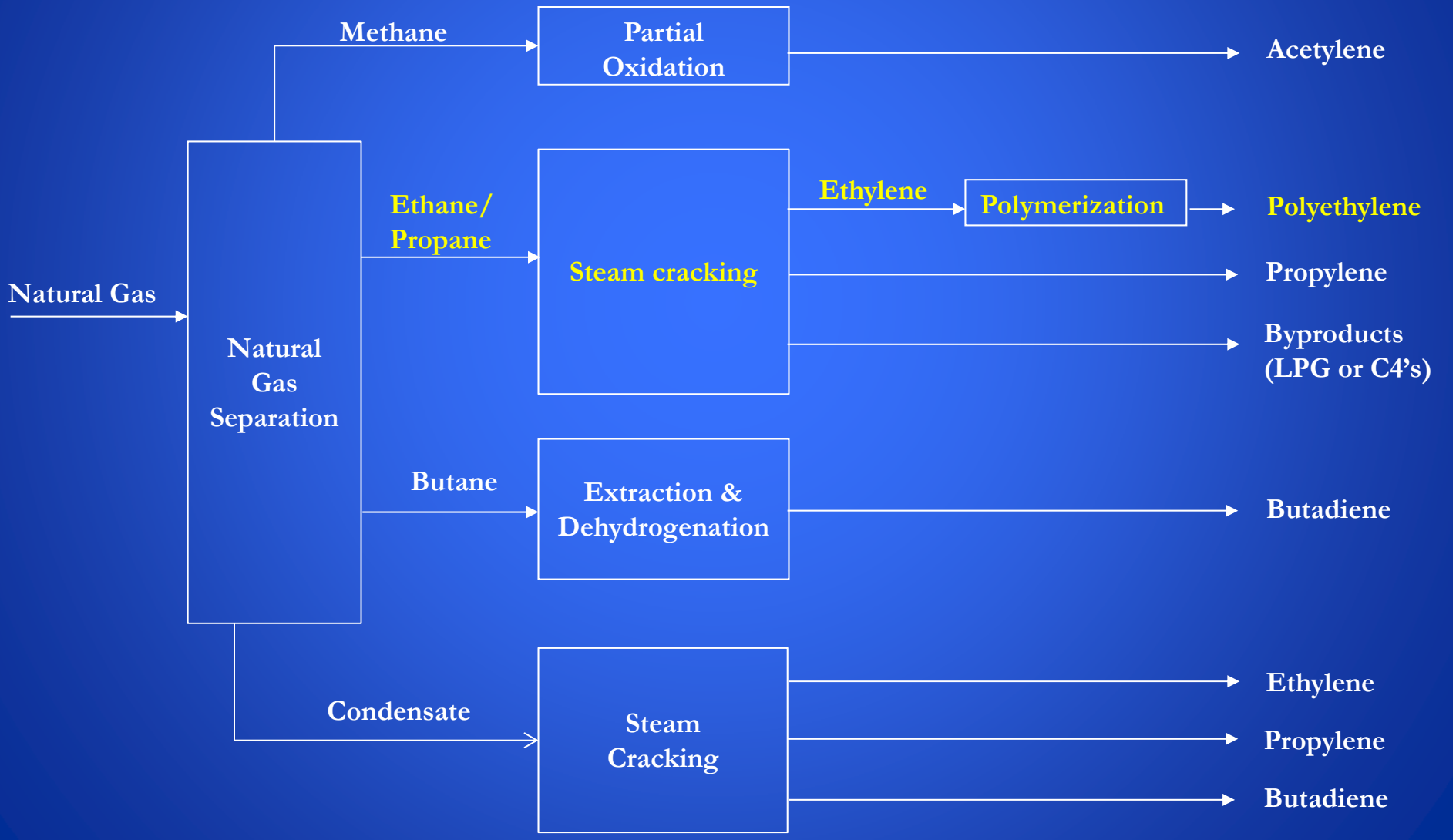
# POLYETHYLENE PRODUCTION TECHNOLOGIES

# ROUTES TO POLYETHYLENE

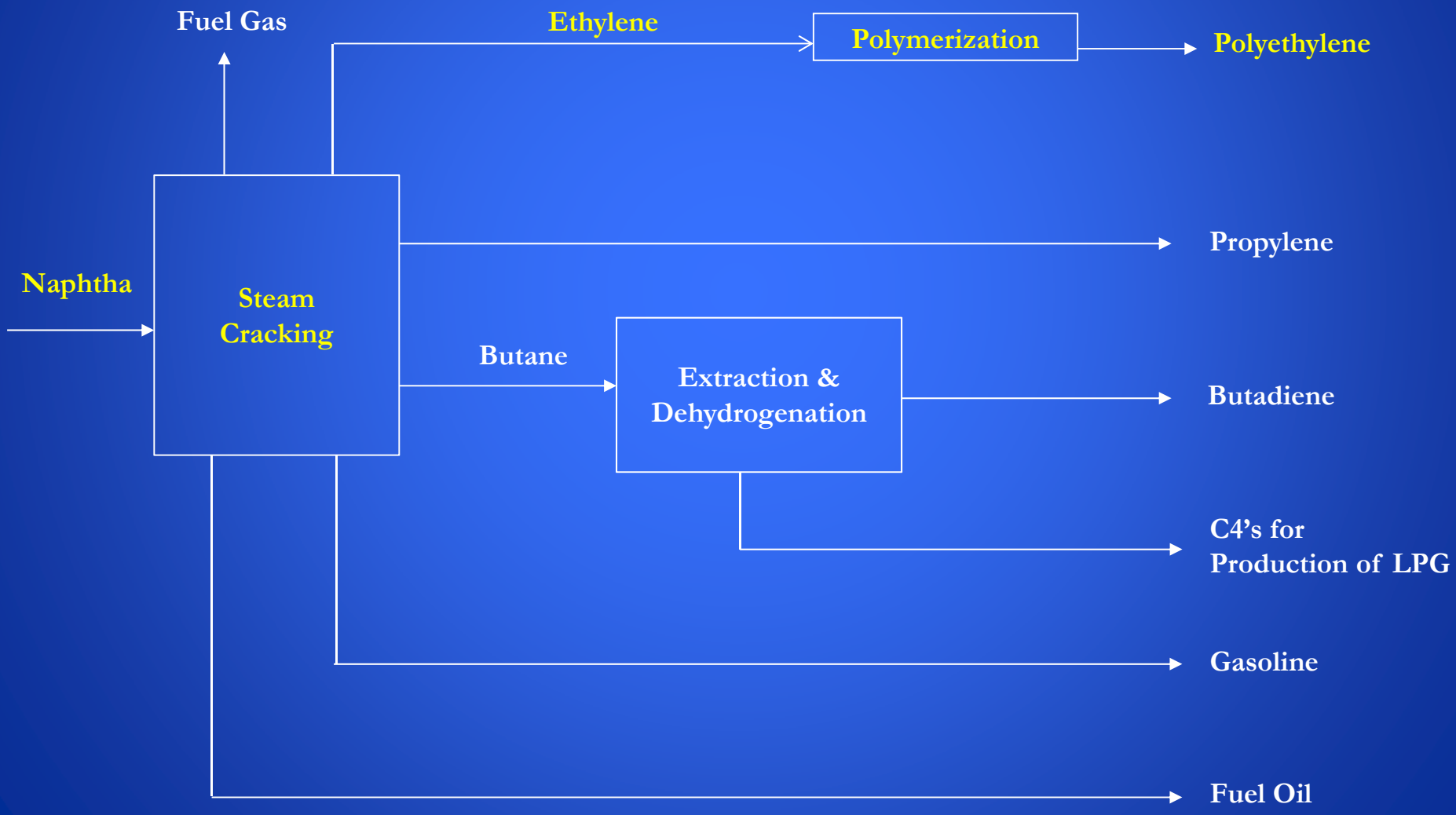
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## 1. From Natural Gas



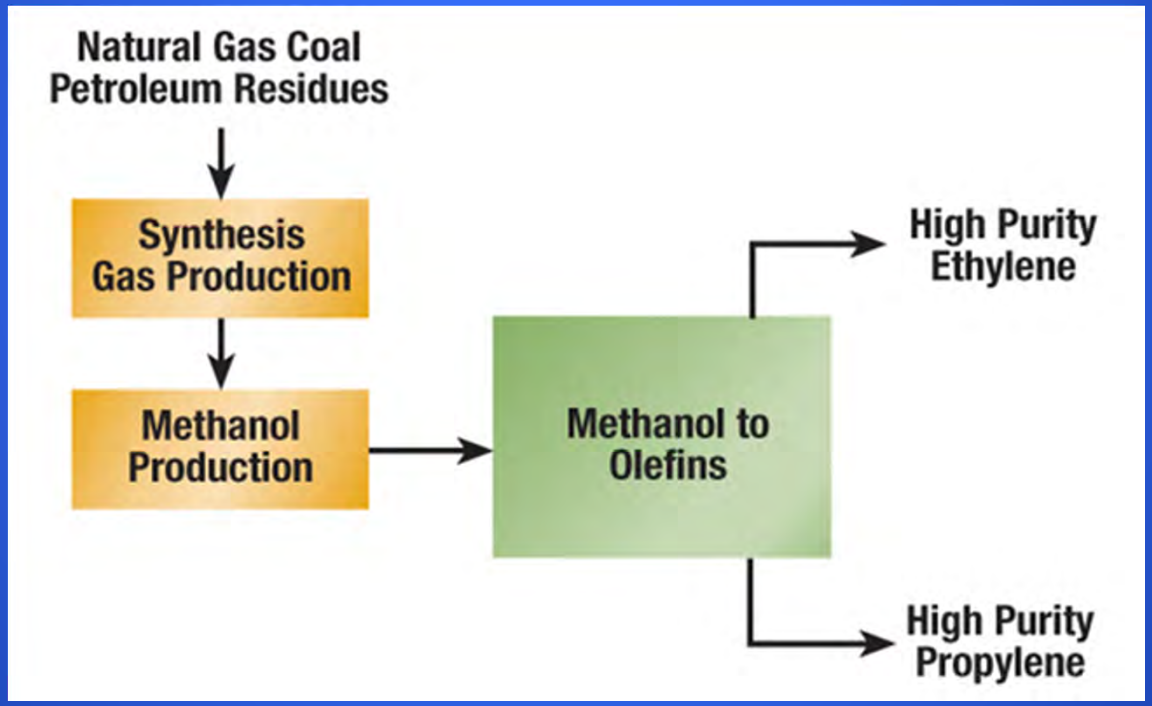
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## 2. From Naphtha



## ➢ Routes to PE New Trends

1. MTO ( Methanol to Olefins)




2. Bio Petrochemicals (Ethanol Dehydration)

# POLYETHYLENE POLYMERIZATION REACTION & TECHNIQUES

# ➢ PE Polymerization Reactions

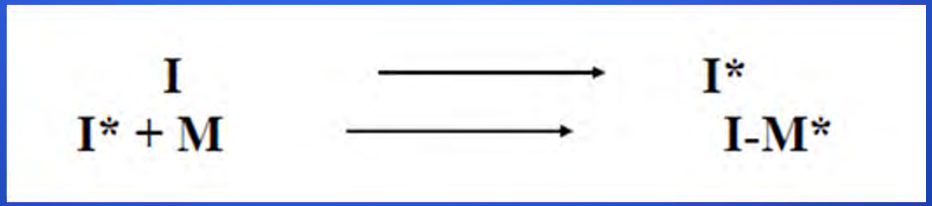
- **Polymerization**

  A reaction in which polymer chain is formed by combining large number of small molecules called "Monomers".

- **Polymerization reaction steps:**

1. **Initiation**

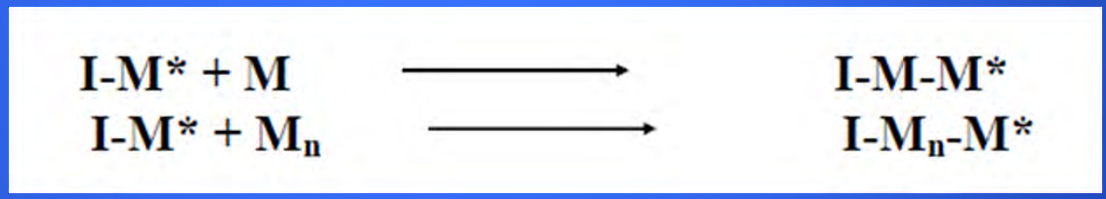
   The trick to get the reaction started is to use a catalyst, initiator or promoter.



## ➢ 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




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**
  - ✓ **Metallocene**

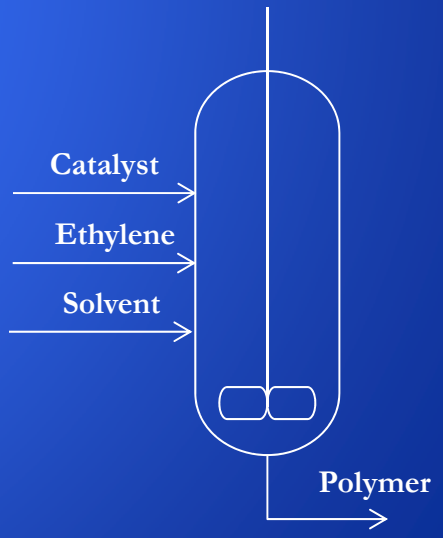
# ➢ PE Polymerization Techniques (cont'd)

## 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

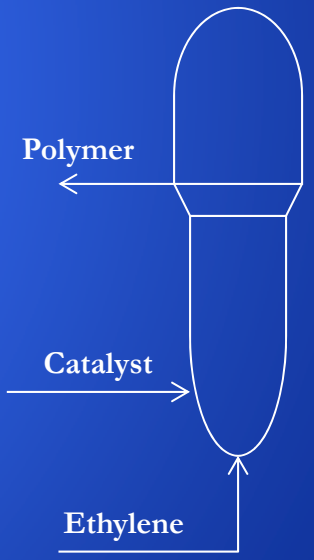
- ✓ Catalyst and polymer formed during production remains suspended in a liquid medium but never dissolving.
- ✓ Polymerization reaction takes place in CSTR or tubular reactor.

# ➢ PE Polymerization Techniques (cont'd)

## 2. Low pressure polymerization (cont'd)

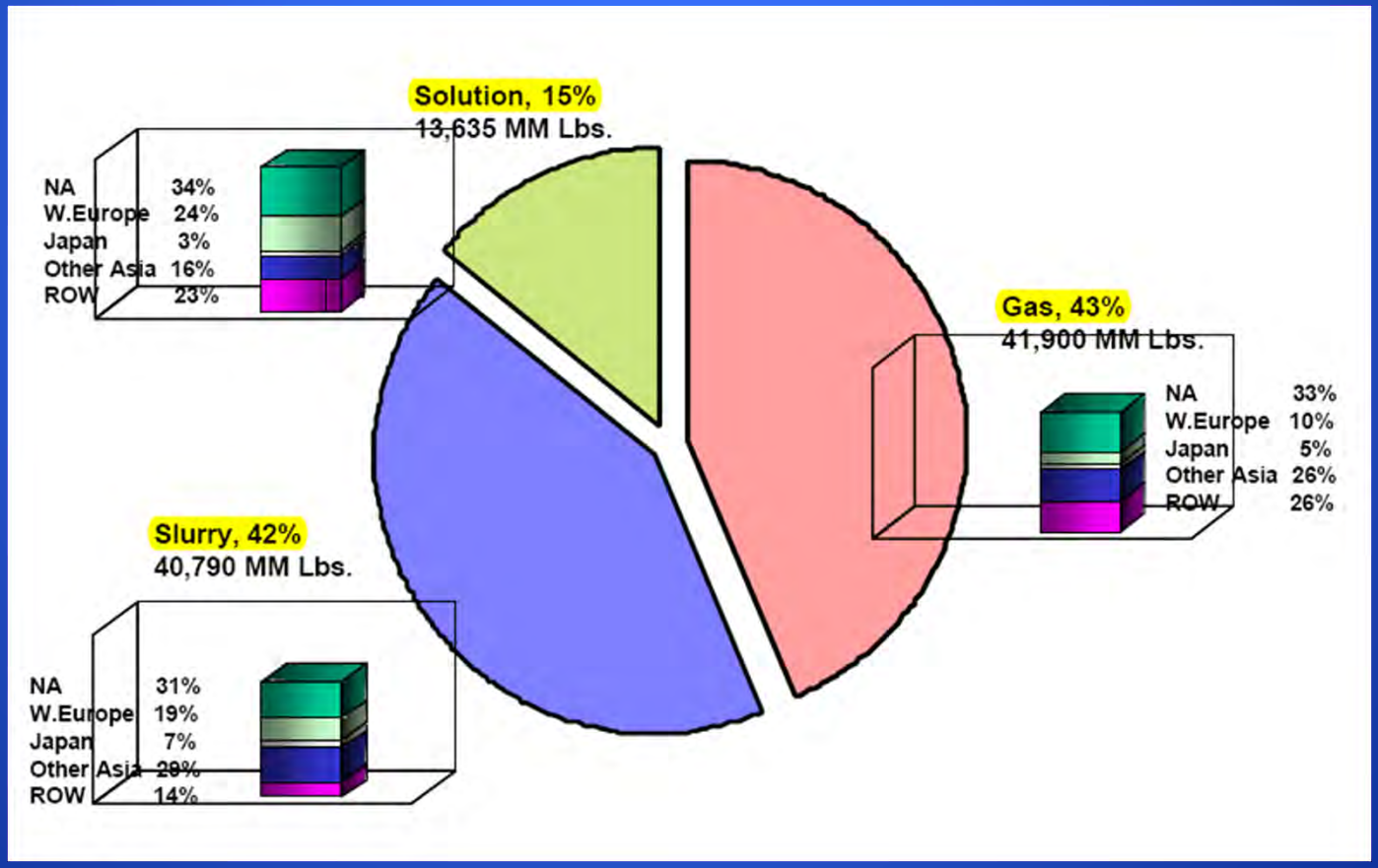
### III. Gas Phase Process

- ✓ No solvent is used.
- ✓ Ethylene monomer and supported catalyst are blown into the reactor.
- ✓ Polymerization reaction takes place in fluidized bed reactor.



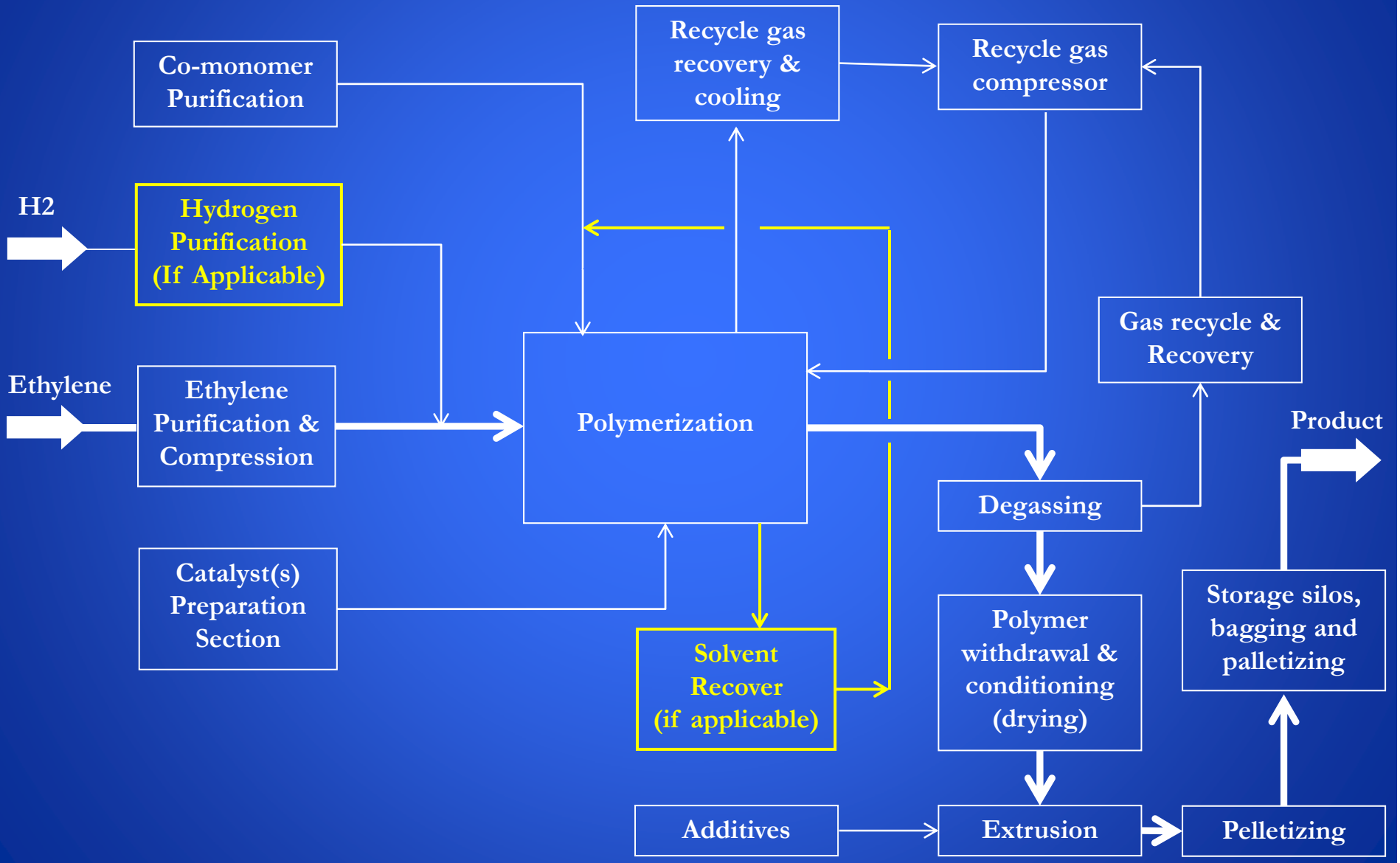
## ➢ PE Polymerization Techniques (cont'd)

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



# PE POLYMERIZATION TYPICAL PROCESS SCHEME

# POLYETHYLENE PRODUCTION TECHNOLOGIES



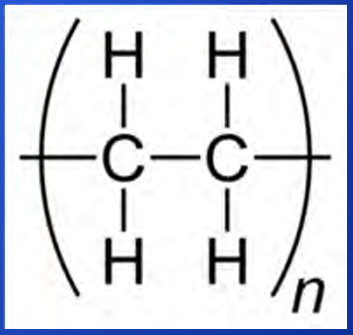
# POLYETHYLENE, GRADES AND PROPERTIES

# POLYETHYLENE PRODUCTION TECHNOLOGIES

- 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 world wide annual production of approximately 150 million metric tons (2013).

- PE is chemically synthesized from molecules that contain long chains of ethylene monomer.



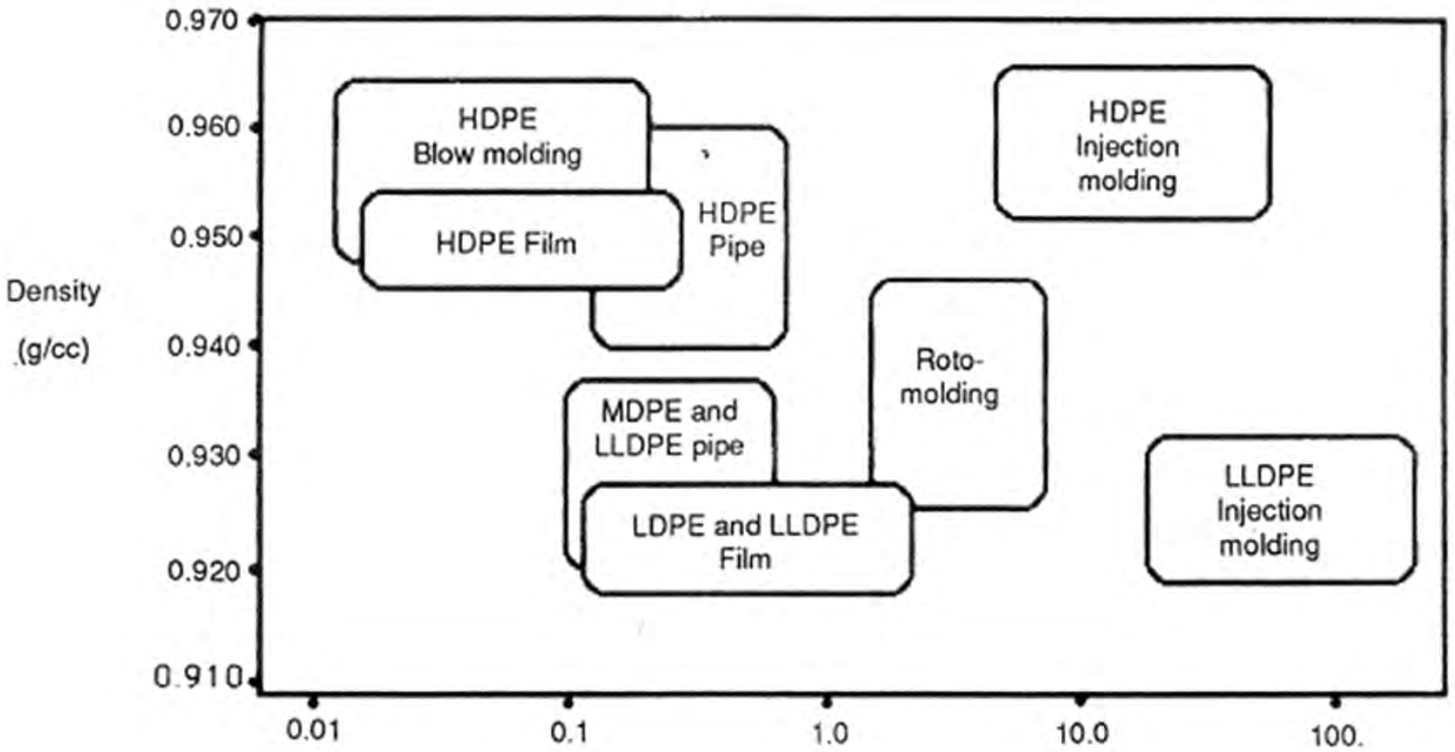
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ Most Important PE Grades Properties

| | HDPE | LLDPE | LDPE |
|---|---|---|---|
| Density, gm/cm³ | 0.94 – 0.97 | 0.926 – 0.94 | 0.91 – 0.925 |
| Crystallinity, % | 80 – 90 | 55 | 50 – 65 |
| Melting Temp. °C | 130 | 125 | 115 |
| Yield Strength, MPa | 20 - 40 | 8 - 45 | 4 - 16 |
| Melt index range (g/10 min) | 0.1 - 100 - 150 | | |

## ➢ Most Important PE Grades Properties (cont'd)

**Polymers, Polyethylene**




Definition of major polyethylene market applications by density and melt index.

## ➢ 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.

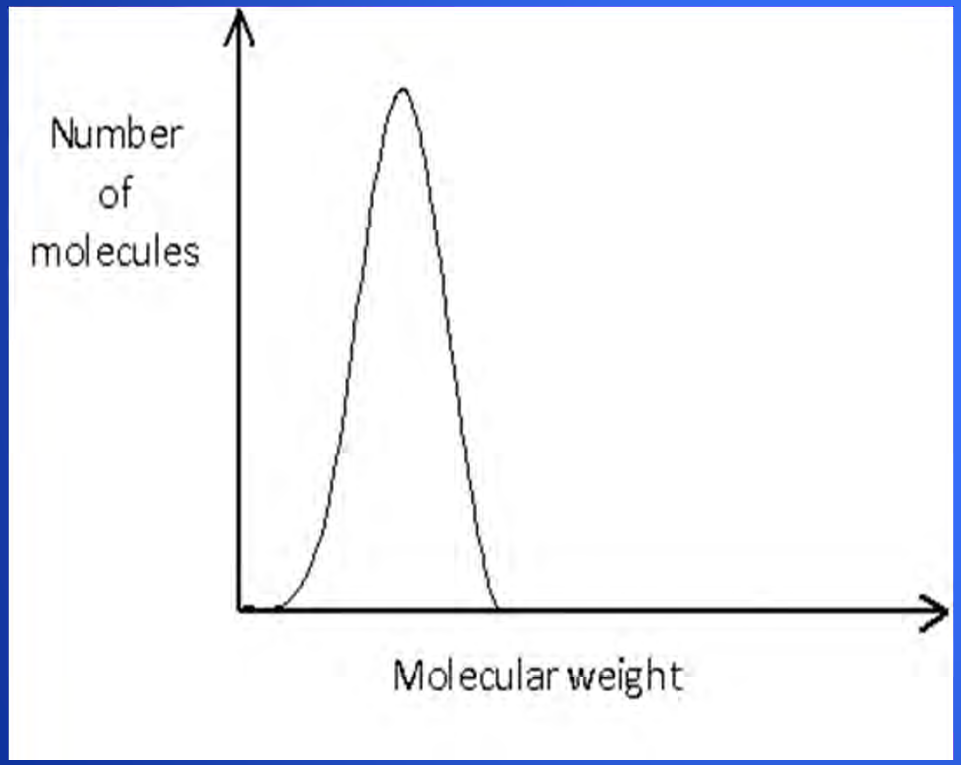
- **BIMODAL** is the combination between LMW and HMW in one reactor.

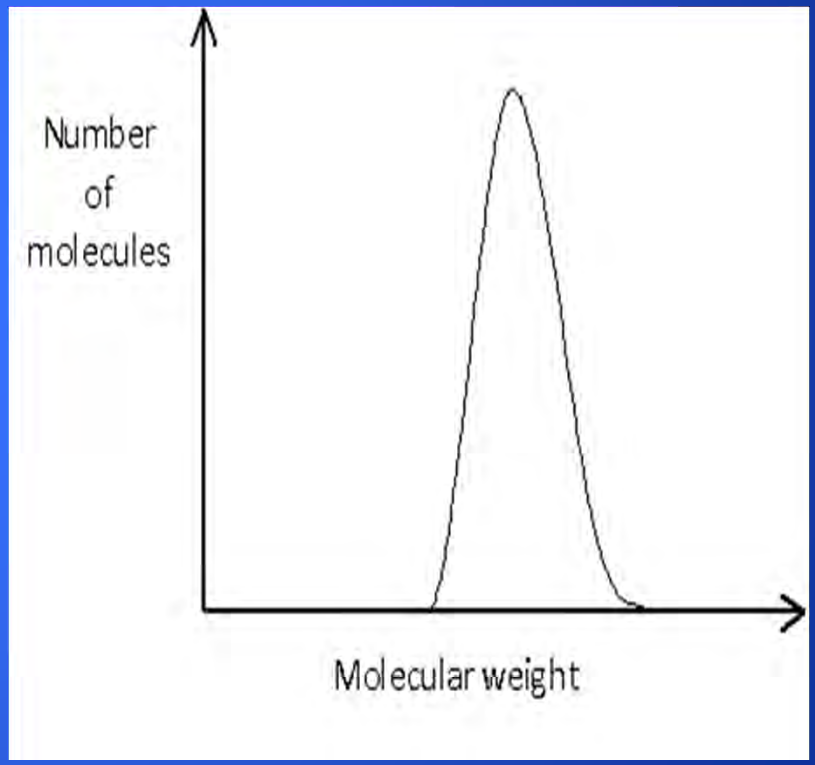
- **Why BIMODAL HDPE ?**

  Light weight containers while maintaining good impact resistance.

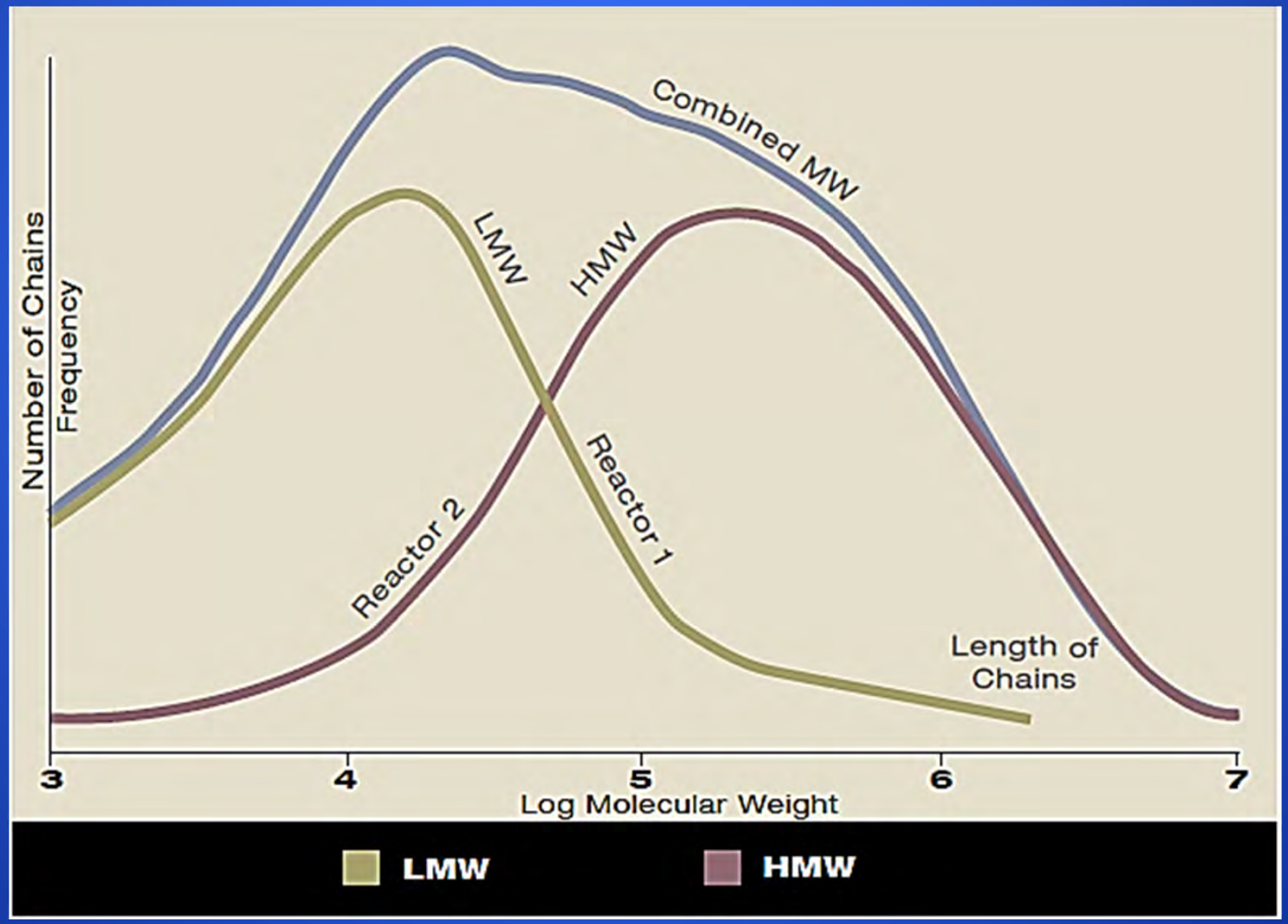
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ UNIMODAL HDPE



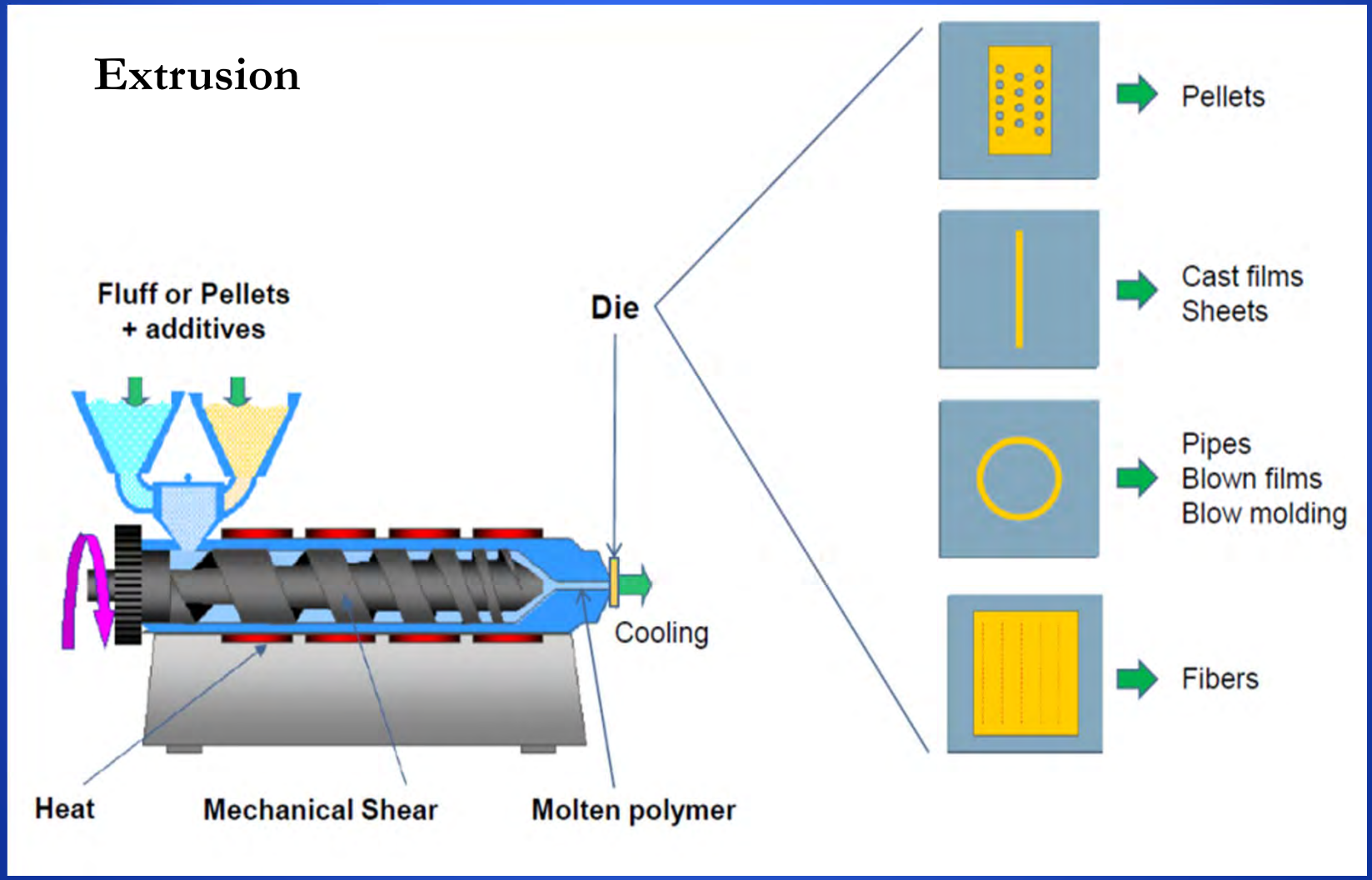



## ➢ BIMODAL HDPE (cont'd)

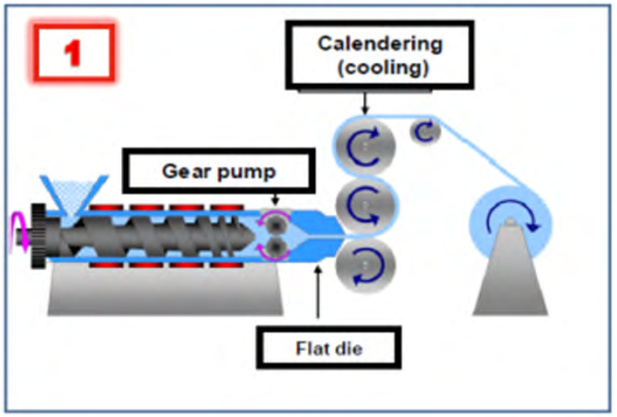


# POLYETHYLENE END USER TECHNIQUES

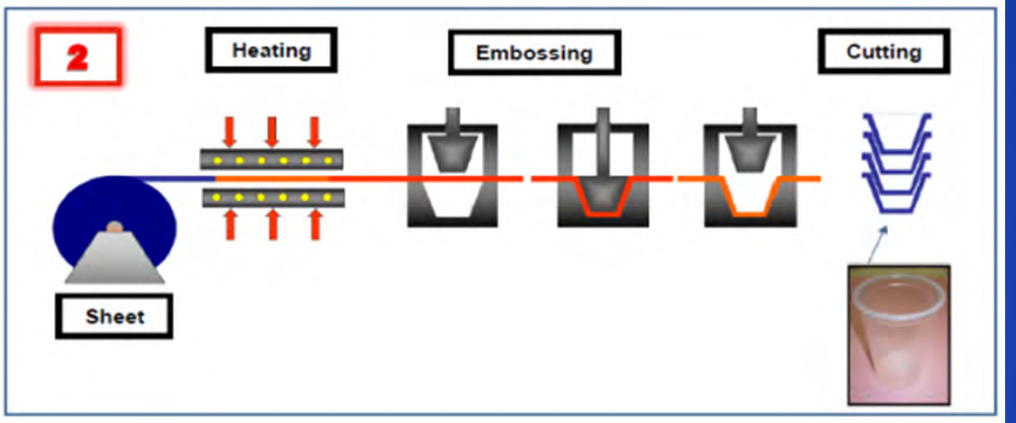
## ➢ End User Processing Techniques



## ➢ End User Processing Techniques (cont'd)

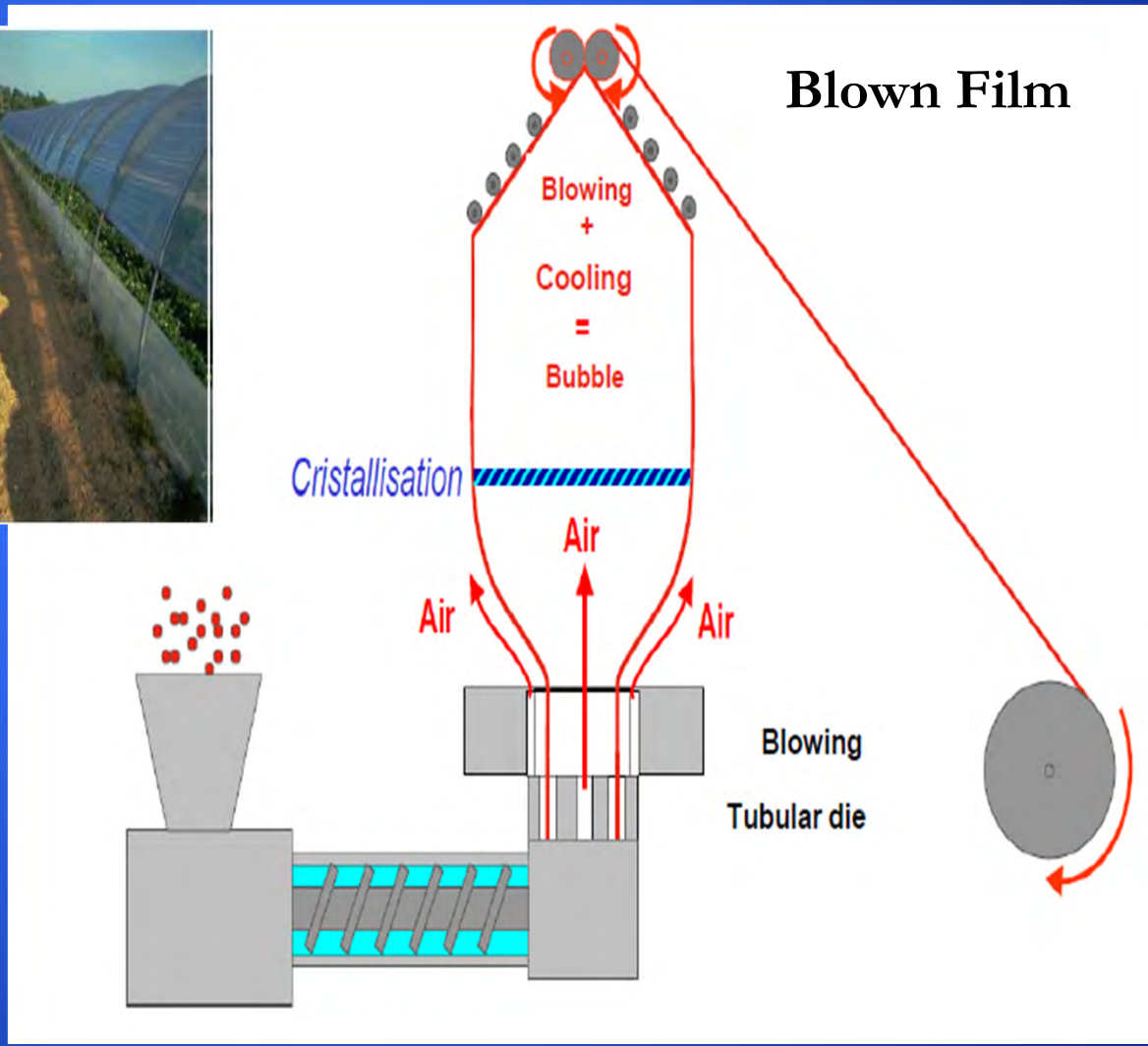



Sheet Extrusion

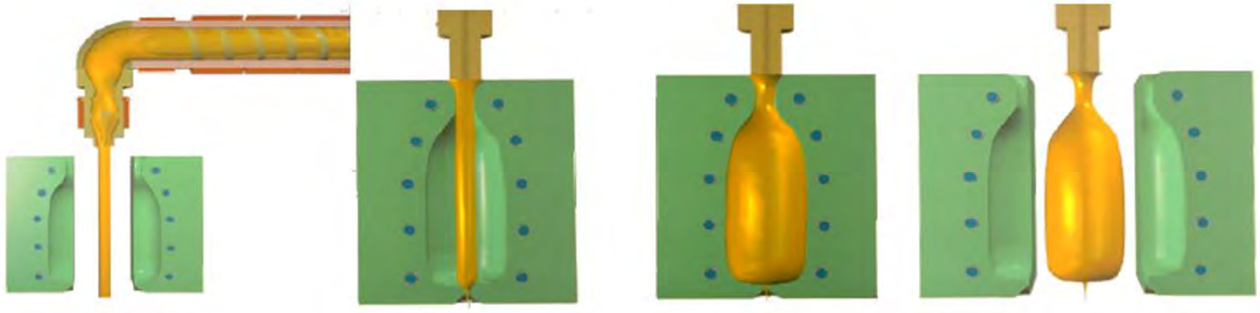



Thermoforming

## ➢ End User Processing Techniques (cont'd)



## ➢ End User Processing Techniques (cont'd)




### Blow Molding

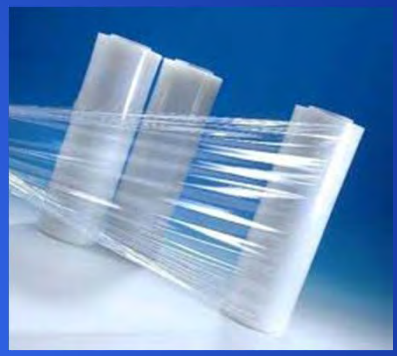



# POLYETHYLENE APPLICATIONS

# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ LLDPE

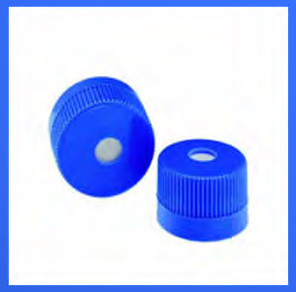
- Heavy duty bags
- Covers
- Buckets and containers
- Stretch films




# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ HDPE

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



# POLYETHYLENE PRODUCTION TECHNOLOGIES

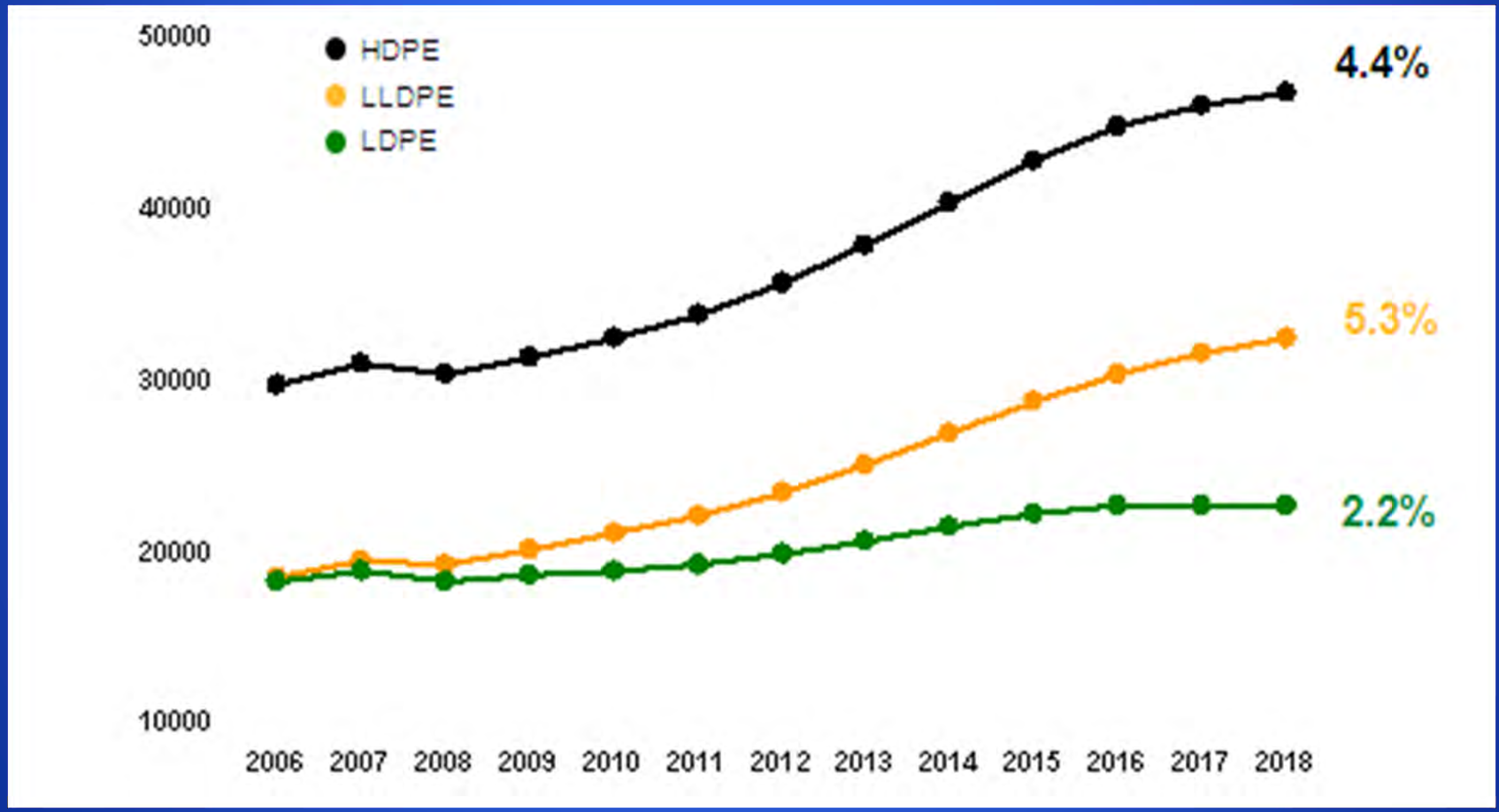
## ➢ LDPE

- Plastic bags
- Dispensing bottles
- Film warps
- Cables insulation
- General purpose containers

# POLYETHYLENE MARKET ANALYSIS

# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ PE Global Demand Growth Rate



## ➢ LLDPE Market Analysis

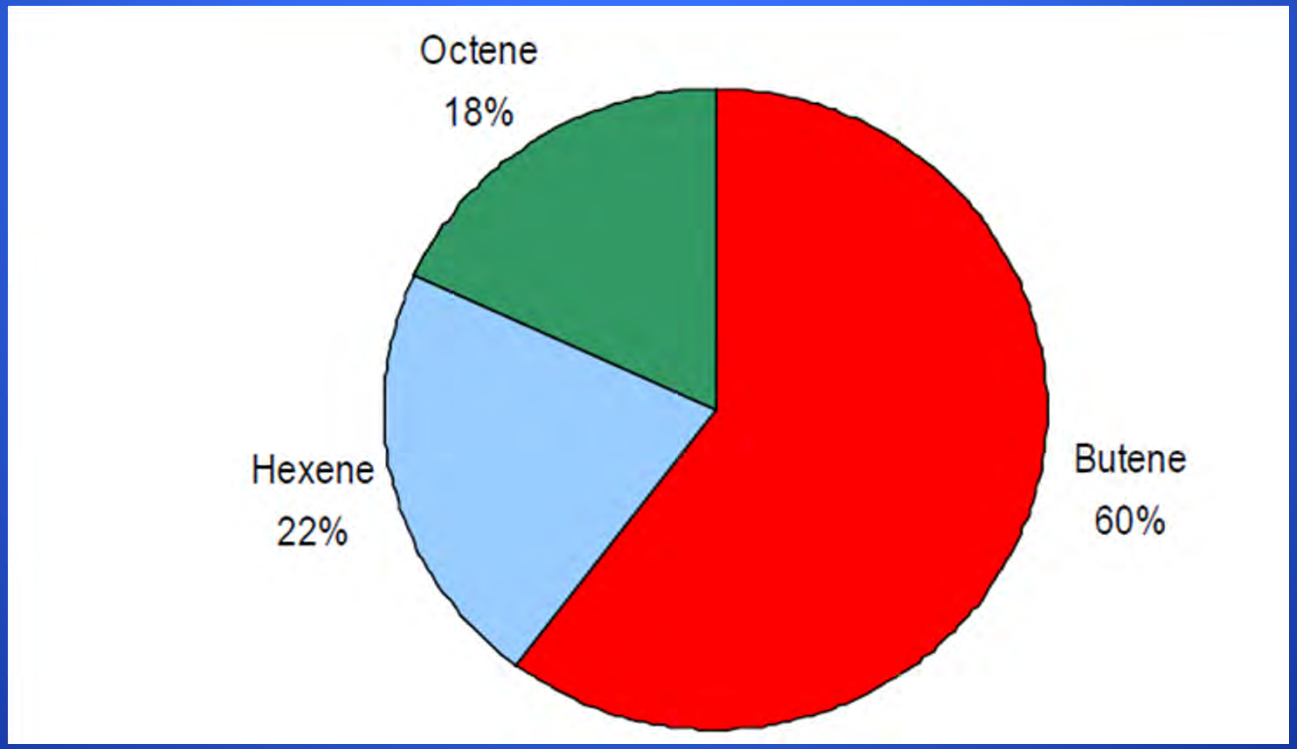
### 1. Global Demand Growth Rate

- 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)

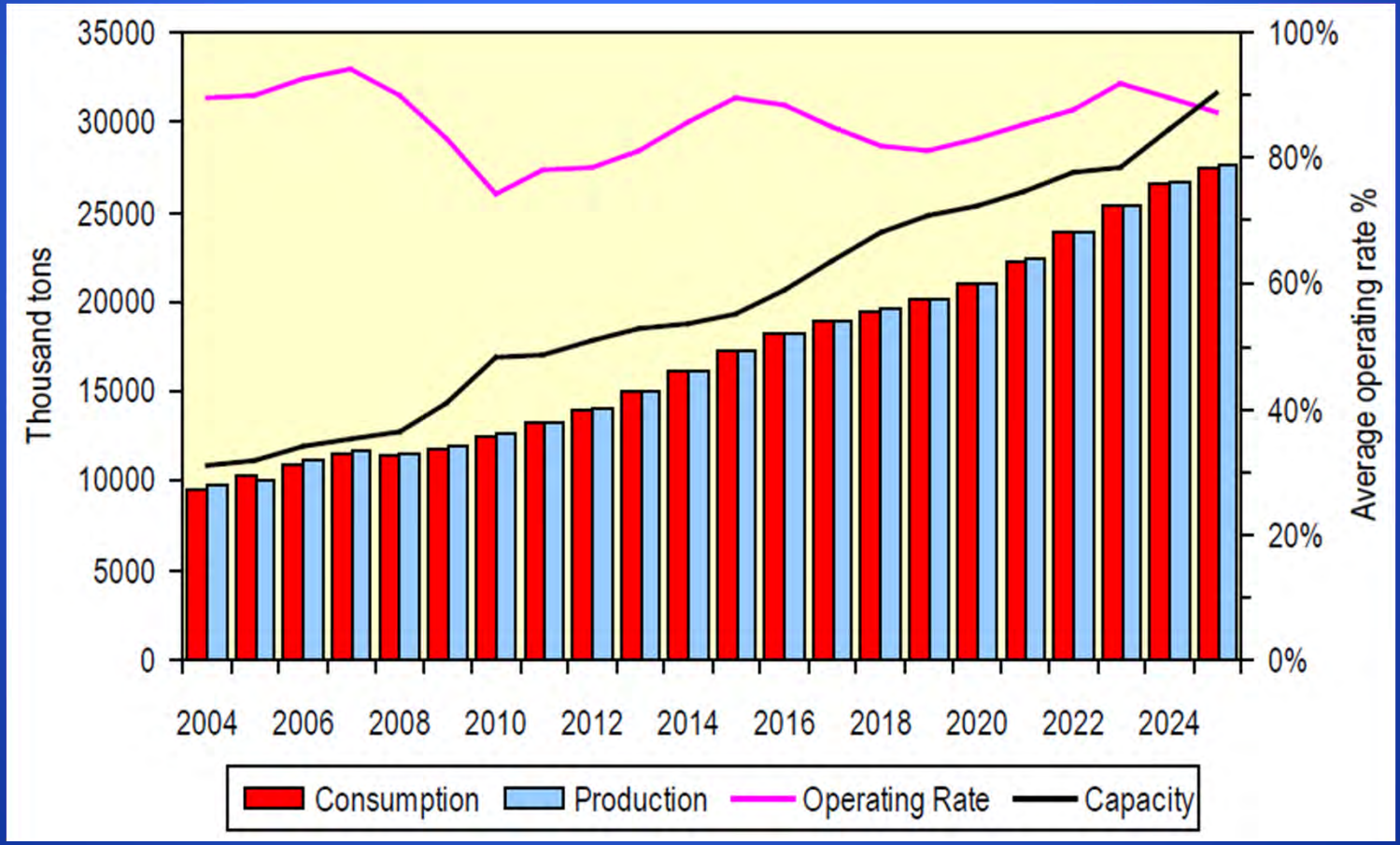
## 2. Global Demand (2013)

- 24.5 million ton



# ➢ LLDPE Market Analysis (cont'd)

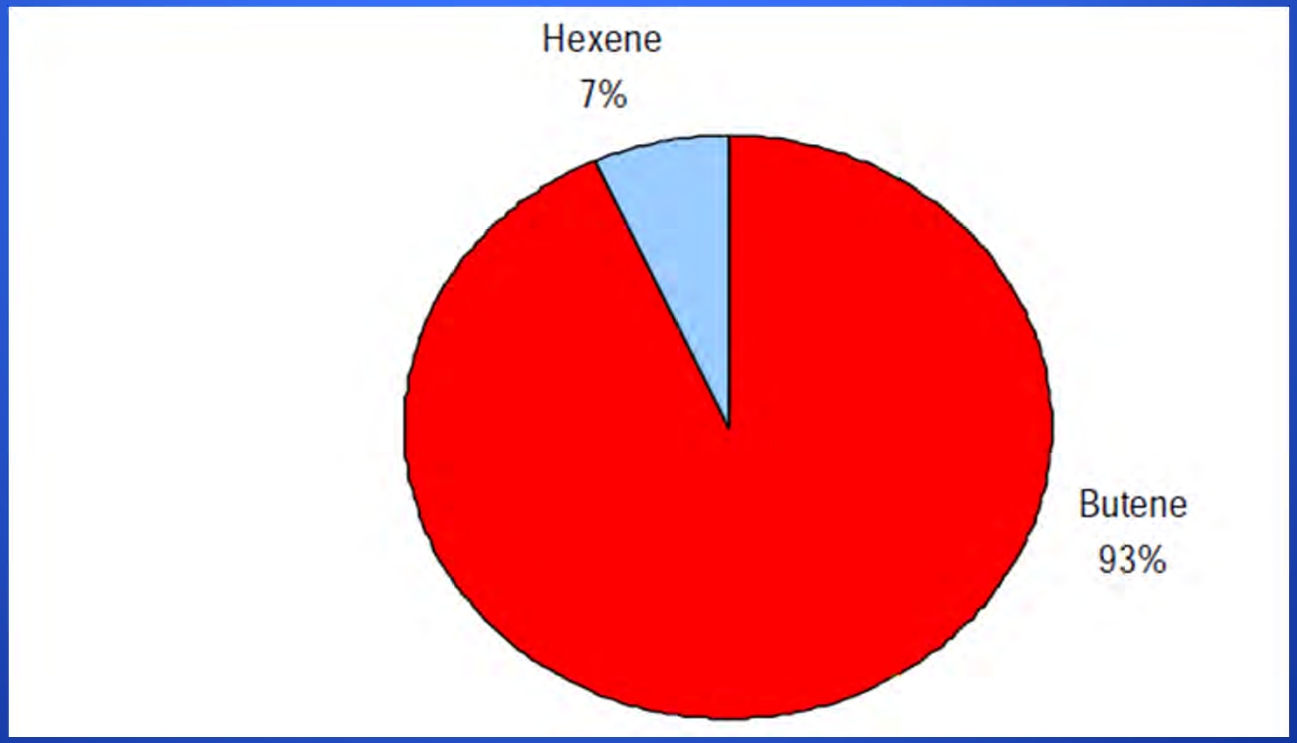
## 3. Global Supply & Demand



# ➢ LLDPE Egyptian Market Analysis (cont'd)

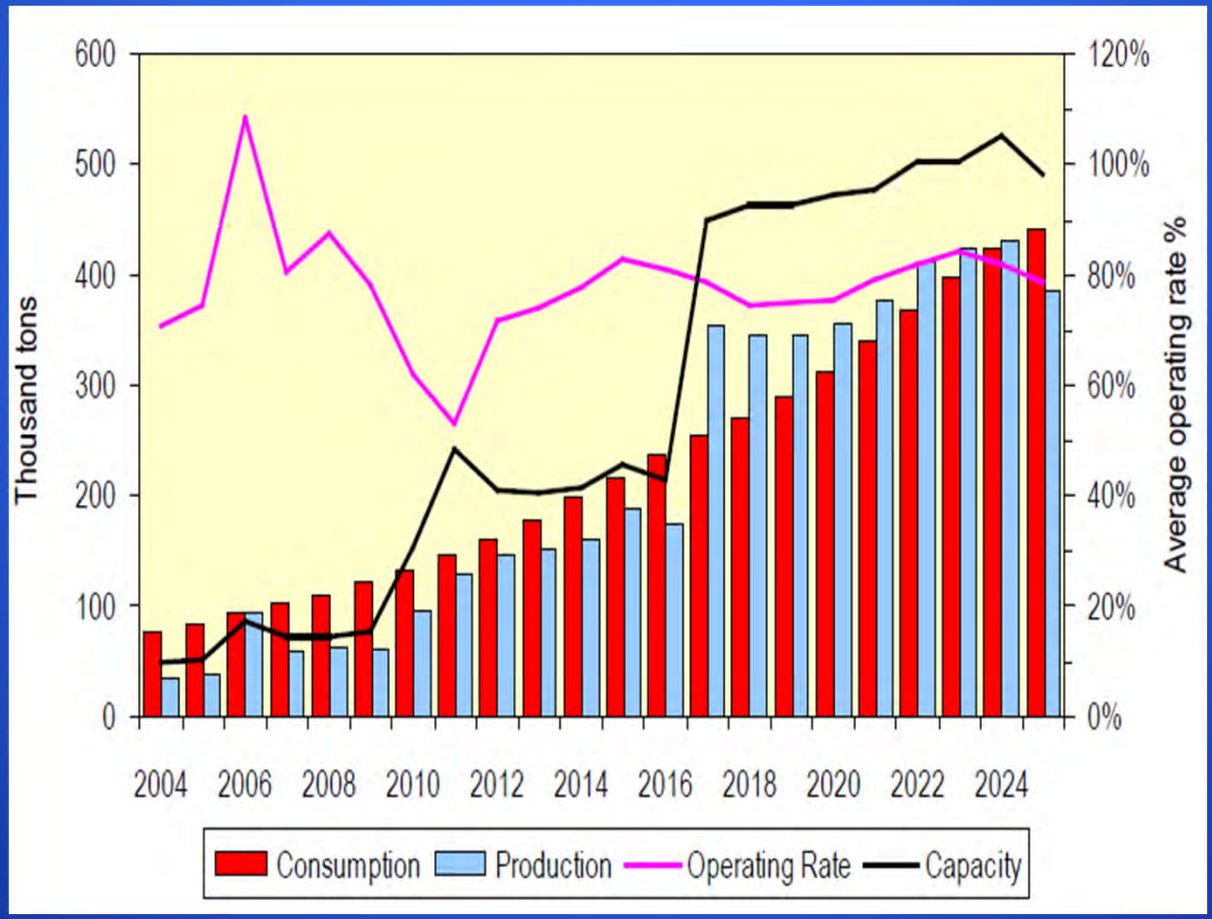
## 2. Local Demand (2013)

- 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)



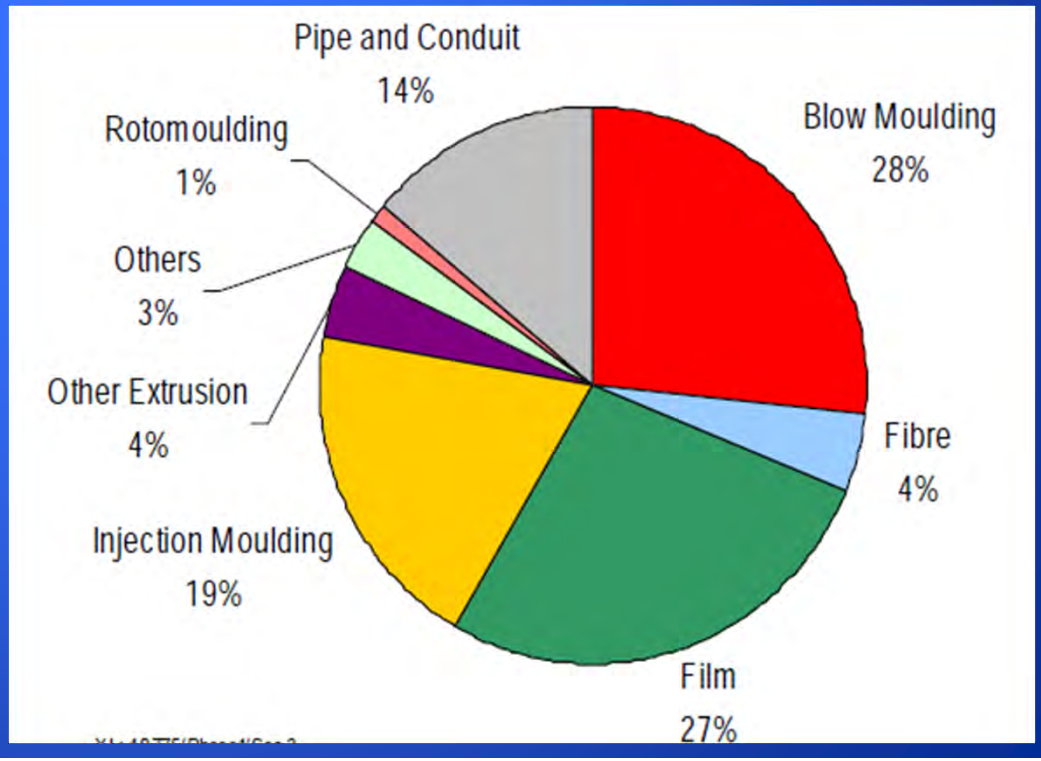
# ➢ HDPE Market Analysis

## 1. Global Growth rate

- 4.4 % annually

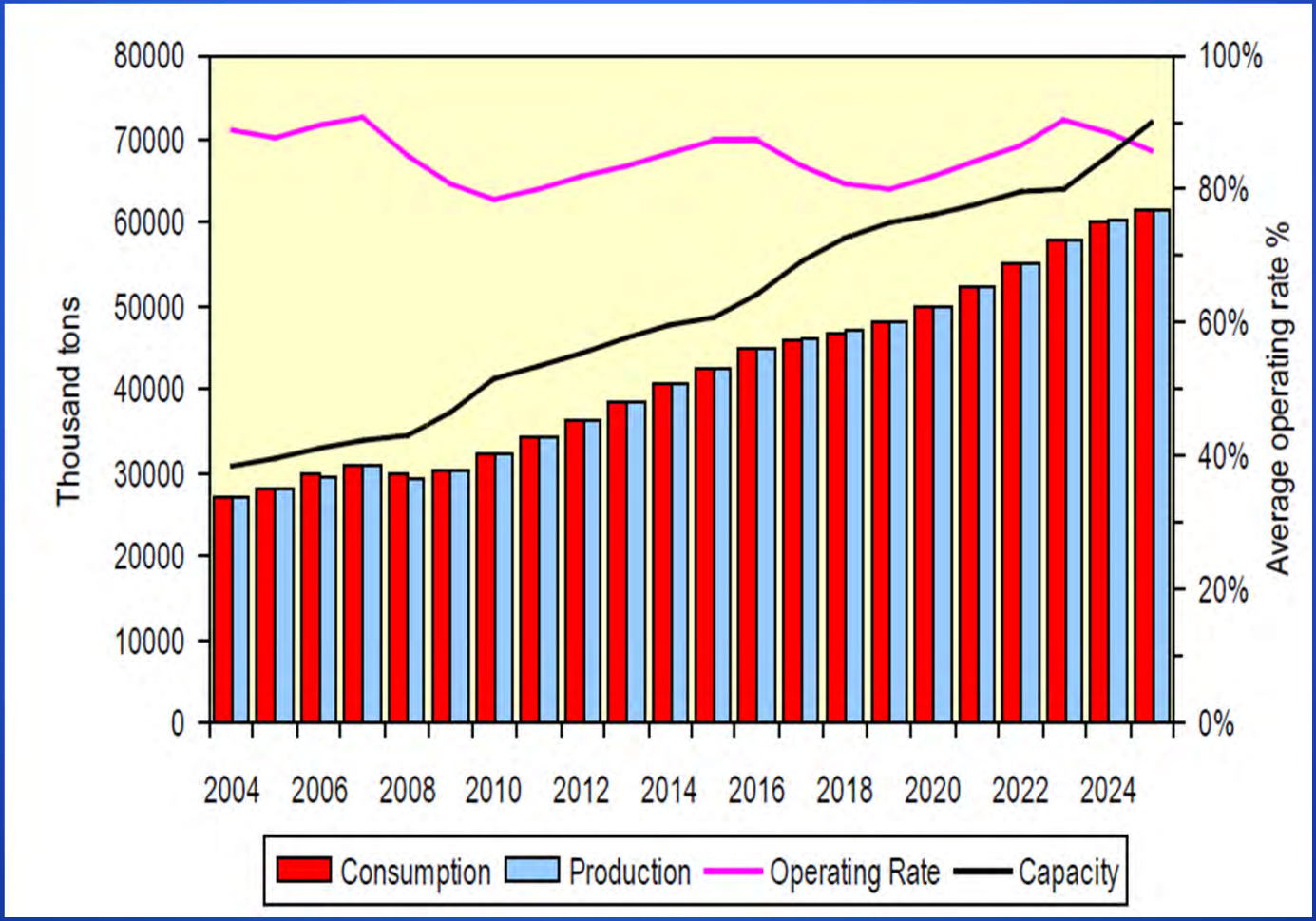
## 2. Global Demand (2013)

- 40.3 million ton



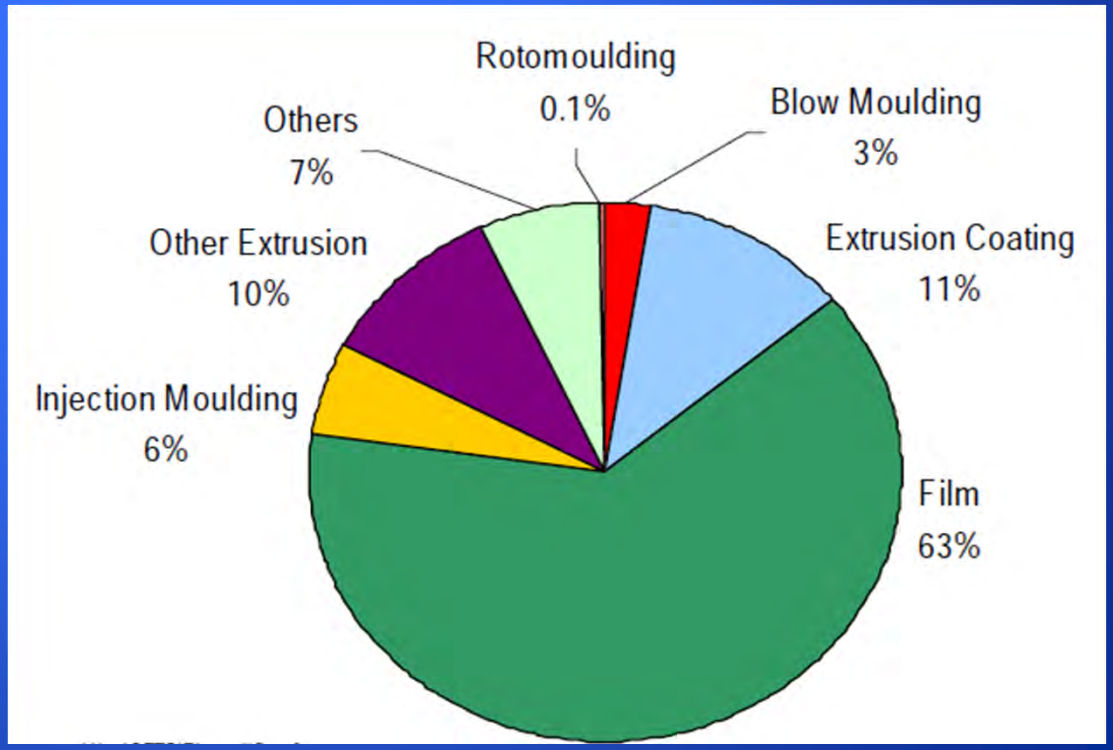
## ➢ HDPE Market Analysis (cont'd)

### 3. Global Supply & Demand



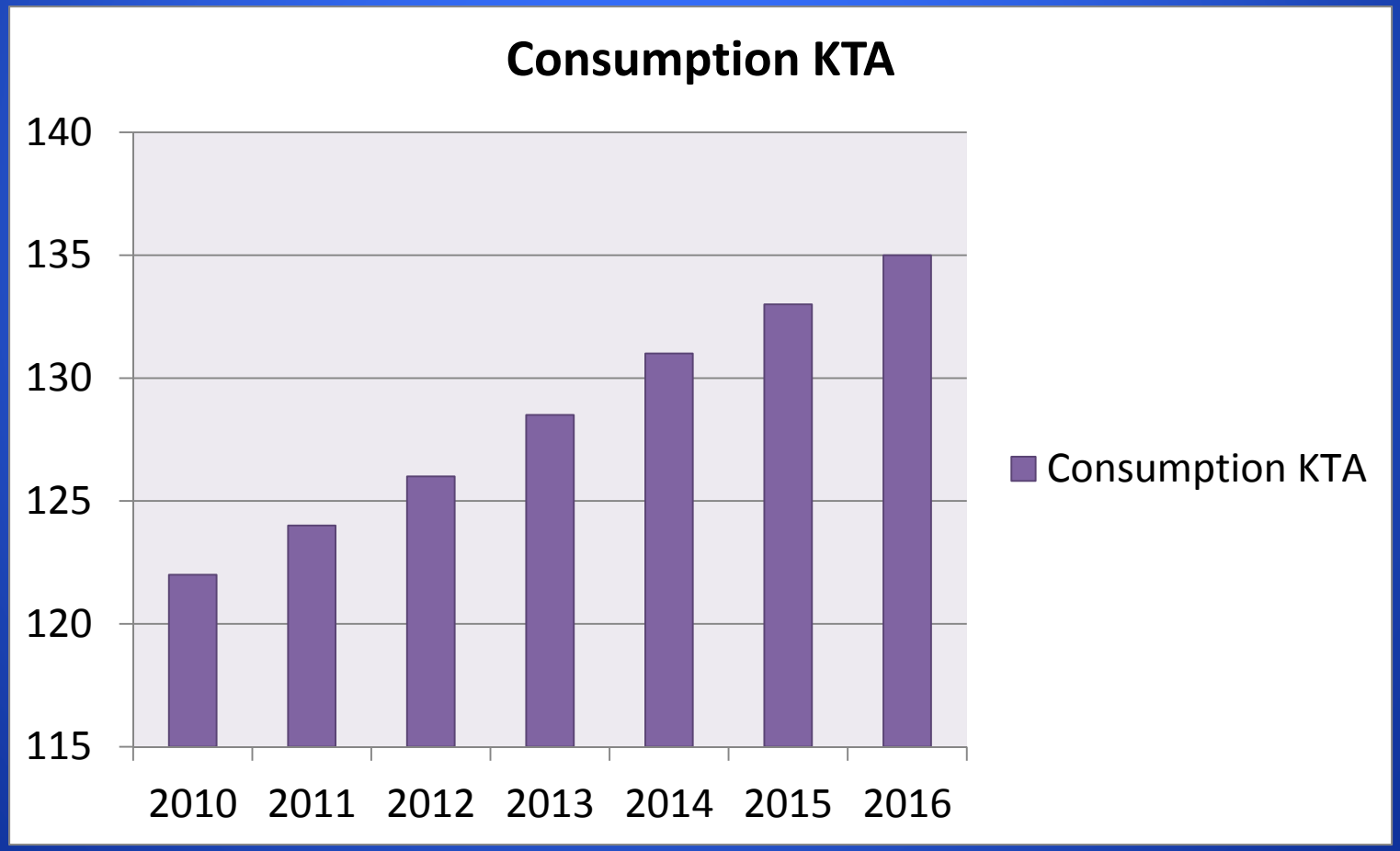
## ➢ LDPE Market Analysis

1. **Global Growth rate**
   - 2.6 % annually
2. **Global Demand (2013)**
   - 20 million ton



## ➢ LDPE Market Analysis (cont'd)

### 3. Local Consumption Growth



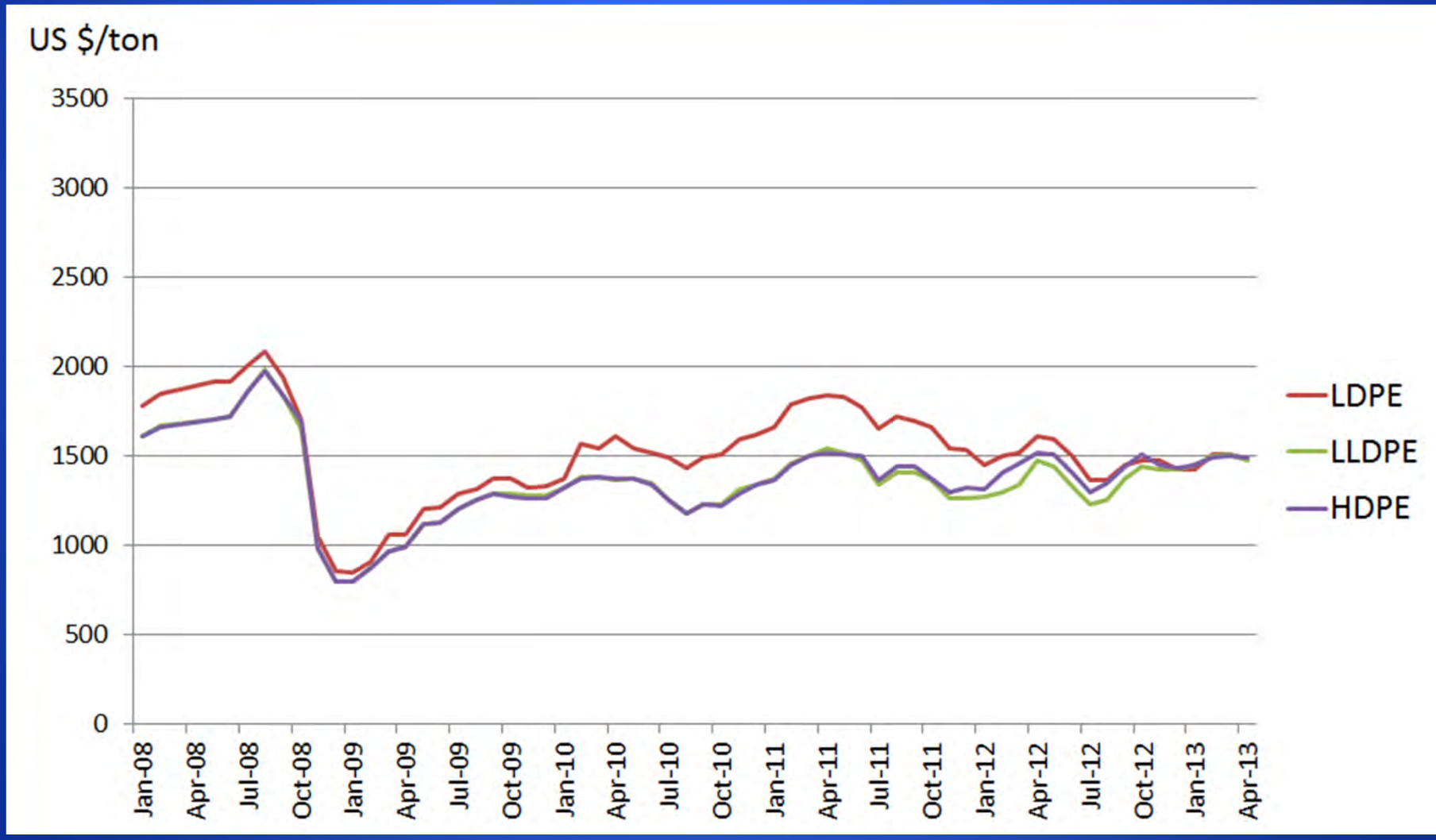
## ➢ PRICING BASIS

- 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 down stream process

# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ PE Grades Pricing History



# POLYETHYLENE TECHNOLOGIES AND FEATURES

# HIGH PRESSURE POLYMERIZATION LICENSORS (LDPE)

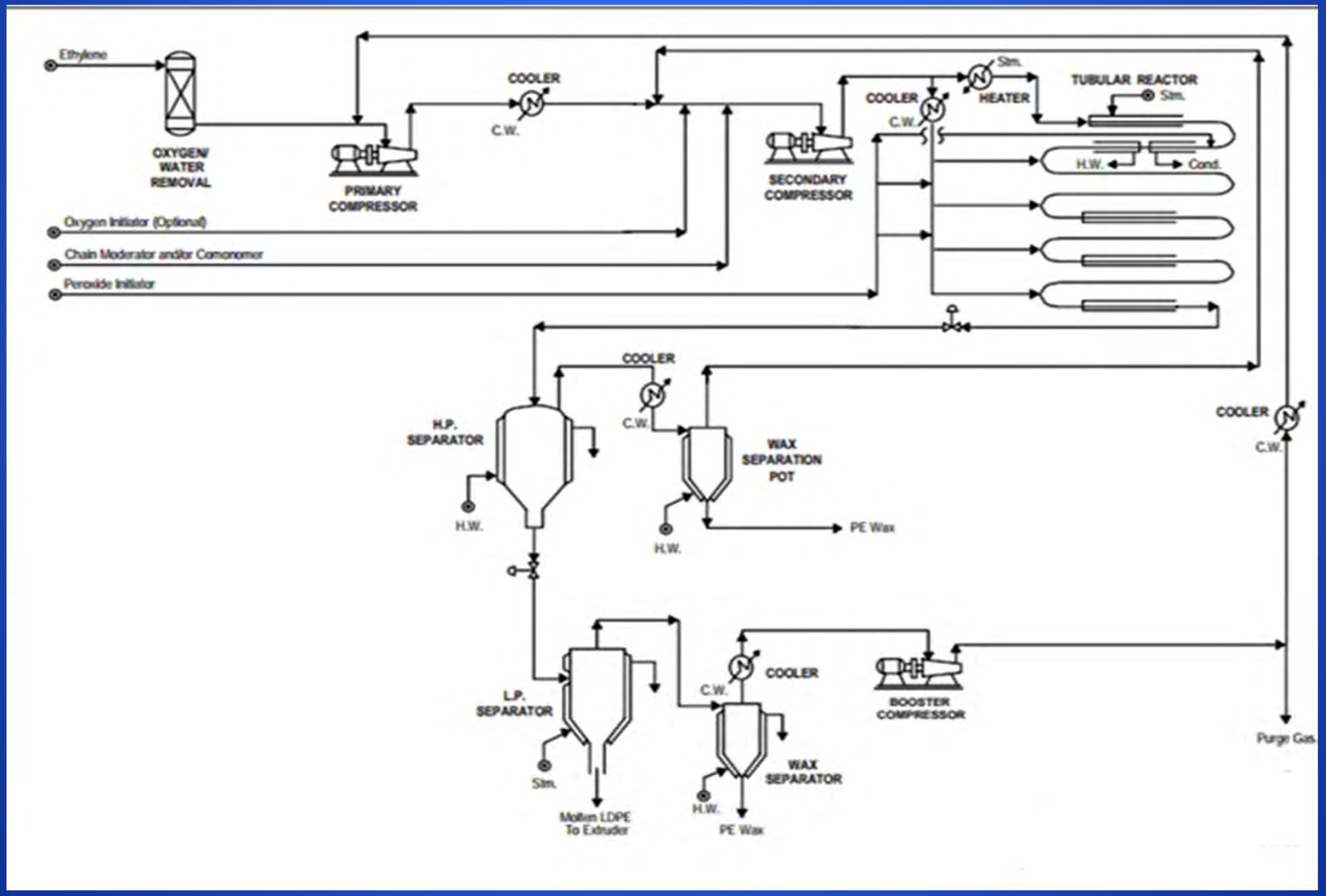
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ 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)

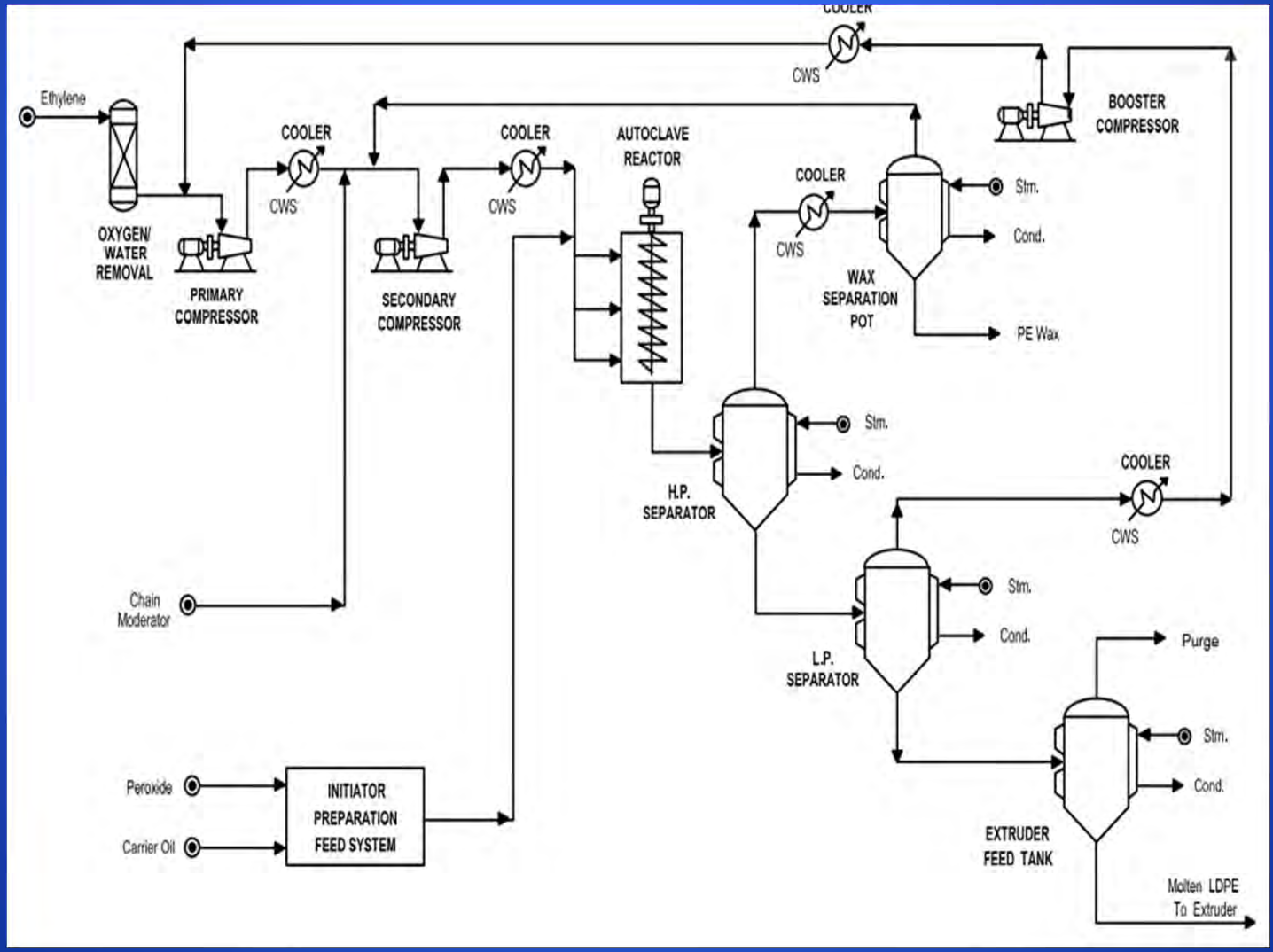
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ 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)

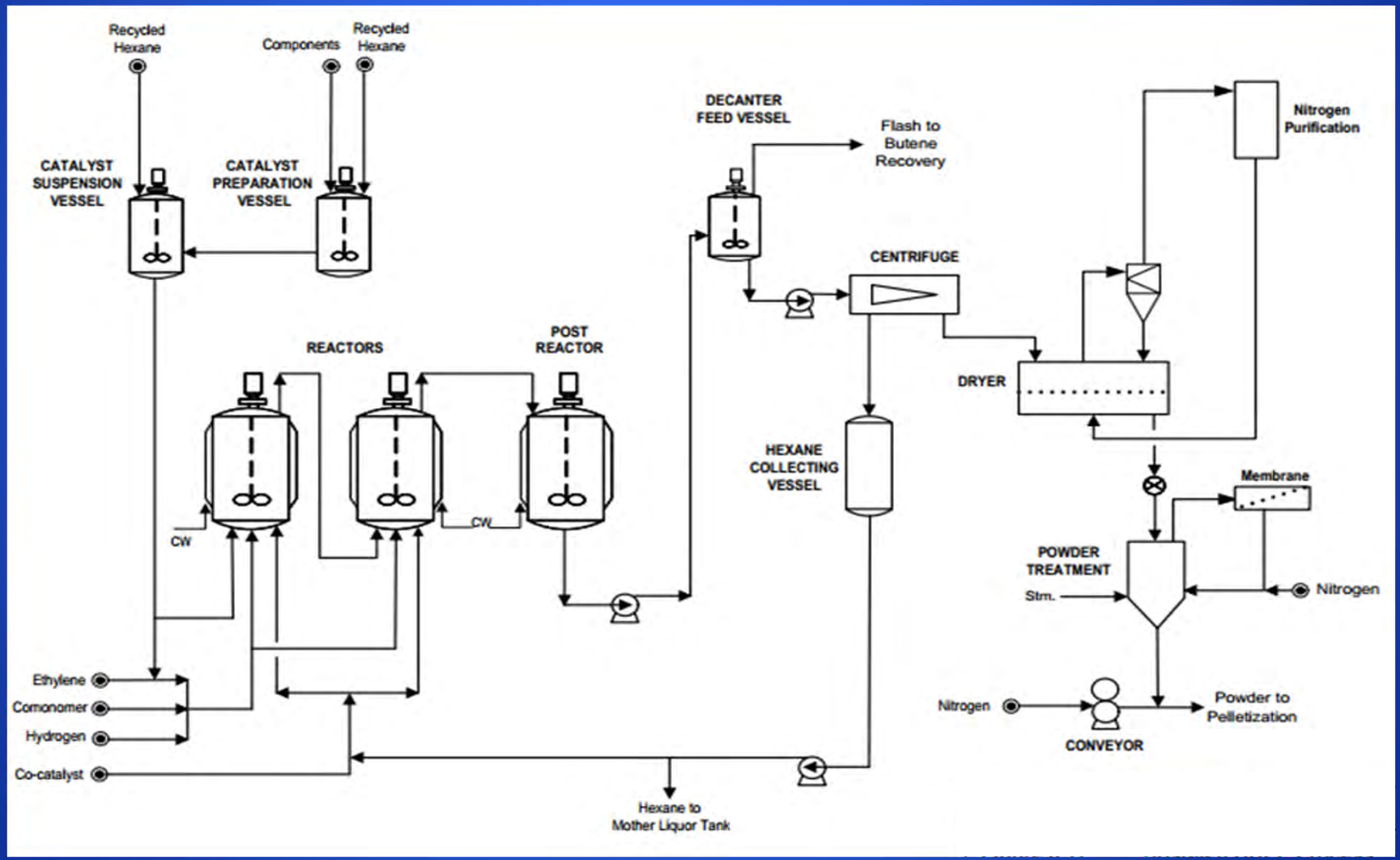
## ➢ Low Pressure Polymerization Licensors (cont'd)

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)

# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ Lyondell Basell Ziegler Slurry Process (HDPE)

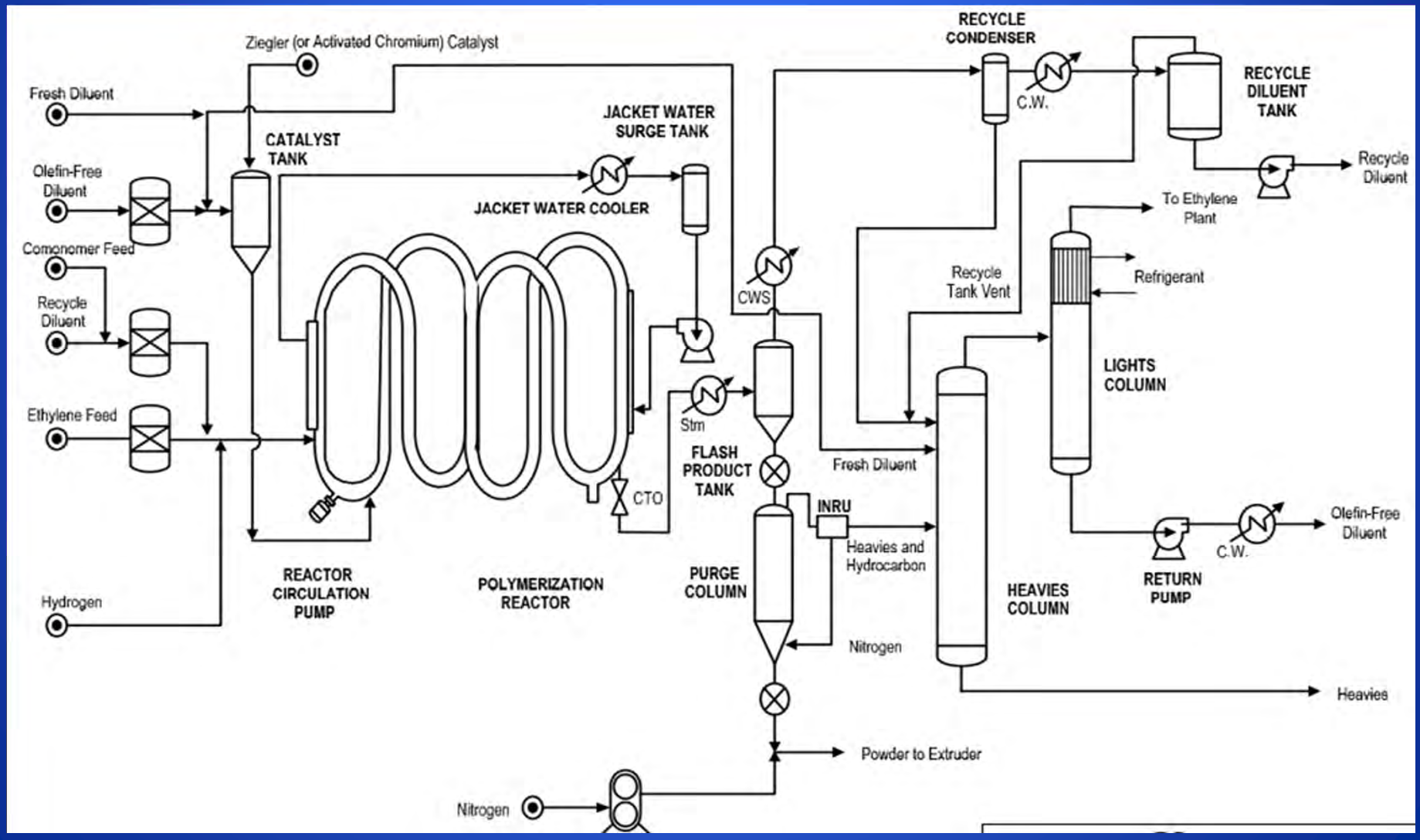


## ➢ Lyondell Basell Ziegler Slurry Process Features

- 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-1only
- 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

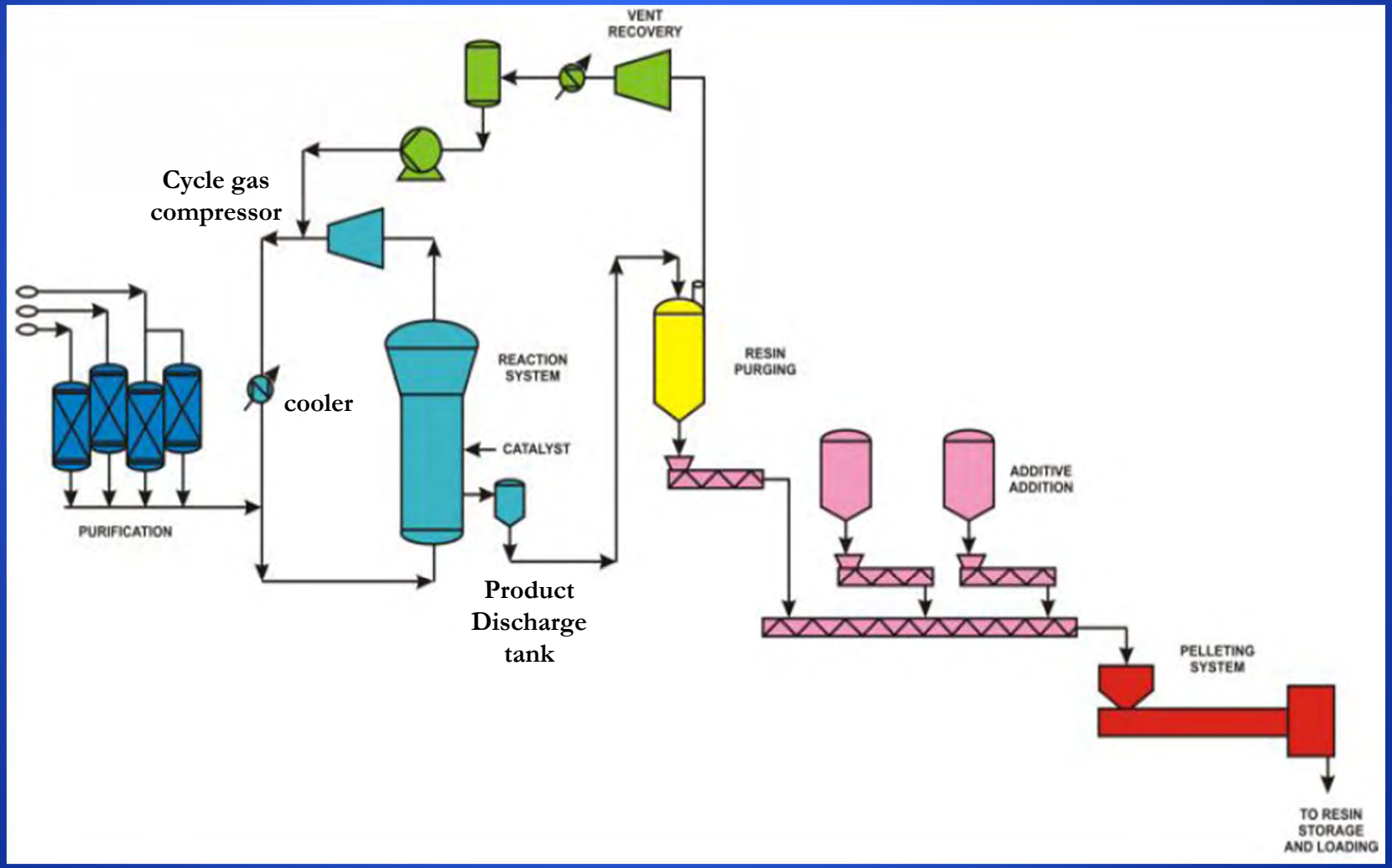
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ Slurry Process Products Slate

| APPLICATION | DENSITY | MELT INDEX (G/10 MIN) |
|---|---|---|
| BLOW FILM | 0.922-0.976 | 0.04 - 5 |
| CABLE | 0.922-0.927 | 0.06 - 0.4 |
| BLOW MOULDING | 0.922-0.960 | 0.08 - 4 |
| INJECTION MOULDING | 0.922-0.979 | 0.7 - 50 |
| ROTO MOULDING | 0.923-0.935 | 4 – 8.5 |
| CAST FILM | 0.922-0.976 | 4 - 70 |
| PIPE | 0.940-0.963 | 0.06 - 0.4 |

# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ Univation (UNIPOL) Gas Phase



## ➢ Univation (UNIPOL) Gas Phase Features

- Three types of catalyst family
  1. Bimodal HDPE (PRODIGY BMC), made up of two catalyst component, 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 process
- 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

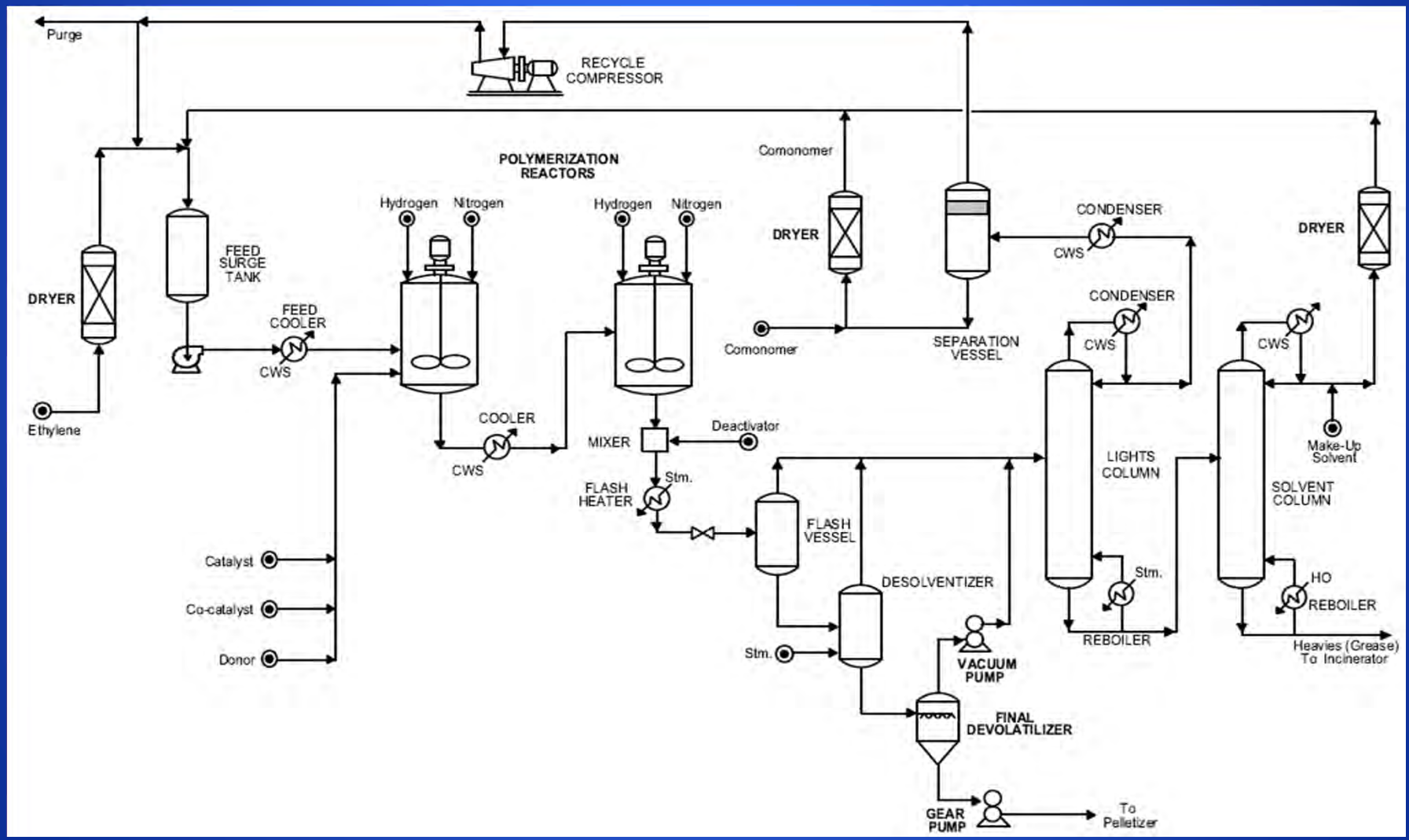
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ Gas Phase Process Products Slate

| APPLICATION | DENSITY | MELT INDEX (G/10 MIN) |
|---|---|---|
| BLOW FILM | 0.885 - 0.965 | 0.085 - 5 |
| CABLE | 0.895 - 0.927 | 0.085 - 0.4 |
| BLOW MOULDING | 0.915 - 0.96 | 0.085 - 0.4 |
| INJECTION MOULDING | 0.89 - 0.97 | 0.85 – 75 |
| ROTO MOULDING | 0.92 - 0.935 | 4 – 8.5 |
| EXTRUSION COATING | 0.905 - 0.922 | 4 – 50 |
| CAST FILM | 0.922 - 0.965 | 5 -75 |
| PIPE | 0.94 - 0.963 | 0.085 - 0.4 |

# 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.

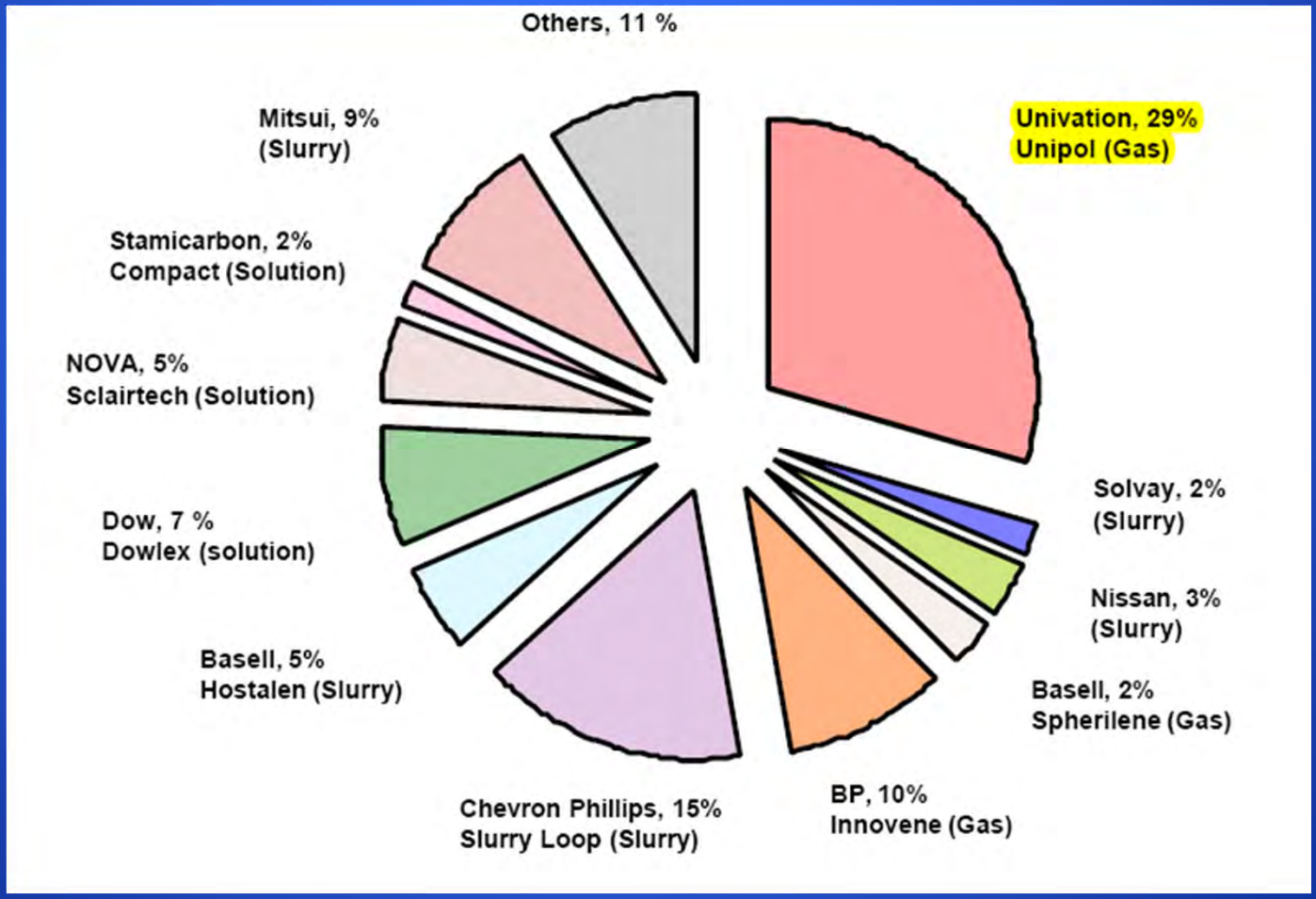
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ Solution Process Products Slate

| APPLICATION | DENSITY | MELT INDEX (G/10 MIN) |
|---|---|---|
| BLOW FILM | 0.885 - 0.932 | 0.7 - 5 |
| CABLE | 0.895-0.928 | 0.7 - 0.4 |
| BLOW MOULDING | 0.915 - 0.932 | 0.7 – 4 |
| INJECTION MOULDING | 0.89 - 0.932 | 0.7 - 200 |
| EXTRUSION COATING | 0.905-0.922 | 4 - 50 |
| ROTO MOULDING | 0.92-0.932 | 4 – 8.5 |
| CAST FILM | 0.925-0.93 | 5 - 70 |

## ➢ Low Pressure Polymerization Licensors (cont'd)

Linear PE Capacity Breakdown By Licensor



# LICENSE EVALUATION CRITERIA

# POLYETHYLENE PRODUCTION TECHNOLOGIES

- **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**

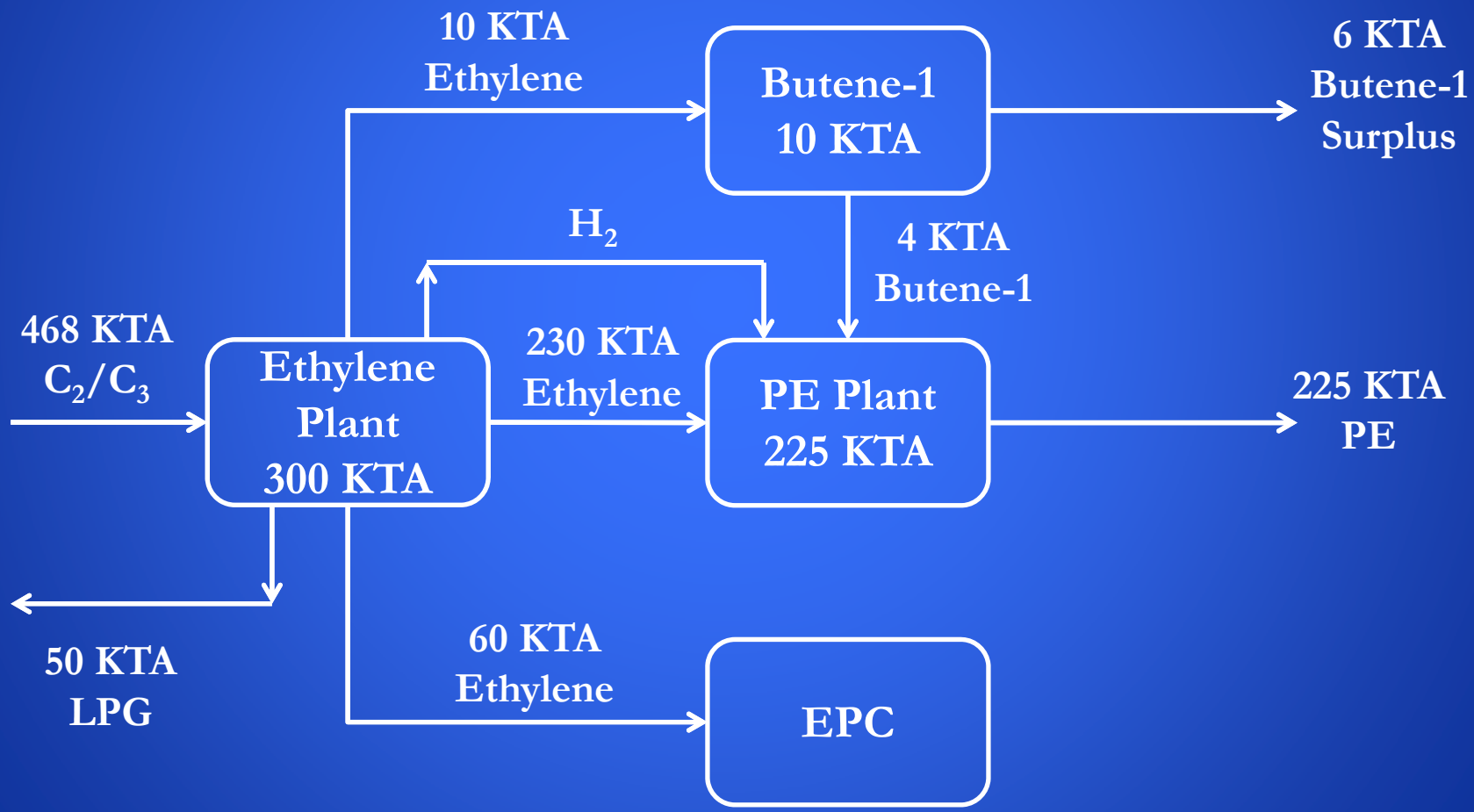
1. Length of campaign
2. Duration of change over
3. Expected off grade quantity
4. Co-monomer used
5. Waste tonnage product
6. No. of grades per application
7. Turn down ratio
8. Start-up time (feed to on-spec)
9. No of catalysts used
10. No of catalyst suppliers
11. Frequency of scale removal from the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

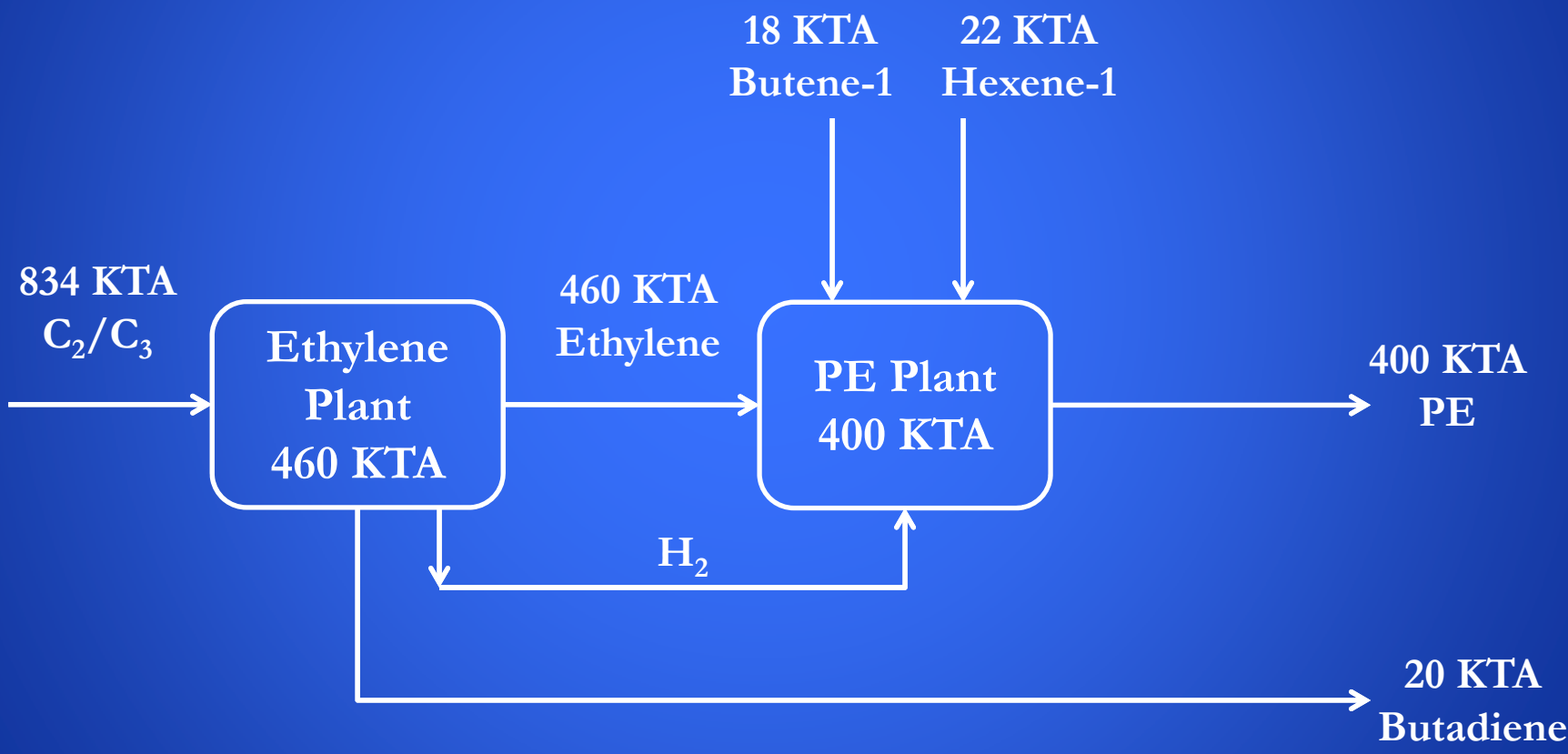
## ➢ SIDPEC Overall Material Balance



# ETHYDCO 400 KTA PE PLANT

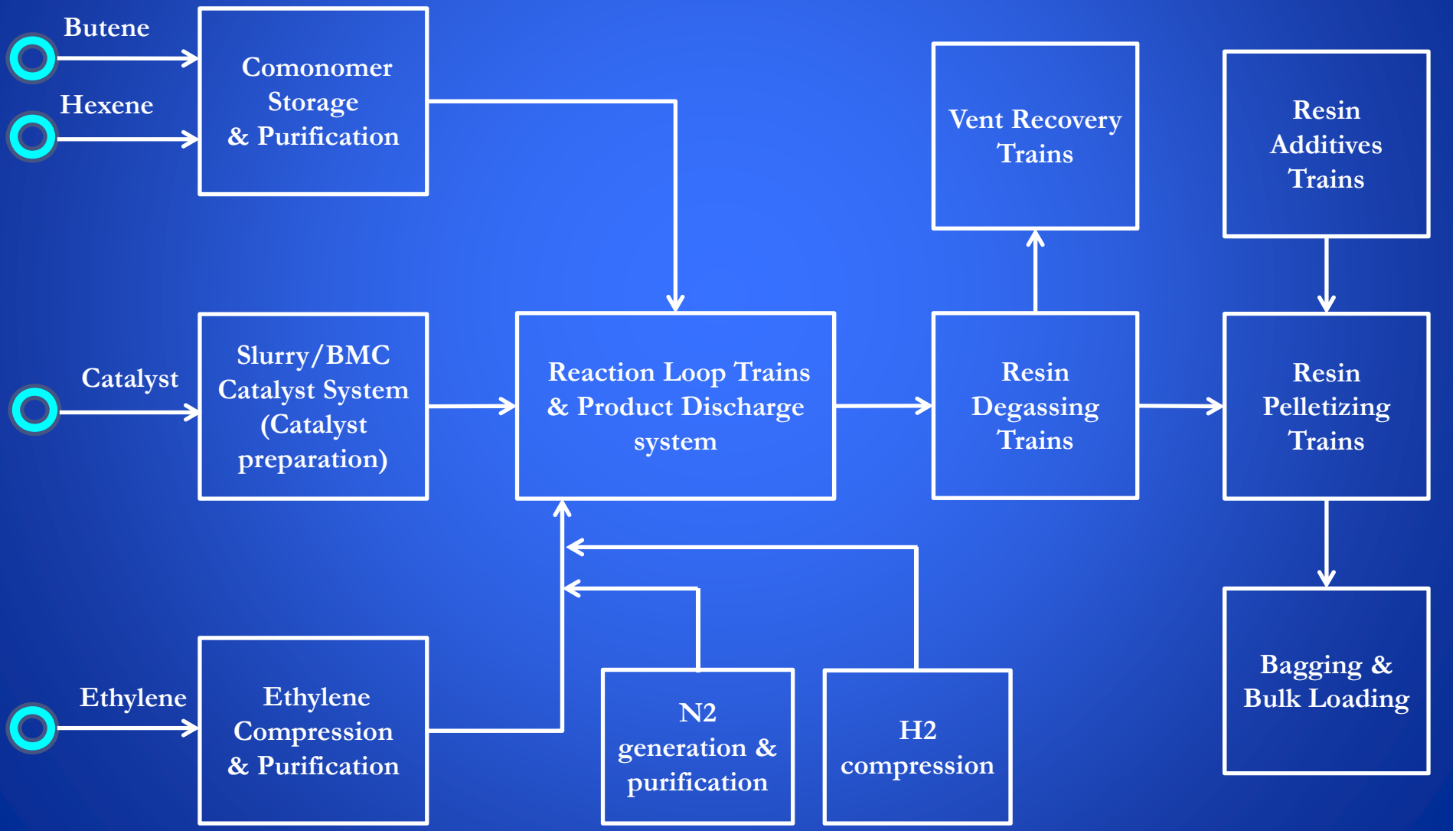
# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ ETHYDCO Overall Material Balance



# POLYETHYLENE PRODUCTION TECHNOLOGIES

## ➢ ETHYDCO 400 KTA PE Plant



# POLYETHYLENE PRODUCTION TECHNOLOGIES

| Ethylene Plant | SIDPEC | ETHYDCO |
|---|---|---|
| **Capacity** | 300 KTA polymer grade Ethylene | 460 KTA polymer grade Ethylene |
| **License** | ABB Lummus Technology | ABB Lummus Technology |
| **Contractor** | TOYO Engineering | TOYO Engineering |
| **Byproducts** | • High Purity $H_2$<br>• LPG<br>• Pyrolysis Gasoline | • High Purity $H_2$<br>• Butadiene<br>• Pyrolysis Gasoline |
| **Main Process Sections** | • Acid gases removal unit ($CO_2$ & $H_2S$)<br>• Pyrolysis & Quenching<br>• Compression, acid gas removal, drying & Hg removal units<br>• Cold box & fractionation<br>• LPG Unit | • Acid gases removal unit ($CO_2$ & $H_2S$)<br>• Pyrolysis & Quenching<br>• Compression, acid gas removal, drying & Hg removal units<br>• Cold box & fractionation<br>• Butadiene Extraction Unit |

# POLYETHYLENE PRODUCTION TECHNOLOGIES

| PE Plant | SIDPEC | ETHYDCO |
|---|---|---|
| Capacity | 225 KTA PE | 400 KTA PE |
| License | BP Innovene gas phase process | Unipol gas phase process |
| EPC Contractor | Samsung – Korea | TOYO Engineering |
| Catalyst | Cr catalyst<br>Ziegler Catalyst | Ziegler Catalyst<br>Cr catalyst<br>Bimodal catalyst |
| Operating Conditions | 28 barg<br>75 – 100 °C | 23 barg<br>50 – 90 °C |
| Co-monomer | Butene-1 | Butene-1<br>Hexene-1 |
| Solvent | Yes, pre-polymerization step<br>N-hexane | No |
| Product slate | HDPE<br>LLDPE | HDPE<br>Bimodal HDPE<br>LLDPE |

# POLYETHYLENE PRODUCTION TECHNOLOGIES

| PE Plant | SIDPEC | ETHYDCO |
|---|---|---|
| **Main Process Sections** | • Catalyst preparation Unit<br>• Feed Purification Unit<br>• Solvent Recovery Unit<br>• Pre-polymerization Unit<br>• Polymerization & degassing Unit<br>• Additives and Pelletizing Unit<br>• Pellets Storage & Bagging | • Catalyst preparation Unit<br>• Feed Purification Unit<br>• Polymerization & degassing Unit<br>• Additives and Pelletizing Unit<br>• Pellets Storage & Bagging |

# THANK YOU