As the world’s largest producer 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, our Avant catalyst range is suitable for all major product applications.

As a rule, process technologies used to make polypropylene are divided into 3 categories – bulk, gas phase and slurry. Although most polypropylene is produced in bulk processes such as Spheripol, gas phase processes represent a significant proportion of global production.

For a number of reasons, catalysts developed for bulk processes, do not necessarily operate well in gas phase processes. A good understanding of the kinetic, mass and heat transfer characteristics of the catalyst is critical to ensure acceptable gas phase polymerization.

Through its predecessor companies, LyondellBasell has operated a significant number of gas phase plants for several decades. All our gas phase plants, whether our own in-house technologies or licensed third-party plants, use only LyondellBasell produced catalysts.

Changing the catalyst used in a polypropylene plant usually requires careful consideration. Such a major change can normally only be justified when product improvement, plant capacity increase and/or cost savings can be realised.

This paper outlines the general differences between gas phase and slurry/bulk processes from a catalyst perspective. The kinetic behaviour of different catalyst families and external donors is also discussed. Finally the link between the catalyst and final product properties is explored.
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 gas phase experience

LyondellBasell and its predecessor companies have a long history in operation of gas phase polypropylene processes. LyondellBasell’s breakthrough Spherizone multi-zone circulating reactor process provides an economical and efficient method of manufacturing a wide range of high-quality polypropylene and novel, propylene-based polyolefinic resins. Since the launch of the Spherizone process in 2004, more than three million tonnes of capacity have been licensed. LyondellBasell operates four Catalloy process plants around the world. This is a non-licensed, proprietary, gas phase process using fluidized bed reactors capable of incorporating ethylene, propylene and butylene in various structures to make products, including but not limited to, supersoft applications, high clarity impact copolymers and very stiff materials.

As BASF was the previous licensor of Novolen, LyondellBasell continues to operate about 600 kt/yr of this technology. This is a vertically stirred gas phase reactor process. In total, LyondellBasell operates more than 1.3 million tonnes of gas phase polypropylene technology. All of these gas phase lines run exclusively on LyondellBasell catalysts.
The global polypropylene production for 2014 was estimated at more than 57 million tonnes.

The chart on the left, represents the polypropylene market broken down by process technology type.

Bulk processes such as Spheripol account for about one half of the total polypropylene produced.

Gas phase processes such as Unipol, Innovene and Novolen account for about 45%, and the balance comes from older slurry processes.

The chart on the right, represents the equivalent catalyst market broken down by process technology type. As indicated by this chart, gas phase technologies have a higher catalyst share compared to their polypropylene volume share. This is related to their lower catalyst yield compared to bulk processes.

It is estimated that in 2014 about 2300 tonnes of catalyst has been produced to serve the global polypropylene business.

Gas phase polypropylene processes are different. Catalysts which have been developed for bulk or slurry processes do not necessarily operate well in the gas phase.

General Features of Gas Phase PP Processes

Compared to bulk and slurry processes, gas phase processes have the following general features:

- Electrostatic charge – dissipation is generally poorer in gas phase processes which makes control of fines more critical; poor powder morphology can cause operability problems (sheets, chunks)
- Non-isothermal reaction – compared to bulk processes, there is a more pronounced temperature gradient inside a gas phase reactor – this non-uniform reaction may have product quality implications
- Lower yield – compared to bulk processes, the catalyst yield is generally lower due to lower monomer concentration (fugacity)
- Hydrogen concentration – in general the hydrogen concentration in the gas phase reactor can be higher due to pressure limitations of bulk systems
- Ethylene concentration – for random copolymer, gas phase processes can run higher ethylene content, due to extraction of solubles in bulk systems (stickiness)

In general catalysts in Gas Phase processes exhibit a lower yield than in bulk processes.

Source: LyondellBasell/Tecnon-Parpinelli
Modern polypropylene catalysts consist of a magnesium dichloride (MgCl₂) or silica support impregnated with titanium tetrachloride (TiCl₄) and an internal donor. The physical form of the catalyst can vary from flake to highly spherical.

The internal donor can be seen as the coarse tuning for product characteristics and external donor as the fine tuning. It is mainly the internal donor that determines the hydrogen response, molecular weight distribution and catalyst kinetic profile. The important distinction between the role of internal and external donors is explained later in this paper.

The 4th generation phthalate internal donor is the workhorse of the polypropylene industry, with a significant majority of all polypropylene made with this catalyst. In the early 1980’s the 3rd generation benzoate system was commercialized and is still used extensively today.

Within the last few years, LyondellBasell has commercialized 5th generation diether and succinate catalysts which are increasingly being used due to their ability to make unique products.

The newer external donors are mainly dialkydimethoxysilanes such as C, P and D-donor.

Older ester based donors such as PEEB are still used frequently in the industry. Although not every internal-external donor combination will work, many combinations are possible, and indeed catalysts utilizing mixtures of internal and external donors make the overall picture very complex.

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

Many internal/external donor combinations exist which affect reactor performance and product properties.
The behaviour of a catalyst in a gas phase reactor depends on many factors, but the most important are reactor design and internal donor used. Gas phase reactors typically utilize either fluidized beds, or vertically or horizontally stirred beds.

The graph on the left shows the kinetic behaviour in isothermal batch mode of diether, succinate, benzoate and phthalate catalysts. Benzoate catalysts exhibit fast decay – they have a very high initial reaction rate and then burn out quickly. This explosive kinetic behaviour can produce a lot of fines and benzoate catalysts require reactivation in the second reactor to produce impact copolymer.

Conversely diether, phthalate and succinate catalysts exhibit slow decay. Typically they have a rather linear time kinetic meaning that they can polymerize for several hours.

In contrast to benzoate catalysts, phthalate, succinate and higher yield diether catalysts do not require reactivation in the second reactor.

The graph on the right shows the dependency of yield on temperature of these four catalysts. Benzoate and diether catalysts tend to deactivate with increasing temperature. This is a very useful feature as the catalyst reaction rate decreases before the polymer melting point is reached. This means the chance of making reactor chunks is minimized during reactor upsets.

Conversely, the reaction rate of phthalate catalysts increases significantly with increasing temperature.

Phthalate catalysts can produce chunks if hot spots exist within the reactor.

Succinate catalysts behave someway between diether and phthalate catalysts.

A complete understanding of catalyst kinetic behaviour is essential to ensure good gas phase reactor performance.
How has LyondellBasell been able to implement its catalysts in such a wide range of gas phase technologies?

The answer lies in our ability to scale-up our catalyst developments.

Our fundamental catalyst research, which includes new donors and supports, is done in our labs in Ferrara, Italy and Frankfurt, Germany.

The first step is normally to investigate the basic properties of the catalyst such as hydrogen and donor response. This is done in our bulk phase autoclaves.

Kinetic investigations such as how the catalyst behaves by varying reaction temperature and time are done in our batch gas phase, fluidized bed reactors.

The next scale-up step is typically to run the catalyst in our fluidized bed pilot plants, which are capable of producing 100’s of kg per day. As well as being able to fully test the products, operational aspects such as reactor control and fouling can also be studied.

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

Gas Phase Catalyst Scale-up

<table>
<thead>
<tr>
<th>Autoclaves: Basic properties</th>
<th>Gas phase poly reactors: Kinetic studies</th>
<th>Gas phase pilot plants: Products studies</th>
<th>Industrial plants: World scale production</th>
</tr>
</thead>
</table>

LyondellBasell has been successful in scaling-up from lab to plant due to its in-house gas phase facilities.
LyondellBasell offers polypropylene catalysts with four different internal donors – the traditional benzoate 3rd generation and phthalate 4th generation catalysts, as well as the more advanced diether and succinate 5th generation catalysts.

**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.

**MW distribution**
The breadth of MWD is normally numerically described by the polydispersity index or PI. High speed fibre applications, such as spun bond or meltblown require a narrow MWD, with a PI less than 3.0. On the other hand, a broader MWD is generally favoured 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 that the catalyst is highly selective with low external donor consumption in order 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).

**Microtacticity**
Measured by NMR and usually expressed as %n-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 xylenic solubility of the polymer.

LyondellBasell’s Gas Phase Catalyst Range

**The internal donor in the catalyst influences:**
- Catalyst yield
- Decay characteristics
- MW distribution
- Selectivity range
- Hydrogen response
- Oligomers content
- Microtacticity

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

Benzoate

Phthalate

Diether

Succinate
To extend product properties in an existing polypropylene line, the operator must work within the constraints of the process, external donor and catalyst.

Starting with MWD, polydispersity index can only be varied by about ±0.1 in one reactor operation. Reactor temperature is the main variable which is usually constrained at the low end by propylene condensation and at the high end by hardware limitations. Small changes in MWD can be achieved by changing the external donor. However to make significant changes in MWD which the final customer can detect, the catalyst must be changed.

For instance changing from diether to succinate catalyst will increase the PI by at least 2 points, which results in a corresponding large increase in stiffness.

For benzoate and phthalate catalysts, the reactor MFR is limited by the maximum reactor hydrogen concentration, which may reduce cooling capacity.

Higher final product MFR is achieved by peroxide cracking during extrusion. Changing the external donor can give a moderate increase in MFR. However diether catalyst can make at least 100 MFR products directly in the reactor, without the use of peroxide.

Finally increasing ethylene content for impact copolymers is an important parameter to increase impact performance. This is typically only achievable by increasing the porosity of the catalyst, which keeps the rubber within the polymer particle to prevent stickiness.

In summary, major changes in product properties can only be achieved by selecting the correct catalyst.

### Degrees of freedom in an existing PP line

<table>
<thead>
<tr>
<th>Property</th>
<th>Process</th>
<th>External Donor</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modify MWD (PI)</td>
<td>± 0.1 *</td>
<td>± 0.2</td>
<td>± 1.5</td>
</tr>
<tr>
<td>Increase reactor MFR</td>
<td>1.2x</td>
<td>1.5x</td>
<td>&gt; 10x</td>
</tr>
<tr>
<td>Increase C2 content</td>
<td>+ 1%</td>
<td>+ 1%</td>
<td>+ 10%</td>
</tr>
</tbody>
</table>

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.

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

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### Avant ZN Catalyst Clustering – Gas Phase Homopolymer

- **Pipe Sheet**
- **BOPP**
- **Injection Molding**
- **Raffia**
- **Cast Film**
- **BCF**
- **Spun Bond**
- **TWIM**
- **Melt Blown**

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 3rd generation benzoate catalysts, although easy to use due to their high temperature and fast decay kinetic profile, are rather limited in terms of yield and hydrogen response.

The 4th generation phthalate catalysts are somewhat more difficult to use, however they make a wider product portfolio at higher catalyst yield, compared to benzoate catalysts.

The 5th generation diether catalysts offer ease of operation and high yield advantages, as well as the ability to make a wide product portfolio.

The 5th generation succinate catalysts are similar to phthalate in operation, and their broad MWD is favoured for high stiffness applications.

Apart from the internal donor chemistry, the other major factor determining operability in gas phase reactors is powder average particle size and particle size distribution. Different gas phase processes have different polymer particle size requirements related to reactor mixing, transport and degassing. In general, a larger catalyst particle will produce a larger powder particle however particle breakage can be a significant effect. This problem is normally minimized by pre-polymerizing the catalyst under mild conditions prior to injecting it into the reactor. Unfortunately, these pre-polymerization facilities are not normally standard in gas-phase processes, and for this reason, LyondellBasell also offers a range of pre-polymerized catalysts.

In general, the use of prepolymerised catalysts improves ease of operation, by reducing polymer fines.

How to choose the right Avant Catalyst?

The catalyst choice is a balance between PP market strategy and process capability.
V. Case studies

Presented below are two case studies of gas phase plants that have converted to LyondellBasell catalysts.

Case Study 1

**Description**
Gas phase PP process using a 3rd generation catalyst system for mainly impact copolymers.

**Motivation for change**
Increasingly demanding market place putting pressure on existing product range.

**Value proposition**
Upgrade to LyondellBasell diether catalyst/external donor combination.

**Result**
- Significant improvement in copolymer impact/stiffness balance
- Significant reduction in manufacturing costs (catalyst + donor)
- Reduction in product odour
- Excellent plant operability

Case Study 2

**Description**
Gas phase PP process using a 4th generation catalyst system for mainly random copolymers.

**Motivation for change**
Major reduction in plant capacity due to lump formation when producing a moderate (3.5%) C2 RCP.

**Value proposition**
Upgrade to LyondellBasell diether catalyst/external donor combination.

**Result**
- Ability to run at above design capacity for this product
- Significant reduction in manufacturing costs (catalyst + donor)

The first case study is a product upgrade example of a gas phase line running a 3rd generation catalyst making mainly impact copolymer. As stated previously, phthalate catalysts are the workhorse of the polypropylene industry and offer a number of product advantages over older catalyst systems. To become more competitive, they wanted to upgrade their product range, but were reluctant to do so due to the perceived poor operability of phthalate systems.

Our solution was a diether catalyst specially modified for the gas phase reactors in combination with a patented external donor.

In this case, the results were an improvement in product properties, at reduced operating cost without sacrificing plant operability.

The second case study is an operational improvement example. This gas phase line was running a 4th generation phthalate catalyst and was having problems with reactor lumps when making random copolymer.

This limited the plant production rate and occasionally caused the line to stop for cleaning.

Our solution was a diether catalyst specially modified for the gas phase reactors in combination with a patented external donor. In this case, the result was an operability improvement coupled with reduced operating cost.
Clearly the benefit of converting to LyondellBasell gas phase catalysts depends on many factors including current product mix, plant configuration and the catalyst system used. However the table below gives an indication of the expected benefit of converting a moderately sized 200 kt/yr gas phase polypropylene plant from phthalate to diether catalyst.

As stated previously, the high yield of diether catalyst means a reduction in donor, TEAL and catalyst consumption which reduces the overall catalyst system costs. Typically this would be around €500,000/yr.

The higher hydrogen response of the diether means a lower hydrogen consumption to make the same products. In case that electrolytic hydrogen is purchased from a third party, €150,000/yr could be saved.

The high temperature deactivation kinetic of diether reduces the chance of reactor sheets and chunks. The reactor cleaning cost associated with two stops per year of three days is typically around €300,000. There may also be a cost associated with loss of production that is covered later. Typically there are also operating savings due to the higher resin bulk density. Removing less hydrocarbon with the resin from the reactor, translates to lower recompression and distillation costs to recover the monomer. These operating savings are estimated at around €150,000/yr.

As stated previously, the benefit of conversion to diether catalyst is dependant on many local factors. However in this typical example, total savings of around €1 million/yr may be expected in a plant of this size.

Other benefits which are more difficult to calculate relate to additional production, assuming of course that additional monomer is available. The contribution margin associated with this incremental production could be as much as €700,000/yr.

Extracting value from the market from a product upgrade is in principle possible, but depends on the local conditions. Sometimes a product upgrade is required just to stay in business.

### Indicative Benefit Breakdown

<table>
<thead>
<tr>
<th>Scenario – conversion of a 200 kt/yr gas phase PP line from a phthalate catalyst to LyondellBasell 5th generation diether catalyst.</th>
<th>million €/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Savings</strong></td>
<td></td>
</tr>
<tr>
<td>Donor + TEAL + Catalyst</td>
<td>0.4–0.6(1)</td>
</tr>
<tr>
<td>H$_2$ consumption</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td>Maintenance/cleaning</td>
<td>0.2–0.4(2)</td>
</tr>
<tr>
<td>Operating (steam/electricity)</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.8–1.4</strong></td>
</tr>
<tr>
<td><strong>Other Opportunities</strong></td>
<td></td>
</tr>
<tr>
<td>Additional production</td>
<td>0.0–0.7(2)</td>
</tr>
<tr>
<td>Product upgrade</td>
<td>market premium?</td>
</tr>
</tbody>
</table>

(1) Actual savings will depend on many factors including product mix, plant configuration and catalyst system currently used.

(2) Elimination of 2 x 3 day shutdowns/yr. Additional production opportunity depends on monomer availability.
VI. Summary

In conclusion, the main points are as follows:

- Gas phase polypropylene processes have special catalyst requirements. Catalysts developed for bulk and slurry technologies will not necessarily operate satisfactorily in gas phase processes.
- LyondellBasell has a long history of developing gas phase polyolefin processes. Our Avant range of gas phase catalysts has been specially designed to ensure good operability, high yield and a wide range of product properties.
- LyondellBasell’s gas phase catalysts are drop-in and commercially available. They are being utilized in many of the gas phase polypropylene technologies currently in operation.
- Conversion to LyondellBasell catalysts has been justified on process operability improvements, product property enhancement and cost reduction considerations.
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