



**Figure 2** Activity response to sudden (orange) and steady (grey) ramps in Fe, with Na and V effects removed

equivalent of only 9,000-10,000 ppm. In this case, catalyst activity is not affected outside of the normal variability baseline. Thus, by keeping steady-state Fe equivalent below 10,000 ppm, there is minimal catalyst activity impact beyond effects from other associated contaminants such as V. Even when Fe levels rise quickly, catalyst activity can still be maintained by increasing the catalyst addition rate to keep steady-state equivalent Fe to below 10,000 ppm.

Controlled activity and operation are key to the future of operating residual feedstocks. The yield objectives for this case study, such as coke, delta coke, slurry, and other unit yields, were achieved while processing this high Fe feedstock.

## BASF

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## Pursue sustainability and improve catalyst performance with magnesium ethoxide when producing polyolefins

Polyolefins consisting of polyethylene (PE) and polypropylene (PP) belong to the top five groups of plastic materials produced globally. Two hundred and twenty million tons of polyolefin plastics are produced annually. This versatile thermoplastic boasts a wide range of end-use applications, spanning pipes, containers, automotive parts, medical devices, and more.

First commercialised in the 1930s, the growth of the polyolefin market share over the decades is due to the discovery of and subsequent improvements to catalysts. Ziegler-Natta-type catalysts, introduced in the 1950s, are still commonly used today for the production of PE and PP. With PE, Ziegler-Natta catalysts account for almost 45% of all polymerisation processes; for PP, it is 95%.

These popular catalysts, however, need a support to achieve their best performance, which is where magnesium ethoxide excels. Marrying performance and cost-effectiveness, this material can assist companies with their sustainability goals.

## Evolution of Ziegler-Natta catalysts

The second generation of catalysts for polyolefin production was introduced in the 1970s when scientists discovered the incorporation of magnesium species into the Ti-Al (titanium-organoaluminium) Ziegler-Natta catalyst. Magnesium significantly increased catalyst activity and increased the catalysts' capability to incorporate a second monomer, a high  $\alpha$ -olefin with four or six carbon atoms, into PE chains.

Ti-Mg-Al (titanium-magnesium-organoaluminium) Ziegler-Natta catalysts revolutionised the polyolefin industry. Current polymerisation processes have been designed based on this version of catalyst.

Polyolefin production can now take place with monomer and comonomer in the presence of Ziegler-Natta catalysts without the need for diluent, significantly reducing the environmental impact.

Additionally, the higher catalyst activity in the range (20,000-60,000 kg polyolefin)/(kg cat) leaves a minimal amount of metal residue in the resin, thereby eliminating the need for residue removal steps.

For PP production, a promoter known as the internal donor was incorporated into the aforementioned Ti-Mg-Al catalyst to selectively produce the useful grades of PP, isotactic PP (iPP), in combination with a second promoter known as the external donor.

## Continued benefits of magnesium ethoxide

The magnesium used in Ziegler-Natta catalyst production takes two forms: magnesium chloride ( $\text{MgCl}_2$ ) and magnesium alkoxide. The latter is mainly in the form of magnesium ethoxide (MgE, for short). In the finished Ziegler-Natta catalyst, most magnesium species exist in the form of  $\text{MgCl}_2$  through a series of chemical transformations.

Looking at propylene polymerisation,  $\text{MgCl}_2$  serves as the catalyst support and is still part of the catalyst's active components. The main composition in the finished catalysts, it utilises its unique crystal structure to disperse titanium and the internal donor, to make a highly active and highly selective catalyst for the production of desired iPP. Evonik provides proprietary olefin polymerisation catalyst components for the manufacture of polyolefin catalysts, comprising both supports and donors.

## Catlyen S

A precursor to a variety of ethylene and propylene polymerisation catalysts, granular MgE – Catlyen S 100 series is a

high-purity material. It can be utilised to conduct particle form technology to obtain the desired catalyst activity, particle size, and particle size distribution for reactor operability.

A Mg-Ti precursor solution, Catylen S 200, allows for the making of morphology in only one step, significantly reducing catalyst production cycle time and debottlenecking plant capacity without capital investment.

Catylen S 300 is a family of morphology-defined spherical MgE particles. These have particle sizes between 10 µm and 35 µm that can be commercially produced. The spherical material can undergo titaniation to become a PE catalyst or, when combined with an internal donor, can be used to produce a PP catalyst.

To enhance sustainability efforts, one of the starting materials in MgE production, ethanol, is being migrated from petroleum-derived ethanol to bio-based ethanol. Currently, half of the ethanol Evonik uses for this production comes from a bio-based source, with further expansion underway.

## Catylen D

Internal donors, essential components of the Ziegler-Natta catalyst system, provide stereoselectivity, hydrogen response, molecular weight, and comonomer incorporation capability while influencing the catalyst activity in the polymerisation of propylene. The recently developed Catylen D 2100 is a phthalate-free and non-aromatic internal donor that enables polyolefin producers to exceed the highest toxicity standards.

## Conclusion

Where would Ziegler-Natta catalysts be without magnesium ethoxide? The support precursor provides a host of performance benefits, rendering the catalyst with high activity, a smooth polymerisation kinetic profile, longer catalyst life, and better comonomer incorporation. This combination allows polyolefin manufacturers to produce value-added specialty polymers, including multimodal polyethylene and polypropylene impact copolymer.

Catylen S and Catylen D are marks of Evonik.

## Evonik Catalysts

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## Specifying waste water treatment unit biomass separation pilot test equipment

### Problem

A Texas Gulf Coast refinery performed a pilot trial testing biomass solids separation. A trailer unit for biomass separation technology was utilised for the trial. The effluent from the pilot is not pumped; it flows out of the unit by gravity. This posed a problem as the effluent from the pilot trailer needed to be routed to the existing solids separation unit a few hundred feet away at a higher elevation than the pilot trailer.

The proprietary Process Engineering ToolS (PETS) was utilised to:

Figure 1 PETS fittings equivalent lengths tool

Figure 2 PETS pipe pressure drop tool

- Size all the process lines to and from the trailer.
- Size the effluent holding tank and determine the working volume.
- Determine the pump's net positive suction head available.
- Determine the pump's required discharge pressure.
- Size a restricting orifice to provide continuous minimum flow spillback.

The speed and ease of PETS enabled the project team to find the equipment needed, get it installed, and perform a successful trial.

PETS was used to determine the fittings equivalent lengths (see Figure 1). After the equivalent length was determined, the pipe pressure drop (see Figure 2) was calculated for all the pipes required for the trial.

The tank sizing tool enabled the engineer to determine that an 8ft (2.4m) diameter and 7ft (2.1m) high tank provided sufficient residence time (see Figure 3). A minimum