Optimization of reaction chemistry for efficient high density polyethylene production

The application of online process gas to HDPE production

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Introduction

Polyolefins, specifically polyethylene and polypropylene, are high-performance plastics derived from ethylene and propylene. Known for their excellent chemical resistance, durability, and flexibility, these materials are essential across a wide range of industries.

They are widely used in packaging solutions such as films, containers, and bags, offering both protection and convenience. In the construction sector, polyolefins play a key role in products like roofing membranes, insulation materials, and piping systems thanks to their resilience and long service life.

In the automotive industry, polyolefins are valued for their light weight, impact resistance, and ability to withstand harsh environmental conditions. This makes them ideal materials for components that require both strength and efficiency.

As sustainability becomes a priority, innovations in polymer processing and the development of biodegradable and recycled-content polyolefins are driving the next generation of material solutions. These developments help manufacturers and consumers meet both performance goals and environmental standards.

In 2024 the polyolefin market volume stood at $231M USD and with an expected growth rate of ~5.29% is forecast to reach $372M by 2034.

The Asia Pacific region dominates this market volume with a share exceeding 50% while Europe and North America make up most of the balance of production.

Polyolefin catalysis

The efficient production of specific polyolefins requires the development and selection of suitable catalysts. This catalyst development is an increasing endeavor by many chemical companies, involving considerable investment in research facilities for catalysis screening. Catalysis screening is carried out on a laboratory scale, using batch reactors, where the polymerization runs are short, in the order of one hour in duration. Typically, there will be multiple batch reactors in a single laboratory, so that experimental data are acquired at maximum possible rate. One important feature of batch reactions for polyolefins, which is different from the continuous processes that are used in plant production, is that steady-state conditions (in terms of ratios of key constituents) are impossible to achieve without on-line process gas analysis.

For example, in the case of polyethylene (PE), where hydrogen is used to terminate the polymer chains, when the reaction is commenced with a specific H_2/C_2H_4 concentration ratio, if no more H_2 is added to the system, the H_2/C_2H_4 ratio is rapidly depleted. The effect of this is that the polymers produced at the beginning of the run will have on average a much lower molecular weight than those produced at the end of the run. The problem is illustrated in Figure 1. This makes it impossible to develop catalysts to run under static conditions to achieve a specific polymer product. The solution is to use on-line analysis combined with system-controlled metering of H_2 introduced via a mass flow controller. This solution has been implemented in some situations, and experimental conditions where stable H_2/C_2H_4 ratios have been maintained. The result is that narrow and symmetrical distribution of polymer molecular weights are achieved. In this way, catalyst screening is being performed in a way that mimics actual steady state plant conditions, thereby generating statistically valid data for catalyst performance.

A similar effect is observed with α-olefins such as 1-butene and 1-hexene, which are used in the PE polymerization experiments to produce the required polymer grades. During production these key components are depleted, but they can be regulated at a constant ratio relative to C_2H_4 by controlled introduction based on on-line analysis.

Analogous regulation schemes (based on H_2/C_3H_6 and 1-butene/ C_3H_6 ratios) are used for polypropylene (PP) experiments. Similarly, C_2H_4/C_3H_6 can be regulated for ethylene-propylene co-polymer production.

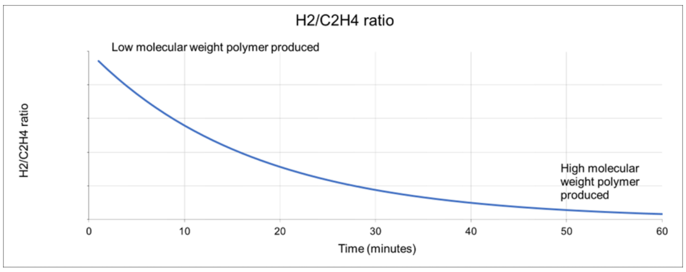

Figure 1. Hydrogen depletion and the effect on polymer molecular weight.

HDPE process data

The ultimate aim of the research referenced above is to produce a polymer with a very tight (heavy) molecular weight distribution with minimum hydrogen consumption. The experiments test different catalysts to achieve this. In this particular instance, research reactors are already working with a factor of 10 less hydrogen than the full-scale plant. Replicating the use of this new catalyst in production reactors will significantly reduce the hydrogen consumption whilst producing significantly denser polymer product. This can be verified through the use of mass spectrometry (MS). Figure 2 shows the ability of MS to measure gas species at the catalyst even at very low concentrations: the H_2 concentration is ~500 parts per million (ppm), while the concentrations of hexene-1 and hexene-2 are ~100ppm or less.

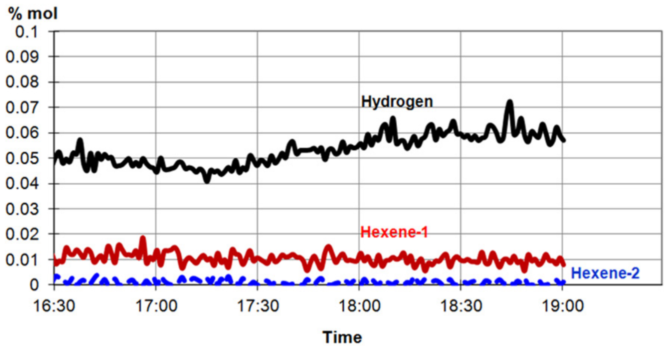

Figure 2. MS analysis of very low concentrations of H_2, hexene-1 and hexene-2.

Analyzer selection

A major polyolefin producer used gas chromatography (GC) to perform online process gas analysis. Due to the requirement for multiple reactors and shortest possible cycle times, this necessitated dedicated GC units for each reactor. However, even in this case the fastest cycle time possible was 5 minutes for analysis up to C-4 (or 8 minutes up to C-6), and regulation was found to be poor. Therefore, MS was considered, as this is known to be a very fast technique, providing typically 20x faster analysis compared with GC.

After exhaustive evaluation of two types of MS the Thermo Scientific™ Prima™ series Process Mass Spectrometer was chosen. The Prima spectrometer is an extremely precise, robust and reliable process gas analyser, of which there are over 1,500 units installed world-wide on chemical plants, pharmaceutical processes, iron and steel works, as well as in research laboratories. Before the Prima series spectrometer was selected for this application, it was evaluated in a comparative trial, where a quadrupole process MS, a process GC and a laboratory GC were also used to analyze a series of samples.

The laboratory GC had been proven to exhibit very high accuracy when tested with a number of different certified gas mixture blends. The results shown in Figure 3 indicate that the Prima series process mass spectrometer is in very close agreement to the laboratory GC. It is evident that the Prima series process MS produced more accurate data than the process GC. However, it is clear that not all types of mass spectrometers are suitable for this type of analysis: the quadrupole MS (QMS) was shown to give poor accuracy for this application; this is due to the poor and unstable response for H_2 exhibited by quadrupole systems, due the low energy of the ion beam, typically 10 eV or less. The Prima series process MS uses a very high ion energy (1000 eV) which results in very high reproducibility and accuracy.

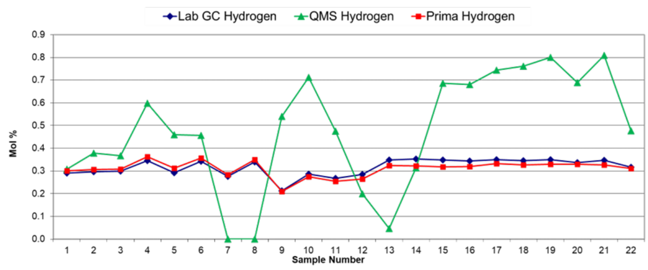

Figure 3. Hydrogen data from lab GC, quadrupole MS and Prima series process MS systems.

Comparison can also be made with the Prima series process MS and process GC, in this instance the subject molecule is ethylene. Figure 4 shows a data set of 55 analysis points from the lab GC and both MS and process GC. For consistency the MS only samples at the same rate as the GCs, but of course MS is capable of providing data at a much faster rate if required.

It is shown that there is generally good agreement with all three analyzers, with the lab GC and MS having closest alignment. The outlier is the process GC where there are several instances of data which disagree with both of the other analyzers.

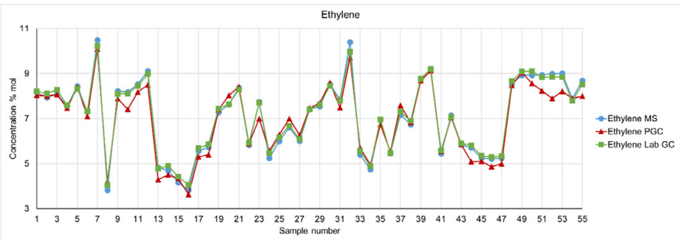

Figure 4. Ethylene data from MS, lab GC and process GC.

Magnetic sector MS technology

The choice of MS technology is important as there are many different types of mass spectrometer, and each has its own unique characteristics. The data shown in this report show that not all have the same levels of performance. The type that has been proven over many decades to have superior analytical performance, as well as the ability to go 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 ensures consistent height measurement while being very tolerant of small variations in peak position. Figure 5 shows the design of a scanning magnetic sector MS.

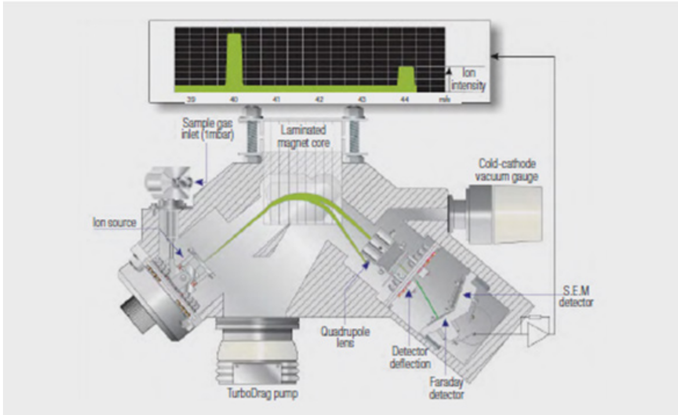

Figure 5. Scanning magnetic sector MS.

Prima PRO Process Mass Spectrometer performance specifications

Our latest model of process MS is the Thermo Scientific™ Prima PRO 710 Process Mass Spectrometer. As well as being very fast, magnetic sector MS is also very precise and able to demonstrate high precision over wide ranges of concentrations. Table 1 shows the performance specification for the Prima PRO 710 MS when measuring a complex mixture of gases common to the polyethylene production process.

Analysis cycle time is 10 seconds, with the addition of time for stream switching and purging the total cycle time for a multi-stream application is ~20s per point.

Table 1. Prima PRO 710 MS performance specification for polyethylene process gases.

	Polyethylene process stream	
	Concentration mol%	Standard deviation mol%
Hydrogen	1	≤ 0.01
Ethylene	7	≤ 0.05
Ethane	1	≤ 0.01
Nitrogen	3	≤ 0.05
n-butane	1	≤ 0.05
1-butene	0.75	≤ 0.01
Isobutane	Balance	≤ 0.05
1-hexane	0.5	≤ 0.005
n-hexane	0.2	≤ 0.005

Summary

The Prima series process mass spectrometer is an ideal system for monitoring process gases in the development of catalysts for the production of polyolefins. This technique is equally effective when moved to full-scale production.

The data generated by the Prima series MS is available in just a few seconds per sample stream and is of a very high precision. With the inclusion of a rapid multi-stream sampler (RMS), a single analyzer can be applied to multiple reactors, making this a cost-effective system with low maintenance and operating expenses.

The latest version Prima PRO 710 mass spectrometer and its predecessors have been in use for a number of years in polyolefin development and manufacturing. Users who had previously used GC for these measurements report the following benefits of MS analysis:

- Narrower and more symmetrical distribution of polymer molecular weights
- More consistent properties due to better control of comonomer
- Excellent reproducibility of trials
- Lower incidence of unreliable trials
- Faster experimental data output
- Easier analytical operation with lower maintenance

Reference

1. Polyolefin market volume and forecast 2025 to 2034, Towards Chem & Materials, May 2025, https://www.towardschemandmaterials.com/insights/polyolefin-market