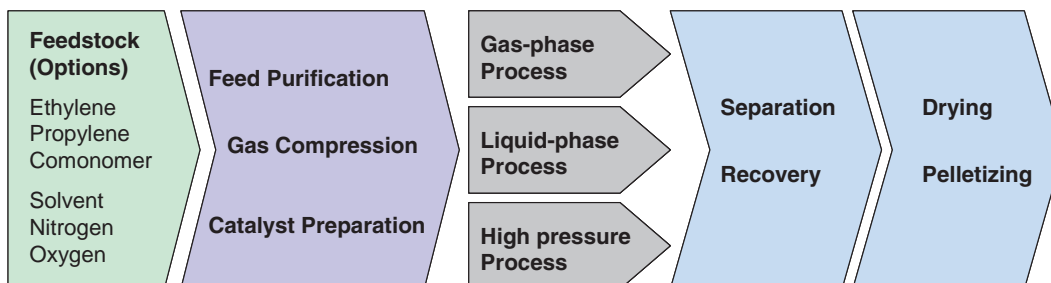


Fig. 1: Generic Polyethylene (olefin) polymerization process, simplified

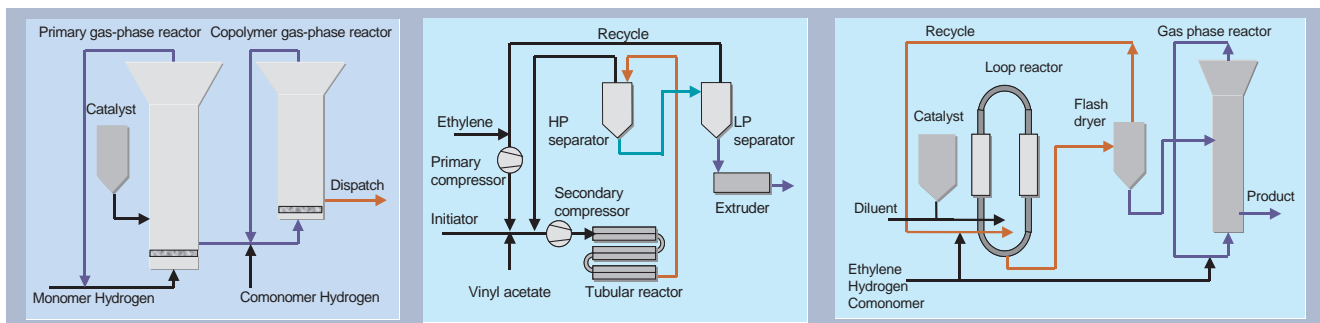


Fig. 2: PE production principles: gas-phase, high-pressure, liquid-phase (from left)

## Liquid-Phase Polymerization

In liquid-phase processes (slurry or suspension, Fig. 2, right) catalyst and polymer particles are suspended in an inert solvent, typically a light or heavy hydrocarbon. Super-critical slurry polymerization processes use supercritical propane as diluent.

Slurry processes run in loop reactors with the solvent circulating, stirred tank reactors with a high boiling solvent or a "liquid pool" in which polymerization takes place in a boiling light solvent. A variety of catalysts can be used in these processes. Processes in solution require, as their last step, the stripping of the solvent.

Supercritical polymerization in the slurry loop provides advantages (e.g. higher productivity, improved product properties) over subcritical polymerization.

Advanced processes combine a loop reactor with one or two gas-phase reactors, placed in series, where the second stage of the reaction takes place in the gas-phase reactors. For bimodal polymers, lower molecular weights are formed in the loop reactor, while high molecular weights are formed in the gas-phase reactor.

Some processes are listed in Table 1.

## High Pressure Processes

In high pressure processes (Fig. 2, center) autoclave or tubular reactors (pressure in excess of 3,000 bar) are used, but the processes are similar, comprising compression, polymerization, pelletizing, and dispatch as major steps. Fresh ethylene enters the reactor and is mixed with the low pressure recycle. After further compression the mixture enters the reactor for polymerization. Oxygen or peroxide may be used as initiators.

A tubular reactor typically consists of several hundred meters of jacketed high-pressure tubing arranged as a series of straight sections connected by 180° bends.

High pressure processes can produce LLDPE homopolymers and vinylacetate copolymers in addition to the normal range of LDPEs.

Some processes are listed in Table 1.

### Gas-phase processes

Lupotech G®	A fluidized-bed process for manufacturing of HDPE, MDPE, and LLDPE
Unipol® PE	A fluidized-bed process for manufacturing of HDPE and LLDPE

### Liquid-phase processes

Hostalen®	A low-pressure slurry process for manufacturing of bimodal HDPE
Borstar® PE	A supercritical slurry process, which combines a loop reactor and a gas-phase reactor
Phillips	A slurry process for manufacturing of HDPE

### High pressure processes (selected)

Lupotech T®	High-pressure process for manufacturing of broad range LDPE
ExxonMobil	High-pressure tubular process for LDPE
Equistar	High-pressure tubular and autoclave processes for LDPE

Table 1: Common PE production processes

# Use of process analyzers

## Analyzer Tasks

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

### Four major applications

Analyzer applications can be divided 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** for ISO compliance
- **Plant monitoring and alarms**  
This application protects personnel and plant from possible hazard from toxic or explosive substances
- **Emission control**  
This application helps to keep emission levels in compliance with local regulations.

## Analyzers and sampling points

Different analyzers are used in ethylene 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 O<sub>2</sub> traces
- Low Explosion Level (LEL) analyzers

## Analyzer installation

Analyzers are installed partially in the field close to the sampling location and/or in an analyzer house (shelter). In modern plants most of the analyzers are interfaced to a plant wide data communication system for direct data transfer from and to the analyzers.

The total number of analyzers installed in a plant varies from plant to plant depending on the type of process, individual plant conditions and user requirements.

An example of typical sampling locations, analyzers, and measuring components and ranges is given in Fig. 3 for a HDPE plant using a gas-phase fluidized bed reactor:

- Feed of monomer, comonomers, catalyst, and additives to the reactor (1-4)
- Cycle gas line (5)
- Product line or feed to a second reactor (6)
- Safety measurements at different locations of the plant (7)

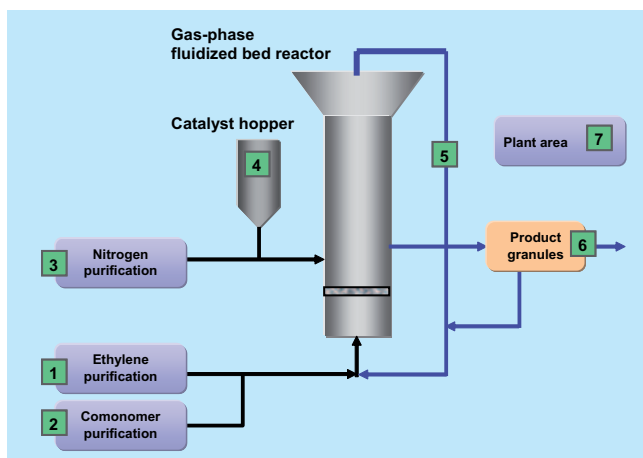


Fig. 3: Typical sampling points of a fluidized-bed HDPE plant

Sampling point	Sampling stream	Component	Meas. Range [ppm]	Suitable Analyzer
1	Ethylene purification	CO	0 ... 2	MAXUM
		CO <sub>2</sub>	0 ... 2	MAXUM
		Methanol	0 ... 10	MAXUM
		Acetylene	0 ... 5	MAXUM
		Total S	0 ... 2	MAXUM
		Ethane	0 ... 400	MAXUM
		Moisture	0 ... 5	TPA
		O <sub>2</sub>	0 ... 2	OXYMAT 6
2	Comonomer purification	Moisture	0 ... 100	TPA
3	Nitrogen purification	Moisture	0 ... 10	TPA
		O <sub>2</sub>	0 ... 10	OXYMAT 6
4	Catalyst feed	O <sub>2</sub>	0 ... 10 %	OXYMAT 6
5	Cycle gas	Nitrogen	0 ... 100%	MAXUM or MicroSAM
		Hydrogen	0 ... 50%	CALOMAT 6
		CO	0 ... 10 ppm	ULTRAMAT 6
		Methane	0 ... 10%	ULTRAMAT 6
		Ethane	0 ... 20%	MAXUM or MicroSAM
		Ethylene	0 ... 100%	MAXUM or MicroSAM
		N-Butane	0 ... 5%	MAXUM or MicroSAM
		ISO-Butan	0 ... 5%	MAXUM or MicroSAM
		1-Butene	0 ... 25%	MAXUM or MicroSAM
		Trans-2-Butene	0 ... 1%	MAXUM or MicroSAM
		ISO-Butene	0 ... 5%	MAXUM or MicroSAM
		CIS-2-Butene	0 ... 2%	MAXUM or MicroSAM
		Hexane	0 ... 10%	MAXUM or MicroSAM
		1-Hexene	0 ... 20%	MAXUM or MicroSAM
		C6 inerts	0 ... 10%	MAXUM or MicroSAM
6	Product	Moisture	0 ... 5	TPA
7	Plant area	Various		

Table 2: Typical measuring components and ranges acc. to Fig. 3

TPA: Third party analyzer

# Siemens Process Analytics at a glance

## Products

### Siemens Process Analytics

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 analysers into automations systems in the process industry.

From demanding analysis tasks in the chemical, oil & 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 analysers 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. 4 to 7), process gas chromatographs (fig.8 to 11), sampling systems and 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 to 20 mA, PROFIBUS, Modbus, OPC or industrial ethernet.



Fig. 4: Series 6 gas analyzer (rack design)

Extractive Continuous Gas Analyzers (CGA)	
ULTRAMAT 23	The ULTRAMAT 23 is a cost-effective multicomponent analyser 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 corrosion-proof 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 ZrO <sub>2</sub> technology to measure smallest oxygen concentrations in pure gas applications.
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 multicomponent device for measuring up to two IR components and oxygen.
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.
In-situ Continuous Gas Analyzer (CGA)	
LDS 6	LDS 6 is a high-performance in-situ process gas analyser. 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 real-time. This enables a pro-active control of dynamic processes and allows fast, cost-saving corrections.

Fig. 5: Product scope „Siemens Continuous Gas Analyzers“



Fig. 6: Series 6 gas analyzer (field design)



Fig. 7: LDS 6 in-situ laser gas analyzer

# Siemens Process Analytics at a glance Products (continued) and Solutions



Fig. 8: MAXUM edition II Process GC



Fig. 9: MicroSAM Process GC

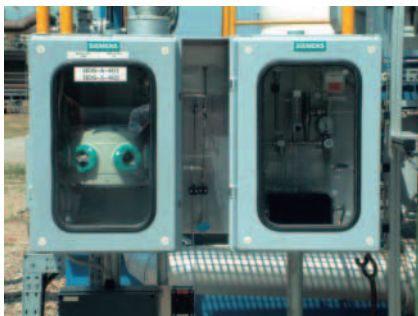


Fig. 10: SITRANS CV Natural Gas Analyzer

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. offshore exploration or direct mounting on a pipeline. The special software "CV Control" meets the requirements of the natural gas market, e.g. custody transfer.

Fig. 11: Product scope „Siemens Process Gas Chromatographs“

## Our solutions

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 analyser cabinets or for installation in analyser shelters (fig. 12). 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 "Our Services".

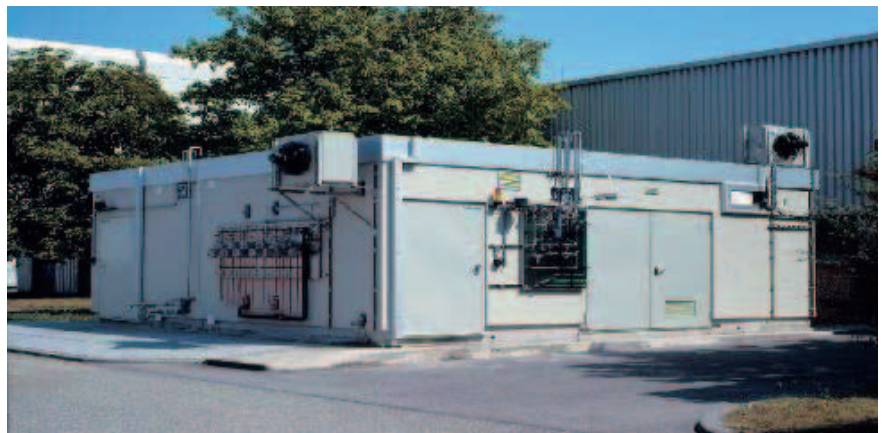


Fig. 12: Analyzer house (shelter)

# Siemens Process Analytics at a glance Solutions (continued) and Services

## Our solutions ...

### Analyzer networking for data communication

Engineering and manufacturing of process analytical solutions increasingly comprises "networking". It is getting a standard requirement in the process industry to connect analyzers and analyzer systems to a communication network to provide for continuous and direct data transfer from and to the analysers.

The two objectives are (fig. 14):

- To integrate the analyzer and analyzer systems seamlessly into the PCS / DCS system of the plant and
- To allow direct access to the analyzers or systems from a maintenance station to ensure correct and reliable operation including preventive or predictive maintenance (fig.13).

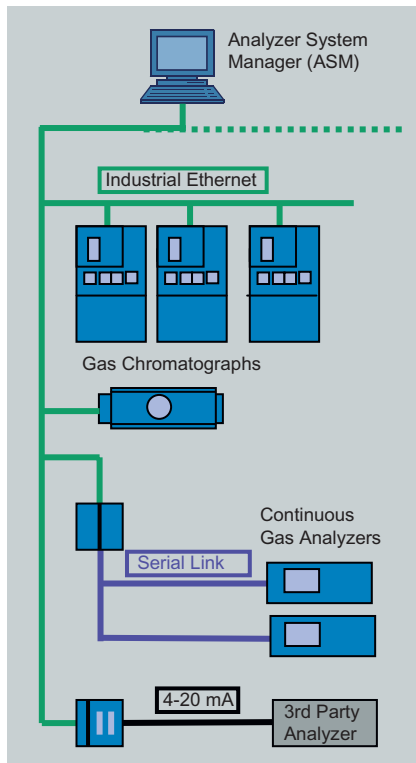


Fig. 13: Communication technologies

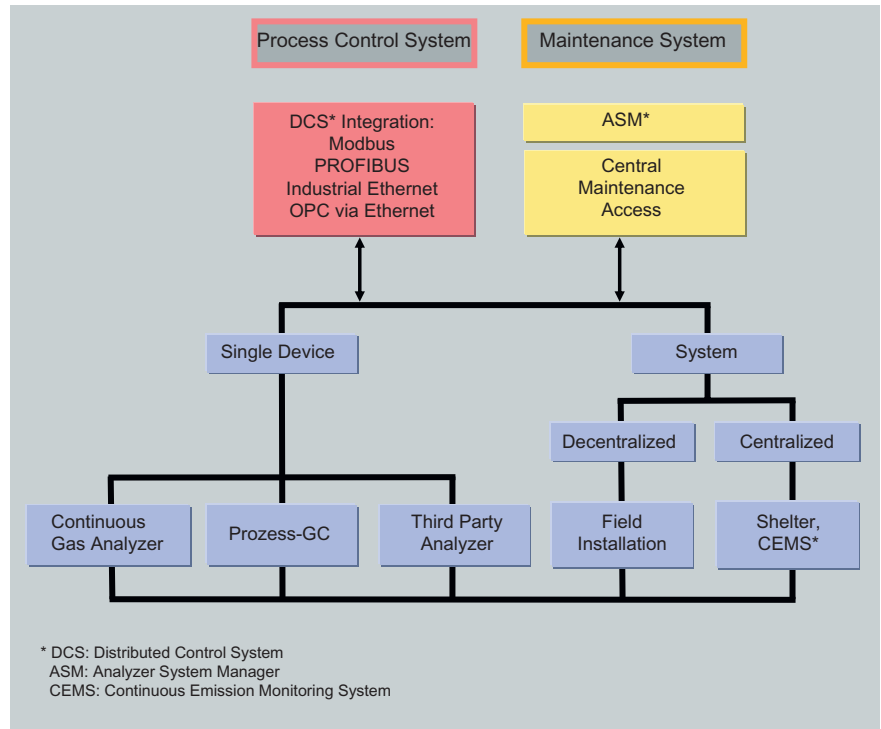


Fig. 14: Networking for DCS integration and maintenance support

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

## Our Services

Siemens Process Analytics is your competent and reliable partner world wide 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.



Fig. 15: Portfolio of services

# Siemens Process Analytics at a glance

## Services, continued

### Our Services ...

#### Service portfolio

Our wide portfolio of services is segmented into Consulting, Support and Service (fig. 15 to 16). It comprises really all measures, actions and advises that may be required by our clients throughout the entire lifecycle of their plant. It ranges from site survey to installation check, from instruction of plant personnel to spare part stock management and from FEED for Process Analytics (see below) to internet-based service Hotline.

Our service and support portfolio (including third-party equipment) comprises for example:

- 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

#### FEED for Process Analytics

Front End Engineering and Design (FEED) 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.

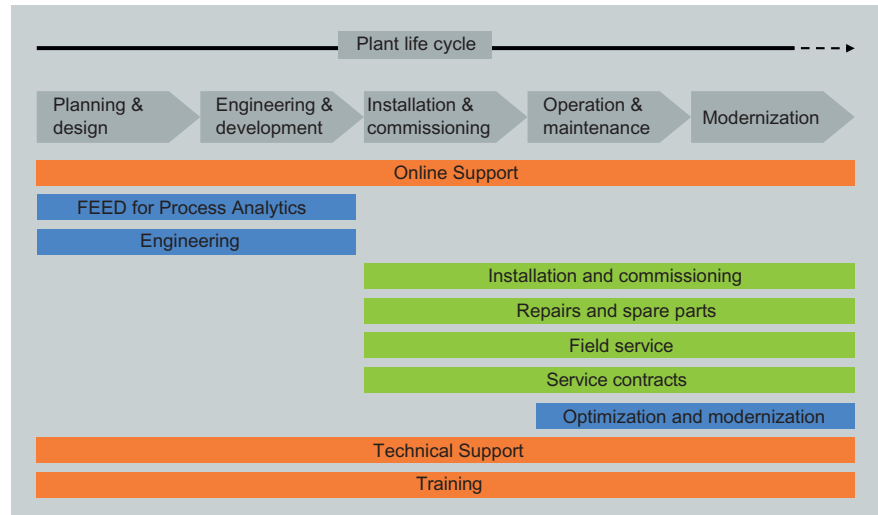


Fig. 16: Portfolio of services provided by Siemens Process Analytics

Based on its expertise in analytical technology, application and engineering, Siemens Process Analytics offer a wide scope of FEED services focused on analysing 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.



# Case Study

## Siemens Process Analytics - Answers for industry



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