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Polyethylene Catalyst and Process Technology Tutorial

SPE RETEC Houston 2017

Townsend Solutions | February 26, 2017

Applications Mega-trends Forecast Markets Strategy Bioplastics
Competition Circular Economy Recycling Premiums Customers

Training

Important Notices

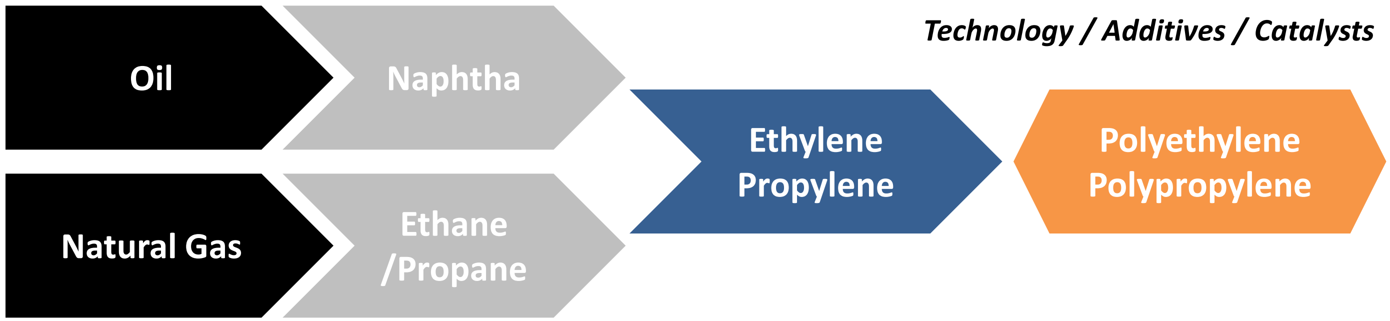
Contents

Session Introduction & Focus

Legislation
Regulation
Environment
Macroeconomics

Polyolefins Value Chain Dynamics

Technology / Additives / Catalysts



To understand and project what may happen to the polyolefin industry, we need to understand what can occur to any influencer of this business, both up & downstream

Properties / Processability / Additives

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Technology Innovation Drives Growth

Polymer technologies that yield substantially better products create value, and this value spurs new demand:

- By making new applications accessible
- By offering greater utility in existing applications

They add value and volume to the industry, and this drives their commercialization. Producers realize this value via higher selling prices for superior products & using unique products to displace competitive materials and break into new markets.

Innovation also drives profitability:

- Innovative new products reap benefits for producers in the form of higher product prices and higher margins.
- Converters, end-users & brand owners reap even larger benefits through a closer match to their needs: faster processing, reduced raw material requirements, greater end-use utility and lower overall costs.

Technology Innovation Drives Growth

Product characteristics and their match to market needs are what make the difference between a standard commodity-priced product and a higher performance premium priced product

- Grade slate depends on process configuration and catalyst capabilities. Price differentials or premiums for higher performing products can be attributed in part (or entirely) to process and catalyst characteristics.

LYB LaPorte Texas plant will utilize new proprietary Hyperzone PE technology. HDPE products produced here will exhibit enhanced properties such as an improved stress crack resistance and an improved balance between stiffness and impact strength. In certain applications, Hyperzone PE resins may allow customers to use less PE resin per unit produced, resulting in improved resource efficiency and savings for customers. --Bob Patel, LyondellBasell CEO and Chairman of the Management Board

Technology: Recent Key Developments

- Multizone PE (LBI's proprietary) types of process development for superior polyethylene products // Trimodal PE
- Low cost metallocene catalyst systems with no or low MAO
- Drop-in Phthalate-Free PP Catalyst (same behavior like 4th Generation PP catalyst)
- Molecular Catalysts for High Temperature Ethylene Copolymers
- (application) 3D Printing (Additive Manufacturing by successive layer formation of objects // 4D Printing (time factor included) - property and shape changes vs. temp, pressure, and moisture led by Self Assembly Lab MIT)

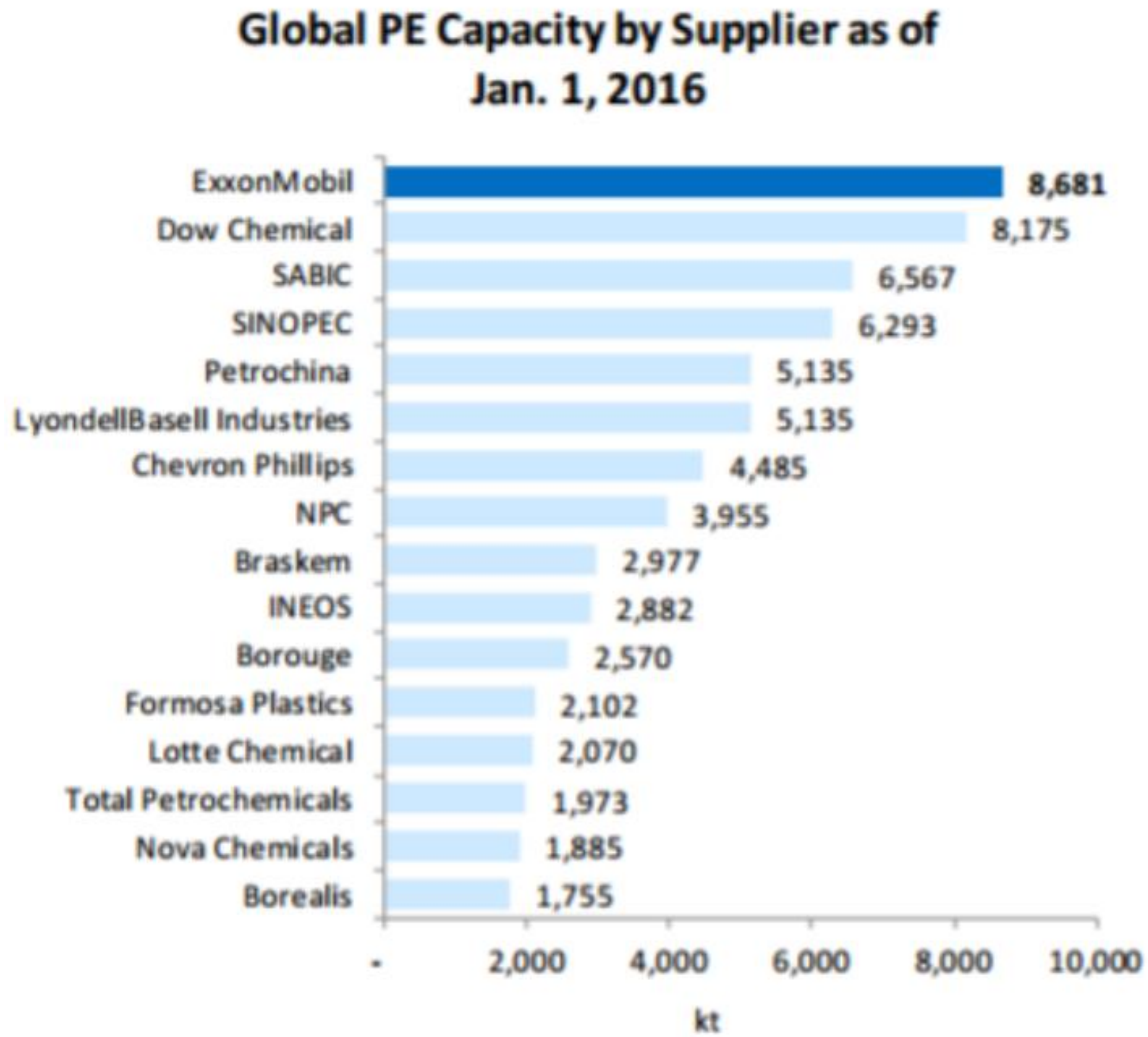
The Polyolefins Industry

PE & PP are the two largest volume polymers in the world

- Annual Global Production of about 150 million tons
  - ˜ 90 million tons PE (HDPE > LLDPE > LDPE)
  - ˜ 61 million tons of PP

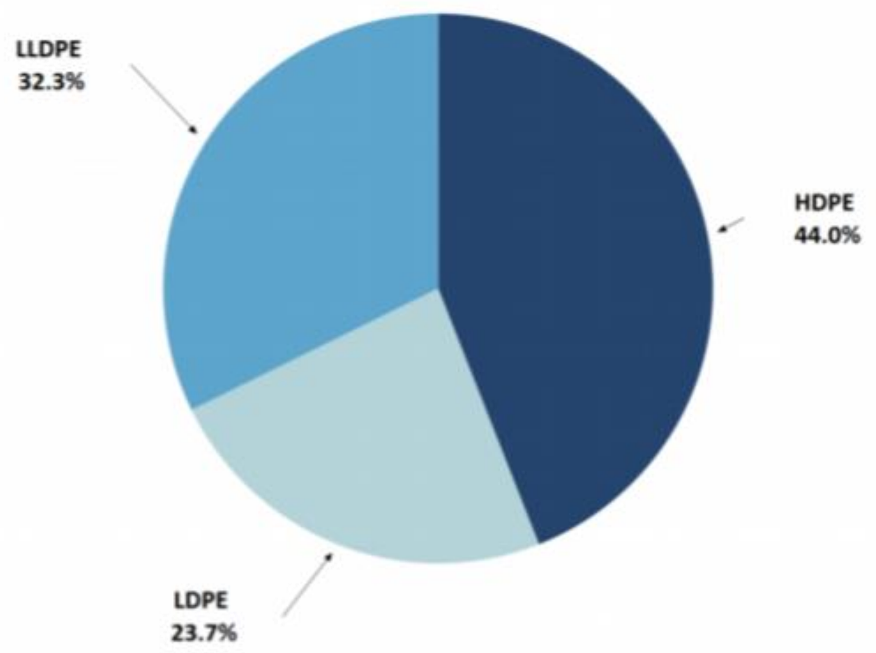
- Polyolefins is estimated to be a roughly $230 billion industry, larger than any other thermoplastic material

The Polyolefins Industry



The Polyolefins Industry

Figure 2.1 – PE Consumption by Resin Type: 2015



Source: Townsend Solutions

The Global HDPE consumption totaled 38,825 kilotonnes or 44.0% of the total PE consumption in 2015 and is forecasted to grow 3.4% in 2016.

The Global LLDPE consumption totaled 28,443 kilotonnes or 32.3% of the total PE consumption in 2015 and is forecasted to grow 5.0% in 2016.

The Global LDPE consumption totaled 20,900 kilotonnes or 23.7% of the total PE consumption in 2015 and is forecasted to grow 2.9% in 2016.

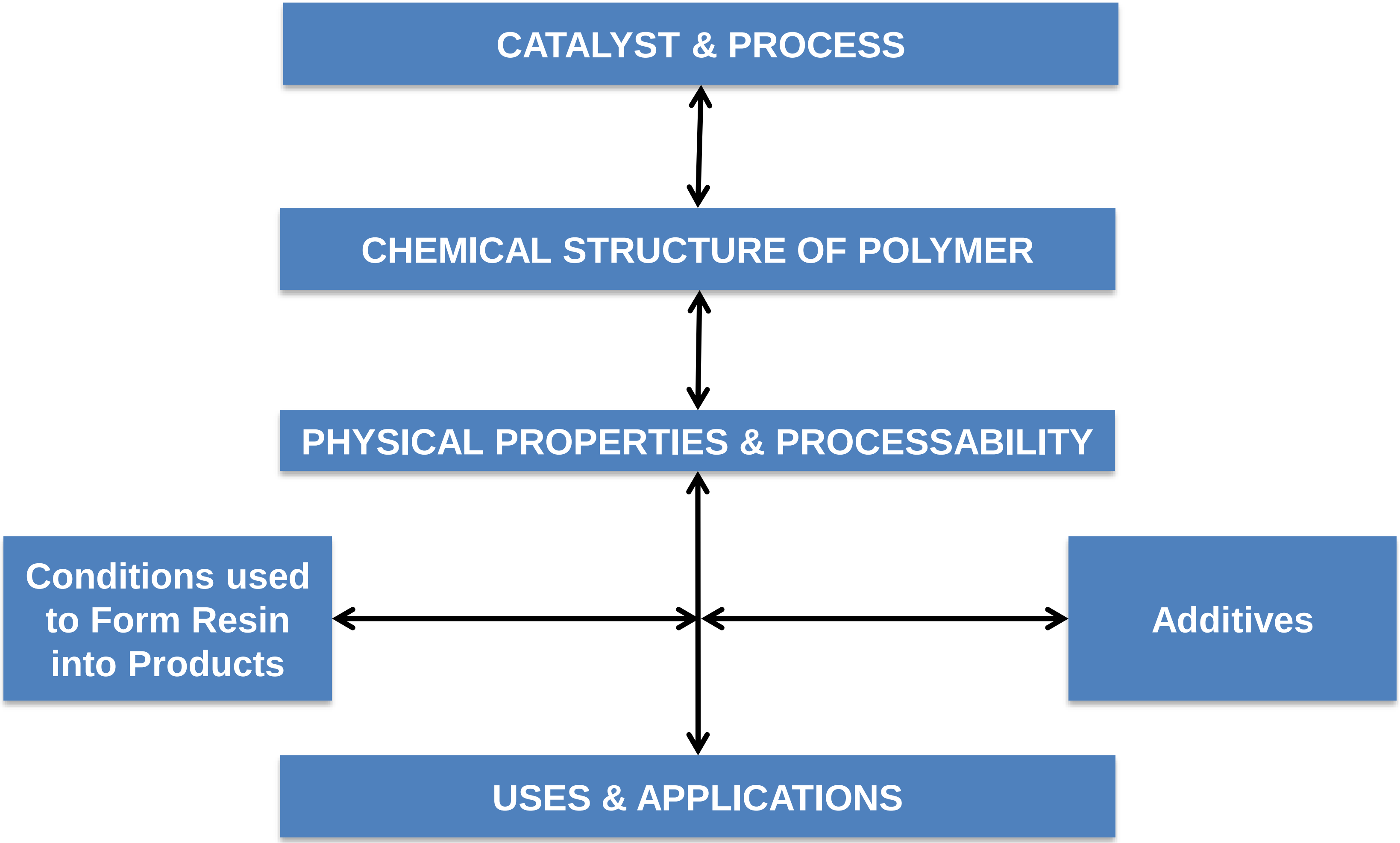
The Polyolefins Industry

Table 2.2 – Global PE Demand Overview by Region: 2015 – 2021, kt

Region	2015, kt	% PE Market Share	Volume Growth 2016 - 2021, kt	% PE VG Share
North America	16,836.8	19.1%	2,813.4	13.8%
Central and South America	4,992.9	5.7%	803.3	3.9%
Western Europe	11,939.4	13.5%	1,578.6	7.7%
Central and Eastern Europe	4,669.7	5.3%	884.8	4.3%
Japan	2,616.7	3.0%	53.2	0.3%
China	23,981.0	27.2%	7,100.0	34.8%
Asia Pacific	9,973.7	11.3%	1,926.5	9.4%
India	4,139.0	4.7%	2,614.0	12.8%
Middle East	5,681.5	6.4%	1,616.8	7.9%
Africa	3,338.4	3.8%	1,013.0	5.0%
Grand Total	88,169.1	100.0%	20,403.6	100.0%

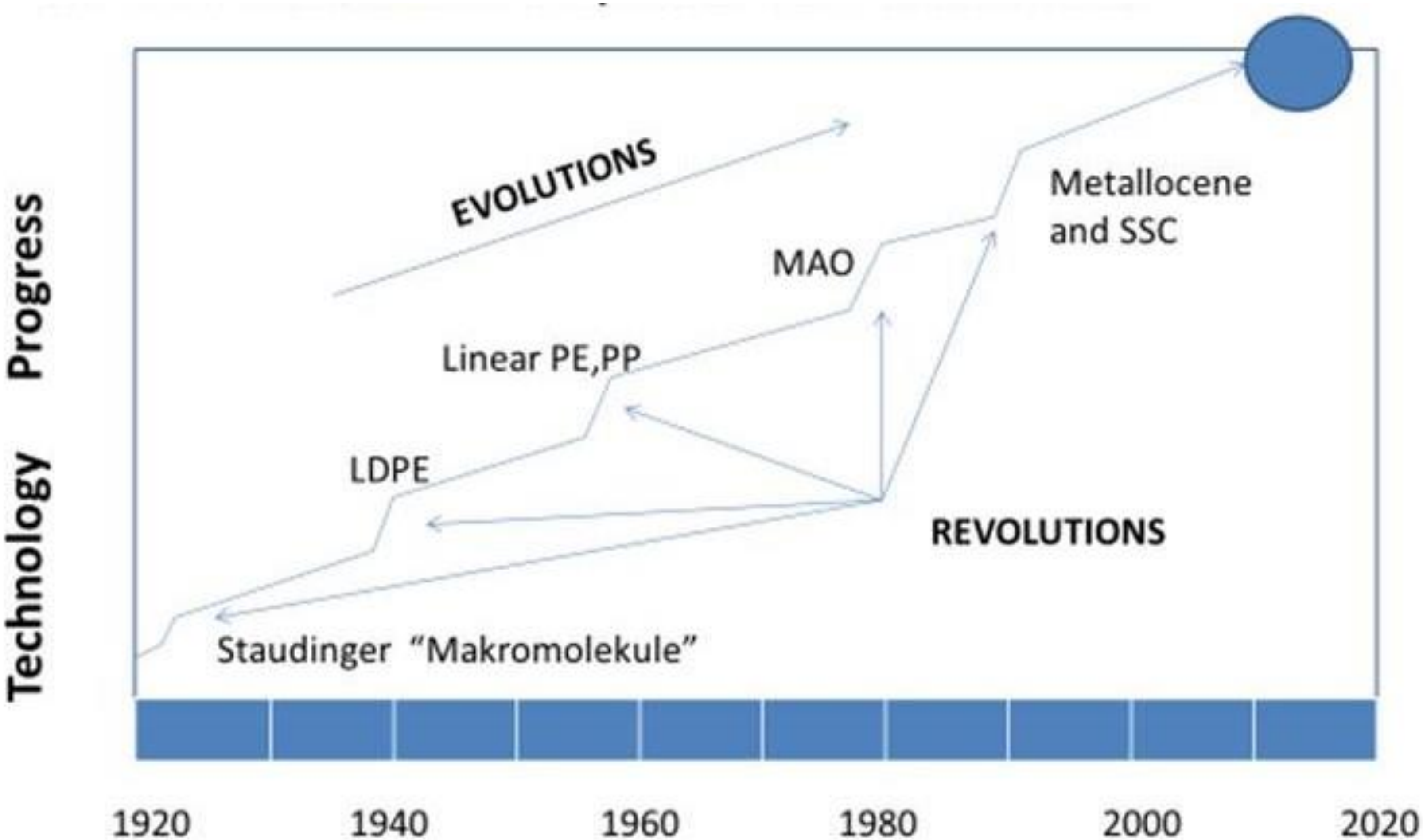
Source: Townsend Solutions

Catalyst Determines Polymer Applications



Polyolefin Development Cycle Process

Gradual Evolution Interspersed with Revolution



Courtesy of Ken Sinclair in MetCon 2000 "Polymers in Transition"

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Catalyst SYSTEM is the Heart of the Engine

Three Types of PE Catalyst Systems

1. **Cr compounds on silica**
   - Typically no co-activator (co-catalyst) is needed
2. **PE Ziegler –Natta**
   - Transition Metal halide, Mg compounds + activator (aluminum alkyls)
3. **Metallocene**
   - Transition metal complex of bisCp or single Cp (bridged or open) with MAO or borate as activator

Catalyst SYSTEM is the Heart of the Engine

Three Types of PE Catalyst Systems

1. **Cr compounds on silica (serendipity)**

    - Cr oxide catalyst on silica. It yields polymer of broad MWD which is suitable for blow molding, pipes, and films. This Cr system was developed by Phillips Petroleum in circa 1951. The Cr system was actually the most versatile catalyst system. When polymerization was conducted in solution process, narrow MWD PE was achieved which is suitable for injection molding and rotomolding applications. Therefore Cr on silica is capable of producing BM, Film, Pipe, Sheet, Injection Molding, and rotational molding products

Catalyst SYSTEM is the Heart of the Engine

Three Types of PE Catalyst Systems

2. **Z-N Based PE Catalysts mostly by Ti/Mg or Ti/Mg on silica (less common)**

    - A great variety of Ti and Mg compounds containing halides were mixed to form high activity PE catalyst. Various of techniques (like spray dry etc.) to improve the morphology. Typically bead-like catalyst particles are preferred as this will lead to bead-like polymers which render higher polymer bulk density and low fines. Triethylaluminum is a typical cocatalyst.

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Catalyst SYSTEM is the Heart of the Engine

Three Types of PE Catalyst Systems

3. Metallocene PE Catalysts

- BisCp M type: like the famed ExxonMobil patent 5,324,800 issued to Welborn et. al. The pie bonding feature was first reported by Paulson, Wilkinson, and Fisher in the 1950's

- One Cp or its analog forms pie bond with the transition metal with nitrogen silyl group to form the complex with constrained geometry to distort the complex and expose the active site for more efficient incorporation of comonomer – an important feature of single-site catalyst system. MAO was found to be critical for high activity for metallocenes

Polyethylene Invention

"I would like to first describe our normal-pressure polymerization experiment, which actually takes about an hour but which has been condensed in the films to a few minutes.

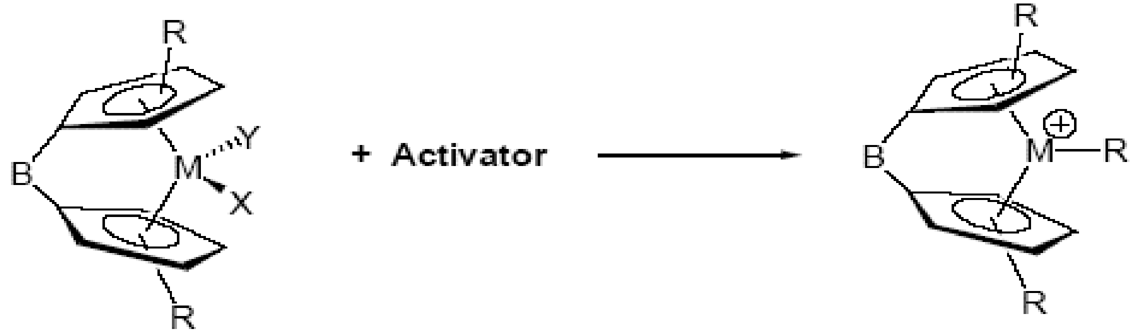
The catalyst is prepared simply by simultaneously pouring, with exclusion of air, two liquid materials **($TiCl_4$ and AlR_3)** into about two liters of a gasoline-like hydrocarbon, after which ethylene is introduced, while stirring. Within an hour one can easily introduce 300-400 liters of ethylene into the two liters of liquid. At the same time, a solid substance precipitates. The addition of some alcohol and by the introduction of air, the precipitate becomes scow-white and can be filtered off. "

Excerpted from 1963 Karl Ziegler Nobel Lecture

Metallocene Catalysts Systems

A. ExxonMobil Metallocene System Bis Cp Zr X2, US 5324800 (Welborn H. etal.) and many others

Metallocene Catalyst are Single-sited Structures



Catalyst Precursor

Active Metal Cation

M: Transition metal, generally from Group IV.

B: Bridge, optional. Used to control 'openness' of front face giving access to metal. Make metallocene stereorigid.

R: Substituents control activity through electron donation and their steric bulk can effect monomer access and orientation.

X, Y: One is abstracted by activator making the metal electron deficient. The other is the active propagation site.

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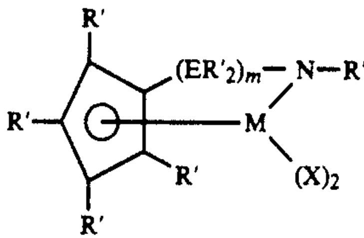
Metallocene Catalysts Systems

B. Dow's Constrained Geometry Catalyst (e.g. US5272236 and 5278272 (Lai, Shih-Yaw et. al.) and many others. It is widely used in Dow's metallocene products

38. The substantially linear olefin polymer of claim **12** wherein (a) is an amidosilane- or amidoalkanediyl- compound corresponding to the formula:



wherein:

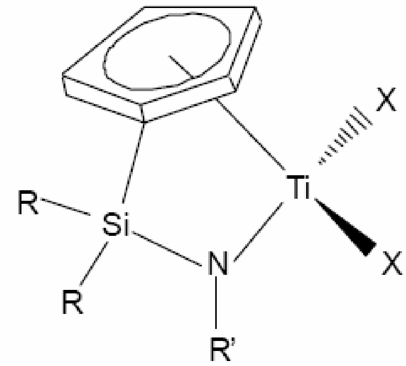
M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, or aryl, of up to 20 carbons; and

m is 1 or 2.

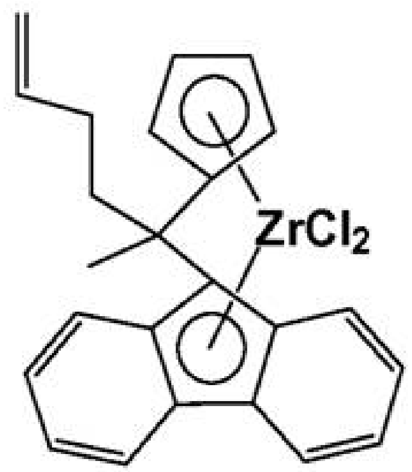


- ✓ Excellent comonomer incorporation.
- ✓ Long-chain branching improves processibility.
- ✓ Embroiled in extensive patent and civil litigation (now settled) between Dow and Exxon.

Metallocene Catalysts Systems

C. CP Chem's high clarity low haze metallocene catalyst system for slurry process

- US61537169 (Welch, Alt et. al.),US7230128,US 6992035,US6482967 etc. Lower left is an example is a bridged Cp fluorenyl metal complex catalyst. Lower right is Figure 4 in US6153716 which demonstrates the low haze (lower line) by unique ethvl branches



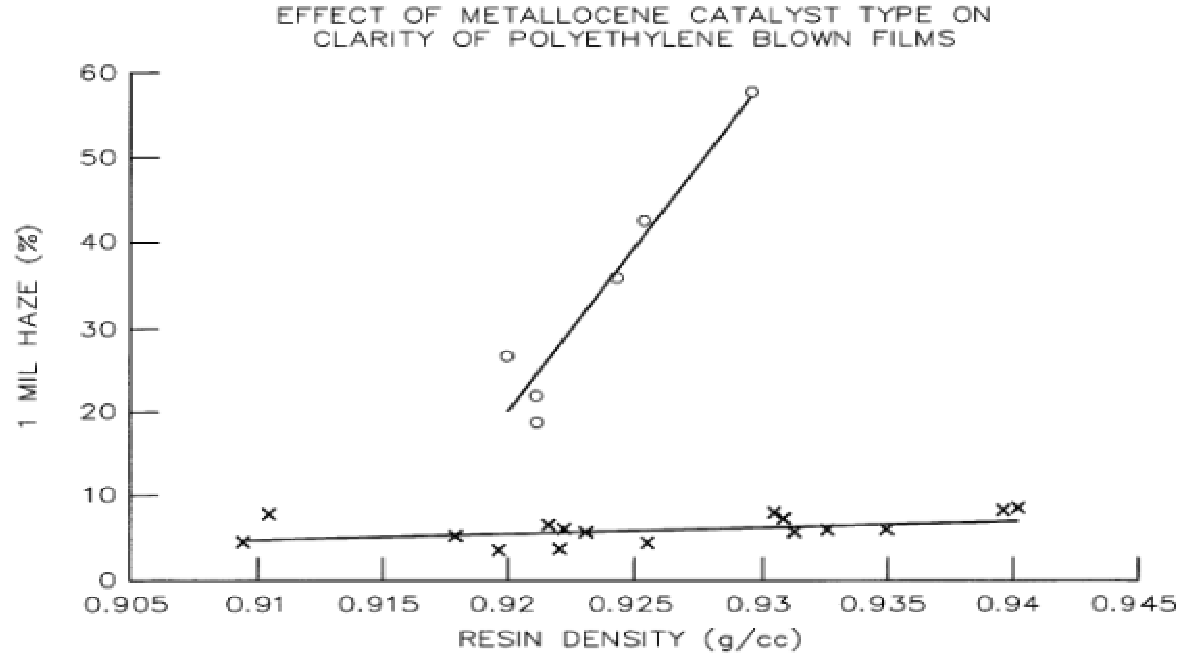


FIG. 4

Metallocene Catalysts Systems

C. CP Chem (continued)

- Polymer Features include low haze, high clarity, dart impact presumably derived from catalyst's extremely good comonomer incorporation efficiency, unique ethyl, butyl branching distribution

- MarFlex mPACT D143, density 0.916 g/c.c. haze 4%, gloss (60 deg) 130, Dart >800 g/mil

- Jun 2014, CP Chem started the construction of a 500. KTA LLDPE metallocene resins plant in Old Ocean, TX for 2017 start-up. Presumably the combination of a specific complex and the superacid technology (slides 27 & 28) will be employed.

Metallocene Catalysts Systems (Activator)

D. CP Chem's Super Acid Support for metallocene catalyst review

- Solid supports such as silica, alumina, alumina-silica etc. are treated with super acid or salts with electron withdrawing anion (e.g. halide) to activate metallocene for high activity without using MAO as activator

- Article by McDaniel et. al., and US6300271, US6107230 etc.

Metallocene Catalyst Systems (Activator)

D. (Continued) CP Chem Super Acid Activator Polymer properties remain the same

- Example (13A in 271):

  Ketzen B alumina, calcined at 600C, H_2SO_4, cal. at 550C activity 1387 g/g/hr. metallocene bis n-butyl $CpZrCl_2$

- CP Chem is currently building a 500 KTA capacity MarTech SL reactor for LLDPE employing its proprietary metallocene super acid technology

Metallocene Catalyst Systems (Activator)

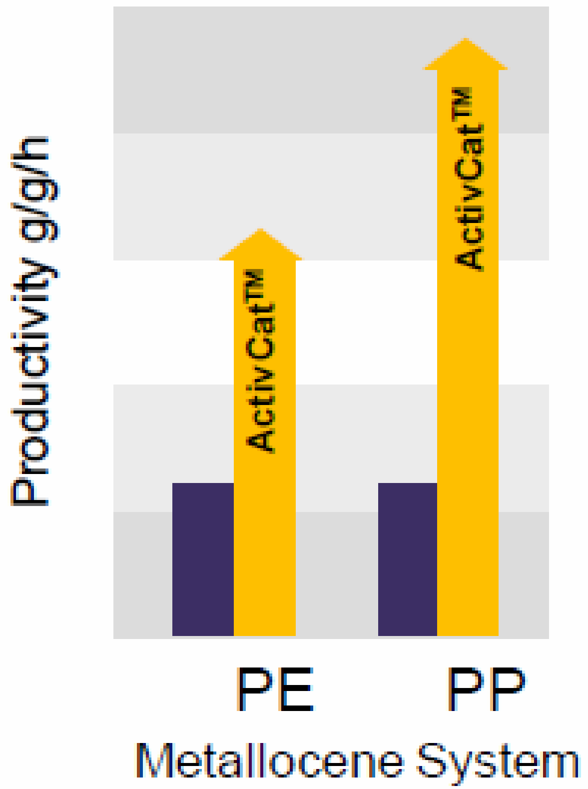
E. Albemarle's ActivCat™

ActivCat™ Technology demonstrated to work with various types of metallocene components used to produce both PP and PE

- This is a versatile technology for supported metallocene system. Basically the complex and MAO are immobilized on support and activated with an di-alkyl Al halide or other counter-anions. The productivity is reported to be doubled per Albemarle.

- References include US8575284 (Luo, L. Et. al.), US8501655, US8354485, and US8088952 etc.

ActivCat™ Transformational Productivity Improvement



Metallocene Catalyst Systems (Activator)

F. Solid MAO commercialization was launched in 2010

(TOSOH FineChem) (PCT/06019 JP2009P/ 006019)

- MAO is made by hydrolysis or thermal decomposition. A Self aggregation technique is employed to prepare solid MAO without any solid support or additives.
- Example:
  Ind2ZrCl2/solid MAO, , Al/Zr = 214, Activity = 10,000 g/g//hr

PE Commercial Process Technologies

(double reactors refer to two reactors in series)

Slurry

- Single Reactor
  - CP Chem
- Multiple Reactors
  - **Cascade stirred tanks**
    Mitsui, Equistar Maruzen
  - **Hostalen APC**
    (3 reactors in series)
  - <u>**Dual loop reactor**</u>
    Ineos
    Total
    CP Chem

Gas Phase

- Single Reactor
  - Univation
  - Innovene G
  - Spherilene S
- Double Reactor
  - Spherilene C
  - Unipol II

Solution

- Single Reactor
  - DSM
  - Nova (Sclairtech)
- Double Reactor
  - Nova (AST)
  - Dow (Dowlex)

The following are for internal use and thus not licensed: Equistar slurry bimodal (LBI), Nippon slurry (Formosa USA), Borstar loop/gas hybrid, LBI (DuPont) solution, DSM solution.

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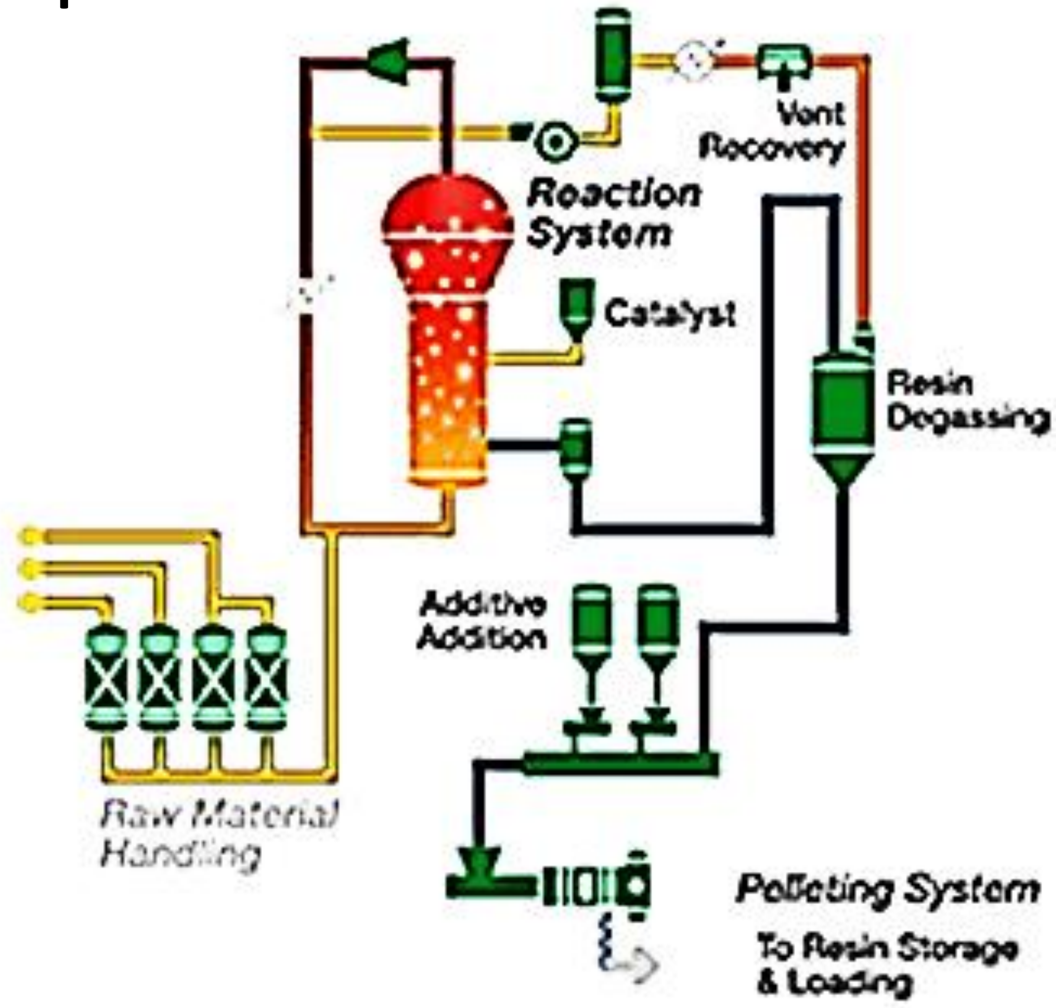
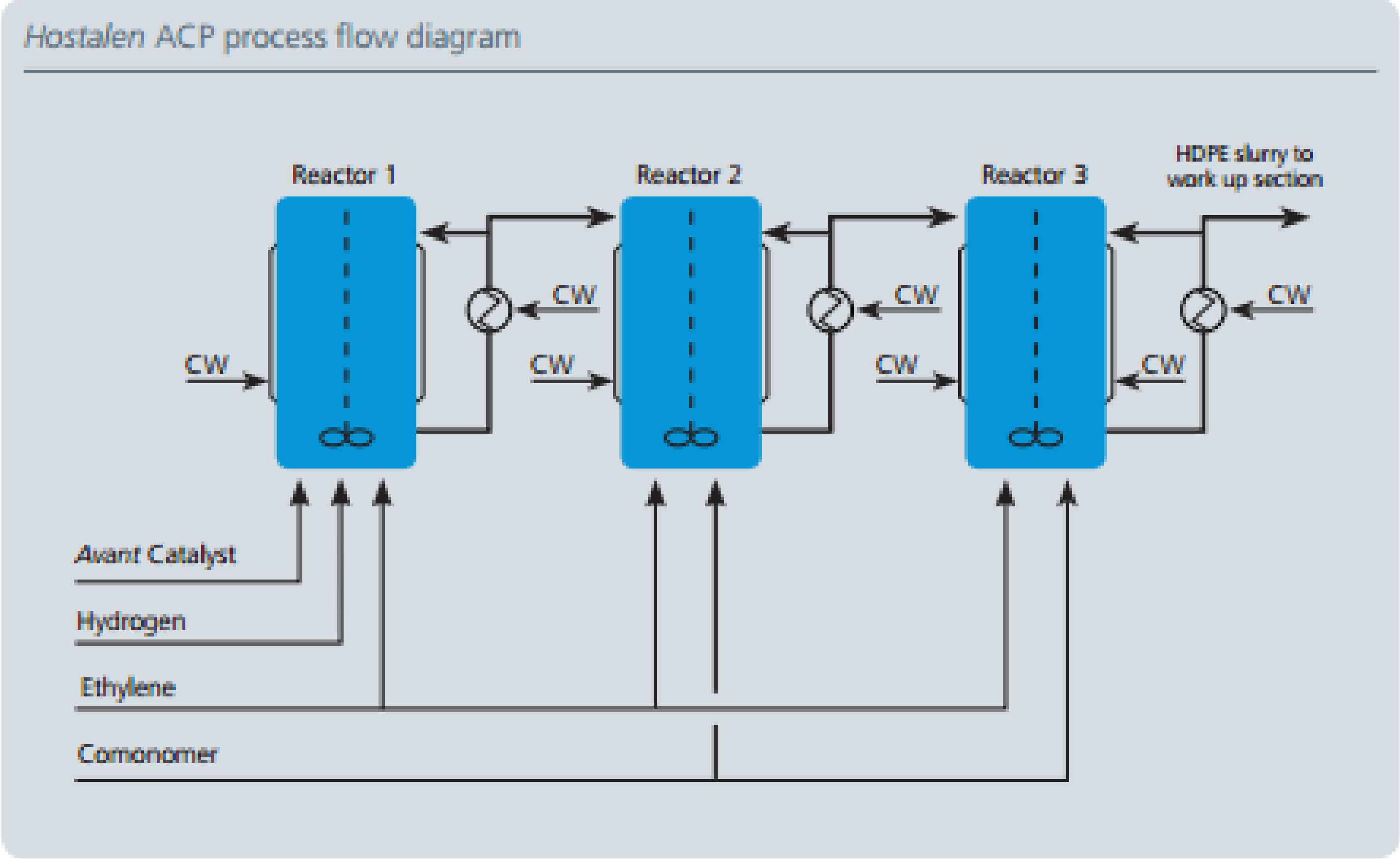
Schematic of Ethylene Polymerization Process – UNIPOL gas phase



Source: Univation

Schematic of LyondellBasell's Hostalen APC Polyethylene Process

- There are 8 million tons of Bimodal and Multi-Modal Slurry Tank Capacities Licensed globally



Source: LyondellBasell Industries

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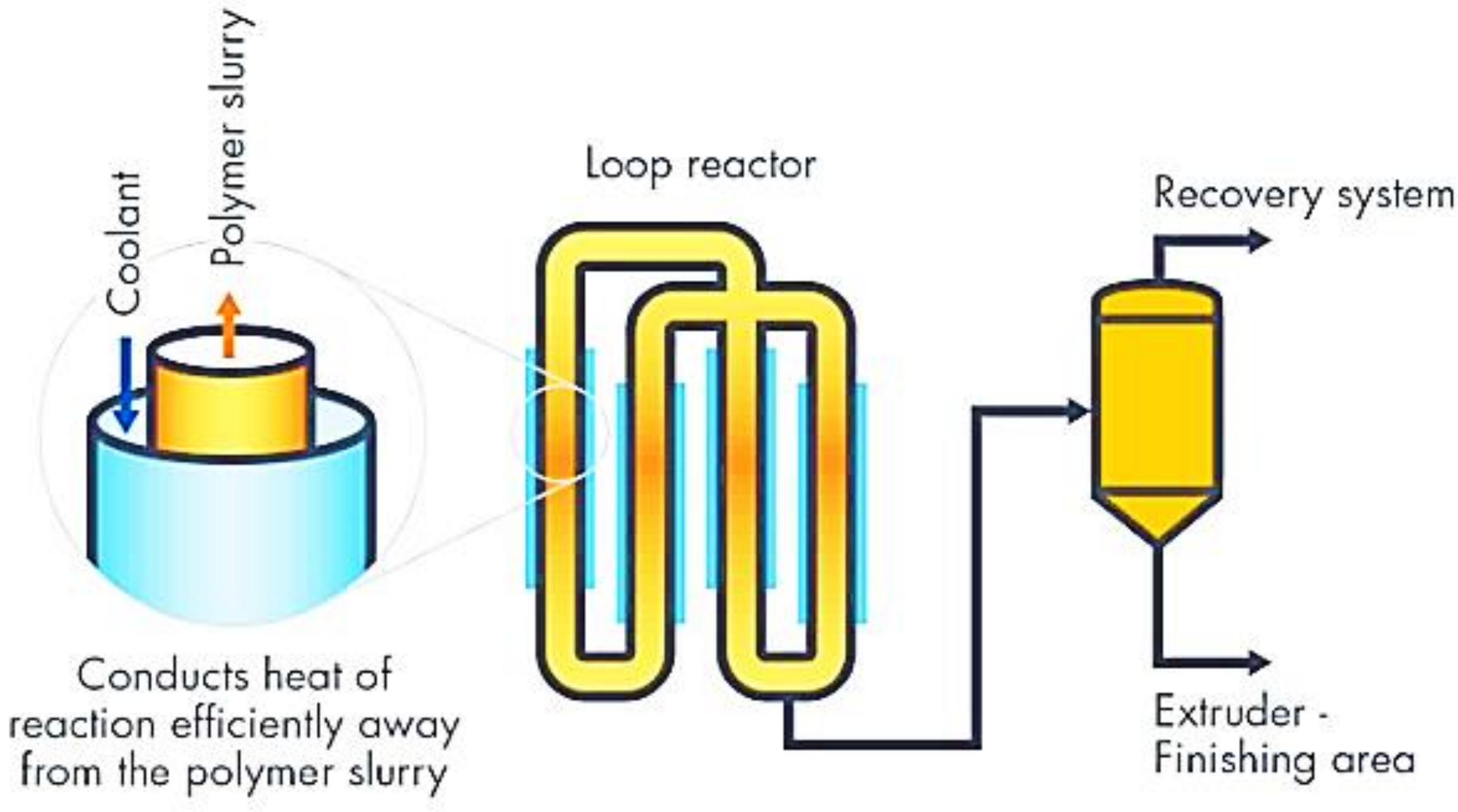
Schematic of CP Chem's MarTech Single Loop (SL) Reactor

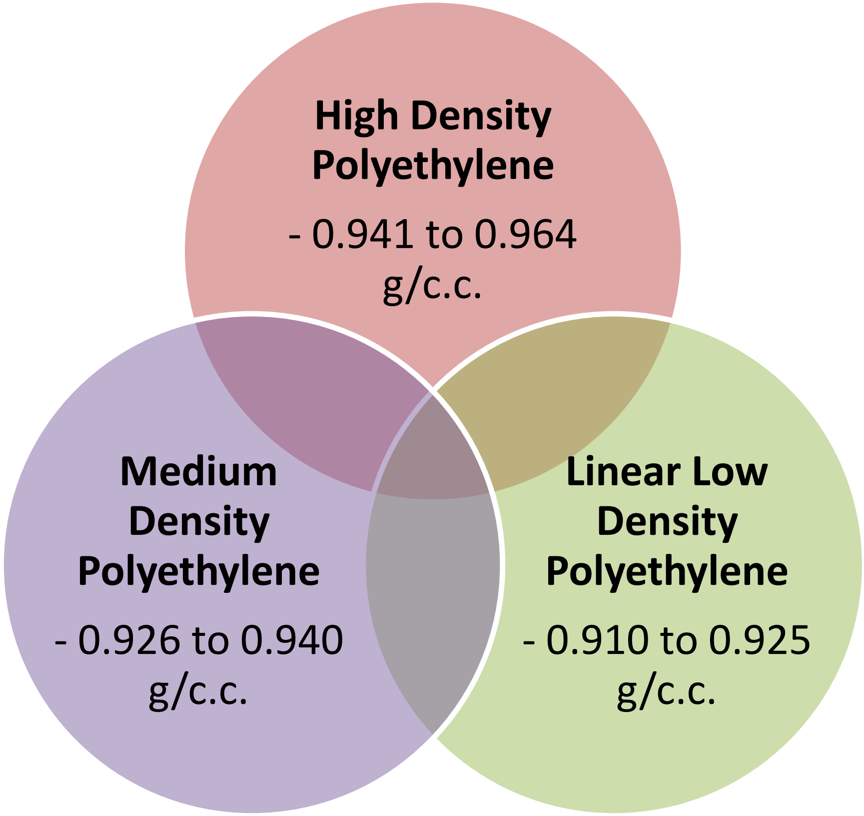


Source: Chevron Phillips Chemical

Fundamentals of Polyethylene

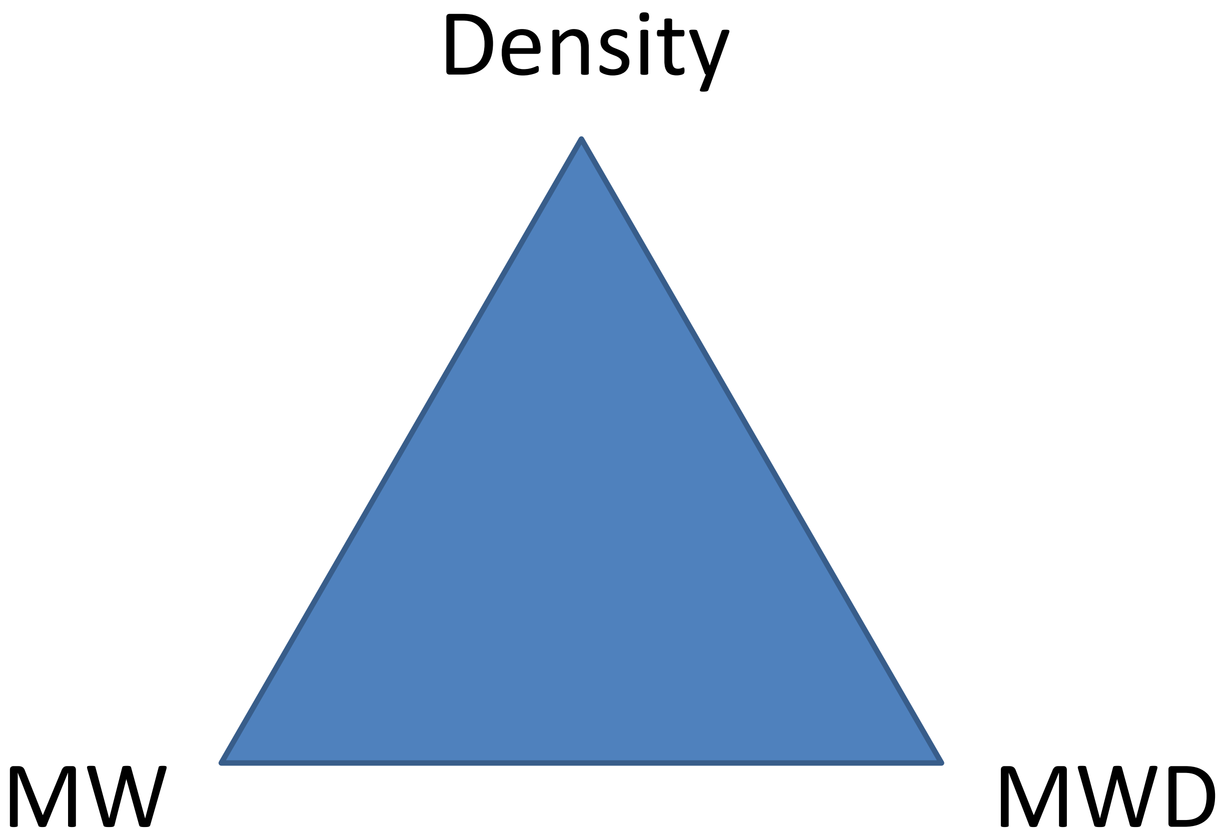
Three key elements define most of the physical mechanical properties and processability of PE

- **Density**
- **Molecular Weight**
- **Molecular Weight Distribution**



LLDPE and MDPE are sometimes lumped together

Fundamentals of Polyethylene



Molecular Weight and Molecular Weight Distribution

1. Molecular weight is often measured by Melt Index defined as # grams extruded out of the orifice of a standard MI index set-up in 10 minutes (ASTM D1238) with 2.16 g. weight on the cylinder

2. For very high MW material it can be also measured by HLMI which means the weight on the cylinder is 21.6 kg.

3. The Ratio of MI20/MI2 is indicative of MWD – an extremely important parameter because it determines the market and applications. The higher the ratio the better the processability and the better the melt strength. Broad MWD PE is more suitable for blow molding, sheet, film, and pipe applications. Narrower MWD PE is more suitable for film, rotomolding, and injection molding applications.

Molecular Weight and Molecular Weight Distribution (continued)

In polyethylene, the HLMI/MI is a practical and very useful measure to indicate the applications and markets

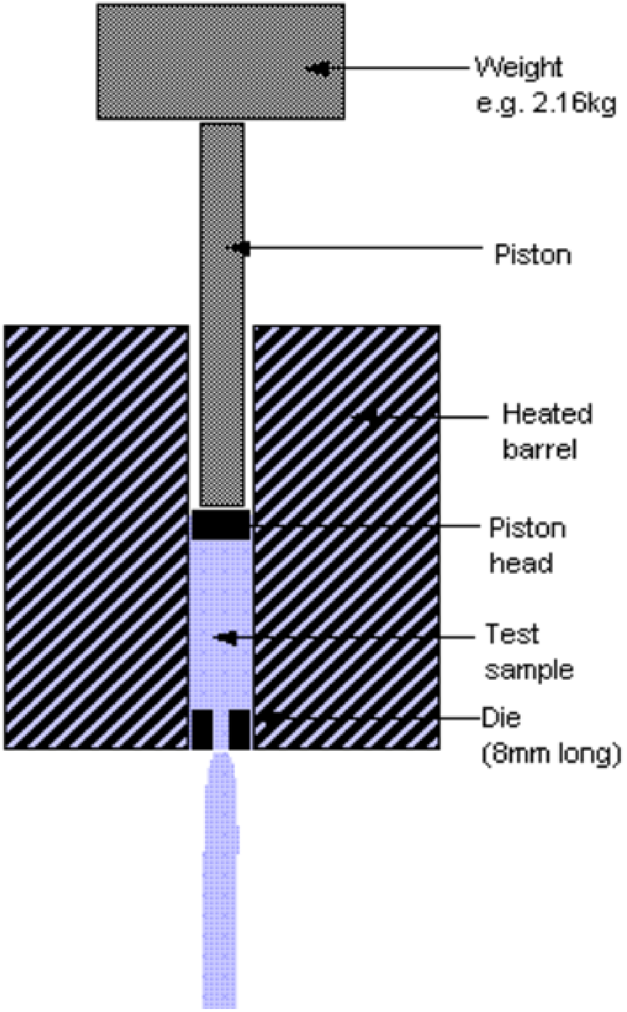
1. Z-N catalyst typically produces PE with HLMI/MI about 25-40. This is suitable for injection molding, rotational molding, and films (LLDPE)

2. Cr based catalyst produces PE with HLMI/MI around 80-120 or higher. It is suitable for blow molding, sheet, films, and pipes (including PE-80)

3. Z-N catalyst in dual reactors produces PE with HLMI/MI around 150 to 200 or higher. It is suitable for high performance pipes (like PE-100), HMW HDPE films etc.

Melt Indexer Machine

Overview of the measurement of melt flow index (MFI)



Molecular Weight Definitions

- The number average molecular weight ($\overline{M}_n$) is **defined** from the expression:

$$\overline{M}_n = \sum M_x N_x / \sum N_x$$

- The weight average molecular weight ($\overline{M}_w$) is **defined** using the second order equation:

$$\overline{M}_w = \sum (M_x)^2 N_x / \sum M_x N_x$$

- So higher molecular weight molecules will play more part. The higher ratio of $\overline{M}_w / \overline{M}_n$ the broader the MWD

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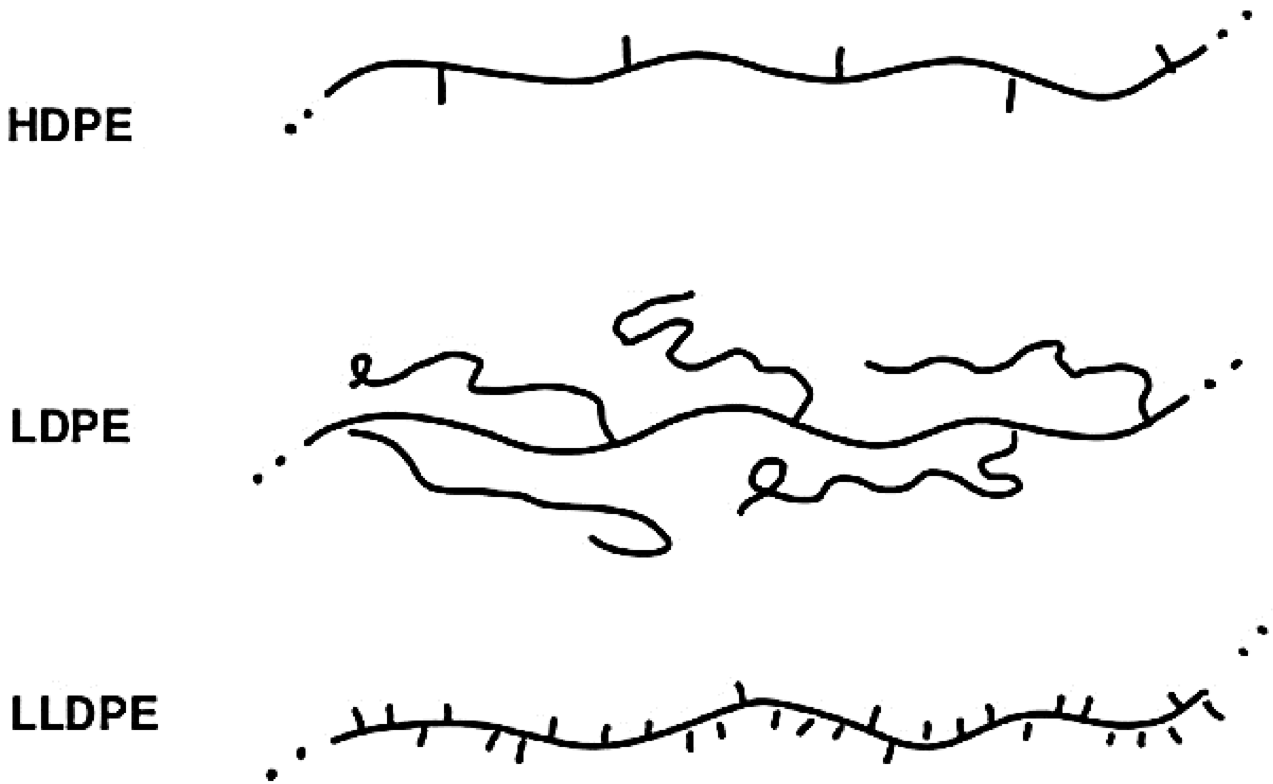
Graphic Representation of Polyethylene Molecules

Topology of Polyethylene



Polymer Specifications Dictate the Converting Process – PE Extrusion

PE Type	Nominal MI	Nominal Density, g/cc	Converters - Extrusion (some cross-over to LPBM)
UHMWPE	0	0.953	Ram extrusion, compression
HDPE	0.05	0.950	PE100, HME HDPE film grocery bags. Grooved feeder is often used.
HDPE	0.1	0.950	Sheet, LPBM (cross-over to BM)
LLDPE	1	0.920	Film
HDPE solution	1	0.958	Film, barrier film for cereal bags

Polymer Specifications Dictate the Converting Process – PE Molding

PE Type	Nominal MI	Nominal Density, g/cc	Converters - Molding Extrusion
HDPE	0.6	0.963	Gallon size milk jug, water or juice bottles
HDPE	0.3	0.952 to 0.956	Detergent bottles, chemical bottles
MDPE	3-6	0.940	rotomolding
HDPE	5-8	0.952	Injection molding, caps, closures, and pallets
HDPE	1	0.957	Injection blow molding

Contents

Polyethylene SWOT Analysis: Major Commercial Processes

- **Single reactor case**
  - Gas Phase
  - Slurry Phase

- **Multiple Reactors**

- **Dual reactors case**
  - Slurry Loops

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SWOT Analysis – UNIPOL PE (single reactor gas phase)

Strengths

- Low cost with no diluent or solvent to recover
- Mechanically less problem due to few moving parts
- Simple design so it requires less capital to build and with less maintenance
- Wide product range in MI
- Mild operating condition (pressure <350 psi and T <115C), so it is relatively safe in operation

Opportunities

- Quick bed change technology developed to speed up the grade change
- Unipol is capable of making bimodal grades when dual site Prodigy catalyst is used in one single reactor
- Univation has sold 8 Prodigy licenses worldwide, 4 in China

Weaknesses

- Takes longer time to change grades due to fluidization mechanism
- Requires larger compressor to recover ethylene
- Less suitable to make specialty grades

Threats

- Other efficient slurry processes are competing with Unipol such as CPChem's MarTech SL
- Other gas phase also compete with Unipol PE such as LBI's Spherilene S and Innovene G

SWOT Analysis – CP Chem PE MarTech SL (single reactor slurry phase)

Strengths

- Efficient cooling by water in the jacket around the loops where the slurry is propelled by high speed pump
- Simplicity of design and the capacity can be increased by extending the height and/or length of the loop pipes
- Excellent change of MI as hydrogen is well dispersed in isobutane
- Fast grade change
- Wide product range in MI

Opportunities

- Recent new plants are of 8 or 16 loops are built which lowers the CAPEX and OPEX significantly
- Slurry process is capable of making very high molecular weight PE
- This technology is extended to double loops to make high performance pipes and HMW HDPE films, we may call them differentiated commodity

Weaknesses

- Isobutane needs to be recovered and requires sufficient energy cost
- Relatively high pressure in the loops (about 700 psi) and high temperature (about 100 C) which needs all safety precautions to ensure safety

Threats

- Other efficient slurry processes are competing with MarTech SL such as UNIPOL, Innovene G, and Spherilene S for some large volume products

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SWOT Analysis – LBI APC (CSTR multiple reactors)

Strengths

- This is a three-reactor cascade reactor technology
- The product properties are excellent and homogeneous better than bimodal products

Opportunities

- Many specialty products can be made by this 3-reactors in series process due to the sell designed and controlled molecules
- This greatly expanded the product envelope. In other words, it enhances processability, stiffness, and impact at the same time

Weaknesses

- CAPEX higher than single or dual reactors
- CAPEX depends on the size of reactors

Threats

- Other processes may approach the product envelope expansion by catalyst route

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SWOT Analysis – CP Chem MarTech DL (dual reactors slurry loops)

Strengths

- Highly efficient heat transfer
- The technology is well developed by Total and CP Chem
- 40 years of manufacturing experience and product development programs with loop reactors
- Strong programs for technology dissemination to licensees
- CP Chem has a rich and successful tradition of licensing loop technology

Opportunities

- It is for selected and strategic licensing opportunities
- It is primarily for domestic market and Americas when the 500 KTA MarTech DL comes on stream by mid year 2017

Weaknesses

- There is a density limitation for MDPE bimodal grades due to solubility
- Isobutane recovery
- HMW HDPE film is a new market for CP Chem and the market is very competitive

Threats

- Innovene S will be a head-to-head competition
- LBI APC is also a strong competing technology

SWOT Analysis – Innovene S

Strengths

- Efficient cooling by hexane in the dual loop configuration
- Specifically for high performance pipe grades and HME HDPE
- Competitive CAPEX and OPEX

Opportunities

- More advanced catalyst development to extend product envelope
- Further cost reduction

Weaknesses

- Products are only for HDPE, MDPE bimodal is difficult due to solubility issue

Threats

- Competing with CP Chem MarTech DL and APC, and Innovene S
- Competing with single reactor technology via dual site catalyst

SWOT Analysis – Mitsui CX (CSTR dual reactor slurry)

Strengths

- Noted for making excellent HMW HDPE film for decades
- Cascade stirred tank reactors in series which are reputed to be reliable to make film

Opportunities

- Improved catalyst may help with the solubles

Weaknesses

- High solubles in hexane diluent
- Not as popular in high performance pipe

Threats

- LBI Hostalen APC gives better product and with excellent operability
- CP Chem MarTech DL and Ineos Technology's Innovene S are competing

Contents

Product Comparison

Dow Continuum HDPE DGDA 2490 BK

Specs, Catalyst, Process	• Density 0.949 g/c.c. and 0.959 g/c.c. (when black is in), MI = 0.06 • Z-N, bimodal
Properties & Processing	• Carbon black filled pipe resin • Extrusion
Market & Applications	• Pipe • High performance pipe: like PE100 or PE4710

LBI HDPE Alathon Product L4904

Specs, Catalyst, Process	• Density 0.949 g/c.c., MI = 0.04, Broad MWD • Z-N based, good processing, High MS
Properties & Processing	• Good ESCR • Extrusion
Market & Applications	• Pipe • High performance pipe like PE100 or PE4710

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Q & A

Thank you!