Application Note

Advancing Process Control and Efficiency During Ethylene Production Using the Thermo Scientific Prima PRO Process Mass Spectrometer

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Key Words

- Steam cracking
- Cracking severity
- Steam-to-carbon ratio
- Selectivity
- Coil outlet temperature (COT)
- Product slate
- Real-time optimization (RTO)
- Advanced process control (APC)
- Rapid multi-stream sampler
- Magnetic sector analyzer
- Return on investment (ROI)
- Total cost of ownership (TCO)

Introduction

Ethylene (IUPAC name: ethene) is the simplest olefin, or alkene, with the chemical formula C_2H_4. Production of more than 150 million tons of ethylene was forecast in 2012, up from 109 million tons in 2006. Approximately 60% of this stock has been used to produce polyethylene with the majority of the remaining stock used to produce ethylene oxide, ethylene dichloride and ethyl benzene.

The market price for ethylene has been extremely volatile, with average prices varying between $950 and $1,450 US per ton during the past 12 months. Over the same period, prices for naphtha, one of the main sources of ethylene, have varied between $695 and $1,080 US per ton. Based on this volatility, the ethylene production unit must respond to rapidly changing market requirements if it is to maintain or increase profitability. To achieve this goal, plants need to maximize uptime and output while operating in a safe and environmentally sound manner.

Thermo Scientific Prima PRO Process Mass Spectrometer

The Ethylene Process

Ethylene production takes place in an olefin furnace which is also used to produce other hydrocarbons in the olefin family, typically 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 to 900°C (1382°F and 1652°F), and high pressure, between 175 and 240 kPa, in a series of tubular furnaces.
Two main types of feedstock are used:

Gas feed (ethane, propane)

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

$$C_3H_8 \rightarrow CH_3CH = CH_2 + H_2$$

Liquid feed (e.g. naphtha)

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

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

There are two alternative methods that a typical ethylene plant can use for effluent gas analysis: process gas chromatography (GC) and process mass spectrometry. This application note will discuss the advantages gained by using the Thermo Scientific™ Prima™ PRO Process Mass Spectrometer for effluent gas analysis. Two benefits achieved can clearly be seen in Figure 1: the reduction of both the footprint and the maintenance required.

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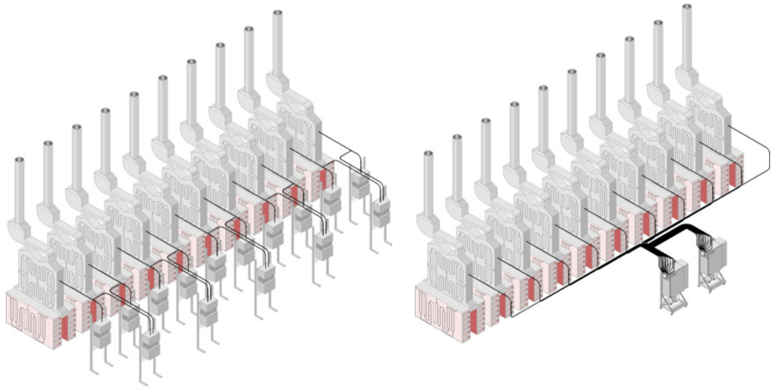


Figure 1.
Two Prima PRO Process Mass Spectrometers (right) used in place of 15 gas chromatographs (left) on ethylene furnaces for effluent gas analysis.

Process Control Requirements

The furnace temperature, also known as the cracking severity, 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 20 components, including the desired product. A number of 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 fuel consumption. It essentially drives the overall profitability of the entire complex.

Key Control Parameters

Steam-to-Carbon Ratio

Apart from the composition of the feedstock and the furnace temperature, the ratio of hydrocarbon to steam fed into the furnace plays a major role in determining the composition of the furnace effluent. This is known as the steam-to-carbon ratio.

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.

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 key propylene derivatives have grown rapidly over the last 10 years, leading to occasional imbalances in supply and demand. Measuring ethylene, propylene and butadiene concentrations in the furnace effluent defines the plant's selectivity.

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

Process Analytical Requirements

Analysis of the furnace effluent provides invaluable information to the plant's process control system:

Coking Rate: hydrogen and methane
Selectivity: ethylene, propylene and butadiene
Severity: n-pentane, iso-pentane and pentene-1

Traditionally, process GC has been used during this process but long analysis cycle times as well as frequent calibration and maintenance intervals limit the usefulness of this technique. A typical ethylene unit comprises eight to 12 furnaces and requires one GC per furnace just to provide a limited analysis of five components with a cycle time of close to three minutes. Furthermore, additional GC analyzers are required to provide a more complete analysis.

Advantages of Mass Spectrometry

Process mass spectrometers offer analysis times measured in seconds rather than minutes and the ability to measure inorganic and organic species over a wide dynamic range.

Figure 2 shows a comparison of furnace effluent analysis by the Prima PRO mass spectrometer compared to a process GC. It analyzes 22 components in 30 seconds, meaning one unit has the capacity to analyze six furnaces in three minutes. The GC is much less efficient and is only capable of analyzing five components in three to six minutes. In addition, the GC does not analyze hydrogen, butadiene or the C5 hydrocarbons, all of which are important to cracker optimization. The Prima PRO mass spectrometer is also more precise; typically around 0.1% relative compared to 0.5% relative for the GC.

Advantages of the Prima PRO Process Mass Spectrometer

While the ethylene process is a challenging application for the majority of process mass spectrometers, the Prima PRO mass spectrometer has been engineered to overcome these challenges by providing unprecedented speed and precision of analysis.

Rapid Multi-Stream Sampling

To effectively monitor all process streams, the mass spectrometer requires a fast, reliable means of switching

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

Figure 2. Comparison of Prima PRO Process Mass Spectrometer versus GC mean data during furnace effluent gas analysis.

between streams. Other technologies use solenoid valve manifolds that have too much dead volume or rotary valves that suffer from poor reliability. The Prima PRO mass spectrometer incorporates a unique rapid multi-stream sampler (RMS) which offers an unmatched combination of sampling speed and reliability and allows sample selection from one of 32 or one of 64 streams. Stream settling times are application-dependent and completely user-configurable. The RMS includes digital sample flow recording for every selected stream which can be used to trigger an alarm if the sample flow drops or if a filter in the sample conditioning system becomes blocked.

The RMS can be heated to 120°C (248°F) and the stream selector position is optically encoded for reliable, software-controlled stream selection. Temperature and position control signals are communicated via the internal network. The RMS has a unique standard three year warranty. There are no other multi-stream sampling devices that offer the same level of guaranteed reliability.

Precision of Analysis

The mass spectrometer is required to monitor a complex mixture of hydrocarbons over a wide range of concentrations. To be used as part of a dynamic plant control strategy, the data must be reliable and available.

The heart of the Prima PRO mass spectrometer is a magnetic sector analyzer which offers unrivalled precision and accuracy compared with other mass spectrometers. Both Thermo Scientific quadrupole and magnetic sector mass spectrometers are available. However, over thirty years of industrial experience have shown the magnetic sector analyzer offers the best performance for industrial online gas analysis. Key advantages of magnetic sector analyzers include improved precision, accuracy, long intervals between calibrations, and resistance to contamination. Typically, analytical precision is between two and 10 times better than a quadrupole analyzer, depending on the gases analyzed and the complexity of the mixture. A unique feature of the Prima PRO mass spectrometer magnet is that it is laminated. It scans as fast as a quadrupole analyzer, offering the unique combination of rapid analysis and high stability. This capability allows for the rapid and extremely stable analysis of an unlimited number of user-defined gases. The scanning magnetic sector is controlled with 24-bit precision using a magnetic flux measuring device for extremely stable mass alignment.

The Prima PRO mass spectrometer features an enclosed ion source that provides high sensitivity, minimum background interference and maximum contamination resistance. The high-energy (1000 eV) mass spectrometer offers extremely rugged performance in the presence of gases and vapors that have the potential for contaminating the mass spectrometer.

Direct Comparison: GC and Prima PRO Process Mass Spectrometer

A major olefin producer investigated the comparative benefits of gas chromatography and mass spectrometry by carrying out a head-to-head evaluation. A single Prima PRO mass spectrometer with a 32-port RMS was compared against a process GC configured with two analytical ovens (figure 3). 12 furnaces were connected but only six were chosen for the evaluation based on their planned availability. The GC analysis time was three minutes for limited component analysis, resulting in a total cycle time of nine minutes. The Prima PRO mass spectrometer needs just 30 seconds for a complete analysis, resulting in a cycle time of three minutes.

Figure 4 contains the data produced during the evaluation. The upper 24-hour plot represents the propylene/ethylene ratio (severity) from the Prima PRO mass spectrometer. The lower plot represents data from the GC. A three-minute mass spectrometry analysis cycle tracked furnace dynamics while the GC was unable to do the same during its nine-minute cycle.

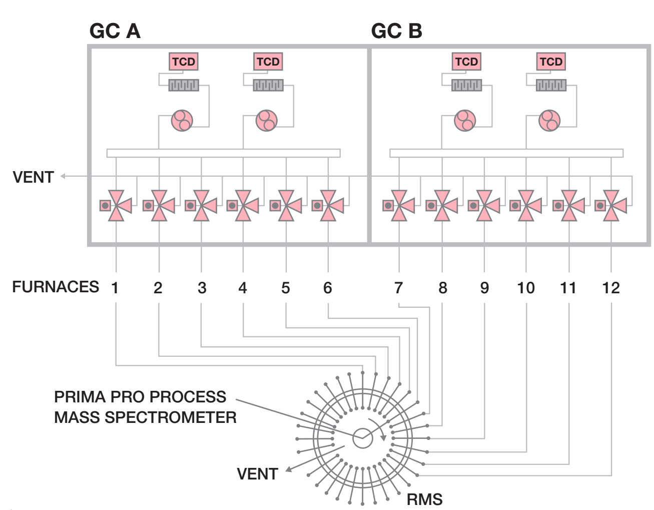
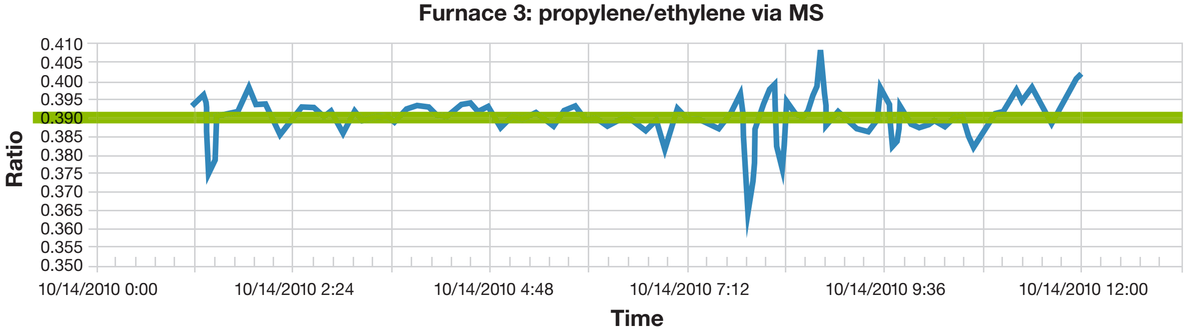


Figure 3.
Setup for the evaluation of the 32-port Prima PRO Process Mass Spectrometer rapid multi-stream sampler versus GCs on an ethylene furnace.



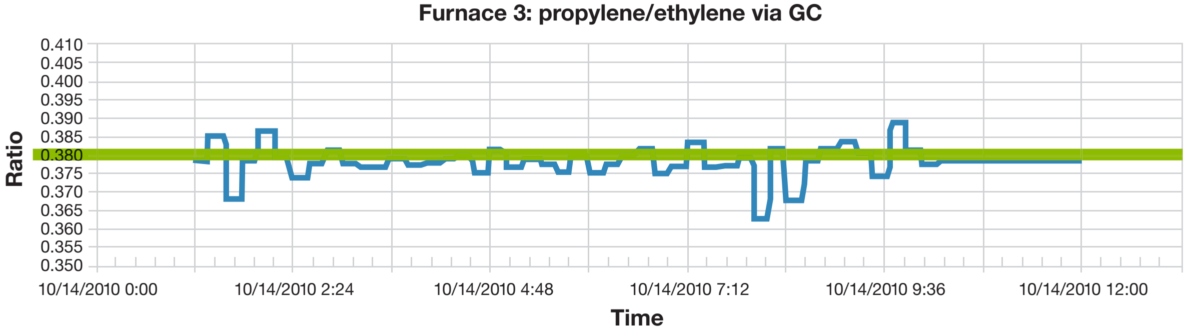


Figure 4.
Comparison of severity data that indicates the Prima PRO Process Mass Spectrometer is capable of tracking furnace dynamics within three minutes.

The GC provided average severity of 0.38 versus 0.39 which was provided by the Prima PRO mass spectrometer. During recalibration of the GC, the customer proved the mass spectrometer was correct. The GC missed a significant transient between 09:00 and 09:30 and was off-line from 10:00 for two hours. The test established a five-day calibration interval for the GC while the Prima PRO mass spectrometer remained stable and did not require recalibration for the duration of the evaluation.

Using Mass Spectrometry Data to Control the Process

The intensely competitive olefin business has led to the development of sophisticated systems to maximize plant profitability. While it is generally accepted that furnace effluent composition data plays a vital role in optimizing parameters such as COT, the poor availability, slow speed and incomplete analysis of a GC has limited its usage in plant modeling systems. COT corrections (or COT bias), which is the difference between calculated COT and actual COT, are based either on estimates of effluent composition or occasional readings at key stages in the process. The Prima PRO mass spectrometer offers a unique combination of a magnetic sector analyzer, RMS multi-stream switching and Thermo Scientific™ GasWorks software to ensure accurate, reliable data. A range of industry standard protocols enable transfer of this data to process control systems. Figure 5 indicates how the Prima PRO mass spectrometer is used for closed-loop control of COT correction.

Summary

Olefin manufacturers need fast, reliable online furnace effluent analysis to control cracking severity and to maximize profits. The furnace effluent analysis cycle time needs to be close to three minutes to track process kinetics in this dynamic process. One Prima PRO mass spectrometer offers this rapid analysis speed along with precision that is on average five times better than process GC.

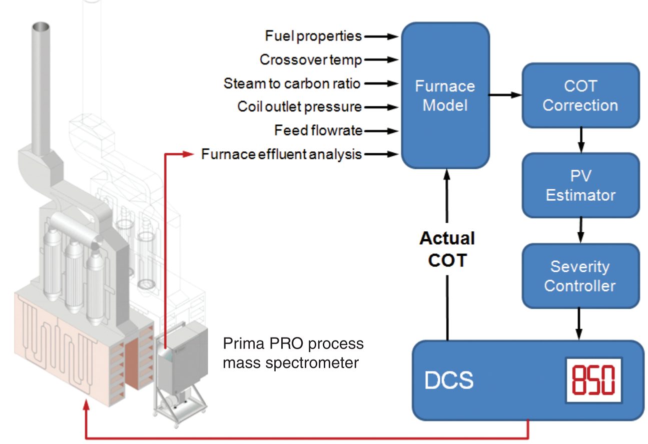


Figure 5.
Closed-loop coil outlet temperature (COT) correction provided by the Prima PRO Process Mass Spectrometer.

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