Catalysts for production of polypropylene

As one of the world's largest producers of polypropylene and associated catalysts, LyondellBasell has experience that stretches back to the original discovery of Ziegler-Natta polymerization.

Developed originally for our benchmark *Spheripol* polypropylene process, and more recently extended to our state-of-the-art *Spherizone* process. *Avant* catalyst has been tailored for non-LYB technologies as well, industrially proven and commercially available for all main third parties technologies. Our *Avant* catalyst range is suitable for all major product applications.

Through its predecessor companies, LYB has and is operating different PP technologies (including solution, bulk and gas phase processes) for several decades. All our bulk and gas phase plants, whether our own in-house technologies or licensed third-party plants, use LYB produced catalysts.

Polypropylene catalyst portfolio

- *Avant ZN* - multi-purpose multi-site Ziegler - Natta catalysts for a broad range of polypropylene products for benchmark and added value applications
- *Avant M* - Single-Site catalysts for the production of specialty metallocene polypropylene products

The powerful combination of leading process technologies and cutting-edge catalysts provides important synergies. LYB as a leading process licensor and catalyst producer, has an extensive understanding of the interaction between catalysts and process technologies.

Catalyst development

LyondellBasell's fundamental catalyst research, is conducted in its R&D labs in Ferrara (Italy) and Frankfurt (Germany).

Modern Ziegler-Natta (ZN) polypropylene catalysts consist of a magnesium dichloride ($MgCl_2$) support complexted with titanium tetrachloride ($TiCl_4$) and an internal donor. The physical form of the catalyst can vary from flake to highly spherical. Through the phenomenon of replication, the polymer product formed in the reactor takes on the basic form of the catalyst.

The internal donor can be seen as the coarse tuning mechanism for product characteristics, while the external donor serves as the fine tuning. It is primarily the internal donor that determines the hydrogen response, molecular weight distribution (MWD), and the catalyst's kinetic profile.

Typically, the catalyst is combined with an aluminum alkyl to activate the active center, and an external donor is added to control selectivity. While the external donor has a more limited influence on the overall catalyst behavior, it plays a key role in adjusting the xylene solubles (XS) and fine-tuning specific product properties to meet targeted performance requirements.

Main catalyst features

Catalyst yield

Operating conditions, such as reactor temperature, pressure and hydrogen concentration influence catalyst yield. Poisons, such as water, oxygen or sulphur compounds negatively affect activity. Catalyst yield is important for product quality as well as economic considerations.

Kinetic profile

How the catalyst yield varies with both time and temperature is a key factor for cascaded-reactor performance.

MW distribution

The breadth of MWD is normally numerically described by the polydispersity index or PI. High speed fiber applications, such as spun bond or melt blown require a narrow MWD, with a PI less than 3.0. On the other hand, a broader MWD is generally favored for BOPP film, with a PI of at least 5.0.

Selectivity range

Refers to the external donor's ability to change the homopolymer XS which is normally controlled in the range of 1–5%. It is important the catalyst is highly selective with low external donor consumption to strike the correct balance between product versatility and economics.

Hydrogen response

Hydrogen is used to control the molecular weight (MFR) of the polymer. It is important for the catalyst to have good hydrogen response so the full range of products can be produced within the operating conditions of the reactors.

Oligomer content

The low MW fraction of the product is important as these light hydrocarbons may be emitted during final product processing (die-drool and fuming) and in final product application (for example food migration).

Microtacticity

Measured by NMR and usually expressed as %m-pentads, microtacticity indicates the degree of stereo-regularity in the polypropylene chain. This is a more precise indication of chain structure than isotacticity which just indicates the xylene solubility of the polymer.

Powder bulk density

The bulk density of the polymer produced is very important for the process, because it has consequences for the maximum throughput of the plant as well as for the economics of its operation. It is a complex function of internal donor characteristics, catalyst support design and operating conditions.

Porosity

The porosity of the catalyst particle plays a crucial role in polypropylene production, particularly in cascaded-reactor systems. High porosity enhances the catalyst's ability to accommodate the formation of bipolymer in the second reactor, allowing it to be effectively incorporated into the polymer matrix. This contributes to better control over polymer morphology and overall reactor performance.

Morphology

Crucial factor in polypropylene (PP) processes is the morphology of the polymer particles, including shape, average size, size distribution, and fines content. The particle size must ensure good mixing in the reactor, efficient pneumatic transport, and effective degassing. Therefore, the particle size must match the process characteristics.

Polymerization

To maintain the morphological integrity of polymer particles, pre-polymerization (initiating the polymerization reaction under mild conditions) can be applied. Some processes include in-line pre-polymerization facilities. For processes without such facilities, LYB offers a range of pre-polymerized catalysts. Overall, the use of pre-polymerized catalysts improves ease of operation by reducing polymer fines.

Major steps in catalyst industrialization

The first step in catalyst development is to investigate the basic properties of the catalysts such as hydrogen response and selectivity response. This is done in bulk phase autoclaves.

Also, kinetic investigations are done on bench-scale reactors which determine the catalyst decay and the behavior at different temperatures. This investigation is then extended to the batch gas phase fluidized bed reactors.

The next scale-up step typically is to run the catalyst in continuous bulk / gas phase pilot plants, capable of producing several hundred kg/day. Here, operational aspects such as reactor control can be tested; it also provides enough product to examine properties for the various applications.

The last step in the process is to conduct trials on a full commercial scale to confirm the pilot results and produce commercial quantities for customer trials.

Only after this rigorous testing has taken place can new catalysts be industrialized in LYB commercial lines.

Catalyst scale-up

LyondellBasell is successful in scaling-up from lab to plant due to its in-house facilities and its technical experts with sound knowledge.

R&D
- laboratory

Solutions for a better tomorrow

R&D
- pilot plant

Throughout the value chain.

Industrial plants trial

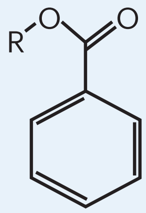
Final application

LYB catalyst chemistry range

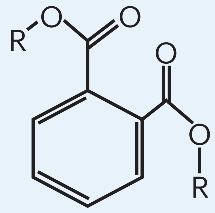
LYB offers polypropylene catalysts with four different internal donors – the benzoate 3rd generation and traditional phthalate 4th generation catalysts, as well as the more advanced diether and succinate or mixed donor catalysts of 5th generation.

Basic catalyst components

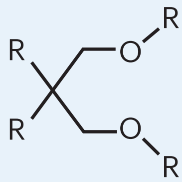
Internal Donors - Catalyst Types



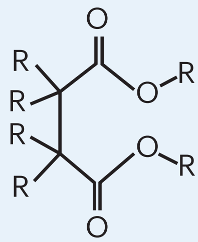
Benzoate



Phthalate

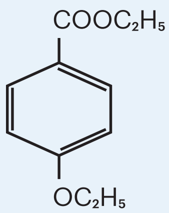


Diether

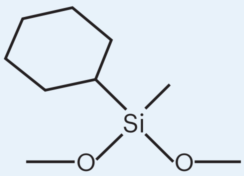


Succinate

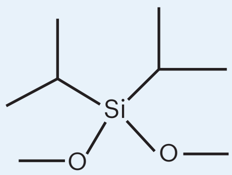
External Donors



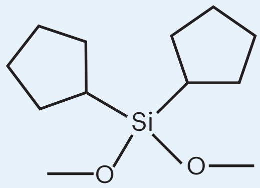
PEEB



CHMMS (C)



DPDMS (P)



DCPDMS (D)

In the early 1980s, the 3rd generation benzoate system was commercialized, but it has since become a niche market. The 4th generation phthalate internal donor, however, has become the workhorse of the polypropylene industry, with the majority of polypropylene being produced using this chemistry.

Since the early 2000s, LYB has commercialized 5th generation diether and succinate catalysts. These are increasingly popular due to their ability to produce unique products.

The latest development involves using both new diether (narrow MWD) and succinate (broad MWD) internal donors in catalyst preparation. This allows for fine-tuning the MWD of the final polymer by adjusting the amounts and ratios of the two internal donors in the catalyst. The resulting catalyst can produce a similar MWD to the phthalate-based catalysts, which were once the most widely used before the market shifted towards non-phthalate catalysts.

The primary external donors are dialkydimethoxysilanes, such as C, P and D-donor. Older ester-based donors like PEEB are now less commonly used in the industry. While not every internal-external donor combination is effective, many combinations are possible, making the overall picture quite complex.

It's also important to recognize that beyond patent protection, know-how and experience are crucial for developing newer internal and external donors.

A thorough understanding of the kinetic, mass, and heat transfer characteristics of catalysts is crucial for ensuring acceptable polymerization in any technology. The behavior of a catalyst in a reactor depends on various factors, with reactor design and the internal donor used being the most significant.

Explosive kinetic behavior can lead to the production of many fines. Diether, phthalate, and succinate catalysts exhibit slow decay, typically showing a rather linear time kinetic, allowing them to polymerize for several hours. Diether catalysts tend to deactivate as temperature increases, which is beneficial because the reaction rate decreases before reaching the polymer's melting point. This minimizes the risk of reactor chunks during upsets.

In contrast, the reaction rate of phthalate catalysts increases significantly with rising temperatures, potentially causing chunks if hot spots exist within the reactor. Succinate catalysts exhibit behavior that falls between diether and phthalate catalysts.

A comprehensive understanding of catalyst kinetic behavior is essential for ensuring optimal reactor performance.

Catalyst selection criteria

To operate an existing polypropylene (PP) line reliably and economically, operators must work within process constraints to enhance product properties using various catalyst and donor choices. Consider how these variables influence product properties.

Regarding molecular weight distribution (MWD), the polydispersity index (PI) can only be adjusted by approximately +/-0.1 in a single reactor operation by altering the reactor temperature or the external donor. However, significant changes in PI detectable by customers require a catalyst change. For example, switching from diether to succinate catalysts can increase the PI by at least two points, resulting in a substantial increase in stiffness.

Design pressure constraints often limit the maximum melt flow rate (MFR) achievable in a bulk reactor when using benzoate or phthalate catalysts. If a higher final product MFR is needed, it is typically achieved through peroxide cracking during extrusion.

Changes in the external donor can moderately increase the MFR. Diether catalysts, due to their high hydrogen response, can produce at least 100 MFR products directly in the reactor without using peroxides, leading to higher product quality.

While all catalyst systems can theoretically produce random copolymers, diether catalysts are preferred for their superior balance between ethylene incorporation and the final xylene solubles (XS) of the product.

Increasing ethylene content in impact copolymers is crucial for enhancing impact performance. This is usually achieved by increasing the catalyst's porosity, which helps retain the rubber within the polymer particle, preventing stickiness.

In summary, major changes in product properties can only be achieved by changing catalysts, while fine-tuning can be accomplished through external donors and plant conditions.

Degrees of freedom in an existing PP line

To extend prodcut properties, the operator must work within the constraints of the process, external donor and catalyst.

Property	Process	External donor	Catalyst	
Modify MWD (PI)	± 0.1*	± 0.2	± 1.5	Diether <-> Succinate
Increase reactor MFR	1.2x	1.5x	> 10x	Diether
Increase C2 content	+ 1%	+ 1%	+ 10%	High porosity

Major changes in product properties can only be achieved by selecting the correct catalyst. **Mono-modal reactor operation*

The choice of internal donor has a significant impact on the catalyst's ability to produce specific polypropylene grades, contributing to the complexity of catalyst performance.

LYB diether catalysts produce very narrow molecular weight distribution (MWD) products. These resins are ideal for applications such as high-speed, low-denier fibers or high-clarity, thin-wall injection molding grades.

Phthalate catalysts and the new mixed donor catalysts produce a broader MWD than diether catalysts and can make a wide range of standard polypropylene grades.

At the broad end of the MWD scale are benzoate catalysts, suitable for BOPP and general injection molding grades. However, their inability to produce high crystallinity homopolymers limits the product window of this catalyst.

LYB succinate catalysts produce an even broader MWD. This catalyst can produce high-crystallinity, high-stiffness, odorless products. Until now, equivalent products were only possible with cascaded reactor technology.

The LYB catalyst range covers the complete spectrum of polypropylene applications.

Comparison of LYB catalyst families

The 3rd generation benzoate catalysts are easy to operate due to their fast decay kinetics at elevated temperatures. However, the catalyst have limited hydrogen response and the catalyst yield is very low.

The 4th generation phthalate catalysts are somewhat more challenging to use but offer a wider product portfolio and higher catalyst yield compared to benzoate catalysts.

The 5th generation diether catalysts provide ease of operation and high yield advantages, along with the ability to produce a specialiazed range of products.

The 5th generation succinate catalysts operate similarly to phthalate catalysts and are favored for high-stiffness applications due to their broad molecular weight distribution (MWD).

The 5th generation mixed catalysts provide the same easy of and high yield as diether catalysts with the similar MWD as phthalate based catalyst with the ability to produce a wide range of products.

Figure 1

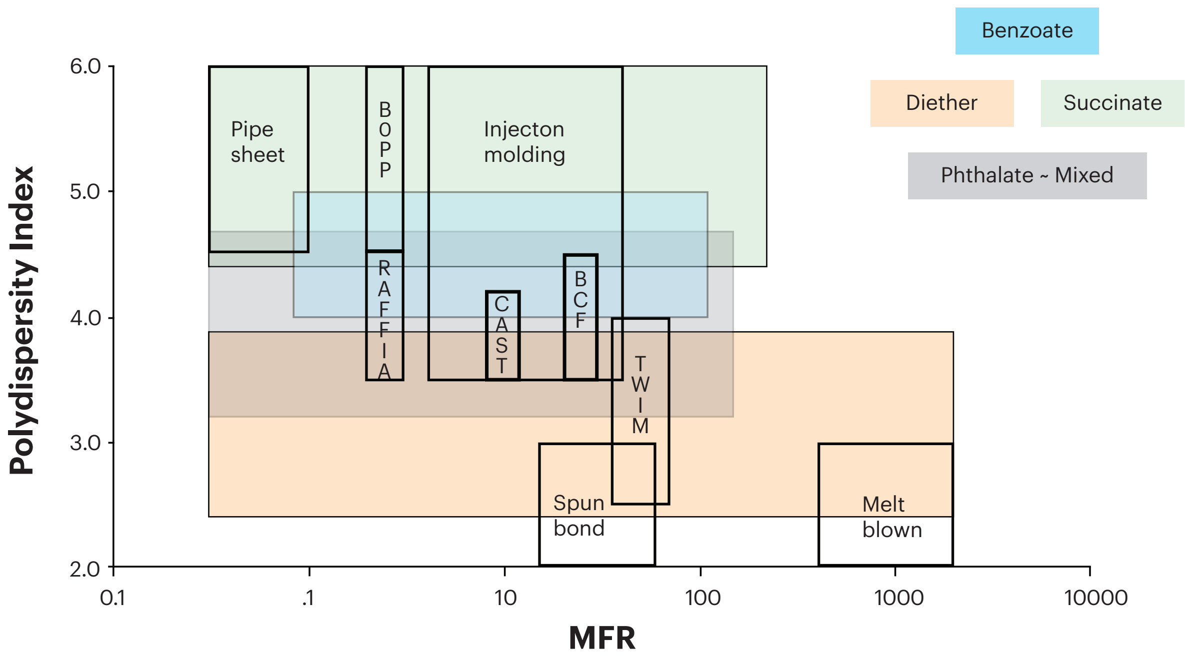
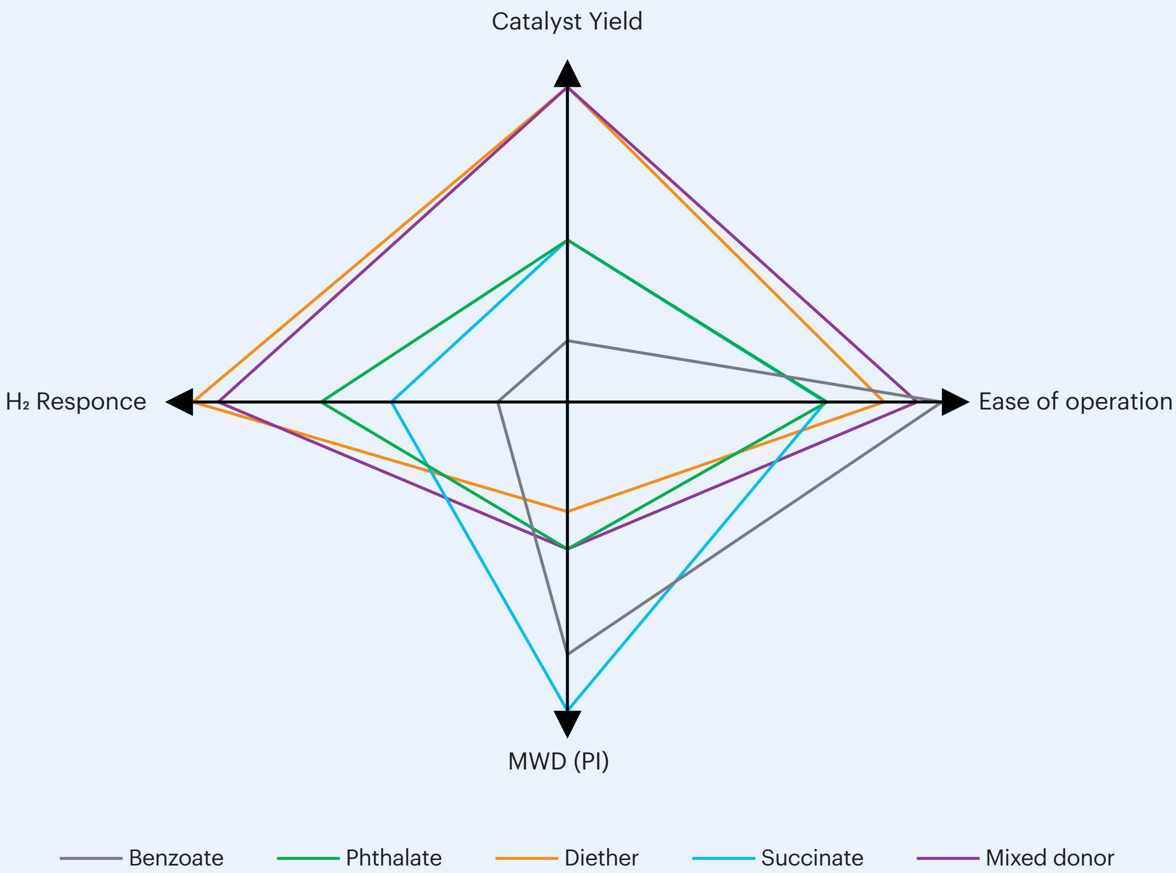


Figure 1 compares LYB catalyst families from a process operation perspective.

The latest generation of mixed donor (diether and succinate) catalysts resembles phthalate catalysts in MWD and facilitate an easy transition from phthalate to nonphthalate catalysts.

Figure 2

How to choose the right *Avant* catalyst?



The catalyst choice is a balance between PP market strategy and process capability

About LYB

LYB has a long-standing history of developing advanced polyolefin processes. Our Avant range of catalysts is specifically designed to ensure excellent operability, high yield, and a diverse range of product properties.

Different polypropylene products and processes have unique catalyst requirements. The LYB catalysts enable producers to create suitable PP powder products efficiently.

The switch to LYB catalysts is often justified by improvements in process operability, enhancements in product properties, and cost reduction benefits.

LYB catalysts are drop-in solutions and are commercially available. They are widely used in many of the polypropylene technologies currently in operation

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