

IMPROVING ETHYLENE CONVERSION *Shortening on-line analysis cycles by using process mass spectrometry improves yields by more than 5%.*

Introduction:

Ethylene represents the single most important building block chemical in the world. It is the basic source for a large variety of industrial products, either directly as polyethylene, or after further reaction with other chemicals.

The large-scale production of ethylene is done by pyrolysis, often referred to as cracking, of hydrocarbon feedstocks in the presence of steam. A complex sequence of unit operations subsequently separates the resultant gas mixtures into their respective fractions.

The modern pyrolysis furnace represents a myriad of technological advancements. Built with fewer construction materials, consuming less feedstock, and requiring less operating manpower, today's plants deliver more than 10 times the capacity of earlier plant designs. But the severe conditions of temperature and pressure required by the pyrolysis of hydrocarbons require a serious look at process monitoring and control.

The process – which involves the complete dehydrogenation of many of the feedstock components – produces a slowly progressing deposition of coke on the internal surfaces of the pyrolysis coil. The coke reduces the heat transfer from the tubes to the gas. As a result, the hydrocarbons partial pressure between the inlet and the outlet of the coil increases over time. Any increase in this pressure drop is detrimental to furnace yields.

For the pyrolysis reactions, hydrocarbons partial pressure and temperature as functions of the coil length and time are of particular importance. The total residence time the gas spends in the pyrolysis coil of a modern furnace is generally in the range of 0.2 to 0.6 seconds. The gas outlet temperature, depending on the feedstock and furnace design, ranges from 770-880° C.

Engineers are particularly interested in controlling the pyrolysis process to maximize the conversion of feedstocks to ethylene while minimizing the stress on the furnace from coking. Achieving this requires careful control of the exit coil temperature.

Process Mass Spectrometers

The use of process mass spectrometers in place of process gas chromatographs as the on-line analysis technique offers engineers significantly better conversion control.

A process mass spectrometer completes a typical stream analysis for 13 components in 5.2 seconds and is capable of measuring unlimited number of components per stream.

Since the mass spectrometer is so much faster than the gas chromatograph, the process conversion is reported virtually in real-time. This allows for tighter control over the furnace leading to higher product yields and lower furnace stress.

Additionally, since the mass spectrometer is able to report stream data in seconds compared to minutes on the gas chromatograph, a single mass spectrometer can be used on multiple sample streams without adversely affecting the cycle time for conversion calculations. This reduces the initial cost and on-going cost of ownership for process analyzers significantly, improves data integrity by eliminating analyzer network complexity, and ultimately simplifies the installation and operation of the system.

In a normal ethylene application, a single mass spectrometer is used to analyze as many as 15 streams with a total cycle time of less than 3 minutes.

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Conversion Control

Conversion control using a mass spectrometer rather than a process gas chromatograph provides real-time measures of the furnace performance and allows for tighter control of the exit coil temperature.

In order to illustrate the dependence of conversion on exit coil temperature, a Questor™ Process Mass Spectrometer from Extrel® CMS was put on-line at the E.I. Dupont ethylene process at Sabine River in Orange, Texas. The mass spectrometer was run in parallel with a

set of 9 process gas chromatographs to illustrate the dynamic nature of the process pyrolysis and determine if the real-time analysis speed of the mass spectrometer could improve the control.

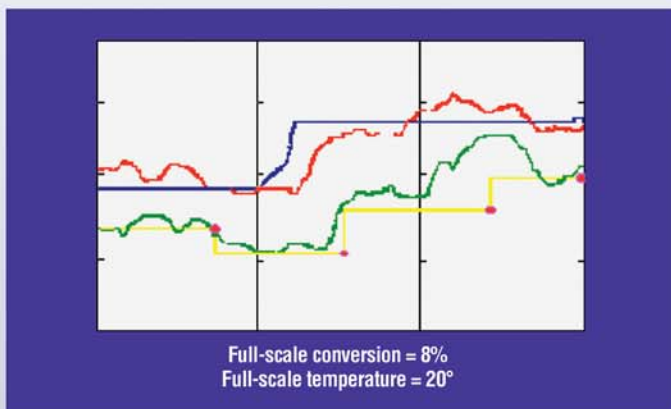
The mass spectrometer completed the analysis of all 13 sample streams in less than 3 minutes. The group of 13 process gas chromatographs completed their analysis loop in 22 minutes.

Exit Coil Temperature

The first objective was to use the speed of the mass spectrometer to determine how quickly conversion responded to a change in the exit coil temperature. There have been debates over the years that the furnace responses to changes in temperature were not immediate.

The process was stabilized at a given exit coil set point and the conversion was tracked to ensure that the process was running stable. The exit coil temperature set point was next changed and the temperature change and conversion change were tracked as the furnace moved towards the new set point.

The results of this test are shown in Figure 1. The blue line reflects the temperature set point while the red line is the actual exit coil temperature measurement. The green line represents the furnace conversion measured by the Questor process mass spectrometer. The yellow line represents the conversion measured by the process gas chromatographs.



The mass spectrometer results showed that the furnace conversion responded to changes in the exit coil temperature within 3 minutes of the set point change. This proved to be much faster than anticipated in the past.

Questor results also demonstrated that conversion tracked temperature in nearly a parallel fashion allowing for very predictable furnace behavior.

While the process mass spectrometer was able to report conversion results that directly related to the changes in exit coil temperatures, the process gas chromatographs were much too slow to adequately track the furnace performance during the dynamic change in temperature.

In fact, the process gas chromatographs failed to report the correct conversion value until the process stabilized at the new temperature set point 90 minutes later.

The significance of tracking conversion real-time under these types of dynamic conditions is realized in the turn around and start-up of the unit.

During start-ups after a turn around, the furnace is run at low feed rates. This often times leads to high conversion rates and high exit coil temperatures. At these stressful conditions the furnace coils coke very quickly, defeating the purpose of the turn around and trading valuable furnace performance. By using the mass spectrometer to track conversion real-time, the exit coil temperature and feed rates can be controlled more closely to avoid furnace stress and bring the unit to full operation more safely and economically. This is impossible under the slow control of process gas chromatographs.

Conversion Control

Once the process is at operating levels, the real-time control of the furnace in a closed loop fashion is critical to maximizing yields and minimizing furnace stress.

The speed of the mass spectrometer in reporting conversion and allowing for real-time control of the furnace is significant.

Using the Questor process mass spectrometer as the on-line analyzer improved the yields more than 5% by reducing the process variance by a factor of 2.

Under normal operating conditions, the process gas chromatographs allowed for control decisions once every cycle (22 minutes). The mass spectrometer provided the same analytical results nearly 10 times faster and allowed for control decisions once every 2.5 minutes.

Figure 2 shows the conversion tracked over 16 hours while the process was controlled in a closed loop fashion using the gas chromatograph cycle of 22 minutes.

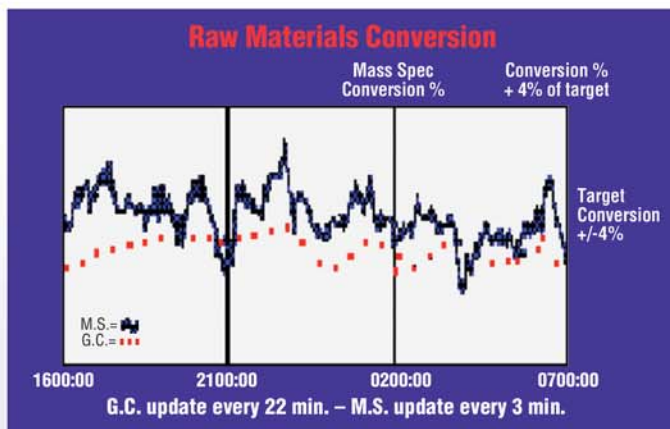


Figure 2

During this same period, the Questor process mass spectrometer was used to monitor conversion in parallel with the gas chromatographs. No control actions were based on the mass spectrometer results.

As shown by the highlighted areas, there were numerous times during the 16 hour run that the conversion values ran above and below the average set points. In many of these instances, the process gas chromatographs failed to report the swing in conversion because they occurred outside of the injection times for the chromatograph's cycle.

Figure 3 shows the same furnace as that used in Figure 2 but this time the conversion control was done using the mass spectrometer's data. The process gas chromatographs were run in parallel to monitor the conversion but their data was not used for control.

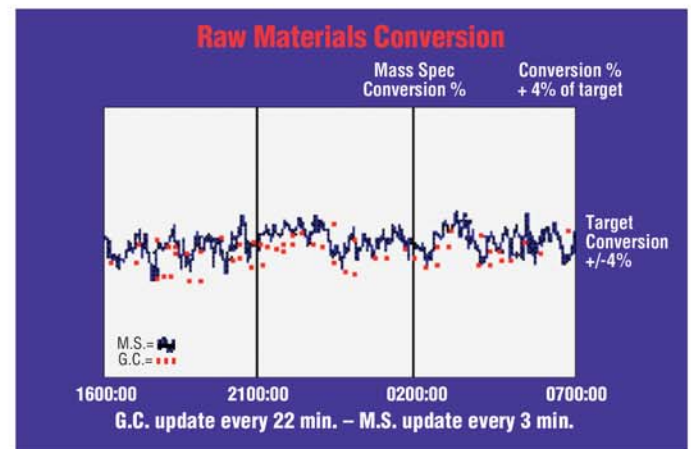


Figure 3

The difference between conversion control using the faster mass spectrometer data and the chromatography data was dramatic.

Under the faster control cycle, with no other changes, conversion over the 16 hour period was controlled at 50% of the process variance of the gas chromatographs. No dramatic swings in conversion were reported because control decisions were made in real-time with respect to the furnace residence time.

This improvement in the conversion control variance allowed for a higher set point (closer to the optimum set point) on the furnace under the mass spectrometer's cycle than that which was possible under the gas chromatograph's.

By moving up the target set point on the furnace without risking the chance of excessive coking, yields improved as well as furnace run times.

The economics of improving process yields and extending furnace run times without re-engineering the plant more than paid for the mass spectrometer.

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Sampling Systems:

The sampling system requirements for the process mass spectrometer are no different than that of a process gas chromatograph. In the examples given here, the mass spectrometer was actually installed by simply placing a tee in the sample line for each gas chromatograph and running a slip stream to the mass spectrometer.

As in any on-line analysis system, it is important to provide the instrument with a representative sample of the process.

Considerations that are important in the use of a mass spectrometer are to ensure that the gas sampler common to ethylene applications is operating properly. One of the advantages of the mass spectrometer is that it can easily monitor for heavy components such as benzene and toluene carryover in the sample conditioning system that indicate improper sampling of the process. This analysis can't be done using the process gas chromatograph because these components significantly extend the analysis time for the gas chromatograph.

Summary:

The use of a process mass spectrometer in the control scheme for today's ethylene processes offers a significant advantage over traditional process gas chromatographs.

The real-time analysis speed of the mass spectrometer allow it to replace multiple gas chromatographs reducing both the initial and lifetime cost of the analyzer system.

The real-time speed of the mass spectrometer offers a control cycle nearly 10 times faster than that of the typical process gas chromatograph. This improves the control frequency leading to tighter process variance and higher target set points under the mass spectrometer.

During start-up or dynamic process upsets, the real-time speed of the mass spectrometer is valuable for controlling furnace coking by allowing for a real-time measure of conversion.

Finally, in case studies of the Questor process mass spectrometer on the E.I. Dupont Sabine River ethylene plant, the process variance was reduced by 50%, target set points were increased, and product yield improved more than 5% under mass spectrometer control.

Typical return on investment on our Ethylene installations is within one month.

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