LDPE Technology

2010

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What is LDPE

- **Low Density PolyEthylene**
- **Typical properties**
  - Density 0,915-0,935
  - Melt index 0,3-20 g/10 min (190 C/2,16 kg)
  - Melting point 120 C
  - Polydispersity 5,5 – 6 (TVK tubular grades)
Application

- Film 65%
- Extrusion coating 10%
- Injection moulding 7%
- Blow moulding 4%
- Other 14%
Application by Properties

- Extrusion Coating
- Injection Moulding
- Film Extrusion
- Blow Moulding

MI, g/10 min/190°C

Density, kg/dm³
History

- LDPE was discovered by ICI in 1933 → autoclave process in 1938
- BASF developed the first tubular process during WW II
- High variation of autoclave and tubular processes by different licensors
- Nowadays licences available up to 400 kt/y plant capacity
- Global consumption in 2009: 18 million t
- TVK LDPE plants
  - 1970 - ICI autoclave process 24 kt/y – debottlenecked to 50 kt/y
  - 1991 - BASF tubular process 60 kt/y
Process Theory 1

- **Free radical reaction**
  - **Initiation**
    \[ I \rightarrow R^\cdot + R^\cdot \]
    Initiators: typically organic peroxides
  - **Propagation**
    \[ R^\cdot + CH_2CH_2 \rightarrow RCH_2CH_2^\cdot \]
    \[ R(CH_2CH_2)_{n-1}CH_2CH_2^\cdot + CH_2CH_2 \rightarrow R(CH_2CH_2)_nCH_2CH_2^\cdot \]
  - **Termination**
    - **Combination**
      \[ R_x^\cdot + R_y^\cdot \rightarrow P_{x+y} \]
    - **Disproportioning**
      \[ R_x^\cdot + R_y^\cdot \rightarrow P_x + P_y \]
Process Theory 2

- Other reactions
  - Chain transfer - important to control molecular weight
    \[ R_x \cdot + \text{CH}_2\text{CH}_2 \rightarrow P_x + R_1 \cdot \] by monomer
    \[ R_x \cdot + M \rightarrow P_x + M \cdot \] by modifier
  - Cracking - results in shorter chains
    \[ R_x \cdot \rightarrow P_y + R_{x-y} \cdot \]
Process Theory 3

Branching - LDPE characterised by high degree of short and long chain branching

- **Short chain branching** – responsible for density
  Intramolecular chain transfer and copolymerisation result in short chain branches

- **Long chain branching**
  Intermolecular chain transfers give long chain branches
LDPE - Autoclave Process

1. **Initiators (Peroxides)**
2. **Autoclave reactor**
3. **Wax separator**
4. **Oil separator**
5. **HP separator**
6. **LP separator**
7. **Extruder**
8. **Degassing**
9. **Bagging Bulk loading**
10. **Secondary compressor**
11. **Primary compressor**
12. **280 bar**
13. **250 C**
14. **0.5 bar**
15. **250 C**
16. **1400 bar**
17. **Ethylene**
18. **250 bar**
19. **Autoclave reactor**

Autoclave Reactor

Autoclave reactor MK 10

L = 4750 mm  d = 18”

Total 725 l

ethylene

Top Zone

2nd Zone

peroxides

3rd Zone

4th Zone

Thermocouple 1 (1st T control)
Thermocouple 2
Thermocouple 3
Thermocouple 4 (2nd T control)
Thermocouple 5
Thermocouple 6
Thermocouple 7 (control 2nd zone T)
Thermocouple 8
Thermocouple 9 (control 3rd zone T)
Thermocouple 10 (control 4th zone T)
LDPE - Tubular Process

Initiator (Oxygen)

Primary Compressor

Secondary Compressor

Preheater

Precooler

Reaction Zone I

Reaction Zone II

HP Separator

HP Recycle

LP Recycle

Purge

Fresh Ethylene

Modifier

250 bar

2400-2900 bar

180-310 C

250 bar

280 bar

250 C

0.5 bar

250 C

280 bar

250 C

Degassing

Extruder

Bagging

Bulk loading

LP Separator
Autoclave vs. Tubular Process

**Autoclave**
- Conversion up to 21% - adiabatic, reaction heat removed by reactant only
- 1300-2000 bar operating pressure
- Higher capacity of hyper compressor
- Organic peroxide initiators only
- Specialty polymer capability – EVA copolymers over 40% vinyl acetate
- Lower reactor capacity – 150 kt/y

**Tubular**
- Conversion up to 36% - reaction heat partly removed by coolant
- 2500-3200 bar operating pressure
- Lower capacity of hyper but higher load
- Cheaper oxygen initiator possible
- Film grades with higher clarity, EVA up to 10% vinyl acetate
- Reactor capacity up to 400 kt/y
Process Steps 1

- **Compression**
  - Increase make up ethylene pressure to reaction pressure
  - Recycle unreacted ethylene
  - Inject modifier and comonomer

- **Reaction**
  - Injection of initiators
  - Control temperatures for required product properties
  - One phase reaction – two phase only at lower pressure and temperature
  - Short residence time – some minutes
Process Steps 2

- **HP separator**
  - Separate melt LDPE and unreacted ethylene

- **LP separator**
  - Remove unreacted ethylene
  - Feed tank for extruder

- **HP recycle**
  - Remove low molecular weight polymer (wax)
  - Cool down recycle ethylene

- **LP recycle**
  - Remove low molecular weight polymer (wax, oils)
  - Cool down recycle ethylene
Process Steps 3

- Extrusion
  - Homogenization
  - Additive dosing
  - Pelletizing
- Degassing
  - Remove residual ethylene (generally less than 1000 ppm) from LDPE – to avoid explosive gas mixtures
Process Control

- Melt index (Molecular weight)
  - $P \uparrow$ MI $\downarrow$ ($M_w \uparrow$)
  - $T \uparrow$ MI $\uparrow$ ($M_w \downarrow$)
  - $[\text{Modifier}] \uparrow$ MI $\uparrow$ ($M_w \downarrow$)

- Density
  - $P \uparrow$ D $\uparrow$
  - $T \uparrow$ D $\downarrow$

- Pressure range: 1300-3000 bar

- Temperature range: 160-310 C
Process Safety

- Risk of decomposition
  - Decomposition: ethylene or polyethylene decomp to C and H₂
  - High temperature, high pressure, contaminations favour decomposition
- Reactor and HP separator in confined area – generally behind concrete wall
- Interlock system to
  - avoid decomposition and
  - protect equipment
- Special metal gaskets at high pressures
- Gas detectors
- Fire fighting system
Key Equipment

- **Compressors**
  - Primary compressor (Booster+Primary)
    - 5 stages
    - 0.1 bar suction; 250 bar discharge
  - Secondary compressor (Hyper)
    - Two stages
    - 250 bar suction; 3000 bar discharge

- **Extruder**
  - Hot melt extruder for homogenization
Hyper Compressor Arrangement

Latest technologies – for best performance
- High pressure packing cups
- Low pressure packing
- Bearings
- High pressure packing
- Oil seals

In-house engineered and manufactured key components – for reliability
- Crosshead frame
- Auxiliary guide
- Burckhardt HyproPack™ – Cartridge system
- Elastic rod coupling
- Plunger coupling
- Central valve
- Burckhardt HyproPul™ – Integrated hydraulic cylinder
- Large cross sections of cooling/flushing piping
- Safety device
- Cylinder tie bolts

Rugged design – for durability
- Crankgear
- Crankshaft
- Distance piece

20
Hyper Compressor Cylinder
Extruder Arrangement

- MAIN MOTOR (3000 kW)
- GEAR REDUCER
- DIVERTOR VALVE
- LPS (LOW PRESS. SEPARATOR)
- GATE VALVE
- SCREEN CHANGER
- CUTTER UNIT
- TEX858-21H SIDE ARM
Single-screw Extruder
## Investment cost
### Basis: USGC 2008Q1

<table>
<thead>
<tr>
<th>Process</th>
<th>Autoclave 135 kt</th>
<th>Autoclave 3x135 kt</th>
<th>Tubular 400 kt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISBL</td>
<td>91,7</td>
<td>231,6</td>
<td>130,1</td>
</tr>
<tr>
<td>OSBL</td>
<td>60,6</td>
<td>142,3</td>
<td>118,4</td>
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<tr>
<td>Other project cost</td>
<td>61,2</td>
<td>160,5</td>
<td>125,1</td>
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<tr>
<td><strong>Total investment</strong></td>
<td>213,5</td>
<td>534,4</td>
<td>373,6</td>
</tr>
</tbody>
</table>

**Specific investment, USD/t**

<table>
<thead>
<tr>
<th>Autoclave 135 kt</th>
<th>Autoclave 3x135 kt</th>
<th>Tubular 400 kt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1581</td>
<td>1320</td>
<td>934</td>
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</tbody>
</table>
## Cost of Production

**Basis: USGC 2008Q1**

<table>
<thead>
<tr>
<th></th>
<th>Autoclave</th>
<th>Autoclave Tubular</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ethylene</strong></td>
<td>1354 USD/t</td>
<td>1354 USD/t</td>
</tr>
<tr>
<td><strong>Catalysts &amp; chemicals</strong></td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td><strong>Additives</strong></td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td><strong>Total raw materials</strong></td>
<td>1376</td>
<td>1376</td>
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<tr>
<td><strong>Power</strong></td>
<td>51</td>
<td>51</td>
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<tr>
<td><strong>Other utilities</strong></td>
<td>9</td>
<td>9</td>
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<tr>
<td><strong>Steam credit</strong></td>
<td>-34</td>
<td></td>
</tr>
<tr>
<td><strong>Total utilities</strong></td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td><strong>Direct cash cost</strong></td>
<td>34</td>
<td>22</td>
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<tr>
<td><strong>Allocated cash cost</strong></td>
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<td>27</td>
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<tr>
<td><strong>Total fixed costs</strong></td>
<td>71</td>
<td>49</td>
</tr>
<tr>
<td><strong>Total cash cost</strong></td>
<td>1507</td>
<td>1485</td>
</tr>
</tbody>
</table>

![Graph showing the cost distribution for different processes](image)

**Graph Notes:**
- **Total fixed costs:**
- **Total utilities:**
- **Total raw materials:**

**Processes:**
- 135 kt Autoclave
- 3x135 kt Autoclave
- 400 kt Tubular
Appendix: Metal Gasket

Schrauben und Sechskantmuttern nach DIN 2510

Nenndruck 360 MPa
Appendix: Hyper compressor cylinder
Appendix: Blown Film Extrusion
Appendix: Extrusion Coating