POLYETHYLENE PRODUCTION TECHNOLOGIES

Routes to Polyethylene
1. From Natural Gas

Natural Gas → Natural Gas Separation → Ethane/Propane → Steam cracking → Ethylene → Polymerization → Polyethylene

Natural Gas Separation → Methane → Partial Oxidation → Acetylene

Ethane/Propane → Extract & Dehydrogenation → Ethylene

Steam cracking → Butane → Butadiene

Steam Cracking → Condensate → Ethylene, Propylene, Butadiene

Byproducts (LPG or C4’s)
2. From Naphtha

Naphtha → Steam Cracking → Butane

Butane → Extraction & Dehydrogenation → C4’s for Production of LPG

C4’s for Production of LPG → LPG

Ethylene → Polymerization → Polyethylene

Polyethylene → Propylene

Fuel Gas → Ethylene

Propylene

Butadiene

Gasoline

Fuel Oil
Routes to PE New Trends

1. MTO (Methanol to Olefins)

2. Bio Petrochemicals (Ethanol Dehydration)
POLYETHYLENE PRODUCTION TECHNOLOGIES

POLYETHYLENE POLYMERIZATION REACTION & TECHNIQUES
PE Polymerization Reactions

- **Polymerization**
  A reaction in which polymer chain is formed by combining large number of small molecules called “Monomers”.

- **Polymerization reaction steps:**
  1. **Initiation**
     The trick to get the reaction started is to use a catalyst, initiator or promoter.
PE Polymerization Reactions (cont’d)

2. Propagation/Growth
The new radical formed in the first step reacts with another monomer molecule to give a new larger radical. This chain growth continue until propagation is terminated

\[
\begin{align*}
I-M^* + M & \rightarrow I-M-M^* \\
I-M^* + M_n & \rightarrow I-M_n-M^*
\end{align*}
\]

3. Termination
Mechanism to stop the propagation
- Dis-propagation
- Recombination
- Chain transfer
PE Polymerization Techniques

The route to PE falls into two categories:

1. **High pressure polymerization**
   - Produces LDPE
   - Operating pressure ranging from 1000 to 3000 barg
   - Operating temperature from 80 to 300 °C
   - Autoclave or tubular reactor
   - Free radical catalysts using initiators (peroxides)
   - Ethylene compression to the reaction pressure through several compression stages with inter stage cooling is a major step.
PE Polymerization Techniques (cont’d)

2. Low pressure polymerization

- Produces LLDPE and HDPE
- Utilizes co-monomer (Butene-1, Hexene-1 or Octene-1)
- Operating pressure ranging from 10 to 80 barg
- Operating temperature from 70 to 300 °C
- 3 types of Catalyst can be used
  - Ziegler/Natta
  - Cr/Mo oxide
  - Metalallocene
PE Polymerization Techniques (cont’d)

2. Low pressure polymerization (cont’d)

There are THREE different processes developed for low pressure PE polymerization

I. Solution Process

- Both catalyst and resulting polymer remain dissolved in a solvent that must be removed to isolate the polymer.

- Polymerization reaction takes place in a CSTR (Continuous Stirred Tank Reactor).
PE Polymerization Techniques (cont’d)

2. Low pressure polymerization (cont’d)

II. Slurry Process

- Catalyst and polymer formed during production remains suspended in a liquid medium but never dissolving.

- Polymerization reaction takes place in CSTR or tubular reactor.
PE Polymerization Techniques (cont’d)

2. Low pressure polymerization (cont’d)

III. Gas Phase Process

✓ No solvent is used.

✓ Ethylene monomer and supported catalyst are blown into the reactor.

✓ Polymerization reaction takes place in fluidized bed reactor.
PE Polymerization Techniques (cont’d)

Regional differences/similarities in the type of process utilized to produce linear polyethylene

- **Solution, 15%**
  - NA: 34%
  - W. Europe: 24%
  - Japan: 3%
  - Other Asia: 16%
  - ROW: 23%
  - Total: 13,635 MM Lbs.

- **Gas, 43%**
  - NA: 33%
  - W. Europe: 10%
  - Japan: 5%
  - Other Asia: 26%
  - ROW: 26%
  - Total: 41,900 MM Lbs.

- **Slurry, 42%**
  - NA: 31%
  - W. Europe: 19%
  - Japan: 7%
  - Other Asia: 26%
  - ROW: 14%
  - Total: 40,790 MM Lbs.
PE POLYMERIZATION
TYPICAL PROCESS
SCHEME
POLYETHYLENE PRODUCTION TECHNOLOGIES

Co-monomer Purification

Ethylene Purification & Compression

Catalyst(s) Preparation Section

Recycle gas recovery & cooling

Recycle gas compressor

Hydrogen Purification (If Applicable)

Gas recycle & Recovery

Polymerization

Degassing

Polymer withdrawal & conditioning (drying)

Additives

Extrusion

Solvent Recover (if applicable)

Storage silos, bagging and palletizing

Pelletizing

Product

H2

Ethylene
POLYETHYLENE PRODUCTION
TECHNOLOGIES

POLYETHYLENE, GRADES
AND PROPERTIES
• PE is a **thermoplastic** polymer, which can be melted to a liquid and remolded as it returns to a solid state.

• PE is the most widely used plastic with worldwide annual production of approximately 150 million metric tons (2013).

• PE is chemically synthesized from molecules that contain long chains of ethylene monomer.
## Most Important PE Grades Properties

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>LLDPE</th>
<th>LDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density, gm/cm³</strong></td>
<td>0.94 – 0.97</td>
<td>0.926 – 0.94</td>
<td>0.91 – 0.925</td>
</tr>
<tr>
<td><strong>Crystallinity, %</strong></td>
<td>80 – 90</td>
<td>55</td>
<td>50 – 65</td>
</tr>
<tr>
<td><strong>Melting Temp. °C</strong></td>
<td>130</td>
<td>125</td>
<td>115</td>
</tr>
<tr>
<td><strong>Yield Strength, MPa</strong></td>
<td>20 - 40</td>
<td>8 - 45</td>
<td>4 - 16</td>
</tr>
<tr>
<td><strong>Melt index range (g/10 min)</strong></td>
<td>0.1 - 100 - 150</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Most Important PE Grades Properties (cont’d)
BIMODAL HDPE

• There is two types of HDPE with respect to molecular weight distribution
  1. Low Molecular Weight (LMW)
  2. High Molecular Weight (HMW)

Both are called **UNIMODAL** HDPE which relates to possessing a unique mode per reactor.

• **BIMODAL** is the combination between LMW and HMW in one reactor.

• **Why BIMODAL HDPE?**
  Light weight containers while maintaining good impact resistance.
POLYETHYLENE PRODUCTION TECHNOLOGIES

- UNIMODAL HDPE

The diagrams show the relationship between molecular weight and the number of molecules, indicating a unimodal distribution.
BIMODAL HDPE (cont’d)
POLYETHYLENE PRODUCTION TECHNOLOGIES

POLYETHYLENE END USER TECHNIQUES
End User Processing Techniques

Extrusion

- Fluff or Pellets + additives
- Heat
- Mechanical Shear
- Molten polymer
- Die
- Cooling
- Pellets
- Cast films
- Sheets
- Pipes
- Blown films
- Blow molding
- Fibers
End User Processing Techniques (cont’d)

Sheet Extrusion

Thermoforming
End User Processing Techniques (cont’d)
End User Processing Techniques (cont’d)

Blow Molding
POLYETHYLENE APPLICATIONS
POLYETHYLENE PRODUCTION TECHNOLOGIES

**LLDPE**

- Heavy duty bags
- Covers
- Buckets and containers
- Stretch films
Polyethylene Production Technologies

- HDPE
  - Hard hats
  - Detergent bottles
  - Natural gas and Water distribution piping
  - Food storage containers
  - Bottle caps
POLYETHYLENE PRODUCTION TECHNOLOGIES

LDPE

- Plastic bags
- Dispensing bottles
- Film warps
- Cables insulation
- General purpose containers
PE Global Demand Growth Rate

- HDPE: 4.4%
- LLDPE: 5.3%
- LDPE: 2.2%
LLDPE Market Analysis

1. Global Demand Growth Rate

- Over the forecast period (2025), Overall LLDPE growth is expected to increase by around 5.3 percent per year.
- Butene-1 is the traditional co-monomer for commodity applications due to its relatively low cost.
- Hexene-1 and Octene-1 for more demanding application.
LLDPE Market Analysis (cont’d)

2. Global Demand (2013)
   - 24.5 million ton
3. Global Supply & Demand

LLDPE Market Analysis (cont’d)

- Graph showing trends in consumption, production, operating rate, and capacity from 2004 to 2024.
2. Local Demand (2013)

- Butene-1 grade demand 167.7 KTA
- Hexene-1 is 13.2 KTA
LLDPE Egyptian Market Analysis (cont’d)

3. Local Supply & Demand (Butene-1)
HDPE Market Analysis

1. Global Growth rate
   - 4.4 % annually

2. Global Demand (2013)
   - 40.3 million ton
3. Global Supply & Demand

HDPE Market Analysis (cont’d)
POLYETHYLENE PRODUCTION TECHNOLOGIES

- **LDPE Market Analysis**
  1. **Global Growth rate**
     - 2.6% annually
  2. **Global Demand (2013)**
     - 20 million ton
3. Local Consumption Growth

- LDPE Market Analysis (cont’d)

![Consumption KTA Diagram]

- Consumption KTA
The primary drives of price are combination of the production costs and supply demand balance.

Factors affecting the price:
1. Prices in other region
2. Relationship to other petrochemical products
3. Profitability of upstream and downstream process
PE Grades Pricing History
POLYETHYLENE PRODUCTION TECHNOLOGIES AND FEATURES
HIGH PRESSURE POLYMERIZATION LICENSORS (LDPE)
High Pressure Polymerization Licensors

- ExxonMobil (Autoclave, Tubular)
- SABIC (Tubular)
- Lyondell Basell (Lupotech T) (Tubular)
- Lyondell Basell (Lupotech A) (Autoclave)
- Polineri Europa (Autoclave, Tubular)
- Mitsubishi (Autoclave)
- Simon Carves (Autoclave)
EXxon Mobil (Tubular)
POLYETHYLENE PRODUCTION TECHNOLOGIES

- Exxon Mobil (Autoclave)
Exxon Mobil (Tubular/Autoclave) Features

• The tubular reactors operate at pressure up to 3,000 bar, where Autoclave reactor operates below 2,000 bar.
• MI range: 0.2 – 150
• Density range: 0.912 – 0.935
• Reactor turn down ratio: 50%
• Short residence times.
• Reactor conversation up to 40%
• Process and mechanical design up to 400 KTA
• Ability to switch from homo-polymers to copolymers
• Product from the tubular process is typically higher in molecular weight and has more short chain branches than LDPE from the autoclave process.
• Produce LDPE homo-polymers and ethylene vinyl acetate (EVA) copolymers.
LOW PRESSURE POLYMERIZATION LICENSORS (HDPE & LLDPE)
POLYETHYLENE PRODUCTION TECHNOLOGIES

➢ Low Pressure Polymerization Licensors

1. Ziegler Slurry Processes (HDPE)
   • Lyondell Basell (Hostalen)
   • Mitsui Chemicals (CX Process)
   • Nippon
   • Equistar

2. Slurry Loop Processes (HDPE and swing LLDPE/HDPE)
   • Chevron Phillips
   • Borealis (BORSTAR) (slurry loop and gas phase in series)
   • INEOS Technologies (Innovene™ S)
3. Gas Phase Processes (HDPE and swing LLDPE/HDPE)
   • Univation (UNIPOL™ PE Process, PRODIGY Bimodal), and UNIPOL unimodal swing process
   • Lyondell Basell (Spherilene), bimodal swing
   • Lyondell Basell (Lupotech G) unimodal HDPE/MDPE
   • INEOS INNOVEN G unimodal swing process

4. Solution Processes (LLDPE)
   • DOW Chemical (DOWLEX)
   • DSM/Stamicarbon (COMPACT)
   • NOVA Chemicals (SCLAIRTECH) (Advanced SCLAIRTECH)
Lyondell Basell Ziegler Slurry Process (HDPE)
Lyondell Basell Ziegler Slurry Process Features

- Catalyst used AVANT Z501 OR ZS509
- Pressure of 5 to 10 atm
- Temperature of 75 to 90 °C
- BUTENE-1 is used as the co-polymer
- Residence time is 0.7 to 2.5 hours per reactor
- Hexane is used as a diluent
POLYETHYLENE PRODUCTION TECHNOLOGIES

- Chevron Phillips (Slurry Loop Process)
Chevron Phillips (Slurry Loop Process) Features

- Two distinct catalysts:
  1. Chromium based catalyst - MI 0.2 to 5
  2. Organometallic - MI 1 to 100
- Isobutene (hydrocarbon) used as diluent
- Co-monomer used is hexane-1 only
- Density range: 0.945 - 0.980
- Reactor turn down ratio: 50% - Short Residence time
- Ethylene conversation per reactor pass is in excess of 96%
- Efficient heat removal
- Hydrogen is used for molecular weight control.
- The reactor consists of a continuous 4, 6, 8, 10, or 12-leg loop to with an axial flow pump, Easily Expandable capacity by extending the reactor length, Single Loop reactor has capacity up 400KTA
## Slurry Process Products Slate

<table>
<thead>
<tr>
<th>APPLICATION</th>
<th>DENSITY</th>
<th>MELT INDEX (G/10 MIN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLOW FILM</td>
<td>0.922-0.976</td>
<td>0.04 - 5</td>
</tr>
<tr>
<td>CABLE</td>
<td>0.922-0.927</td>
<td>0.06 - 0.4</td>
</tr>
<tr>
<td>BLOW MOULDING</td>
<td>0.922-0.960</td>
<td>0.08 - 4</td>
</tr>
<tr>
<td>INJECTION MOULDING</td>
<td>0.922-0.979</td>
<td>0.7 - 50</td>
</tr>
<tr>
<td>ROTO MOULDING</td>
<td>0.923-0.935</td>
<td>4 – 8.5</td>
</tr>
<tr>
<td>CAST FILM</td>
<td>0.922-0.976</td>
<td>4 - 70</td>
</tr>
<tr>
<td>PIPE</td>
<td>0.940-0.963</td>
<td>0.06 - 0.4</td>
</tr>
</tbody>
</table>
Univation (UNIPOL) Gas Phase

- Cycle gas compressor
- Cooler
- Product Discharge tank
Univation (UNIPOL) Gas Phase Features

- Three types of catalyst family
  1. Bimodal HDPE (PRODIGY BMC), made up of two catalyst components, one for low Mwt, and the other for high Mwt (advanced catalyst)
  2. Ziegler-Natta for narrow MWD HDPE and LLDPE
  3. Chrome-based for medium to broad MWD HDPE and LLDPE
- Co-monomer used: Butane-1/Hexene-1
- MI range: 0.01-150
- Density range: 0.9-0.970
- The range of products properties as above is not available with competing other processes
- Reactor turn down ratio: 50%
Univation (UNIPOL) Gas Phase Features (cont’d)

- Produces the widest range of (LLDPE), (MDPE) and (HDPE) having conventional, Metallocene, and new bimodal catalyst systems of unimodal or bimodal molecular weight distribution (MWD) using a single, low-pressure, gas-phase reactor.
- Ability to produce the broadest and most versatile product line
- No diluents or solvent used, there is no aqueous waste stream to handle
- Few piece of equipment
- UNIVATION process is a joint venture between DOW chemical and Exxon Mobil
- Union Carbide is a current subsidiary of the Dow chemical
### Gas Phase Process Products Slate

<table>
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<tr>
<th>APPLICATION</th>
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</thead>
<tbody>
<tr>
<td>BLOW FILM</td>
<td>0.885 - 0.965</td>
<td>0.085 - 5</td>
</tr>
<tr>
<td>CABLE</td>
<td>0.895 - 0.927</td>
<td>0.085 - 0.4</td>
</tr>
<tr>
<td>BLOW MOULDING</td>
<td>0.915 - 0.96</td>
<td>0.085 - 0.4</td>
</tr>
<tr>
<td>INJECTION MOULDING</td>
<td>0.89 - 0.97</td>
<td>0.85 – 75</td>
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<tr>
<td>ROTO MOULDING</td>
<td>0.92 - 0.935</td>
<td>4 – 8.5</td>
</tr>
<tr>
<td>EXTRUSION COATING</td>
<td>0.905 - 0.922</td>
<td>4 – 50</td>
</tr>
<tr>
<td>CAST FILM</td>
<td>0.922 - 0.965</td>
<td>5 -75</td>
</tr>
<tr>
<td>PIPE</td>
<td>0.94 - 0.963</td>
<td>0.085 - 0.4</td>
</tr>
</tbody>
</table>
POLYETHYLENE PRODUCTION TECHNOLOGIES

- DOW Chemical Solution Process (LLDPE)
DOW Chemical Solution Process (LLDPE) Features

- Co-monomer used: Octene-1/ Butene-1
- MI range: 0.9-200
- Density range: 0.89-0.945
- Reactor turn down ratio: 50%
- Molecular weight distribution and ability to produce bimodal resins.
- Over 90 percent ethylene conversion per pass.
- The DOWLEX technology is not available for third party licensing, but is available through joint ventures.
### Solution Process Products Slate

<table>
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<td>0.915 - 0.932</td>
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</tr>
<tr>
<td>ROTO MOULDING</td>
<td>0.92-0.932</td>
<td>4 – 8.5</td>
</tr>
<tr>
<td>CAST FILM</td>
<td>0.925-0.93</td>
<td>5 - 70</td>
</tr>
</tbody>
</table>
Low Pressure Polymerization Licensors (cont’d)

Linear PE Capacity Breakdown By Licensor
LICENSE EVALUATION CRITERIA
Technology License screening criteria is categorized into:

- Licensing
- Commercial Experience
- Investment Cost
- Cost of Production
- Utility Consumption
Technical Evaluation Criteria

• Experience

1. Total Polyethylene similar plant experience list
2. Process of Polyethylene plant experience list
3. Experiences in the Middle East
4. Experience in Egyptian market
Technical Evaluation Criteria (cont’d)

- Process
  1. Length of campaign
  2. Duration of change over
  3. Expected off grade quantity
  4. Co-monomer used
  5. Waste tonnage product
  6. No. of grades per application
  7. Turn down ratio
  8. Start-up time (feed to on-spec)
  9. No of catalysts used
  10. No of catalyst suppliers
  11. Frequency of scale removal from the reactor
  12. Over-all conversion rate
Commercial Evaluation Criteria

1. Cost
   - License Fee
   - Basic Engineering: Preparation of ITB for EPC
   - Review of key documents

2. Technical support

3. Terms of payments

4. Aggregate liability

5. Schedule of work

6. Variable Cost
   - Ethylene, Co-monomer, Catalyst, Chemicals, Pelletizing additives
   - Utilities (Cooling water, Electric power, Steam …etc)
SIDPEC 225 KTA PE PLANT
POLYETHYLENE PRODUCTION TECHNOLOGIES

SIDPEC Overall Material Balance

- Ethylene Plant 300 KTA
- C₂/C₃ (468 KTA)
- Ethylene (230 KTA)
- Butene-1 (10 KTA)
- H₂ (230 KTA)
- Butene-1 Surplus (6 KTA)
- PE Plant 225 KTA
- Ethylene (50 KTA)
- LPG (60 KTA)
- EPC (60 KTA)
- PE (225 KTA)
- Butene-1 (4 KTA)

Flow Diagram:
1. Ethylene Plant 300 KTA
   - C₂/C₃ (468 KTA)
   - Ethylene (230 KTA)
2. Butene-1 10 KTA
   - Ethylene (10 KTA)
   - H₂ (230 KTA)
3. PE Plant 225 KTA
   - Butene-1 (4 KTA)
4. EPC
   - Ethylene (50 KTA)
   - LPG (60 KTA)
5. PE (225 KTA)
   - Butene-1 Surplus (6 KTA)
ETHYDCO 400 KTA PE PLANT
Ethydco Overall Material Balance

- 834 KTA C₂/C₃
- 460 KTA Ethylene
- 18 KTA Butene-1
- 22 KTA Hexene-1
- 400 KTA PE
- 20 KTA Butadiene
POLYETHYLENE PRODUCTION TECHNOLOGIES

ETHYDICO 400 KTA PE Plant

- Butene
- Hexene
- Catalyst
- Ethylene

- Comonomer Storage & Purification
- Slurry/BMC Catalyst System (Catalyst preparation)
- Ethylene Compression & Purification
- Reaction Loop Trains & Product Discharge system
- N2 generation & purification
- H2 compression
- Vent Recovery Trains
- Resin Degassing Trains
- Resin Additives Trains
- Resin Pelletizing Trains
- Bagging & Bulk Loading
<table>
<thead>
<tr>
<th>Ethylene Plant</th>
<th>SIDPEC</th>
<th>ETHYDICO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>300 KTA polymer grade Ethylene</td>
<td>460 KTA polymer grade Ethylene</td>
</tr>
<tr>
<td>License</td>
<td>ABB Lummus Technology</td>
<td>ABB Lummus Technology</td>
</tr>
<tr>
<td>Contractor</td>
<td>TOYO Engineering</td>
<td>TOYO Engineering</td>
</tr>
</tbody>
</table>
| Byproducts    | • High Purity H₂  
• LPG  
• Pyrolysis Gasoline | • High Purity H₂  
• Butadiene  
• Pyrolysis Gasoline |
| Main Process Sections | • Acid gases removal unit (CO₂ & H₂S)  
• Pyrolysis & Quenching  
• Compression, acid gas removal, drying & Hg removal units  
• Cold box & fractionation  
• LPG Unit | • Acid gases removal unit (CO₂ & H₂S)  
• Pyrolysis & Quenching  
• Compression, acid gas removal, drying & Hg removal units  
• Cold box & fractionation  
• Butadiene Extraction Unit |
<table>
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<tr>
<th>PE Plant</th>
<th>SIDPEC</th>
<th>ETHYDCO</th>
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<tbody>
<tr>
<td>Capacity</td>
<td>225 KTA PE</td>
<td>400 KTA PE</td>
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<tr>
<td>License</td>
<td>BP Innovene gas phase process</td>
<td>Unipol gas phase process</td>
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<tr>
<td>EPC Contractor</td>
<td>Samsung – Korea</td>
<td>TOYO Engineering</td>
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<tr>
<td>Catalyst</td>
<td>Cr catalyst Ziegler Catalyst</td>
<td>Ziegler Catalyst Cr catalyst Bimodal catalyst</td>
</tr>
<tr>
<td>Operating Conditions</td>
<td>28 barg 75 – 100 °C</td>
<td>23 barg 50 – 90 °C</td>
</tr>
<tr>
<td>Co-monomer</td>
<td>Butene-1</td>
<td>Butene-1 Hexene-1</td>
</tr>
<tr>
<td>Solvent</td>
<td>Yes, pre-polymerization step N-hexane</td>
<td>No</td>
</tr>
<tr>
<td>Product slate</td>
<td>HDPE LLDPE</td>
<td>HDPE Bimodal HDPE LLDPE</td>
</tr>
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</table>
## POLYETHYLENE PRODUCTION TECHNOLOGIES

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<tr>
<th>PE Plant</th>
<th>SIDPEC</th>
<th>ETHYDICO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main Process Sections</strong></td>
<td><strong>Catalyst preparation Unit</strong>&lt;br&gt;<strong>Feed Purification Unit</strong>&lt;br&gt;<strong>Solvent Recovery Unit</strong>&lt;br&gt;<strong>Pre-polymerization Unit</strong>&lt;br&gt;<strong>Polymerization &amp; degassing Unit</strong>&lt;br&gt;<strong>Additives and Pelletizing Unit</strong>&lt;br&gt;<strong>Pellets Storage &amp; Bagging</strong></td>
<td><strong>Catalyst preparation Unit</strong>&lt;br&gt;<strong>Feed Purification Unit</strong>&lt;br&gt;<strong>Polymerization &amp; degassing Unit</strong>&lt;br&gt;<strong>Additives and Pelletizing Unit</strong>&lt;br&gt;<strong>Pellets Storage &amp; Bagging</strong></td>
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</table>
THANK YOU