HDPE Technology
Content

- HDPE, MDPE and LLDPE – linear polyethylene
- Application
- History
- Catalysts
- HDPE processes
- Process control
- Process safety
- Key equipment
- Investment cost
- Cost of production
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**

- **LLDPE**
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, 2012

- Global: HDPE/MDPE 35.5 million t and LLDPE 24 million t
- Domestic: HDPE 90 thousand t and LLDPE 17 thousand t

TVK HDPE plants

- 1986: Phillips slurry loop process 140 kt/y, debottlenecked to 190 kt/y
- 2004: Mitsui slurry, cascade reactor technology 200 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

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

- **HDPE/MDPE**
  - Melt index limit
  - Best for blow moulding and pipe grades

- **Gas phase processes**

- **Solution processes**
  - High quality film grades

- **Slurry processes**
  - 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
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
ChevronPhillips Slurry Loop Process Characteristics

- **Catalyst:** chromium, Ziegler, (metalallocene)
- **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 TVK
Polymerization
Phillips Process at TVK
Additivation and Pelletizing

1. Extruder hopper
2. Additive blender
3. Premix feeder
4. CIM
5. Extruder
6. Main feeder
7. Dewatering screen
8. Spin dryer
9. Classifier
10. Rotary feeder
11. Air blower
12. Pellet water tank
13. Pellet water pump
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
Slurry Process
Reaction Heat Removal
Process Control

- **Melt index**
  - Ziegler catalyst
    \[
    \frac{[H_2]}{[Et]} \uparrow \quad \text{MI} \uparrow
    \]
  - Chromium catalyst: \( T, [Et], [H_2] \)
    \[
    T \uparrow \quad \text{MI} \uparrow
    \]
    \[
    [Et] \uparrow \quad \text{MI} \downarrow
    \]
    \[
    [H_2] \uparrow \quad \text{MI} \uparrow
    \]

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

- **Molecular weight distribution**
  - Catalyst type
  - Reactors operated at different parameters
Process Safety

- Risk of high volume liquid hydrocarbon
- Interlock system
  - Emergency kill to prevent reaction runaway – except for CSRT
  - Action valves automatically operated by predefined process parameters to separate/blow-down equipment
- Closed blow-down system
  - Pressure safety valves, blow-down valves release to closed system, connected to
  - Flare to burn blown hydrocarbon
- Double mechanical seal on pumps in liquefied gas service
- Gas detectors
- Fire fighting system
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

Series 9510 Internal Anti-Friction Bearing Option

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

Series 9520 Internal Sleeve Bearing Option

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

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.
Decanter Centrifuge
CMP Extrusion Line Arrangement
CMP Elements
Mixing in CMP

Gate Open
GP Suction Press.: Low
Weak Mixing
(Low ESP)

Gate Open

Gate Close
GP Suction Press.: High
Strong Mixing
(High ESP)

Gate Close
## Investment Cost
**Basis: WE 2010 Q1**

<table>
<thead>
<tr>
<th>Process</th>
<th>LLDPE (Gas phase)</th>
<th>HDPE (Gas phase)</th>
<th>HDPE (Slurry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>325</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>ISBL</td>
<td>98</td>
<td>94</td>
<td>88</td>
</tr>
<tr>
<td>OSBL</td>
<td>49</td>
<td>47</td>
<td>44</td>
</tr>
<tr>
<td>Total investment</td>
<td>147</td>
<td>141</td>
<td>132</td>
</tr>
</tbody>
</table>

**Specific investment cost, EUR/t**
- LLDPE: 452 EUR/t
- HDPE: 470 EUR/t
- HDPE: 440 EUR/t
### Cost of Production

**Basis: WE 2010 Q1**

<table>
<thead>
<tr>
<th></th>
<th>LLDPE</th>
<th>HDPE</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>851,8</td>
<td>927,8</td>
<td>927,8</td>
</tr>
<tr>
<td>Comonomer</td>
<td>96,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalysts &amp; Chemicals</td>
<td>19,9</td>
<td>19,9</td>
<td>17,9</td>
</tr>
<tr>
<td><strong>Total raw materials</strong></td>
<td>967,9</td>
<td>947,7</td>
<td>945,7</td>
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<tr>
<td>Power</td>
<td>28,9</td>
<td>26,9</td>
<td>29</td>
</tr>
<tr>
<td>Other utilities</td>
<td>7</td>
<td>8,4</td>
<td>13,5</td>
</tr>
<tr>
<td>Steam credit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total utilities</strong></td>
<td>35,9</td>
<td>35,3</td>
<td>42,5</td>
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<tr>
<td>Direct fix costs</td>
<td>17,1</td>
<td>15,8</td>
<td>18,2</td>
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<tr>
<td>Allocated fix costs</td>
<td>13,7</td>
<td>14,7</td>
<td>14,2</td>
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<tr>
<td><strong>Total fixed costs</strong></td>
<td>30,8</td>
<td>30,5</td>
<td>32,4</td>
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<td><strong>Total cash costs</strong></td>
<td>1034,6</td>
<td>1013,5</td>
<td>1020,6</td>
</tr>
</tbody>
</table>

![Graph showing the cost breakdown](image-url)
Appendix: Typical Mechanical Seal

- Rotary Seal
- Packing
- Stationary Seal
- Packing
- Spring
- Rotary Seal
- Ring
- Stationary Seal
- Ring
Appendix: Blow Moulding
Appendix: Pipe Extrusion