HDPE Technology

Including MDPE and LLDPE

2010

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Content

- HDPE, MDPE and LLDPE – linear polyethylenes
- 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/MDPE
- 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
- Global consumption, 2009
  - HDPE/MDPE 30 million t/y
  - LLDPE 19.2 million t/y
- 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

Solution processes

High quality film grades

Gas phase processes

Slurry processes

Loop slurry only with density limit

LLDPE
Gas Phase Process
Polymerization

Catalyst Feed Tank

Nitrogen

Polymerization Reactor

85-110°C
20-25 bar

COOLER
C.W.

RECYLE BLOWER

ETHYLENE

O₂/H₂O REMOVAL

FEEDER

PRODUCT DEGASSING TANKS

COOLER

GUARD BED

COOLER

C.W.

COMONOMER SEPARATOR

VENT RECOVERY

VENT SYSTEM

COOLER
C.W.

BIN VENT FILTER

PURGE BIN

CLASSIFIER

Polymer Powder
Gas Phase Process
Additivation and Pelletizing
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
Solution Process

Polymerization Reactors

150-250 °C
30-100 bar

Solution Process
Solution Processes

Characteristics

- Catalyst: Ziegler, (metallocene)
- Polymerisation 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
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
Phillips Process at TVK
Polymerisation

- Hexene-1 Comonomer
- Ethylene Compressor
- Flash Gas Compressor
- Isobutane Distillation and Purification
- Flash Gas Filter
- Dryer
- Purge Column
- Powder silo
- Loop Reactor
- Circulating Pump
- Catalyst
- Settling Legs and Product Take off Valves
- Ethylene Purification
- Ethylene
Slurry Process
CSTR- Cascade Stirred Reactor
Slurry Process - CSRT
Reactor and Surroundings
Catalyst: Ziegler, (metalallocene)
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
Process Control

- **Melt index**
  - Ziegler catalyst
    - \([H_2]/[Et]\uparrow\rightarrow MI \uparrow\)
  - Chromium catalyst: \(T, [Et], [H_2]\)
    - \(T \uparrow\rightarrow MI \uparrow\)
    - \([Et] \uparrow\rightarrow MI \downarrow\)
    - \([H_2] \uparrow\rightarrow MI \uparrow\)

- **Density**
  - \([\text{comonomer}] \uparrow\rightarrow D \downarrow\)

- **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

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

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
Decanter Centrifuge

- Planetary gear
- Screw conveyor
- Bowl
- Feed
- Liquid discharge
- Solid discharge
CMP Extrusion Line Arrangement
CMP Elements
Mixing in CMP

- Gate: Open, GP Suction Press.: Low → Weak Mixing (Low ESP)
- Gate: Close, GP Suction Press.: High → Strong Mixing (High ESP)
## Investment Cost
### Basis: USGC 2008Q1; 400 kt

<table>
<thead>
<tr>
<th>Technology Product</th>
<th>Solution LLDPE</th>
<th>Gas phase LLDPE</th>
<th>Gas phase HDPE</th>
<th>Slurry loop HDPE</th>
<th>Slurry CSTR HDPE</th>
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### Specific investment, USD/t

| USD/t | 933 | 782 | 779 | 879 | 926 |
# Cost of Production

**Basis:** USGC 2008Q1; 400 kt

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<thead>
<tr>
<th>Technology</th>
<th>Product</th>
<th>Solution</th>
<th>Gas phase</th>
<th>Gas phase</th>
<th>Slurry loop</th>
<th>Slurry CSTR</th>
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Appendix: Typical Mechanical Seal

Product

Rotary Seal Packing

Stationary Seal Packing

Spring

Rotary Seal Ring

Stationary Seal Ring
Appendix: Blow Moulding
Appendix: Pipe Extrusion