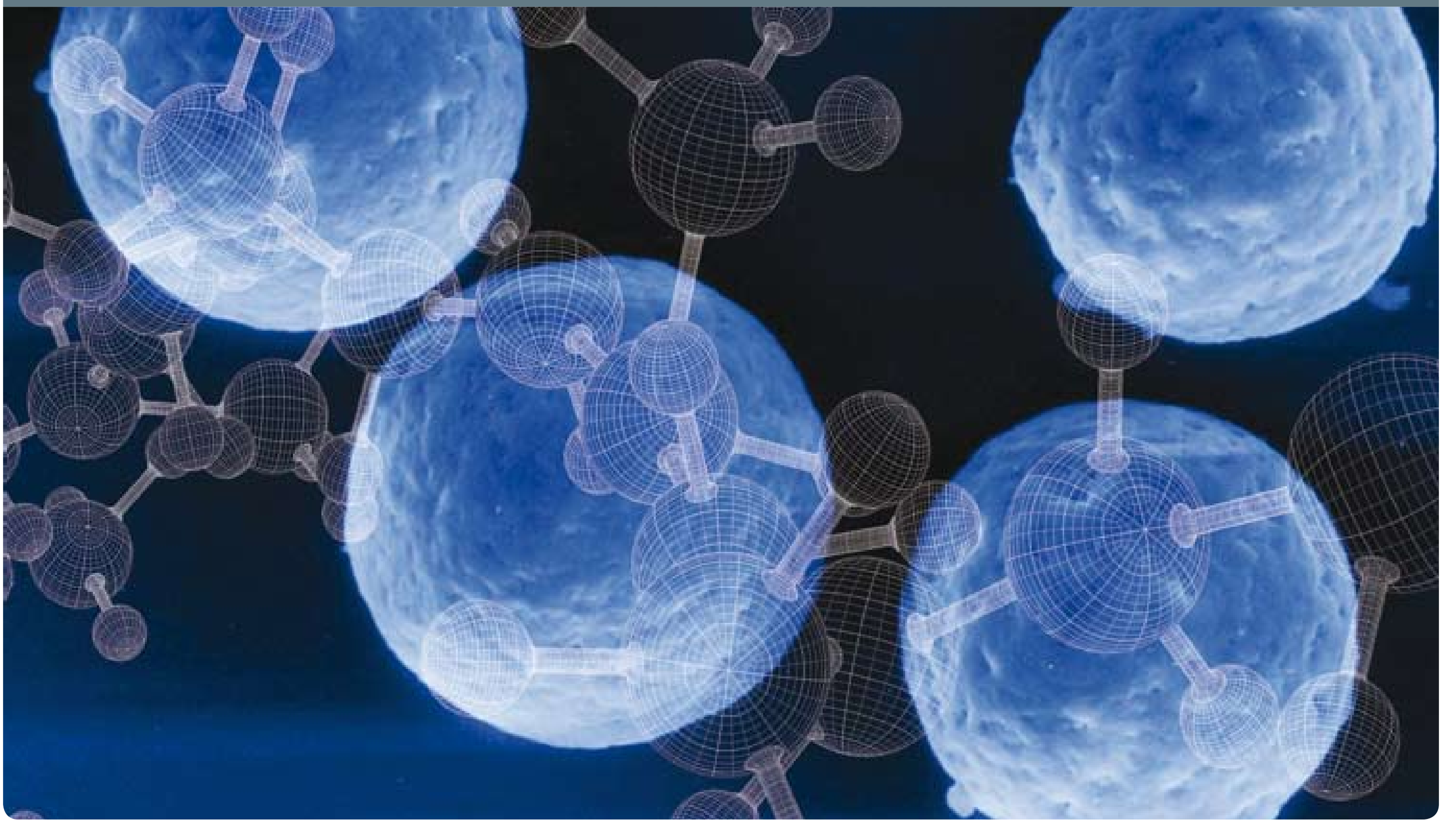
Optimized Ziegler-Natta Catalysts for Bulk PP Processes



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I. Introduction

As the world's largest producer of polypropylene (PP) and associated catalysts, LyondellBasell has experience that dates back to the original discovery of the Ziegler-Natta polymerization of olefins. Developed originally for the benchmark *Spheripol* process, and more recently extended to the state-of-the-art *Spherizone* process, the company's Avant catalyst range is used to make all the major product applications.

Polypropylene process technologies can be divided into three major categories: bulk, gas-phase and slurry processes. The majority of the world's PP production capacity utilizes bulk processes, followed by gas-phase processes and slurry processes respectively, with the latter in the process of becoming obsolete.

Within the category of bulk processes, an additional distinction can be made between the type of polymerization reactor in use – loop reactor(s) or stirred tank reactor(s) (CSTRs).

In addition to world-class *Spheripol* plants LyondellBasell has operated through its predecessor companies and joint ventures, a variety of other bulk plants for several decades. All of these plants use the company's *Avant* catalysts.

Changing the catalysts used in a PP plant requires careful consideration. This type of major change typically can only be justified if substantial benefits in product characteristics, plant throughput and/or costs can be achieved.

This brochure provides information about the variety of catalysts that are tailored for use in bulk processes other than *Spheripol*, highlighting aspects relevant to the operation of PP plants and focusing on products manufactured using different catalyst types.

Topics

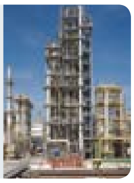
II. LyondellBasell Technology Business

Polyolefin technology licensing and catalyst manufacturing are key elements of the LyondellBasell Technology business.

Licensed Polypropylene technologies

Spheripol
Leading polypropylene technology for the production of homopolymer, random and heterophasic copolymers

Spherizone
Latest-generation polypropylene technology, based on a multi-zone reactor for the production of polypropylene and novel polyolefins

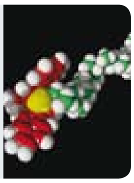


Metocene
Innovative add-on technology for the production of specialty polypropylene products using single-site catalyst systems

Polypropylene catalyst portfolio

Avant ZN
Multi-purpose catalysts for a broad range of demanding value applications

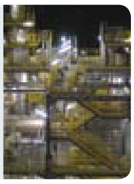
Avant M
Single-site catalysts for the production of specialty polypropylene products



Licensed Polyethylene technologies

Lupotech
Leading high-pressure tubular and autoclave processes for the production of LDPE and EVA copolymers

Hostalen
Leading low-pressure slurry process for the production of high-end multimodal HDPE



Spherilene
Advanced swing-gas-phase process for the production of LLDPE, MDPE, monomodal and bimodal HDPE

Polyethylene catalyst portfolio

Avant Z
Catalysts for leading multimodal HDPE grades in slurry technologies. Controlled morphology catalysts for full range of LLD+MD+HD products in gas-phase technology

Avant C
Chromium catalysts for a broad range of HDPE applications

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

III. LyondellBasell's PP Bulk Technology Experience*

For decades, LyondellBasell has operated plants that utilize a variety of PP bulk processes.

LyondellBasell operates three PP plants that utilize the LIPP process, which uses a CST reactor to produce homopolymer and random copolymer grades. Through its joint ventures, LyondellBasell also operates several Hypol lines which use a combination of CSTRs and gas-phase reactors, and a Showa Denka loop plant with two loop reactors. With a total capacity of 720 kt/a, the plants use LyondellBasell's *Avant* ZN catalysts.

In addition, LyondellBasell has been supplying *Avant* ZN catalysts to third -party bulk plants for decades.

* Exclusive of *Spheripol* process capacity

LyondellBasell's Experience in Bulk PP Processes

LIPP

HYPOL**

** Operated under license agreement

In 2008, global PP production exceeded 52 million tonnes. Of this quantity, approximately 55% is produced using the *Spheripol* process and other bulk processes. Gas-phase processes account for 38% of the total volume, while the remaining 7% is produced using slurry processes.

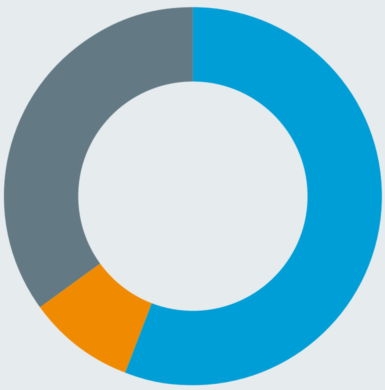
Of the bulk capacity, approximately two-thirds is produced using the *Spheripol* process and about one-third using other bulk processes.

General characteristics of bulk PP processes:

- Bulk processes use very even polymerization conditions (temperature within 0.5 °C) which translates into high product consistency.
- High catalyst yields are achieved due to very high monomer concentration.
- Hydrogen concentration is limited by either design pressure (CSTR) or solubility (Loops).
- Maximum temperature in the reactor is limited by the design pressure.

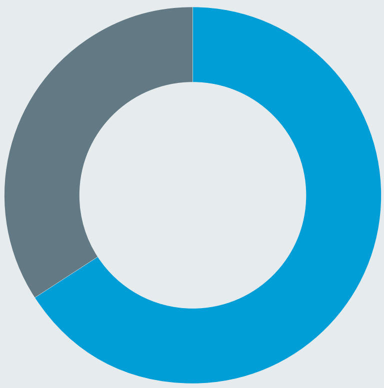
Market breakdown by process technology – 2008

2008 PP Market



Total 52.1 million tonnes
Bulk 55% **Slurry 7%** **Gas Phase 38%**

2008 Bulk Market



Total 28.5 million tonnes
***Spheripol* 66%** **Other Bulk 34%**

IV. LyondellBasell's Bulk Catalyst Range

Modern PP catalysts for bulk processes consist of a magnesium dichloride ($MgCl_2$) support, which is treated with a mixture of $TiCl_4$ (Titanium tetrachloride) and an internal donor to yield the final catalyst. The physical form of the catalyst can range from amorphous flakes to highly spherical. Through the phenomenon of replication, the polymer product formed in the reactor takes on the basic form of the catalyst. Typically the catalyst is combined with an aluminium alkyl for the activation of the active center and an external donor for selectivity control, also known as the selectivity control agent (SCA).

The internal donor is the single most important factor that determines a number of main characteristics such as activity, hydrogen response, selectivity and the kinetic profile which is very important for the operability of the plant. The external donor influences these characteristics to a lesser extent and is primarily used to control the xylene solubles (XS) of the products as well as to fine-tune product properties.

There are four catalyst families for bulk processes in LyondellBasell's portfolio, based on different internal donors:

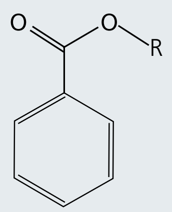
- Third-generation ethylbenzoate (EB) catalysts that were commercialized in the early 1980s.
- A catalyst family using phthalates as the internal donor; these catalysts represent the workhorse of the PP industry.
- More recently LyondellBasell has commercialized fifth-generation diether and succinate catalysts that are increasingly being used due to their operational and product property advantages.

A large number of external donors are used in combination with these catalysts. Whereas EB catalysts would typically use PEEB (para-ethoxy ethylbenzoate) as a selectivity control agent, the other families typically use dialkyldimethoxysilanes as an external donor. A large variety of donors can be used; C, P and D donors are included in the formulas shown below. In addition, catalyst systems that use mixtures of internal or external donors are used, which render the overall picture very complex.

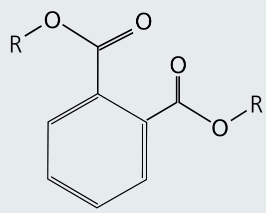
It is important to recognize that patent protection is in force for many of the newer internal and external donors.

Basic Catalyst Components

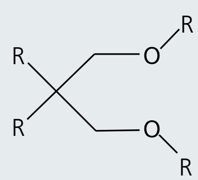
Internal Donors – Catalyst Types



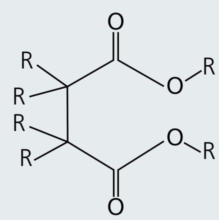
Benzoate



Phthalate

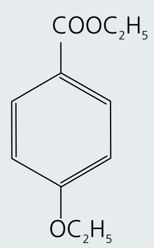


Diether

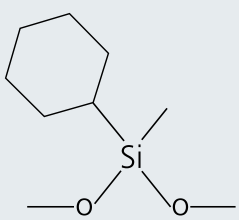


Succinate

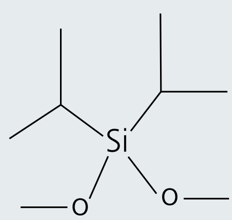
External Donors



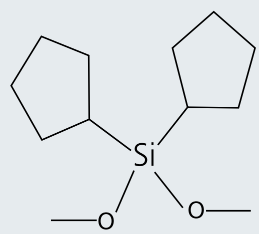
PEEB



CHMMS (C)



DPDMS (P)



DCPDMS (D)

Many internal/external donor combinations exist which affect reactor performance and product properties

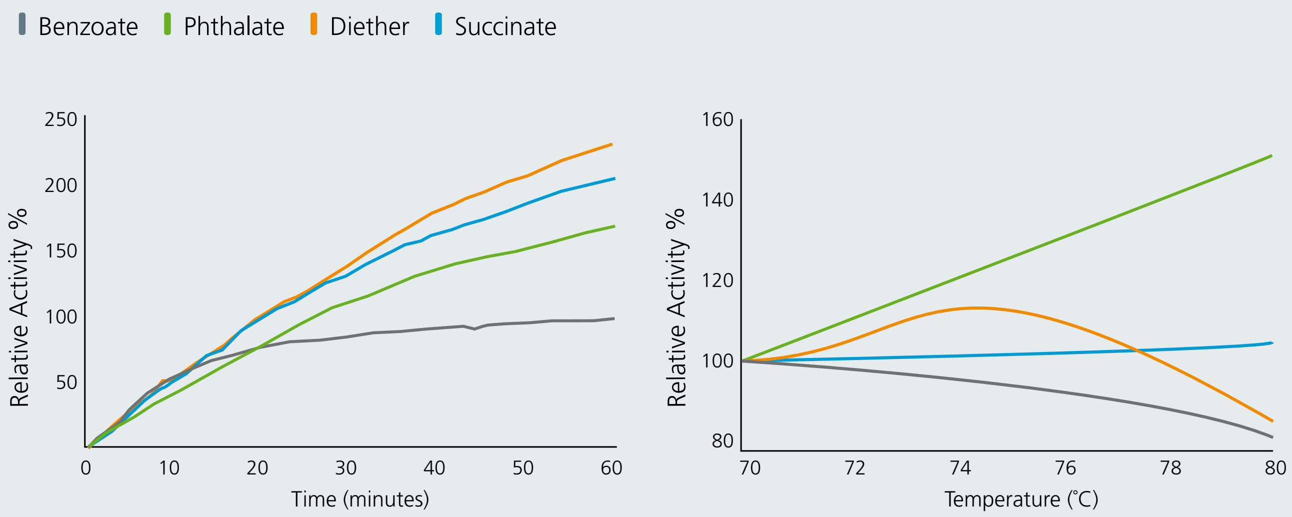
Catalyst Kinetics

The behavior of a catalyst in a bulk reactor is mainly determined by the internal donor that is used to make the catalyst. Both the relative level of activity and the decrease of the activity with time (the catalyst decay) are mainly determined by the internal donor. EB catalysts show rapid decay after a high initial activity, whereas phthalate, diether and succinate catalysts exhibit a relatively low rate of decay. This is shown in the graph on the left, representing batch experiments with the different catalyst families.

Understandably, this has consequences for the relationship between reactor-residence time and effective catalyst yield.

Another very important aspect of the kinetics is the behavior at different temperatures. As illustrated in the graph on the right, the catalyst families differ considerably in this respect. In the commercially relevant temperature range between 70 and 80 °C, the activity of EB and diether catalysts begins to diminish, dropping from 70 to 80 °C, whereas the succinate catalyst activity remains constant and the phthalate catalyst activity increases up to 80 °C. The relevance of this characteristic is related to the extent to which a polymer particle is deactivated during processing steps downstream of the reactor(s). High residual activity in these circumstances can lead to blockages in the downstream equipment, which makes catalyst types with lower activity at higher temperatures easier to run in a plant.

How does the catalyst behave in a reactor?



A complete understanding of catalyst kinetic behaviour is key to ensuring good plant performance

How does LyondellBasell implement its catalysts in various technologies?

The answer lies in the company's ability to rapidly scale up its catalyst developments.

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

The first stage of the company's catalyst testing investigates the basic properties of the catalysts such as hydrogen response and selectivity response. This is done in bulk autoclaves.

Also kinetic investigations are done on bench-scale reactors. These determine the catalyst decay and the behavior at different temperatures.

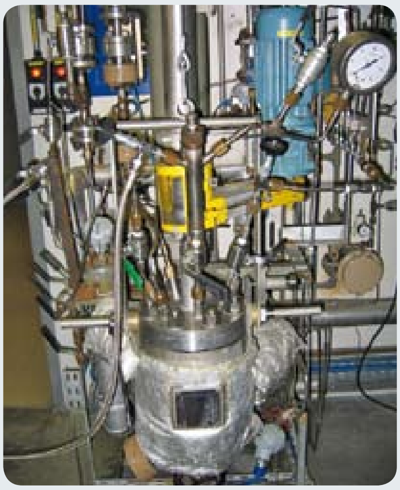
The next scale-up step typically is to run the catalyst in continuous bulk pilot plants, capable of producing several hundred kg/day. Here, operational aspects such as reactor control can be tested; it also provides enough product to examine properties for the various applications.

The final 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 LyondellBasell's commercial lines.

Catalyst Scale-up

Autoclaves:
Basic properties



Bulk pilot plant:
Product studies

Industrial plants:
World scale production

LyondellBasell has been successful in scaling-up from lab to plant due to its in-house facilities.

LyondellBasell offers PP catalysts with four different internal donors – the well known benzoate and phthalate catalysts as well as the more advanced diether and succinate (fifth generation) catalysts.

Catalyst Yield

Operating conditions such as reactor temperature, hydrogen concentration and residence time influence the catalyst yield. Poisons including a long list of polar contaminants, notably oxygen and sulphur containing compounds, can negatively influence catalyst yield.

Kinetic Behavior

Both the decay characteristics of the catalyst as well as its temperature dependence determine the behavior in the reactor and in the downstream section of the plant.

Powder Bulk Density

The bulk density of the polymer produced is very important in bulk processes, 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.

Hydrogen Response

Hydrogen is used to control the average molecular weight (expressed as MFR) of the polymer. The catalyst must have a good hydrogen response so that the full range of products can be produced within the constraints of the hardware.

Selectivity range

Selectivity refers to the external donor's ability to influence the product, which is normally controlled in the range of 1–5% wt. The catalyst must be highly selective with low external donor concentration to exhibit a good balance between product versatility and economics.

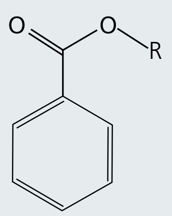
Oligomer content

The low molecular weight fraction of the polymer is important, as these light hydrocarbons are relatively volatile and can be emitted during final product processing in the form of die drool and fuming.

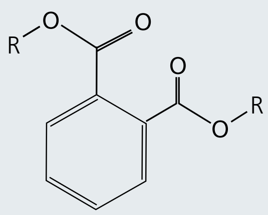
LyondellBasell's Bulk Catalyst Range

The internal donor in the catalyst influences:

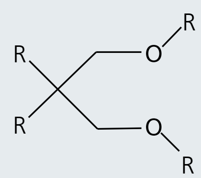
- Catalyst yield
- Decay characteristics
- MW distribution
- Selectivity range
- Hydrogen response
- Oligomers content
- Microtacticity



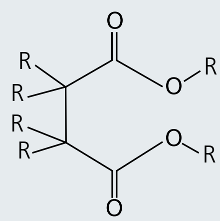
Benzoate



Phthalate



Diether



Succinate

The *Avant* ZN catalyst range includes all these internal donors and uses highly spherical supports

Molecular weight distribution

The width of the molecular weight distribution (MWD) is normally expressed by the polydispersity index, or PI. Different product applications require a different PI. Whereas fiber applications in general require a narrow distribution with a PI less than 3.5, a broader distribution is generally favored for BOPP film with a PI of at least 4.5.

Microtacticity

The microtacticity is a measure of the stereo-regularity of the polymer chain.

It is measured by NMR and expressed as the percentage of n-pentads. Note that this is not equivalent to the XS.

To operate an existing PP line reliably and economically, the operator must work within the constraints of the process to extend product properties using different catalyst and donor choices.

Let us consider how product properties can be influenced by these variables.

With regard to MWD, the polydispersity index can only be varied by approximately +/-0.1 in one reactor operation by changing the reactor temperature or the external donor. However, to make significant changes in the PI that the customer can detect, a change in catalyst is required. For instance, changing from diether to succinate will increase the PI at least two points, which will result in a corresponding large increase in stiffness.

Constraints in design pressure frequently limit the maximum MFR that can be obtained from a bulk reactor when using benzoate or phthalate catalysts. If a higher final product MFR is required this is normally achieved by peroxide cracking during extrusion. Changes in the external donor can give a moderate increase in the MFR. Diether catalysts can by virtue of their high hydrogen response make at least 100MFR products directly in the reactor without the use of peroxides, leading to a higher product quality.

Finally the usefulness of the various catalysts to produce random copolymers can be mentioned. Although in principle all of the catalyst systems can be used to make random copolymers, diether catalysts are preferred because of their superior balance between the amount of ethylene incorporated and the final XS of the product.

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

Degrees of freedom in an existing PP line

To extend product 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

Major changes in product properties can only be achieved by selecting the correct catalyst

* Mono-modal reactor operation

As stated previously, there are many internal-external donor combination possibilities and thus the overall catalyst picture is quite complex. In order to put this into perspective, the relationship between LyondellBasell's catalysts (used in one reactor setup) and the major homopolymer applications is shown in the graph below.

Starting from the left hand side, LyondellBasell's diether catalysts produce very narrow MWD products. These resins are ideal for such applications as high speed, low denier fibres or high clarity, thin wall injection molding grades.

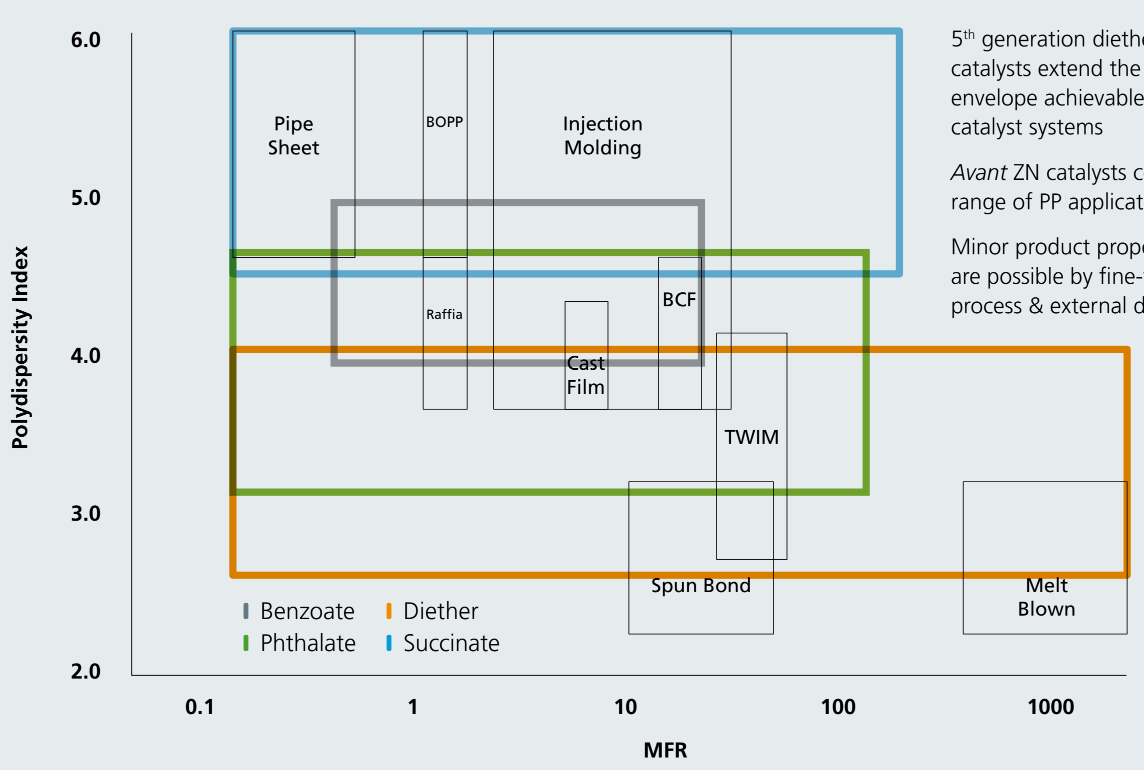
Phthalate catalysts produce broader MWD than diether catalysts, and are capable of making a wide range of standard polypropylene grades.

LyondellBasell's new succinate catalysts produce even broader MWD. This catalyst is capable of producing high crystallinity, high stiffness odourless products. Until now, equivalent products were only possible with cascaded reactor technology.

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

LyondellBasell's catalyst range covers the complete spectrum of polypropylene applications.

Avant ZN Catalyst Clustering – Homopolymer



5th generation diether & succinate catalysts extend the product envelope achievable with older catalyst systems

Avant ZN catalysts cover a wide range of PP applications

Minor product property changes are possible by fine-tuning the process & external donor

The graph below compares LyondellBasell's catalyst families from a process operation point of view.

The third-generation benzoate catalyst, although very easy to use due to its rapid decay and high temperature deactivation, is rather limited in terms of selectivity and hydrogen response.

The fourth-generation phthalate catalysts are definitely more of a challenge to operate in a bulk process, but the advantage is a wider product portfolio.

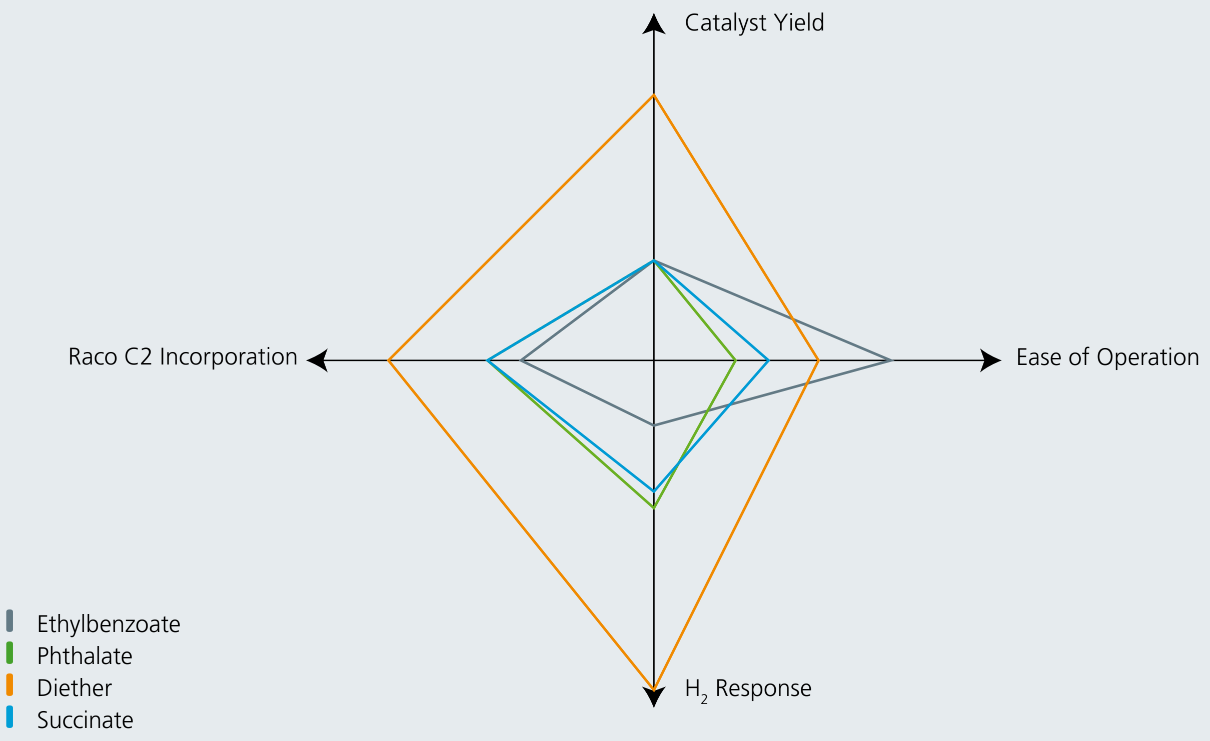
Fifth-generation diether catalysts offer ease of operation and a high yield, combined with the ability to make a wide product portfolio.

The fifth-generation succinate catalysts are easier to operate compared to phthalate catalysts, and their broad MWD combined with low xylene solubles is favored for high-stiffness applications.

Apart form the internal donor chemistry, another very important aspect that determines operability in bulk processes is the morphology of the polymer particles, including particle shape, average particle size, particle size distribution and fines content. The particle size has to enable good mixing in the reactor, efficient pneumatic transport and good degassing behavior. For this reason the particle size must match the characteristics of the process.

To preserve the morphological integrity of the polymer particles, pre-polymerization (start of the polymerization reaction under mild conditions) can be applied. Some bulk processes are equipped with in-line pre-polymerization facilities. For processes that are not equipped with such facilities, LyondellBasell offers a range of pre-polymerized catalysts.

How to choose the right *Avant* Catalyst?



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

V. Case studies

The following information contains descriptions of two case studies where bulk processes have been converted to LyondellBasell catalysts.

The first case study is an example of an improvement in operational aspects, with a loop reactor plant that used phthalate catalysts to produce homopolymer and high ethylene content random copolymer. The operation was hampered by reactor fouling issues which limited capacity and occasionally caused the line to stop for cleaning.

Following an upgrade to a LyondellBasell diether/external donor, plant operations were smooth and fouling was eliminated. Plant capacity increased significantly because of a better heat transfer coefficient. Notwithstanding the lower residence time, the catalyst yield increased by 20%, resulting in a lower production cost.

The second case study deals with a product upgrade in a line comprised of a bulk CSTR followed by a stirred gas phase reactor to produce a full range of products. The line used a phthalate catalyst; increasing demand for high-performance products was the motivation for change. The solution was an upgrade to fifth-generation succinate catalysts in combination with a patented external donor. The result was a significant improvement in homopolymer and impact copolymer properties at a higher catalyst yield coupled with excellent plant operability. Ultimately, better operability along with improved product properties at reduced costs were achieved.

Case Studies

Case study 1	Case study 2
Description	**Description**
Bulk loop process using phthalate for homopolymer and high ethylene raco.	CSTR with gas-phase reactor using phthalates to produce the full product range
Motivation for change	**Motivation for change**
Reactor fouling issues hampered operation	Increasingly demanding market
Value proposition	**Value proposition**
Upgrade to LyondellBasell diether catalyst/external donor combination	Upgrade to LyondellBasell succinate catalyst/external donor combination
Result	**Result**
Smooth operation without fouling Significant capacity increase Catalyst yield increase	Significant improvement in product properties (impact/stiffness) Catalyst yield increase Improved operability

Obviously, the benefits of changing to LyondellBasell bulk process catalysts depend on a number of factors including current product mix, plant configuration and the catalyst system currently in use. The table below gives an indication of the benefits that can be expected in the conversion of a 200 kt bulk plant from phthalate to diether catalysts.

The high yield of diether catalysts means that less catalyst and donor will be consumed, which reduces catalyst system costs. Typically this could be a savings in the order of € 500.000/yr. Higher hydrogen response leads to hydrogen savings and peroxide savings used for chemical cracking, since the higher melt index out of the reactor is attainable. This savings can be estimated at between € 200.000–300.000.

The deactivation of the catalysts that takes place at higher temperatures is a positive aspect of the diether catalyst compared to phthalate catalysts. This characteristic will lead to significantly less problems in downstream equipment, avoiding downtime and cleaning costs. The maintenance costs associated with downstream equipment blockages can be estimated at € 200.000/yr. The gain in occupancy that is achieved by avoiding downtime of the plant can be easily be valued at approximately € 900.000/yr

As stated previously, the incentive for a catalyst change is highly dependent on the specific plant characteristics under consideration, such as bottlenecks and business strategy.

However, this typical example indicates that savings of around 1 million €/yr are feasible in a plant of this size.

Other factors that may increase the maximum hourly throughput of the plant (notably the bulk density of the polymer) can be of great value because normally the extra throughput can be achieved without changing hardware.

Finally the improved product quality can offer additional value. Although it could be difficult to extract this value from the market, an upgrade may be required just to stay in business in a competitive environment.

Indicative Benefit Breakdown

Scenario, conversion of a 200 kt/y bulk PP line from phthalate catalyst to LyondellBasell fifth-generation diether catalyst	**million €/yr**
Savings	
Catalyst + donor	0.5(1)
H_2 + peroxide	0.3
Maintenance/cleaning	0.2
Total	**1.0**
Further potential benefits	
Increased production	0.9(2)
Product quality improvement	premium?

(1) Actual savings dependent on product mix, plant configuration and catalyst currently used.

(2) Assuming no propylene constraint.

VI. Summary

LyondellBasell has a long history of developing and implementing Ziegler-Natta catalysts for PP processes. The company's catalyst range is extensive and addresses a variety of different product applications.

Our experience in a wide range of processes ensures that we can adapt catalyst characteristics to optimally fit the requirements of each process.

LyondellBasell's commercially available catalysts for bulk processes are drop-in, and have been in use for many years in different commercial bulk plants around the world.

Conversion to LyondellBasell catalysts has demonstrated that process operability improvements, product property enhancements and conversion cost reductions can be achieved.

About LyondellBasell

LyondellBasell Industries is one of the world's largest polymers, petrochemicals and fuels companies. We are the global leader in polyolefins technology, production and marketing; a pioneer in propylene oxide and derivatives; and a significant producer of fuels and refined products, including biofuels. Through research and development, LyondellBasell develops innovative materials and technologies that deliver exceptional customer value and products that improve quality of life for people around the world.

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