HDPE Technology
The Linear Polyethylene Family

- HDPE, MDPE, LLDPE: linear polyethylenes
- Classification by density – determined by short chain branching through comonomer content

Properties
- Melt index: 0.03 - >100 g/10 min (190 C/2.16 kg)
- Melting point: 120-140 C
- Polydispersity (TVK grades)
  - Monomodal: 6-8
  - Bimodal: 10-20
**Application**

**HDPE end-use**
- Film: 26%
- Fibre: 5%
- Injection moulding: 18%
- Blow moulding: 27%
- Pipe: 16%
- Others: 8%

**LLDPE end-use**
- Film: 81%
- Injection moulding: 5%
- Rotomoulding: 5%
- Other extrusion: 5%
- Others: 0%
Application by properties

- LLDPE INJECTION MOULDING
- MDPE YARN FILAMENTS
- LLDPE-MDPE-HDPE WIRE AND CABLE (Medium to broad MWD)
- HDPE FILM PIPES
- HDPE INJECTION MOULDING
- LLDPE BLOWN & CAST FILM
- HDPE BLOW MOULDING
- MDPE ROTOMOULDING

Legend:
- Narrow MWD
- Medium MWD
- Broad MWD
History

- HDPE discovered in 1951 by P. Hogan and R. Banks
- Mid 1950s: commercial HDPE production in slurry process (Hoechst) and solution process (Phillips Petroleum)
- 1961: slurry loop reactor technology by Phillips Petroleum
- 1968: first gas phase process by Union Carbide
- Mid 1970s: first LLDPE process by Union Carbide
- Various processes available up to 400 kt/y capacity

Consumption, 2015
- Global: HDPE 39 million t and LLDPE 28 million t
- Domestic: HDPE 90 kt and LLDPE 25 kt

MPK (TVK) HDPE plants
- 1986: Phillips slurry loop process 140 kt/y, debottlenecked to 200 kt/y
- 2004: Mitsui slurry, cascade reactor technology 200 kt/y (presently 220 kt/y)
Catalysts

- Chromium
  - Silica supported hexavalent Cr
  - Activation at high temperature before use
  - Cocatalyst not necessary
  - Medium to broad molecular weight distribution

- Ziegler(-Natta)
  - MgCl$_2$ supported TiCl$_4$
  - Metal alkyl cocatalyst necessary
  - Narrow molecular weight distribution
  - Preferred for bimodal products in cascade reactor technology → very broad MWD

- Metalallocene (single site)
  - Still developing
  - Cocatalyst necessary
  - Very narrow molecular weight distribution
  - Bimodal capability in single reactor technology
Processes and Products

Gas phase processes

Solution processes

Slurry processes

HDPE

Melt index limit
Best for blow moulding and pipe grades

High quality film grades
Loop slurry only with density limit

LLDPE
Gas Phase Processes

Characteristics

- Catalyst: chromium, Ziegler, (metallocene)
- Fluidized bed reactor
  - 70-110°C
  - 15-30 bar
  - Long residence time
- Swing technology: LLDPE – HDPE capability
- Simple process design
- Low investment and operating cost
- Bimodal capability with two reactors
Gas Phase Process
Polymerization

Critical Resources:
- Catalyst feed tank
- Comonomer treater
- Ethylene treater
- Reactor
- Degassing tank
- Gas blower
- Comonomer separator
- Purge column
- Blow down
- Ethylene and nitrogen separation

Processes:
- Ethylene
- Nitrogen

Output:
- Product to powder silo
Gas Phase Process
Additivation and Pelletizing
Solution Processes
Characteristics

- Catalyst: Ziegler, (metallocene)
- Polymerization takes place in solution
  - 30-130 bar
  - 150-300 C
  - Short residence time
- Broad product range: LLDPE – HDPE
- Bimodal capability with cascade reactors
- Higher investment and operating cost
Solution Process
ChevronPhillips Slurry Loop Process Characteristics

- Catalyst: chromium, Ziegler, (metallocene)
- Chromium catalyst activation
  - Fluidized bed activator
  - Heat treatment in air at 600-870 °C
- Reaction in loop reactor
  - 85-105 °C; 42 bar
  - 3-6 % ethylene concentration
  - Isobutane diluent
  - Heat removed by coolant in reactor jacket – very good surface/volume ratio
- Flash separation
  - 10 bar; 80 °C
- Degassing
  - 85 °C; 0,1 bar
ChevronPhillips Slurry Loop Process Polymerization
Phillips Process at MPK (TVK)
Polymerization
Phillips Process at TVK
Additivation and Pelletizing
Slurry Process - CSRT
Process Characteristics

- Catalyst: Ziegler, (metallocene)
- Low reaction pressure and temperature
  - 6-8 bar, 70-90°C
- Reaction heat removed by
  - Overhead condensators
  - Slurry coolers
  - Reactor jacket
- Bimodal product capability
  - Different molecular weight polymer in 1st and 2nd reactor
  - Comonomer built into high molecular weight polymer
- Diluent and polymer separation by centrifuge
- Diluent cleaning for low polymer removal
Slurry Process
CSRT- Cascade Stirred Reactor Technology
Slurry Process – CSRT Reactor and Surroundings
Process Control

- **Melt index**
  - Ziegler catalyst
    \[
    \frac{[\text{H}_2]}{[\text{Et}]} \uparrow \quad \text{MI} \uparrow
    \]
  - Chromium catalyst: T, [Et], [H\(_2\)]
    \[
    T \uparrow \quad \text{MI} \uparrow \\
    [\text{Et}] \uparrow \quad \text{MI} \downarrow \\
    [\text{H}_2] \uparrow \quad \text{MI} \uparrow
    \]

- **Density**
  \[
  [\text{comonomer}] \uparrow \quad \text{D} \downarrow
  \]

- **Molecular weight distribution**
  - Catalyst type
  - Reactors operated at different parameters
Key Equipment

- Reactors
  - Loop with axial circulating pump
  - Gas phase
- Decanter centrifuge – in CSTR only
- Extrusion line
Reactors

- **Loop reactors**
  - Long jacketed pipe – straight vertical sections interconnected by elbows at top and bottom
  - Built in axial pump to circulate slurry
  - Good surface to volume ratio – easy reaction heat removal

- **Gas phase reactors**
  - Vertical pressure vessel with increased top section to reduce polymer carry over
  - Long residence time
  - Reaction heat removed by external heat exchanger in recycle gas stream
  - Difficult reaction control
Loop Reactor Circulating Pump

Series 9510 and 9520 Internal Bearing Axial Flow Propeller Pumps

Available in 16", 18", 20", 22", 24", and 30" discharge sizes

Self-contained thrust bearing oil cooler.

Single, double, tandem, or double/tandem mechanical seals available in cartridge or cartridge/canister design and include a reverse balance feature.

Series 9510 Internal Anti-Friction Bearing Option

Inner Bearing/Seal Cartridge

Propeller

Propeller Cap

Self-aligning anti-friction bearing and inboard mechanical seal mounted in cartridge/canister assembly for ease of maintenance.

A wide range of standard flange ratings and flange facings are available; custom flanges available as specified.

Series 9520 Internal Sleeve Bearing Option

Sleeve Bearing

Shaft Sleeve

Propeller

Propeller Cap

Mechanical Seal Cartridge

Thrust Bearing Cartridge
Decanter Centrifuge

- Planetary gear
- Screw conveyor
- Bowl
- Feed
- Liquid discharge
- Solid discharge
CMP Extrusion Line Arrangement
CMP Elements
## Investment Cost
**Basis: WE 2015Q2**

<table>
<thead>
<tr>
<th>Process slurry</th>
<th>Capacity, kt/yr</th>
<th>Investment costs (million EUR)</th>
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<tbody>
<tr>
<td>ISBL</td>
<td>115</td>
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<tr>
<td>OSBL</td>
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<td><strong>Total investment:</strong></td>
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<tr>
<td><strong>Specific investment, EUR/ton</strong></td>
<td><strong>683</strong></td>
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## Cost of Production
Basis: WE 2015Q2

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<tr>
<th>Process</th>
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<td>Capacity, kt/yr</td>
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<tr>
<td>Production costs</td>
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<td>Raw materials</td>
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<td>Total cash cost</td>
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