Raman spectroscopic analysis of slurry polymerization

Success story Borealis' monitoring of polypropylene and polyethylene grades during olefin polymerization reactions in continuously fed loop reactors

Endress+Hauser
People for Process Automation

Challenges & results

Customer challenges

Polyolefins such as polypropylene (PP) and polyethylene (PE) are invaluable commodities in major industries. Even the slightest changes in production parameters have a significant impact on polymer properties and require rigorous process control.

Polypropylene and polyethylene are usually produced by slurry, gas-phase, hybrid or solution polymerization. Gas-phase polymerizations are typically monitored by gas chromatography (GC) which has become a commoditized technology for this type of process monitoring. However, GCs are not suitable for slurry polymerization for loop reactors or stirred autoclaves because vaporizing a liquid with high solid content (polymer powder) is difficult.

An alternative analysis technique is needed for the polymerization process of polyolefins, especially to monitor monomer and comonomer concentrations during batch polymerizations despite temperature gradients and increasing solid polymer content over the course of the reaction.

Summary of results

Endress+Hauser's Raman spectroscopy analyzer system demonstrated the potential capacity to monitor the polymerization reaction in slurries, where other gas technologies are not fit for purpose.

The results of this study confirmed that the data provided by Raman spectroscopy could potentially improve process understanding and control, with the goal of achieving specific properties of the material consistently within specification.

The next step of the project will be upscaling to plant scale, with these expected benefits:

- **Production yield:** limits off-specification material production when switching between grades and allows for faster switching
- **Production uptime:** prevent unplanned shutdowns due to close monitoring of the reaction process

Polymerization process of polyolefins explained

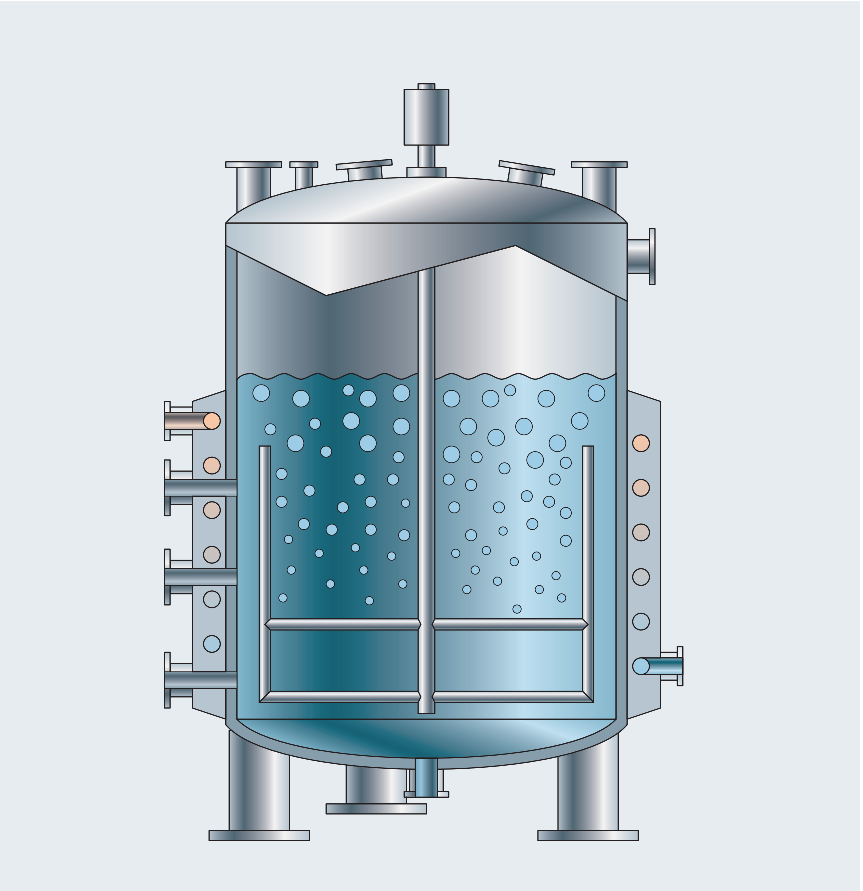
The slurry polymerization process of olefins occur in continuously fed loop reactors. Monomers (propylene, ethylene) are mixed with reactants (hydrogen) for molecular weight control, together with diluent and catalyst. Control of the depletion of reactants and formation of the polymer products over the course of the polymerization process supports the improvement of process control and product quality.

Prior to moving to process conditions, process analytical technologies are tested on small lab-scale reactors – stirred autoclaves – that are suitable for slurry and gas-phase polymerizations. Lab-scale experiments offers the ability to vary multiple parameters and acquire data for optimizing the upscale from lab to process.

Conditions are evolving during the polymerization reaction, such as significant temperature gradients in the order of magnitude of Δ 60˚ C, and an increase of solid polymer content.

The main reaction components are propylene, ethylene, hydrogen, and a catalyst. As the polymerization progresses, the liquid components are consumed and form the solid polypropylene.

Polyethylene plant in Porvoo, Finland



Lab-scale reactor – temperature controlled, designed for future upscaling to pilot plant from lab to process

Process analysis improvements during slurry polymerization

Borealis sought an innovative solution to track monomer and reactant depletion and polymer product formation in a slurry, with the goal of:

- **Increasing production efficiency:** Continuous operation and high-grade quality are crucial for the profitability of 24/7/365 manufacturing processes. Without precise monitoring, off-specification materials may be produced, especially after shutdowns or during grade transitions, leading to reduced-value sales or costly disposal.
- **Improving product quality:** Real-time monitoring of polymer output helps to keep material production in spec.
- **Reducing downtime:** A major challenge is caused by unplanned, costly shutdowns, such as when pipes become plugged during the reaction process. Enhanced monitoring of anomalies during the polymerization process can help limit such downtime.

Our solution

Borealis chose to partner with Endress+Hauser because of its established history as a trusted provider for Raman spectroscopy in ATEX environments.

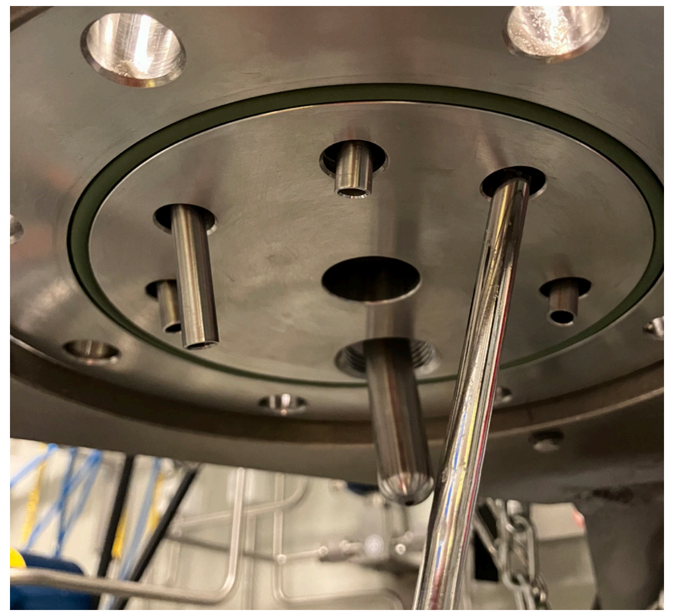
The first phase of the project was to use Raman spectroscopy at a lab-scale reactor for monitoring slurry polymerization. The test was conducted using an Endress+Hauser Raman Rxn analyzer suitable for the ATEX environment, with an immersion probe located inside the reactor. Success at the lab scale could then justify further investment and evaluate implementation at subsequent pilot and manufacturing scales.

The Raman system consisted of the following components:

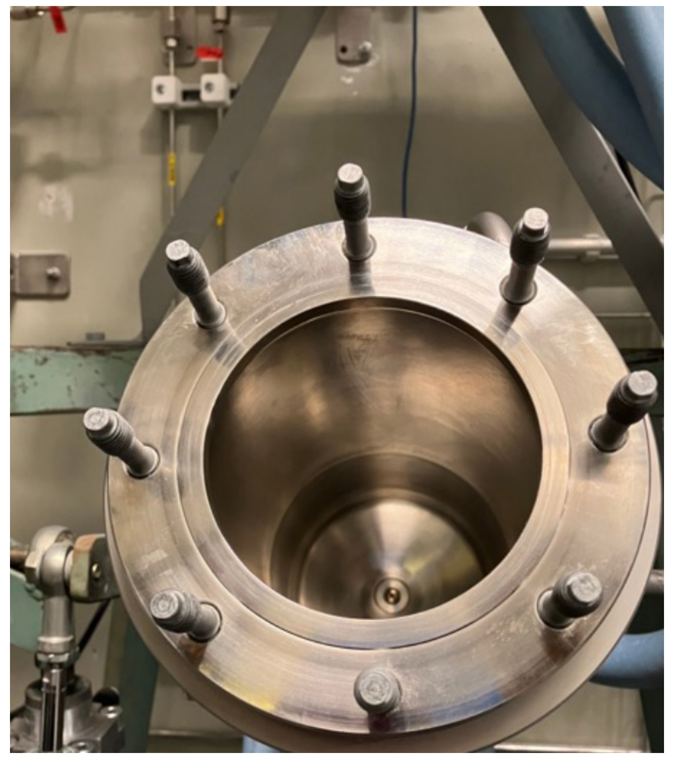
- Raman Rxn2 analyzer – 532 nm ATEX
- Rxn-40 immersion probe

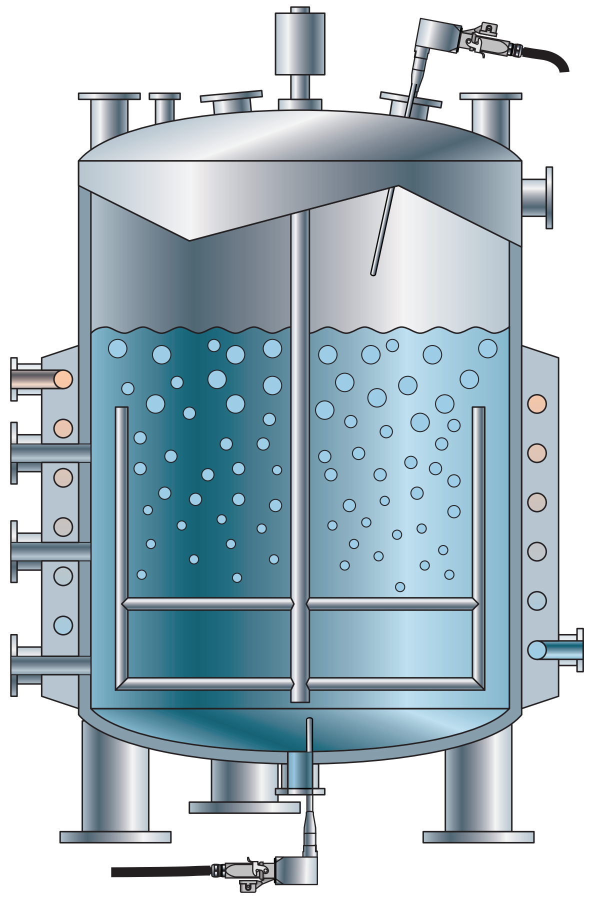
For the lab-scale reactor, Endress+Hauser advised that the placement of the probe was an important consideration, as the volume of the liquid phase tends to drop below the sampling area of the probe for a time until the additional component feeds raised the level volume back in contact with the probe tip. This challenge becomes less of a concern when scaling up to pilot or manufacturing scales since the probe will be placed in the stream.

(Top) Raman Rxn-40 probe
(Bottom) Raman Rxn2 analyzer
532 nm ATEX



The Raman probes were immersed in a lab-scale reactor designed for future upscaling to the pilot plant. With a 10m fiber cable, the Raman probes were connected to the Raman analyzer located in a controlled room.





Stirred autoclave

Endress+Hauser
People for Process Automation

Raman measurements snapshot at lab scale

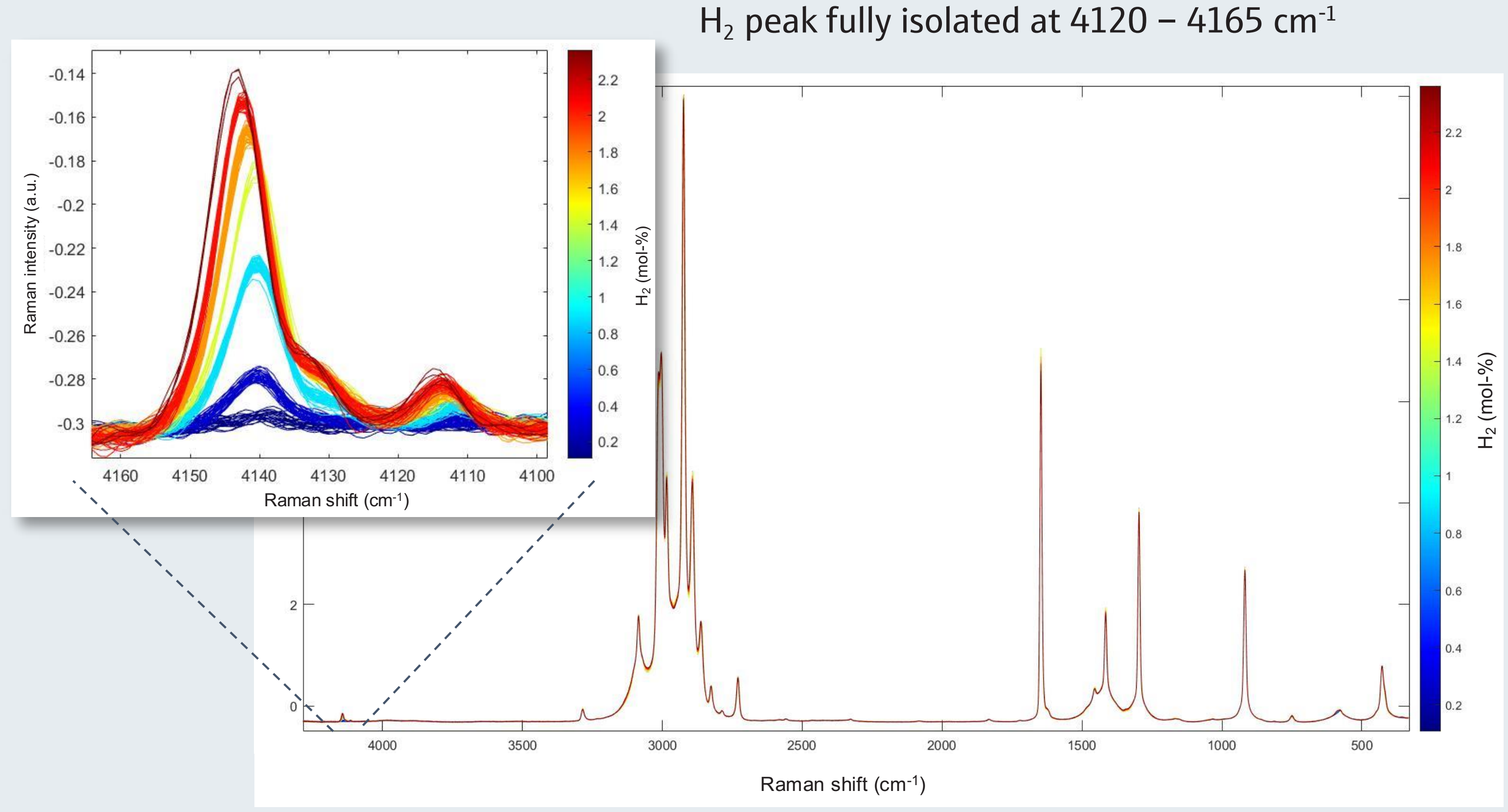
Slurry polymerization is a multi-phase (liquid, solid, and gas) mixture reaction that occurs very fast (within an hour), making it difficult to monitor in real time with a conventional technique in an ATEX environment.

Raman spectroscopy was found to be very sensitive when monitoring inline during the course of the reaction. Not only could concentrations of propylene and polypropylene be quantified, but also low-level additions of H_2, which is of particular interest for estimating the melt flow rate (MFR) governing the physico-chemical properties of the synthesized polymer.

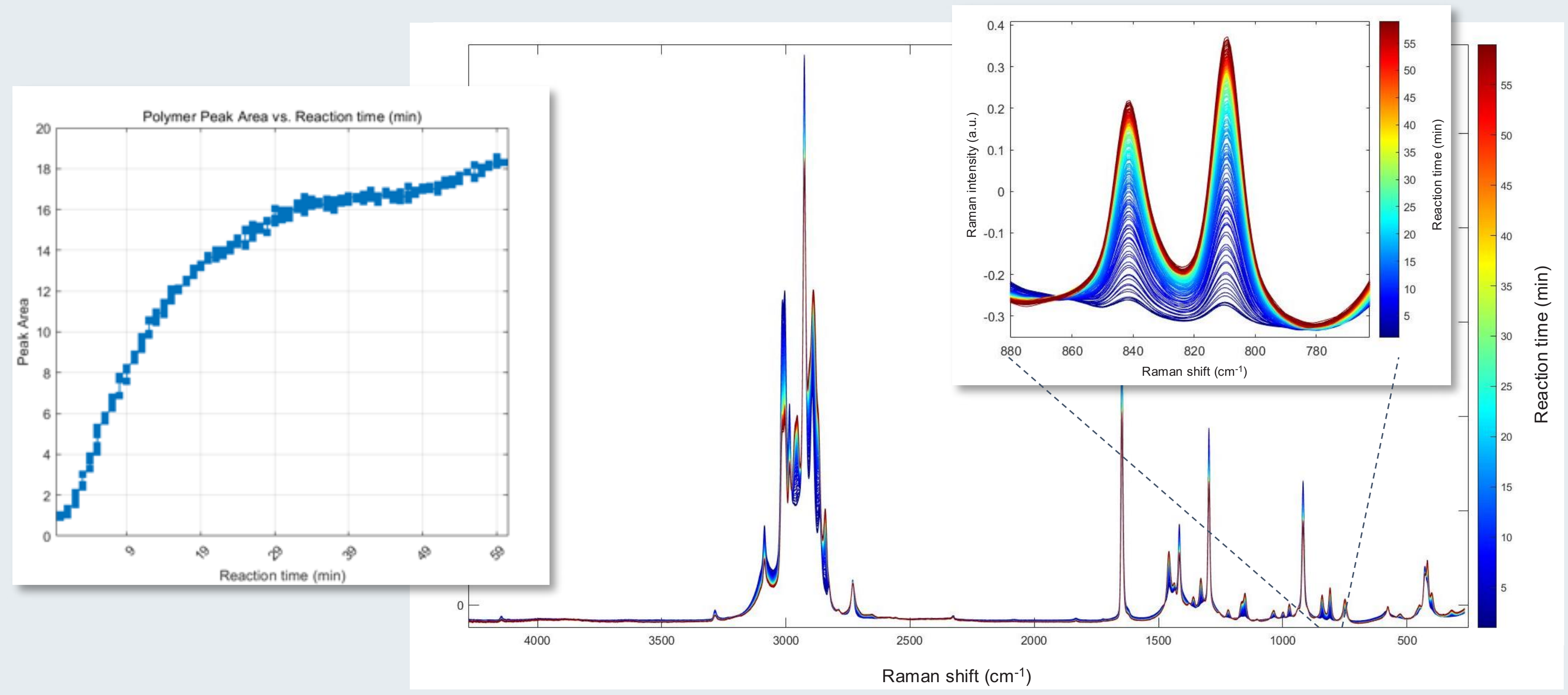
An Endress+Hauser Raman analyzer equipped with a 532 nm wavelength laser allowed the acquisition of a broad spectral range for detecting all compounds of interest in the liquid, solid and gas phases. This included high sensitivity and well-resolved peaks relevant to detect low levels of H_2 with an optimum excitation range of such diatomic gas molecules.

Borealis partnered with Endress+Hauser to support the design of experiments and corresponding data analysis for an application feasibility study at lab scale. Chemometrics such as principal component analysis (PCA) or peak area methods were used for trending. In addition, quantitative analysis was successfully performed using univariate modelling. Spectral data were collected and modeled to simulate the monomers' addition, polymer formation, and H_2 addition during polymerization.

H_2 peak fully isolated at 4120 – 4165 cm^{-1}



Raman spectra with different H_2 concentrations during a polymerization reaction



Raman spectra monitoring polymer formation within 60 minutes

Polymer band at 780– 875 cm^{-1}

Conclusion

Endress+Hauser Raman spectroscopic analyzer systems offer real-time, non-destructive measurements in a slurry mixture for process characterization and feedback control. Results confirmed the potential for using Raman spectroscopy to improve process understanding and control, with the aim of achieving specific properties of the material consistently within specification.

Success at the lab scale provided justification for Borealis to further invest and evaluate implementation at subsequent pilot and manufacturing scales.

"The knowledge and know-how of Endress+Hauser to apply optical analysis in the petrochemical and polymer sectors was instrumental in improving our polymerization process development. Beyond the technology itself, the chemometrics expertise provided by Endress+Hauser's application scientists during the feasibility tests confirmed the capacity of Raman technology to measure, in situ, the chemical composition of the liquid phase in a polymer slurry. As a bonus, we are able to collect information about the polymer while it is being produced, which is inaccessible by other means.

We are now confident that the Raman solutions developed at the laboratory-scale reactor will address the upscaling challenges of plant-scale processes and will provide significant financial and safety benefits for industrial production."

Alexander Standler
Expert online gas analyzer
Borealis Polyolefine GmbH Linz, Austria

About Borealis

Borealis is one of the world's leading providers of advanced and sustainable polyolefin solutions. In Europe, Borealis is also an innovative leader in polyolefins recycling and a major producer of base chemicals. Borealis is headquartered in Vienna, Austria. The case study is based on a work performed with Borealis Polymers Oy, located in Porvoo, Finland.

Airview of Borealis location in Porvoo, Finland

www.addresses.endress.com

CS01924C/66/EN/01.24

Endress+Hauser
People for Process Automation