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Improved process analytics at the ethylene plant by upgrading to online mass spectrometry (MS)

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Introduction

Ethylene (C_2H_4, also known as ethene) is the most used petrochemical product; its reactive double bond makes it the ideal building block for more downstream products than any other. In 2026 global ethylene production stands at around 200 million metric tons annually.[1] Driven by demand for plastics, single-use packaging, and consumer goods, this production is forecast to continue to grow at an annual rate of ~6% in the period to 2035.

The value of ethylene varies substantially by region: The gulf coast of the USA has much lower production costs due to the abundant availability of low-cost shale gas, while Europe by contrast is characterized by high regional energy prices. The result is that prices of USA-produced ethylene stand at ~$600 per MT while the same product in Europe has a price exceeding $1,300 per MT.[2]

In Europe the feedstock is predominantly naphtha, and this carries a significant penalty as the price of naphtha tracks global crude oil prices. This means European producers absorb the full impact of geopolitical oil price spikes, keeping their core raw material costs heavily elevated.

While the USA has an advantage in terms of production margins, these margins are only around $200 per MT,[3] and margins are roughly half of this in the European market. In Asia, where there is a glut of supply, the margins are barely positive at all. Clearly, operating efficiency during production is essential to making ethylene production profitable.

The ethylene process

Ethylene production typically takes place in an olefin furnace that is also used to produce other hydrocarbons in the olefin family, including propylene (C_3H_6) and butadiene (C_4H_6). The hydrocarbon feed is pyrolized, or "cracked," with steam at a high temperature, between 750°C and 900°C (1,382°F and 1,652°F), and high pressure, between 175 and 240 kPa, in a series of tubular furnaces. Two main types of feedstocks are used:

Gas feed (ethane, propane)

$C_2H_6 \rightarrow CH_2{=}CH_2 + H_2$

Liquid feed (e.g., naphtha)

$C_nH_{2n+2} \rightarrow CH_2{=}CH_2 + C_3H_6 + C_4H_8 + C_nH_{2n+2}$

Residence time in the furnace is extremely short, typically 0.08 to 0.25 seconds.

Process control requirements

A variable known as cracking severity, which is largely a function of furnace temperature, determines the type of olefin produced. Higher temperatures favor ethylene, while lower temperatures favor propylene and butadiene.

The energy transfer through the furnace coils is determined by the burner firing rate and the furnace draft pressure. The plant can therefore operate on a campaign basis, producing various olefins based on market demands, feedstock costs, and energy prices.

The furnace effluent product stream is quenched in a heat exchanger. It contains a range of eight to twenty components, including the desired product. Several additional refining and purification steps then take place, but it is the furnace effluent that defines not only the product yield, or slate, but the total plant efficiency and the amount of fuel consumption. It essentially drives the overall profitability of the entire complex.

Key control parameters

Steam-to-carbon ratio

The ratio of hydrocarbon to steam fed into the furnace plays a major role in furnace optimization. Steam acts as a diluent that impacts the reaction selectivity. Steam also continuously reacts with solid carbon deposits inside the radiant coils actively cleaning these tubes during normal operation.[4] The generation of steam is also a costly endeavor; excess steam consumption wastes valuable fuel gas and adds operating costs with no benefit to plant output. Additionally, rising carbon taxes and the financial impact of emissions trading schemes strongly incentivize ethylene producers to limit the burning of fuels that generate carbon emissions.

Coil outlet temperature (COT)

The COT is the key factor in defining the cracking severity of the furnace. It plays a vital part in real-time optimization (RTO) and advanced process control (APC) systems. Adjusting COT is a balance between maximizing production and protecting furnace equipment. Automated systems manage this adjustment using several operational levers including fuel gas pressure and flow, feedstock flow rate, draft and excess air control, and the distribution of heat among the floor and wall burners. Traditionally the furnace effluent gas analysis provided by gas chromatography (GC) was available only at several-minute intervals due to the cycle time of GC. Even with an individual GC instrument dedicated to each and every furnace, this lag time means that cracking severity would be controlled by use of a COT bias derived from a comparison of the actual COT and calculated COT in an open loop mode (reliant on internal predictions rather than measured effluent concentration data). Switching to the ultra-fast analytical system of mass spectrometry (MS) allows the multi-variable predictive control models to receive actual effluent concentrations in very short intervals enabling closed loop control. Figure 1 shows the basic schematic of the closed loop COT correction with MS providing the full effluent stream gas compositions.

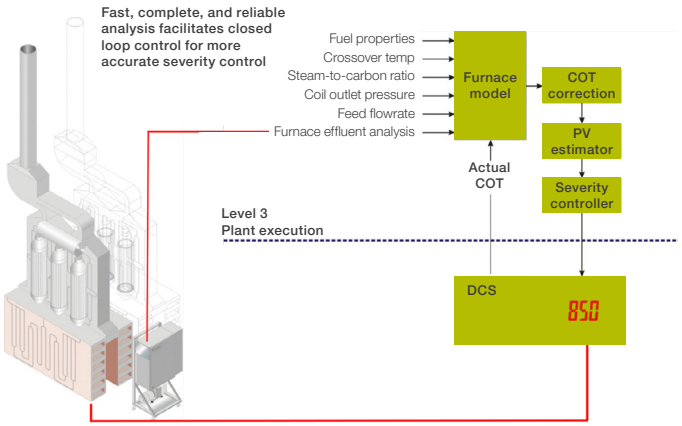


Figure 1. Closed loop COT correction by mass spectrometry.

Selectivity

The furnace needs to be able to switch output between the various olefins quickly and efficiently. Traditionally, ethylene was the most important product, but ethylene plants increase their profit margins through the production of propylene. Measures of ethylene, propylene, and butadiene concentrations in the furnace effluent define the plant's selectivity. This selectivity can be related to the severity of the pyrolysis reaction. For liquid feedstocks such as naphtha, this may be determined by measuring n-pentane in the feedstock and the furnace effluent. The feedstock analysis is typically performed off-line, whereas the furnace effluent is measured on-line. n-Pentane is usually selected since it is present in most light liquid feedstocks and cannot be formed in the pyrolysis of other compounds in a side reaction. The dissociation of n-pentane represents the cracking

severity and is defined as the natural log of the inverse of 1-σ, where σ is the n-pentane conversion factor.

Real-time optimization (RTO) models change severity set points considering feedstock analysis, feedstock costs, market conditions, or downstream requirements.[5] These are tracked through a measure known as kinetic severity function (KSF), which combines multiple metrics into a single value. Here are some examples of kinetic severity functions and their applications:

KSF	= 1.7	maximize propylene
	= 2.3	maximize butadiene
	= 2.7	maximize combined olefins
	= 3.9	maximize ethylene

Coking rate

Coke forms when hydrogen atoms are removed from hydrocarbon radicals, leaving a layer of elemental carbon or coke. It is the final step in a series of unwanted side reactions, beginning with dehydrogenation of ethylene to acetylene, methyl acetylene, and propadiene (MAPD). This process results in olefin yield loss and contamination to the olefin product. The by-products must be removed downstream using palladium-based hydrogenation reactors, which are expensive and difficult to operate.

Small molecules then combine to form larger structures such as cyclo-diolefins and aromatics. These structures condense during the gas phase and settle on the inner walls of the furnace tube, producing a layer of hard coke. If this coke is allowed to build up, the temperature of the furnace tube wall will rise, affecting cracking severity and potentially causing the tubes to fail.

The furnace must be taken offline for decoking, which involves the use of high-pressure air or an air/steam mixture. Shutting down the furnace not only reduces the plant's availability, but it also subjects the internal surfaces of the tubes to great stress. Optimal plant control strategies seek to minimize coke formation and predict when decoking needs to be scheduled.

One paper published in *Industrial & Engineering Chemistry Research*[6] presents a kinetic model for coke deposition during the steam cracking of naphtha. In this model, gas species concentrations in the process fluid are the primary drivers determining the rate and composition of coke formation. The model relies on the fact that different gas-phase molecules have vastly different propensities to form coke. Unsaturated and aromatic species generated during naphtha cracking act as primary coke precursors while saturated light gases contribute significantly less. Models such as this are dependent on the availability of reliable, accurate, continuous, and timely reporting of the concentrations of gas components in the furnace fluid. No modern ethylene plant operates without such gas analysis.

Furnace effluent analyzer selection

When an analyzer technology must be selected, the two principal options are GC and MS, as these are the only systems that are able to report precise effluent stream gas compositions supported by traceable calibration. However, these analyzers have very different characteristics: a process GC has a cycle time of several minutes to report a process sample of hydrocarbons, while process MS will report the same concentration data in a matter of seconds. GC has an advantage of being able to separate individual species of interest from those that are not required for analysis, so this technique can report on a subset of the gas components—MS generally needs to quantify all the components in the sample—but even this methodology leaves the GC with a cycle time typically 10 times slower than MS. Table 1 shows a comparison of furnace effluent data obtained by MS and GC. Note that the MS reports 22 components in 30 seconds and the GC reports 5 components in ~5 minutes.

While a GC could be configured to report all components in the sample stream, the cycle time of such a measurement would not be compatible with the need to follow the dynamics of the process. The GCs in this example would provide the basics for cracking severity control on a one-GC-per furnace basis. Additional GC instruments with an extended analysis method would be required to provide the complete composition measurements required by the APC model.

Using a single MS to report the entire gas compositions from multiple furnaces can significantly reduce capital investment as well as ongoing operational and maintenance costs.

Liquid feed ethylene cracker	MS mean	GC mean
Hydrogen	13.4136	
Helium	0.0011	
Methane	28.6200	28.9980
Acetylene	0.3768	
Ethylene	27.5646	26.9372
Ethane	4.7831	4.5889
Hydrogen sulfide	0.0188	
Methyl acetylene	0.2928	
Propylene	12.7321	12.9908
Propane	0.3246	0.3879
1,3 Butadiene	2.9312	
Isobutene	3.5980	
Isobutane	0.3046	
1,3 Cyclopentadiene	0.9627	
Isoprene	0.7922	
Pentene-1	0.5557	
Isopentane	0.1951	
N-Pentane	0.8675	
Benzene	0.7501	
Hexadiene	0.2226	
Hexene-1	0.4439	
Hexane	0.2489	

Table 1. Comparison of MS and GC data reported from the effluent of a liquid feed cracker. MS reported 22 species while GC reported only five.

Comparison of mass spectrometry and gas chromatography

A major olefin producer investigated the comparative benefits of GC and MS by carrying out a head-to-head evaluation. A single Thermo Scientific™ Prima™ PRO Mass Spectrometer with a 32-channel Rapid Multi-Stream Sampler (RMS) was compared against a process GC configured with two analytical ovens. Twelve furnaces were connected but only six were chosen for the evaluation based on their planned availability (see Figure 2). The GC analysis time was three minutes for limited component analysis, resulting in a total cycle time of nine minutes. The Prima PRO MS required just 30 seconds for a full component analysis, resulting in a cycle time of three minutes.

Figure 3 contains data produced during the evaluation. This chart shows the propylene:ethylene ratio (severity) reported by MS and GC analyses. Comparison of the data trends from MS and GC clearly shows how process dynamics are routinely missed by the GCs due to their much longer measurement interval while the MS effectively reports transient variations in real time.

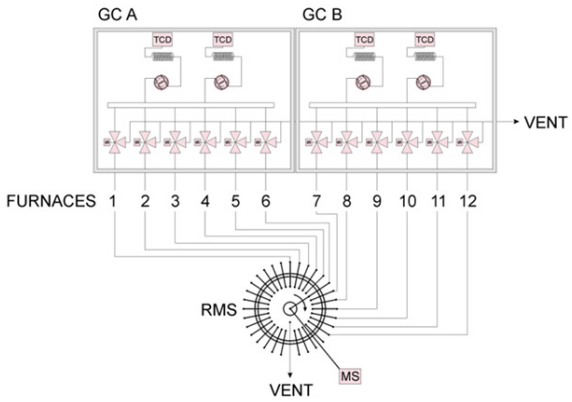


Figure 2. Setup for the evaluation of the 32-stream Prima PRO Process MS versus GCs on six ethylene furnaces.

Long-term stability study

Following calibration of both MS and CG, data were collected to determine the comparative stability of the two technologies. The results of the 17-day test can be seen in the plots of the propylene:ethylene ratios shown in Figure 4. The two analyzers tracked each other very well for the first five days then the data started to drift apart, eventually resulting in a relative error of 2.4%. By validating the analyzers against traceable calibration standards, it was found that the GC had drifted from its calibration. This difference was corrected by re-calibration of the GC.

During the 17-day period the GC generated 2,050 data points compared to 12,300 generated by the MS.



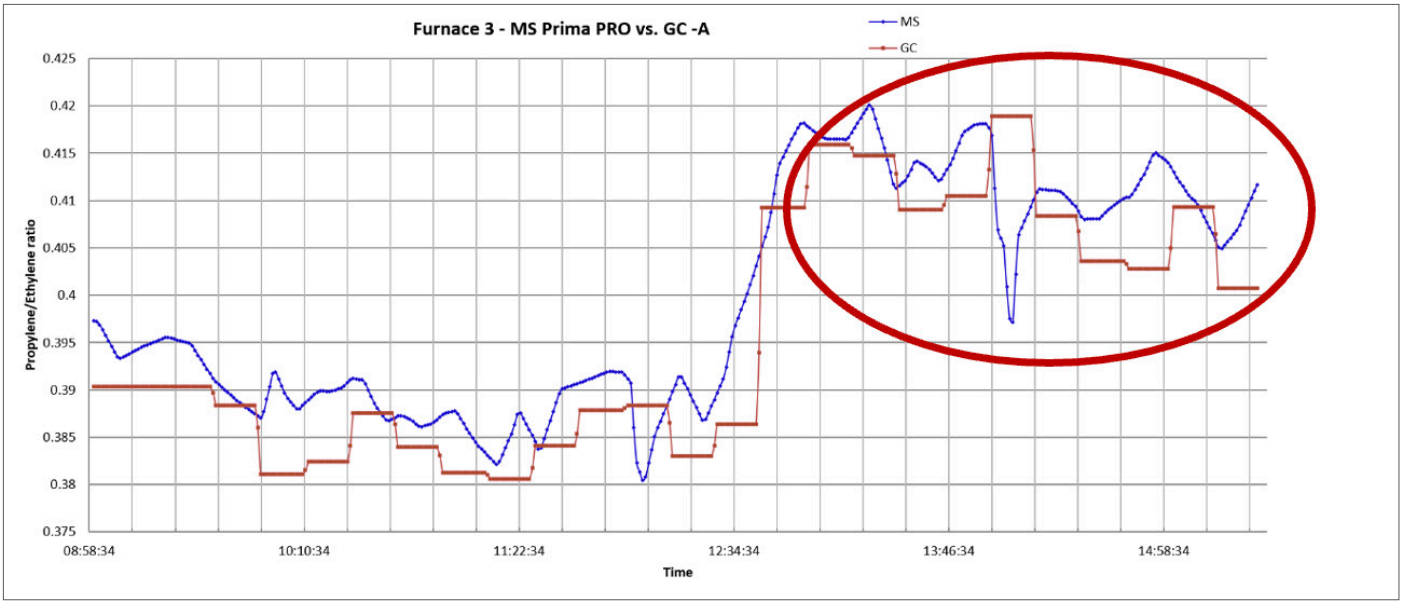


Figure 3. Propylene:ethylene (severity ratio) reported by MS and GC showing significant errors in GC data when rapid changes in cracking severity occur.

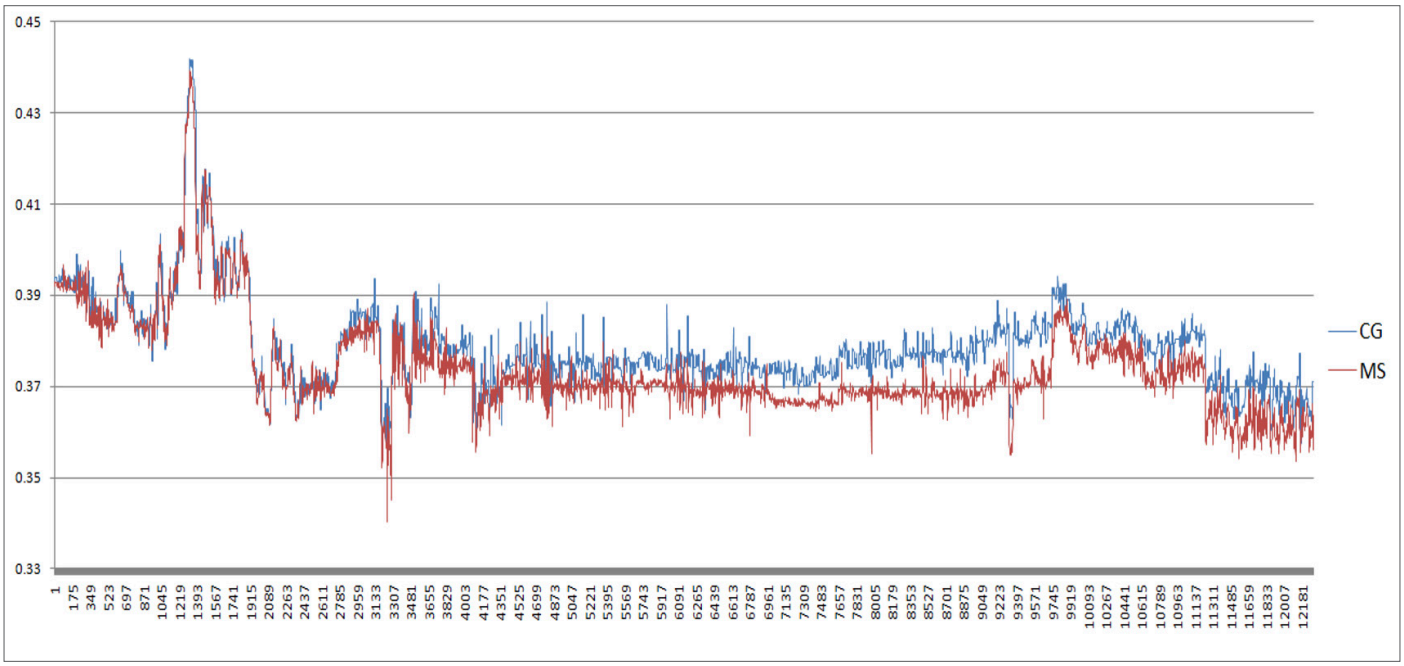


Figure 4. The results of 17 days of analysis showing the drift of GC, which was later corrected by recalibration.

Magnetic sector MS technology

The choice of MS technology is important as there are many different types of mass spectrometers. Each has its own unique characteristics. The type that has been proven over many decades to have excellent analytical performance, as well as longer periods between calibration and maintenance, is the scanning magnetic sector MS. The scanning magnetic sector MS separates positively charged ions generated from the sample gas molecules in a variable magnetic field prior to measuring the current generated by ions of each mass at a Faraday detector. The spectral peaks produced in the magnetic field have a very symmetrical shape with a flat top. The height of a peak is directly proportional to component concentration, and its flat top helps ensure consistent height measurement while being very tolerant to small variations in peak position. Figure 5 shows the design of a scanning magnetic sector MS.

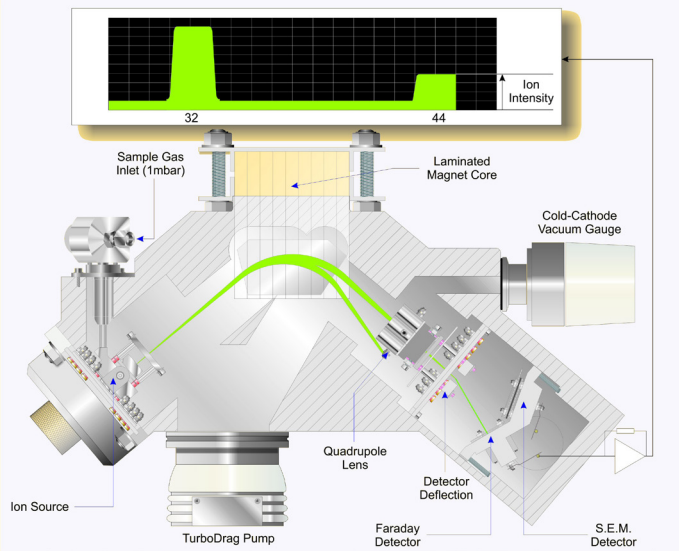


Figure 5. Scanning magnetic sector MS schematic.

Prima PRO 710 high-performance process MS

The latest process MS from Thermo Fisher Scientific is the Thermo Scientific™ Prima™ PRO 710 Process Mass Spectrometer. (See Figure 6). The Prima PRO 710 MS has the same scanning magnetic sector analyzer favored by all of the Thermo Scientific™ Prima™ series MS instruments, and it has been upgraded to include an intuitive touchscreen graphical user interface providing in-person operation, simplified maintenance, and real-time data access. Multi-role user permissions allow for enhanced security and control, allowing operators to customize settings based on their specific needs. All Prima PRO 710 analyzers are housed in self-contained temperature-controlled cabinets suitable for installation in general purpose environments or certified for operation in Zone-1 hazardous areas.



Figure 6. The Thermo Scientific Prima PRO 710 high-performance process MS. General purpose cabinet configuration is shown here.

Multi-stream sampling

A fundamental advantage of MS over GC is the very short measurement cycle time, but this can only be reliably maintained if the analyzer is equipped with a stream selector able to take advantage of this analyzer speed without failure and without the requirement for frequent maintenance. The Prima PRO 710 mass spectrometer is fitted with the rapid multi-stream sampler (RMS), which has an outstanding combination of sampling speed and reliability and allows selection from 1 of 32 or 1 of 64 streams. Stream settling times are user-configurable and can be as short as five seconds between measurement cycles. The RMS includes digital sample flow recording for every selected stream. This can be used to activate an alarm if the sample flow drops (e.g., in the event a filter in the sample conditioning system becomes blocked, the alarm would be triggered).

The RMS can be temperature controlled up to 120°C and the position of the stream selector is optically encoded for reliable, software-controlled stream selection. Temperature and position control signals are communicated to the analyzer software via the Prima PRO instrument's internal network.

The RMS is shown in schematic form in Figure 7. It has a three year warranty as standard. More than 1,000 of these stream selectors are in operation at process facilities worldwide and have consistently demonstrated outstanding long-term reliability.

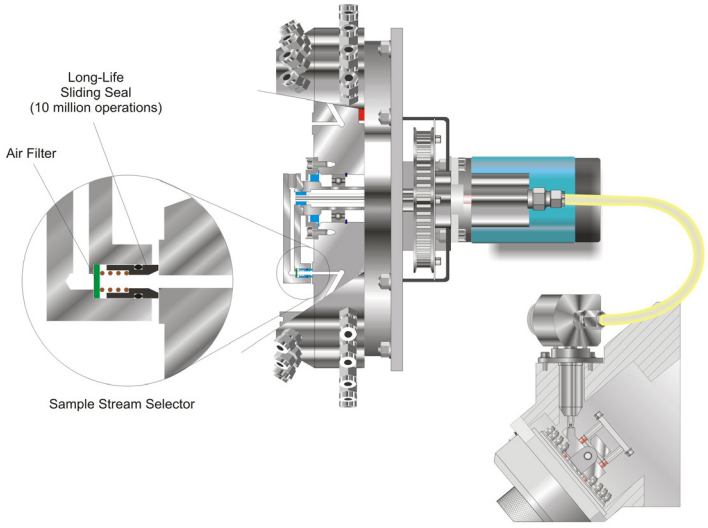


Figure 7. The schematic of the 64-stream rapid multi-stream sampler (RMS) of the Prima PRO 710 process MS.



Summary

Ethylene producers need fast, reliable on-line furnace effluent analysis to control cracking severity, optimize selectivity, and maximize profits. The furnace effluent analysis cycle time needs to be short enough to track process kinetics in this dynamic process. The installation of a single Prima PRO mass spectrometer offers analysis cycle times that are significantly shorter than that of process gas chromatography. Even when multiple GCs are used to reduce overall cycle times, the Prima PRO MS still retains a time advantage while also lowering capital investment and reducing long-term operating costs.

The Prima PRO process mass spectrometer, equipped with the rapid multi-stream sampler for fast and reliable process stream sampling, has demonstrated reliability at more than 1,000 installations in the most demanding industrial environments.

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