LDPE Technology
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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

LDPE end-use

- Film: 63%
- Injection moulding: 6%
- Extrusion coating: 11%
- Other extrusion: 10%
- Others: 10%

Other extrusion
Application by Properties

- **EXTRUSION COATING**
- **FILM EXTRUSION**
- **INJECTION MOULDING**
- **BLOW MOULDING**

**Density, kg/dm³**

- MI, g/10 min/190 ℃

**ML, g/10 min/190 ℃**

- 100
- 10
- 1
- 0.1

- 0.915
- 0.92
- 0.925
- 0.93
- 0.935
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

Consumption in 2015
- Global: 20.5 million t
- Domestic: 60-65 thousand t

MPK (TVK) LDPE plants
- 1970 - ICI autoclave process 24 kt/y – debottlenecked to 50 kt/y
  – closed in 2009
- 1991 - BASF tubular process 60 kt/y (presently 65 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

\[ R_x \cdot + \text{CH}_2\text{CH}_2 \rightarrow \text{P}_x + R_1 \cdot \] by monomer

\[ R_x \cdot + \text{M} \rightarrow \text{P}_x + \text{M} \cdot \] by modifier

- Cracking – results in shorter chains

\[ R_x \cdot \rightarrow \text{P}_y + R_{x-y} \cdot \]
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
Autoclave Reactor

Autoclave reactor MK 10
L = 4750 mm  d = 18"

Total 725 l

Top Zone

2nd Zone

3rd Zone

4th Zone

ethylene

peroxides

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
- LP Separator
- Extruder
- HP Recycle
- LP Recycle
- 280 bar
- 250 C
- 0.5 bar
- 250 C
- 2400-2900 bar
- 180-310 C
- 250 bar
- Bagging
- Bulk loading
- Degassing
Reactor temperature profile
TVK, BASF tubular plant
SPC: Lupotech TM process
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% or higher - 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 Control

- **Melt index (Molecular weight)**
  - $P \uparrow$ MI $\downarrow$ ($M_w \uparrow$)
  - $T \uparrow$ MI $\uparrow$ ($M_w \downarrow$)
  - [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 decomposes to C, CH₄ 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; 250-300 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 HyproPull™ – Integrated hydraulic cylinder
- Large cross sections of cooling/flushing piping
- Safety device
- Cylinder tie bolts

Rugged design – for durability
- Crankgear
- Crankshaft
- Distance piece
Hyper Compressor Cylinder

- main packing and compression chamber located in an assembly cartridge
Extruder Arrangement

MAIN MOTOR (3000 kW)

GEAR REDUCER

LPS (LOW PRESS. SEPARATOR)

GATE VALVE

TEX65α-21H SIDE ARM

DIVER TOR VALVE

SCREEN CHANGER

CUTTER UNIT
Single-screw Extruder
# Investment cost

**Basis:** WE 2015Q2

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<tr>
<th>Process</th>
<th>tubular</th>
<th>autoclave</th>
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<td><strong>Capacity, kt/yr</strong></td>
<td>325</td>
<td>100</td>
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<th>Investment costs</th>
<th>million EUR</th>
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<td>OSBL</td>
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<td><strong>Total investment:</strong></td>
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<td><strong>Specific investment, EUR/ton</strong></td>
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Cost of Production
Basis: WE 2015Q2

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<td>Capacity, kt/yr</td>
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<td>Raw materials</td>
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<td>Total cash cost</td>
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<td>1099</td>
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Appendix: Autofrettage

- Special treatment of high pressure parts: introduction of intrinsic stresses in the wall by plastic deformation with the result of stress reduction under operating conditions and longer lifetime.
- Autofrettage is performed by high pressure - up to 1000 MPa - in short time.
Appendix: TVK LDPE-2 high pressure piping
Appendix: blown film extrusion