SIEMENS

Gas and Liquid Analysis in Ethylene Production Plants

Application Note Process Analytics

Ethylene

Ethylene, $H_2C=CH_2$, the lightest olefin, is a colorless, flammable gas. It is a very important starting material for the production (polymerization) of many petrochemical end products such as fibers, plastics, resins, etc.
Thermal cracking of hydrocarbons is the principal route for industrial production of ethylene. Valuable by-products including propylene, butadiene, and benzene are also obtained during the cracking process. Selectivity for a desired product scope is an important objective in the design of cracking furnaces.
Cracking furnaces are tubular reactors, known also as crackers or steam crackers. Modern reactors are arranged in vertical rows with a capacity of a single furnace well over 100,000 t/yr.The basic reaction proceeds in the pyrolysis coils of the radiant section of the furnace.

Production of ethylene

Common feedstocks for ethylene production are naphta, natural gas or ethane. The entire production process including distillation of the different by-products varies in detail depending on feedstocks, contractors and technologies applied. In thermal cracking technology the process can be split into five major sections, see box below.
Cracking reactions are endothermic with heat supplied by firing fuel gas and/or oil in a large number of side-wall or floor burners of the furnace. Since only about 50 % of the fired energy is absorbed during the cracking process, considerable amount of energy can be extracted from the flue gas of the furnace (when passing through the convection section) to preheat the feed.

A number of environmental and safety objectives must be considered during ethylene production. Flue-gas emissions such as NO_x and SO_2 must be reduced in integrated DENOX and scrubbing units. Waste water and solid process waste resulting from severals plant units has to be treated properly including incineration before disposal.
Personnel and plant safety objectives are also stringent because ethylene is highly flammable and explosive over a wide range of mixtures with air.
Ethylene production is a complex process and thus an ethylene plant consists of up to 30 single units as shown in fig. 1.

Steps of ethylene processing (fig. 1)

- **Cracking** of preheated naphta or other feeds in a group of cracking furnaces with steam added as a diluent to the feed to minimize the formation of coke and to improve selectivity. Inlet temperature is kept between 500 and 700 °C depending on the feed, outlet temperatures are 750 to 950 °C.
- **Quenching** (fast cooling) of the reaction mixture leaving the furnace in quench coolers, also called transferline exchangers (TLE), with valuable high pressure steam generated as by-product The TLE outlet temperature is 350 - 650 °C depening on feedstock and design.
- **Separation** between pyrolysis gasoline and pyrolysis fuel oil
- **Removal** of water and acid gases (CO_2 and H_2S) from pyrolysis gas in a multi-stage compressor
- **Final drying, cooling and distillation** of the pyrolysis gas in a system of several units and thus **production** of the different products including ethylene

Measuring tasks

Process analyzers are a very important part of ethylene plant field instrumentation. Analyzer measuring tasks are grouped into

- Process control and optimization
- Product quality control
- Personnel and plant safety control
- Environmental compliance control

50-100 analyzers may be installed in one plant, measurements include furnace flue gas, cracked gas, steam systems, water and condensate sytems, feedstock quality, stack and water emission, ambient air quality, etc. Continuous and reliable process control including the use of analyzers is especially critical in ethylene production because cracking reactions change as the run proceeds.

Application of Siemens process analyzers

Siemens is known for its wide product line of gas and liquid analyzers as well as gas chromatographs, which are highly qualified and successfully tested for use in ethylene plants, see table 1 and 2. Siemens is able and very much experienced to engineer and to deliver the entire analytical equipment as system supplier or to deliver just the analyzers either to another system integrator or directly to the end user, in case of upgrading, for instance. The key analyzers with their features and benefits are described briefly in the following.

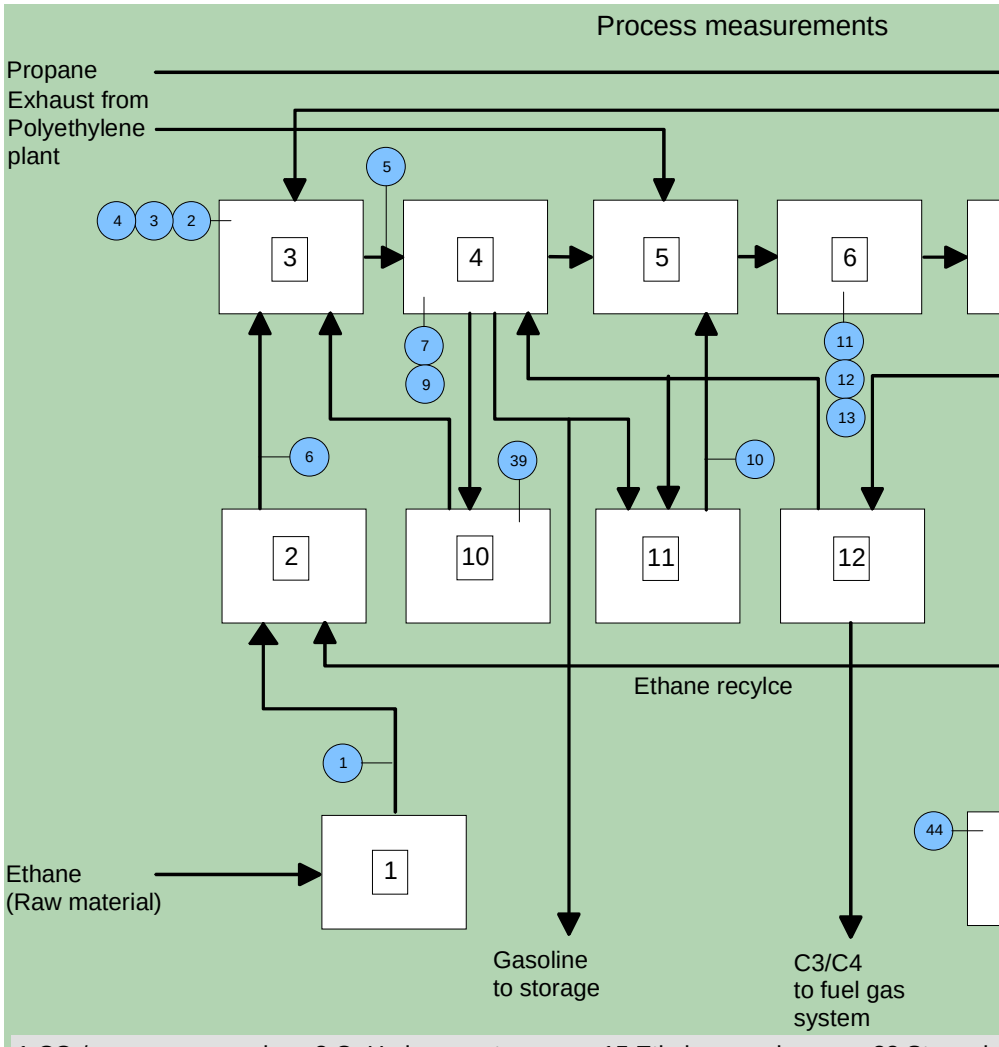

Fig. 1 Ethylene production process flow chart (typical example)

The **OXYMAT 6** is a gas analyzer that 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 microflow sensor and converted into the measuring signal. Thus, the OXYMAT 6 does not contain any moving parts. The sample stream gas also does not come into contact with the microflow sensor, which ensures an extremely long life time and high operating stability. The OXYMAT is listed by many end-users for safety measurements.

Features OXYMAT 6	Benefits
Simple and robust design without moving parts	High operating reliability and service life; very low maintenance and spare parts requirements; High availability
Strictly linear measuring principle	High measuring precision and flexibility
Measuring principle allows differential measurement against a freely selectable comparison gas concentration No electronic zero suppression	Very small measuring ranges for high (absolute) concentrations and thus very high measuring precision
Minimum drift (0,5 % of span in 3 months)	Very high measuring precision Seldom needs for recalibration
SIPROM GA software package for remote control and maintenance Interface for PROFIBUS PA (Option)	Easily integrated into automated systems

Table 1 OXYMAT 6 features and benefits

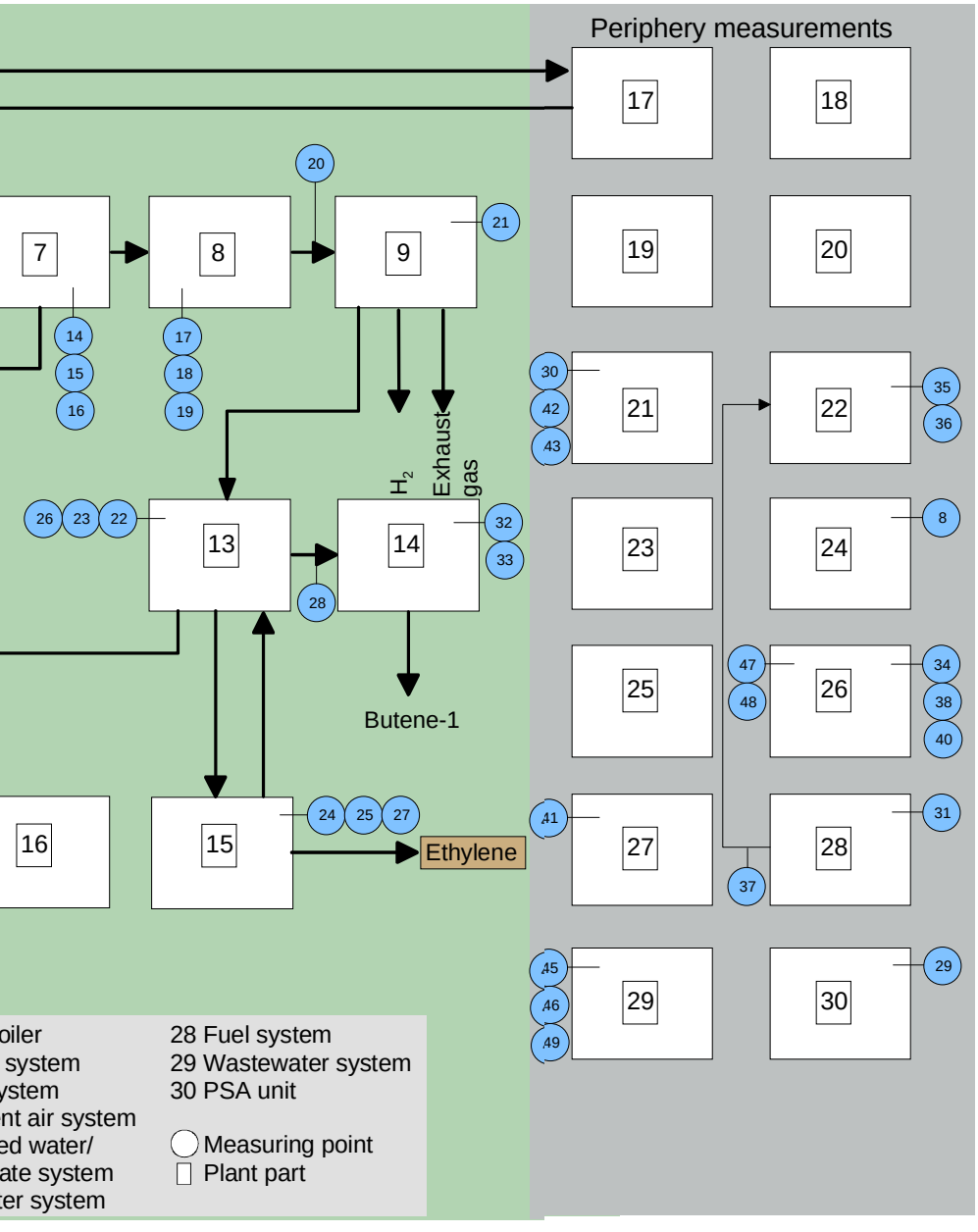

Fig. 2 Ethylene plant (cracker)

Fig. 3 Series 6 gas analyzer in field housing

Features ULTRAMAT 6	Benefits
Dual-layer detector with variable optical path length setting (Optocoupler)	Maximum selectivity und thus measuring precision. Can be optimized for actual analysis task
Detector uses microflow sensor with no moving parts to generate the measuring signal	No microphony effects; very low signal noise; High measuring accuracy
Extremely stable mechanical design Electronical and physical parts separated gas tight in one robust IP 65 housing	Very high operational reliability and life time
SIPROM GA software package for remote control and maintenance Interface for PROFIBUS PA (Option)	Easily integrated in automated systems
Can be extended for simultaneous measurement of 1-4 NDIR gas components Can be combined with the OXYMAT 6 Oxygen Analyzer in one housing	Lower costs thanks to processing of several measuring tasks with one device

Table 2 ULTRAMAT 6 features and benefits

The **ULTRAMAT 6** is a gas analyzer that operates according to the non-dispersive infrared principle (NDIR). It is designed to perform highly selective concentration measurements of infrared-sensitive gases. The ULTRAMAT 6 uses the two-beam alternating light principle with a measurement and comparison cell, dual-layer detector, and optical coupler.This optical bench design produces an extrenely narrow absorption curve minimizing the influence of overlapping spectra. Thus an unparalleled analytical precision is obtained.

MP	Measuring point location	Measuring task	Measuring component	Measuring range	Measuring equipment
1	Before ethane preheater	Feed control	CO_2	0 ... 100 ppm	ULTRAMAT 6FEx
2	Cracking furnace, flue gas	Furnace control	O_2	0 ... 8 %	Zirconia probe
3	Cracking furnace,flue gas	Furnace control	CO NO (NO_2) O_2	0 ... 200 mg/m3 0 ... 250 mg/m3 0 ... 8 mol%	ULTRAMAT 23 ULTRAMAT 23 OXYMAT 6
4	Cracking furnace	Furnace control	CO_2	0 ... 5000 molppm 0 ... 5 mol%	ULTRAMAT 6F Exp.
5	After cracking furnace	Furnace control	H_2 CH_4 C_2H_2 C_2H_4 C_2H_6 C_3H_6 C_3H_8 Sum C4	0 ... 40 mol% 0 ... 30 mol% 0 ... 2 mol% 0 ... 40 mol % 0 ... 50 mol% 0 ... 5 mol% 0 ... 5 mol%	PGC 302 edition II or Advance MAXUM
6	Ethane preheater outlet	Feed control	H_2 CH_4 C_2H_2 C_2H_4 C_2H_6 C_3H_6 C_3H_8 Sum C4	0 ... 40 mol% 0 ... 30 mol% 0 ... 2 mol% 0 ... 40 mol % 0 ... 50 mol% 0 ... 5 mol% 0 ... 5 mol%	PGC 302 edition II or Advance MAXUM
7	Wash water pumps	Process water control	pH	pH 2 ... 12	SIPAN
8	Outlet process steamsuperheater	Process steam control	pH	pH 2 ... 12	SIPAN
9	Process water stripper	Process water control	pH	pH 2 ... 12	SIPAN
10	Off-gas scrubber outlet	Scrubber control	CO_2 CO	0 ... 5 molppm 0 ... 5000 molppm	PGC 302 edition II ULTRAMAT 6F Exp.
11	Crackes gas dryer	Dryer control	H_2O	0 ... 5 molppm	NA
12	Crackes gas dryer	Dryer control	H_2O	0 ... 5 molppm	NA
13	Crackes gas dryer	Dryer control	H_2O	0 ... 5 molppm	NA
14	C2/C3 separator	Product stream control	C_2H_2 Sum C3	0 ..10000 molppm 0 ... 3000 molppm	PGC 302 edition II or Advance MAXUM
15	C2/C3 separator	Product stream control	C_2H_6	0 ... 1000 molppm	"
16	C2/C3 separator	Product stream control	Sum C3	0 ... 3000 molppm	"
17	C2 at dryer	Product stream control	C_2H_2	0 ... 10 molppm 0 ... 100 mol ppm	"
18	C2 at dryer	Product stream control	H_2O	0 ... 5 molppm	NA
19	C2 at dryer	Product stream control	H_2O	0 ... 5 molppm	NA
20	Before demethanizer		CO C_2H_4	0 ... 3000 molppm 0 ..10000 molppm 0 ... 5 mol%	PGC 302 edition II or Advance MAXUM
21	Demethanizer	Product stream control	CH_4	0 ... 2000 molppm	PGC 302 / Adv. MAXUM
22	Ethane/Ethylene separator	Product stream control	C_2H_4	0 ... 5 mol%	"
23	Ethane/Ethylene separator	Product stream control	C_2H_6	0 ... 10 mol%	ULTRAMAT 6F Ex
24	Ethylene refrigerant system	Product stream control	H_2O	0 ... 5 molppm	NA
25	Ethylene refrigerant system	Product stream control	H_2O	0 ... 5 molppm	NA
26	Ethane/Ethylene separator	Product stream control	CH_4 C_2H_2 C_2H_6	0 ... 1000 molppm 0 ... 10 molppm 0 ... 1500 molppm	PGC 302 edition II or Advance MAXUM
27	Ethylene refrigerant system	Product stream control	CH_4 C_2H_2 C_2H_6	0 ... 300 molppm 0 ... 10 molppm 0 ... 1000 molppm	PGC 302 edition II or Advance MAXUM
			CO CO_2	0 ... 2 mol ppm 0 ... 5 molppm	PGC 302 edition II or Advance MAXUM
			NH_3	0 ... 1 molppm	NA (MIPANQ)
			MeOH PrOH Carbonyl	0 ... 1 molppm 0 ... 1 molppm 0 ... 1 molppm	PGC 302 edition II or Advance MAXUM
			H_2O	0 ... 2 molppm	NA
			O_2	0 ... 5 molppm	NA

Table 3 List of sampling points (ref. fig. 1), measuring conditions and analyzers

MP	Measuring point location	Measuring task	Measuring component	Measuring range	Measuring equipment
28	Before Butene-1 unit	Product stream control	CH_4 C_2H_2 C_2H_6	0 ... 1000 molppm 0 ... 10 molppm 0 ... 1000 molppm	PGC 302 edition II or Advance MAXUM
			CO CO_2	0 ... 2 mol ppm 0 ... 5 molppm	PGC 302 edition II or Advance MAXUM
			NH_3	0 ... 1 molppm	NA (MIPANQ)
			MeOH PrOH Carbonyl	0 ... 1 molppm 0 ... 1 molppm 0 ... 1 molppm	PGC 302 edition II or Advance MAXUM
			H_2O	0 ... 2 molppm	NA
			O_2	0 ... 5 molppm	NA
29	PSA unit	Crack control	CO	0 ... 5 molppm 0 ... 100 molppm	ULTRAMAT 6F Ex
30	Chilled water system	Plant safety control	HC C3,C4		ULTRAMAT 6F Ex
31	Fuel gas to furnaces	Fuel quality control	Density	0 ... 5 kg/m^3	NA
32	Butene-1 unit	Product stream control	CH_4 C_2H_4 C_2H_6 C_4H_8	0 ... 3,5 Wt% 0 ... 1000 Wt% 0 ... 5 Wt% 0 ... 50 Wt%	PGC 302 edition II or Advance MAXUM
33	Butene-1 unit	Product stream control	C_2H_4 C_2H_6 C_4H_8 C_4H_{10} (N) C_6H_{12} (M) C_6H_{12} (E)	0 ... 500 ppmWt 0 ... 100 ppmWt 0 ... 1000 ppmWt 0 ... 5000 ppmWt 0 ... 100 ppmWt 0 ... 100 ppmWt	PGC 302 edition II or Advance MAXUM
34	Boiler feedwater/condensate system	Steam system control	TOC	0 ... 10 molppm	NA
35	Boiler Stack	Emission control	CO NO (NO_2) O_2	0 ... 5000 molppm 0 ... 1000 molppm 0 ... 10 mol%	ULTRAMAT 23
36	Boiler combustion control	Combustion control	O_2	0 ... 10 mol%	Zirconia probe
37	Fuel gas to boiler	Fuel quality control	Wobbe ind.		NA
38	Boiler feedwate/condensate system	Steam system control	diss. O_2	0 ... 100 microg/l	SIPAN
			pH	6 ... 12 pH	SIPAN
			Conductiv.	0 ...350 microS/cm	SIPAN
39	HP-steam	Steam system control	diss. O_2	0 ... 100 microg/l	SIPAN
			pH	2 ... 12 pH	SIPAN
			Conductiv.	0 ...10 microS/cm	SIPAN
40	Boiler feedwate/condensate syst.	Plant safety control	TOC	0 ... 5 molppm	NA
41	Clean water system	Personel safety	Cl residue	0 ... 5 molppm	NA
42	Clean water system	Personel safety	HC	0 ... 5 molppm	FIDAMAT
43	Wasserfilter	Watersystem control	Conductiv.	0 ... 1000 microS/cm	SIPAN
44	Air separation unit	N_2 control	O_2	Traces	NA
45	Waste water system	Environmental control	pH	pH 2 ... 12	SIPAN
46	Waste water system	Environmental control	Turbidity	5 ... 1000 NTU	NA
47	Boiler feedwater/condensate syst.	Plant safety control	TOC	> 5 ppm	NA
48	Boiler feedwater/condensate syst.	Plant safety control	Conductiv.	0 ... 350 microS/cm	SIPAN
49	Waste water system	Environmental control	Diss. O_2	0 ... 8 mg/l	SIPAN

Table 3, continued

The **PGC 302 edition II** is a dual-channel single or double-oven gas chromatograph desig-ned for installations in hazardous and non hazardous areas. Its double-oven technology, a large selection of detectors, separating columns, and evaluation methods as well as its valveless column switching makes the PGC 302 an extremely powerful and flexible chromatograph.

Features PGC 302 edition II	Benefits
Single or double-oven device with one or two channels for use in areas with or without explosion hazards	Optimum adaption to actual analysis tasks Extremely cost efficient
Can be retrofitted to include second oven	Low-cost expansion capability
5 detectors, including highly sensitive HID for measuring traces in high purity gases	Highly flexibel for optimum adaption to actual analysis task
Several evaluation methods, including area normalization, internal and external standard, 100% method	Extremely precise analysis results
Valveless column switching function	Greater analysis capabilities, lower maintenance requirements

Table 4 PGC 302 edition II features and benefits

SIPAN features	Benefits
All from one hand: Analyzers in 2- and 4-wire technology, with and without Ex-protection, sensor and fittings	Flexible engineering, low installation requirements, branch specific solutions even for critical applications and in corrosive sample streams
Extensive diagnosis functions Logbook Redundand measurement	Cost reduction by extended maintenance and calibration periods. Extended operatioanal reliability by alarm/pre-alarm status signals Documentation of important events
Individual and user specific temperature compensation	Highest measuring accuracy even for lowest conductivity ranges because of non-linear temperature calibration line
Remote switching of measuring parameters (4 sets)	Highest dynamic range, accuracy and flexibility, very simple parameterization
HART communication and interface to PROFIBUS PA/Simatic PDM	Offline parameterization from the office desk, extended functionality and diagnosis. Sensor, measuring ranges etc. can be parameterized

Table 5 SIPAN liquid analyzer features and benefits

SIPAN stands for the extensive family of Siemens liquid analyzers, available in 2 and 4 wire technology, for hazardous and non hazardous areas, for measurements of pH, conductivity, ORP, and dissolved oxygen, as plug-in unit or in field housing. With interfaces to both HART and PROFIBUS SIPAN offers acces to the two leading field communication technologies in process industry.

Fig. 4 SIPAN Liquid Analyzer

User benefits

Process analyzers in an ethylene plant are of extreme importance for correct, efficient and safe plant operation. The analyzers themselves must be of very high quality and reliability and their integration into the plant requires a high level of know how and engineering expertise.
With this in mind Siemens can provide the user with outstanding performance and value, because

- most of the analyzers required are manufactured by Siemens and known for their utmost quality and
- Siemens as analyzer system and analyzer house supplier has solved the etylene (steam cracker) application several times successfully and has thus achieved intensive experience.

Fig. 5 Process Gas Chromatographs PGC 302 edition II (left) and MAXUM (right)

Siemens AG
Automation and Drives Group (A&D)
Process Automation and Instruments
D-76181 Karlsruhe
Tel. (+49) 721 595-38 89
Fax (+49) 721 595-39 50
http://www.processanalytics.com

Siemens Aktiengesellschaft
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