HDPE Technology

Including MDPE and LLDPE

2010

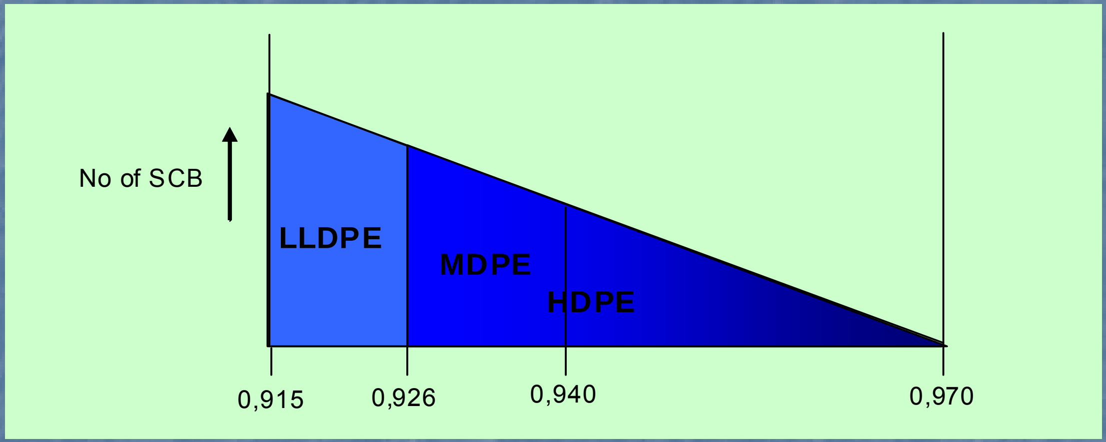
Előadó: Ádám Csaba

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

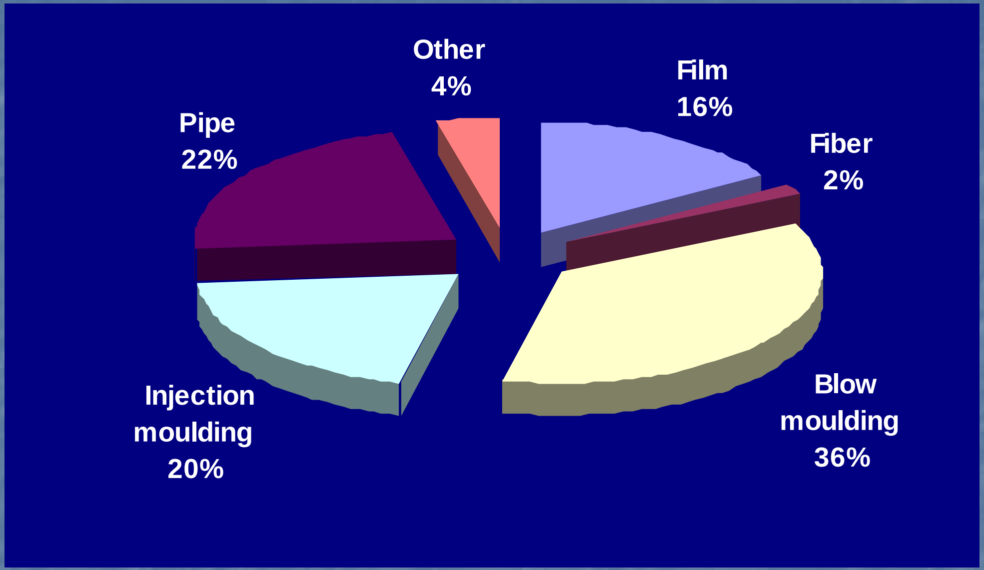
- HDPE, MDPE, LLDPE: linear polyethylenes
- Classification by density – determined by short chain branching through comonomer content



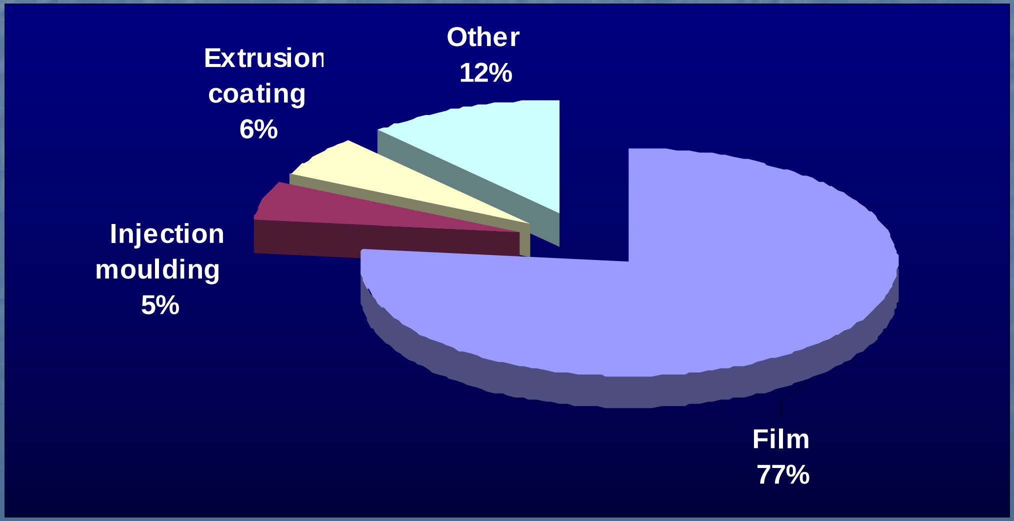
- Properties
  - Melt index 0,03 - >100 g/10 min (190 C/2,16 kg)
  - Melting point 120-140 C
  - Polydispersity (TVK grades)
    - Monomodal 6-8
    - Bimodal 10-20

Application

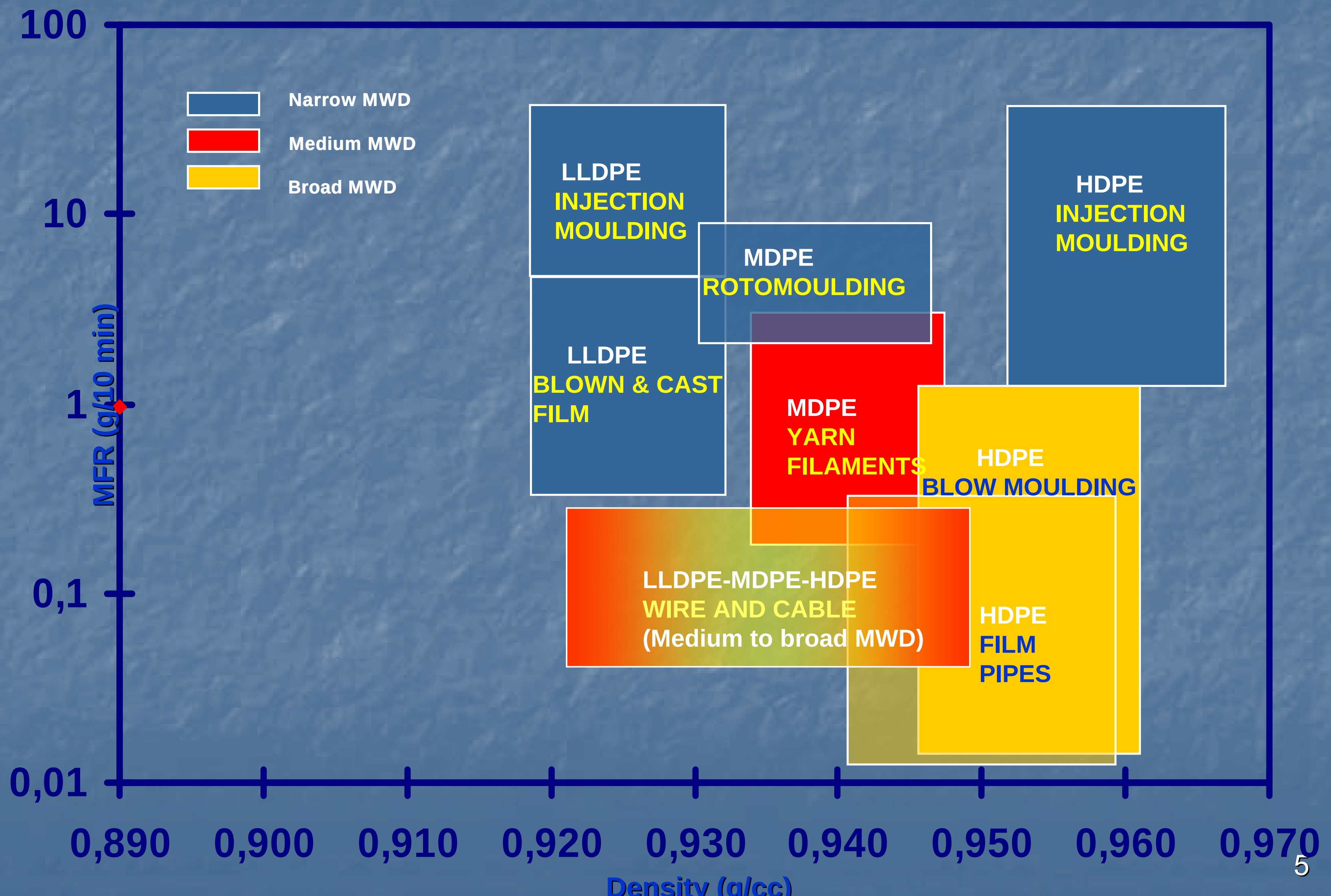
- HDPE/MDPE



- LLDPE



Application by Properties



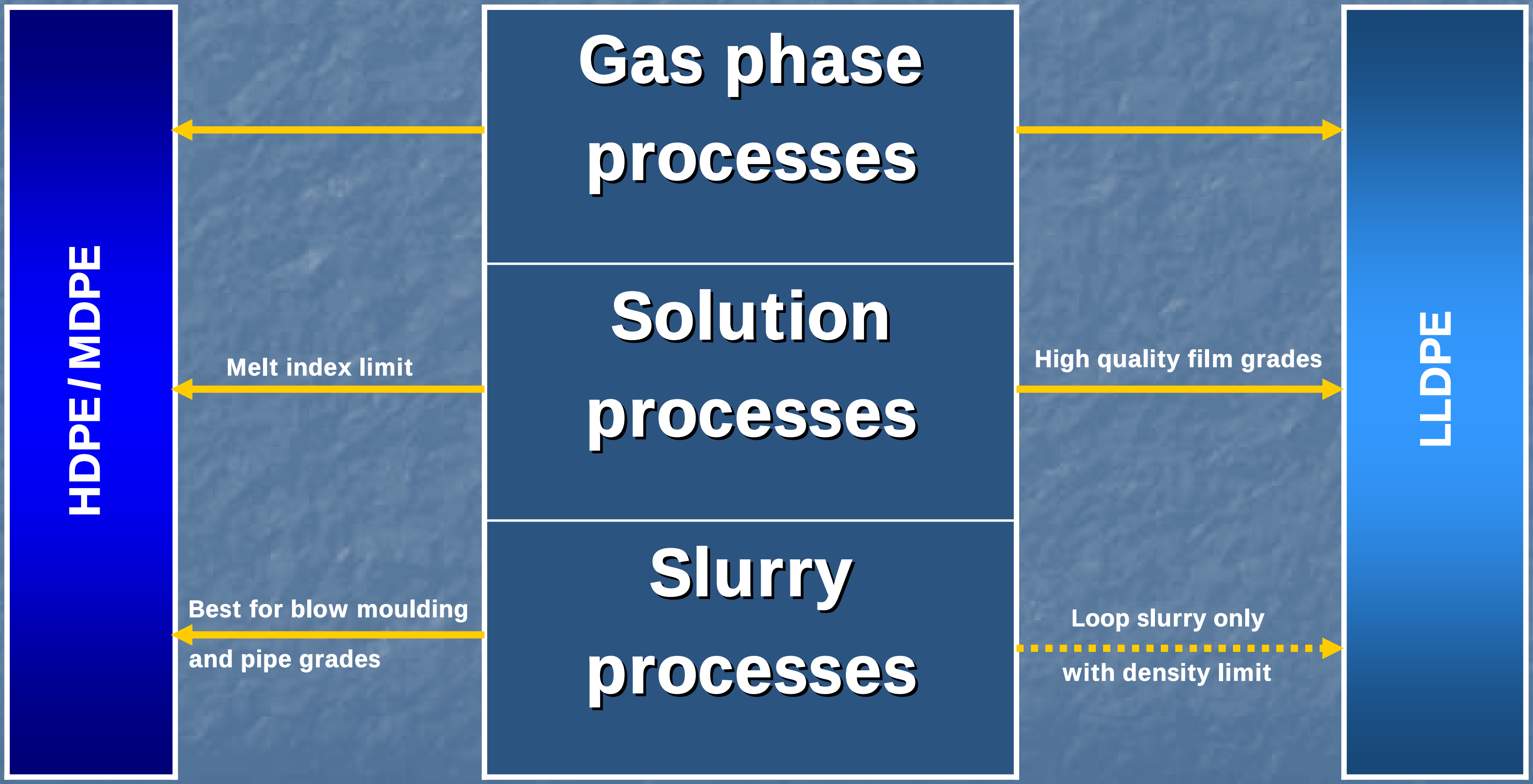
History

- 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

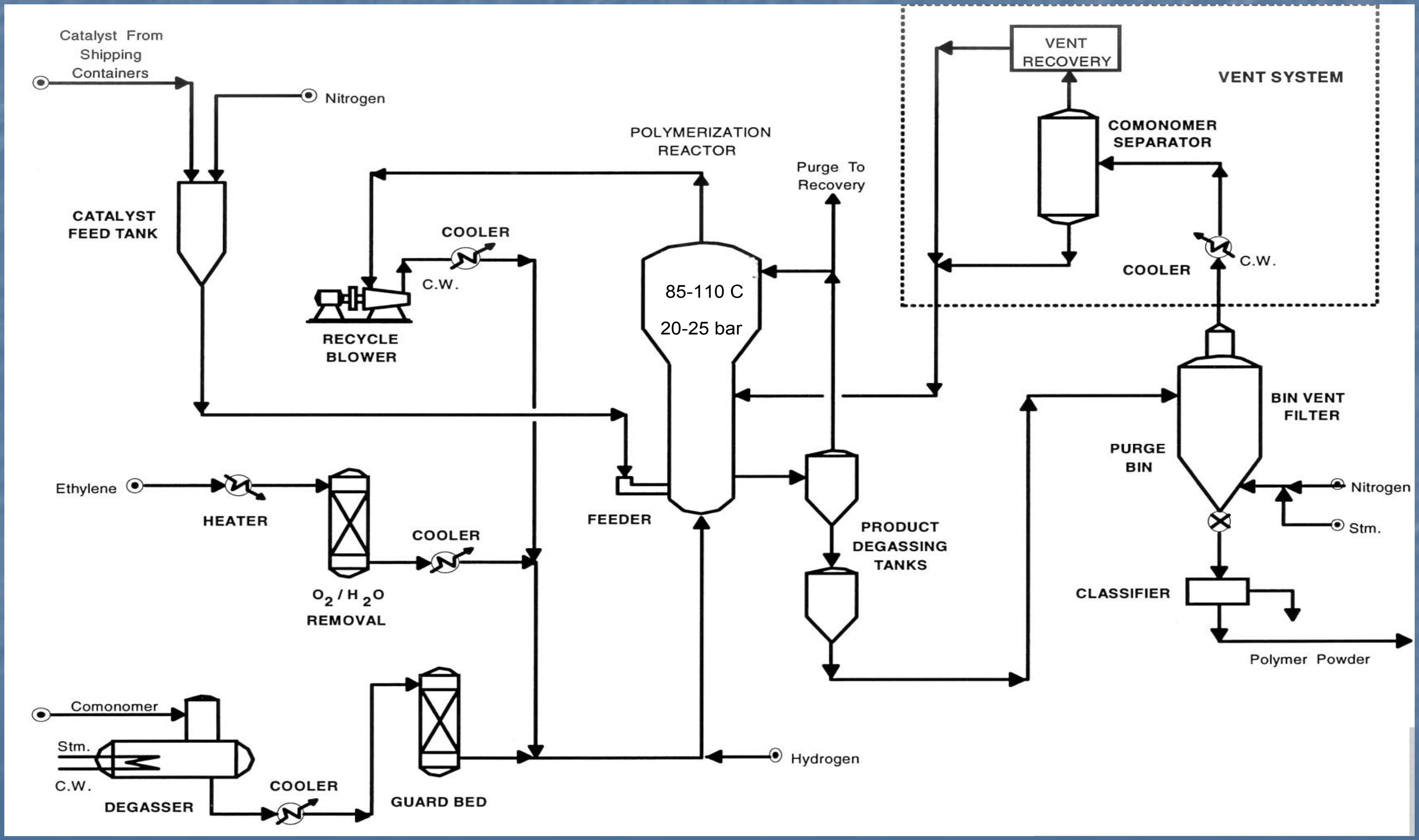
Catalysts

- 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

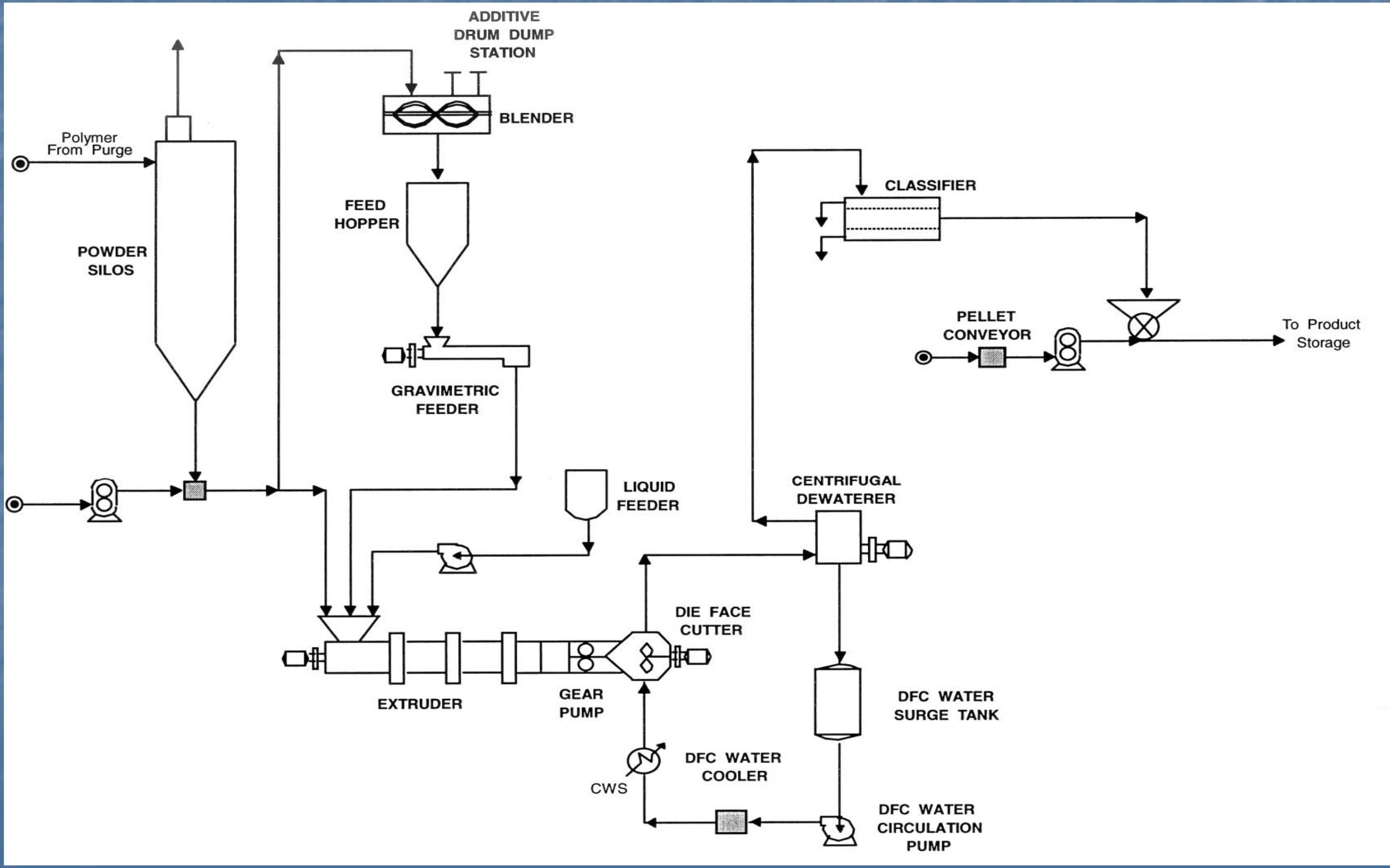
Processes and Products



Gas Phase Process
Polymerization



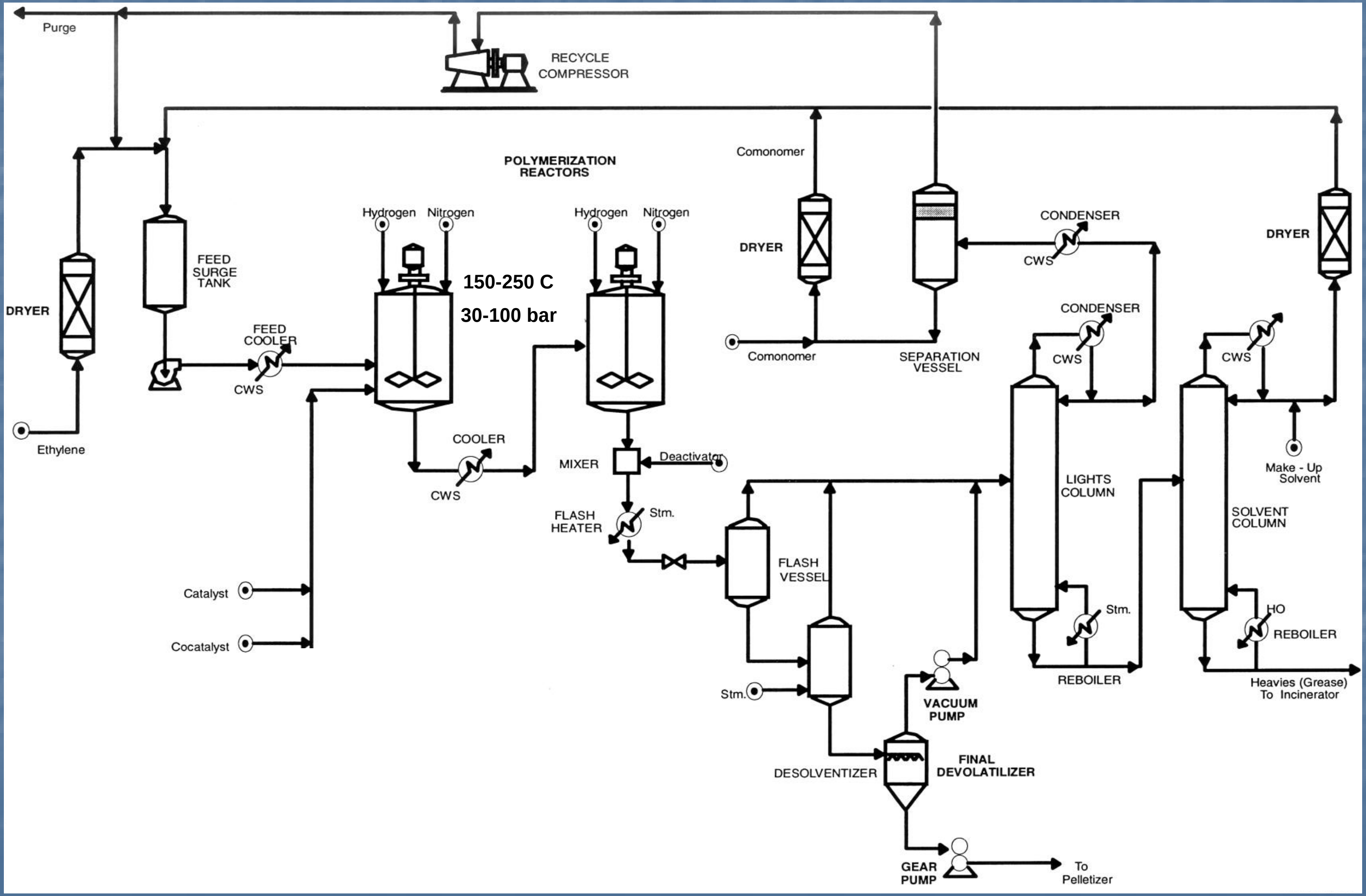
Gas Phase Process
Additivation and Pelletizing



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

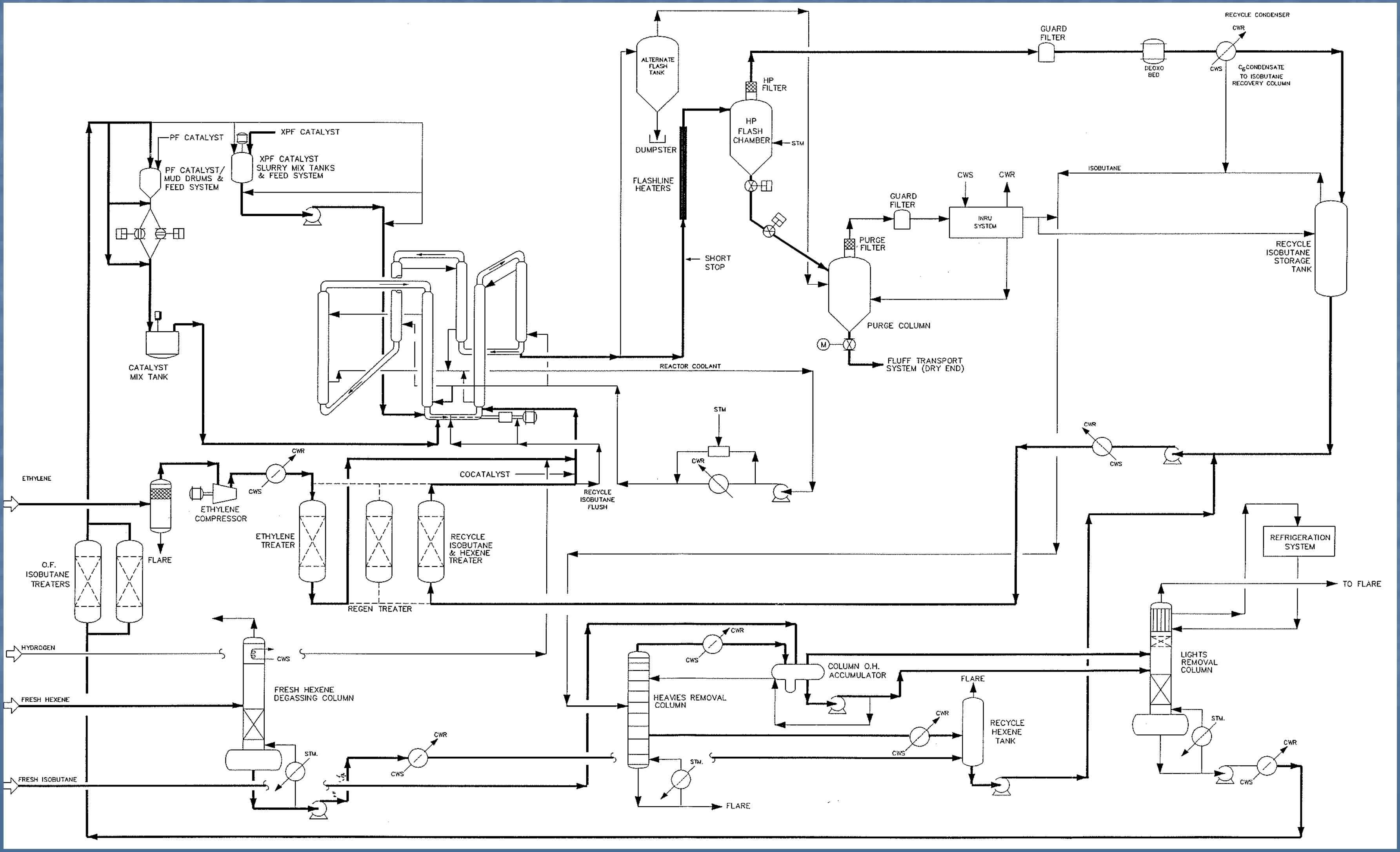
Solution Process



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

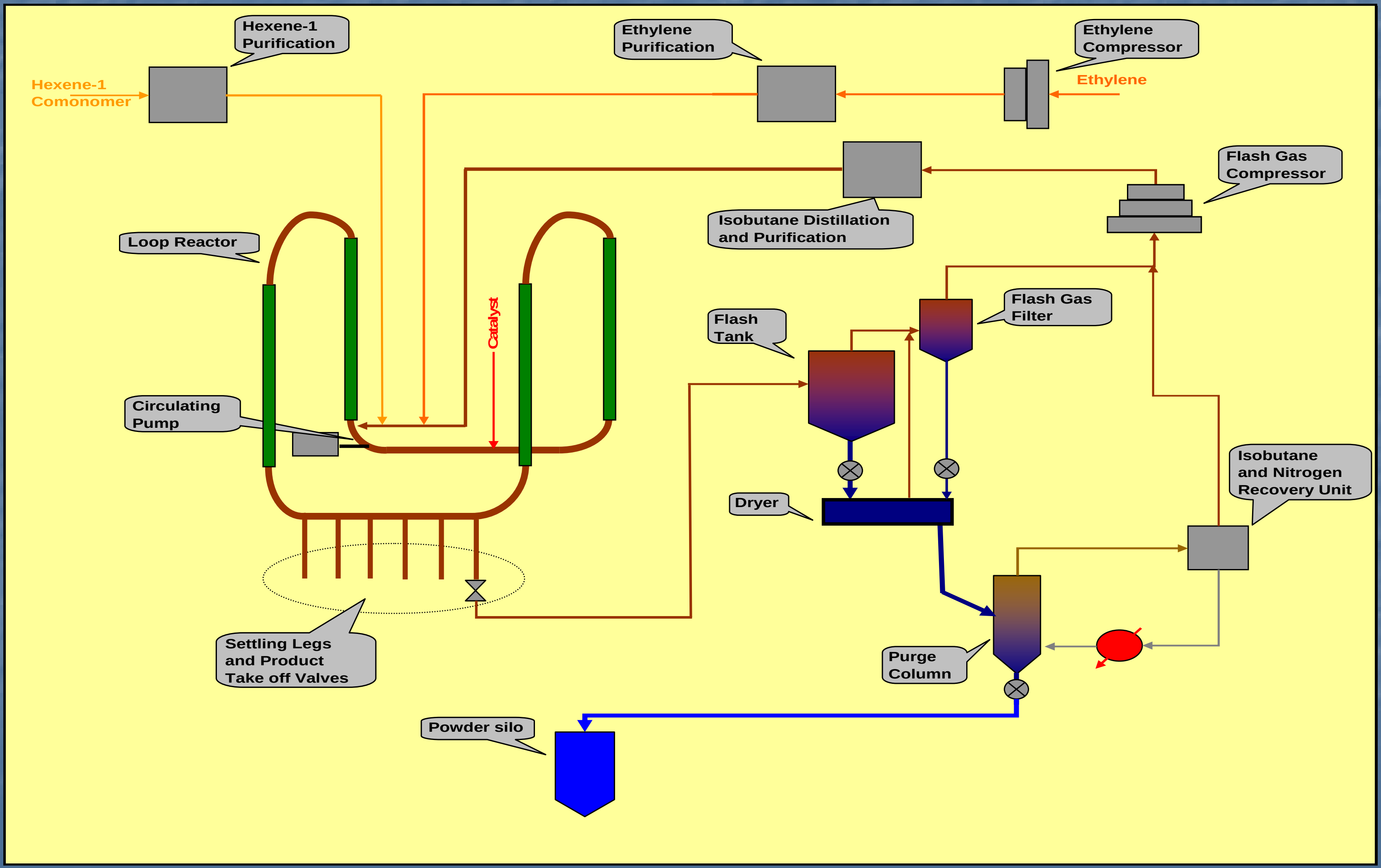
ChevronPhillips Slurry Loop Process



ChevronPhillips Slurry Loop Process Characteristics

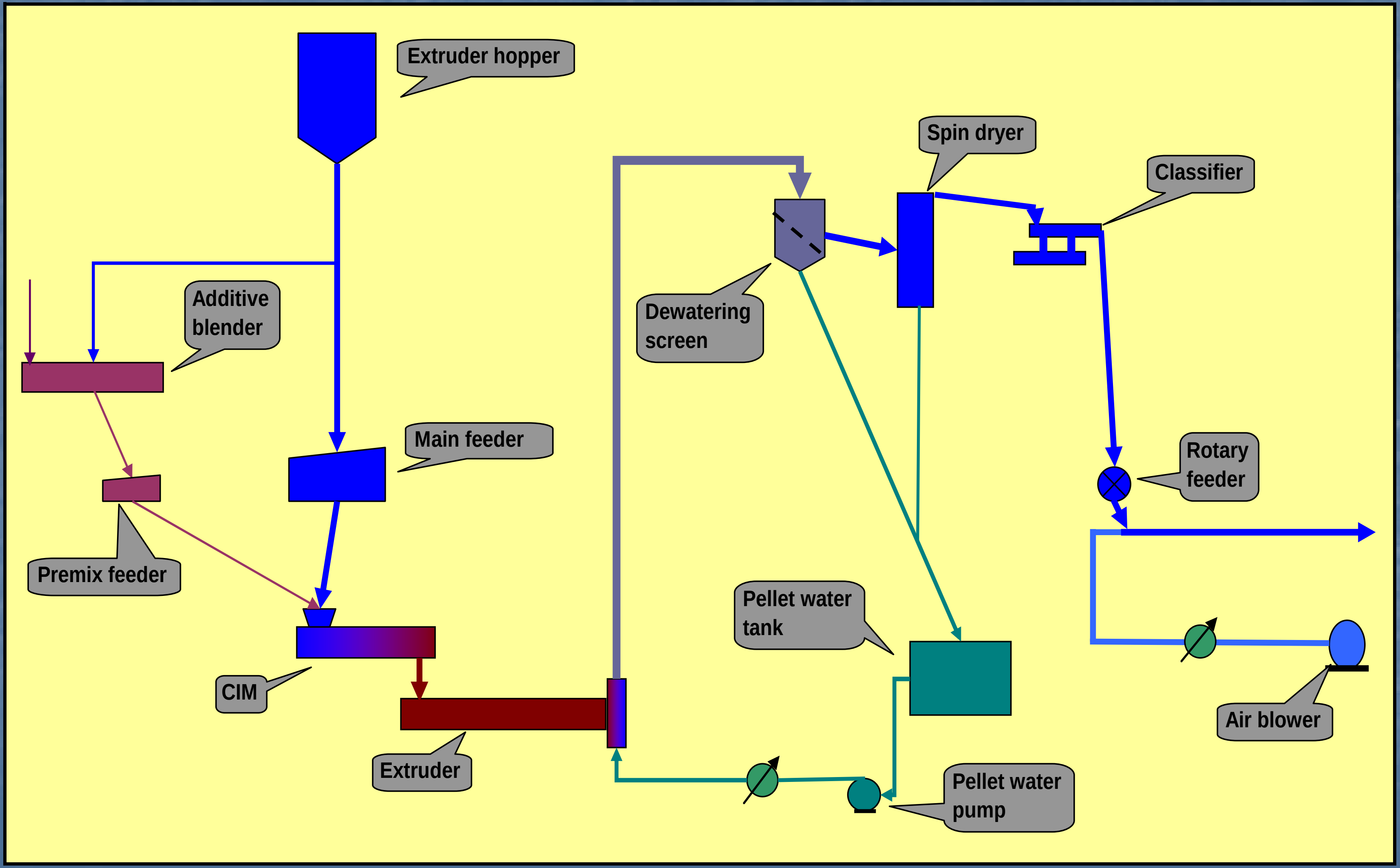
- Catalyst: chromium, Ziegler, (metallocene)
- Chromium catalyst activation
  - Fluidized bed activator
  - Heat treatment in air at 600-870 C
- Reaction in loop reactor
  - 85-105 C; 42 bar
  - 3-6 % ethylene concentration
  - Isobutane diluent
  - Heat removed by coolant in reactor jacket – very good surface/volume ratio
- Flash separation
  - 10 bar; 80 C
- Degassing
  - 85 C; 0,1 bar

Phillips Process at TVK
Polymerisation

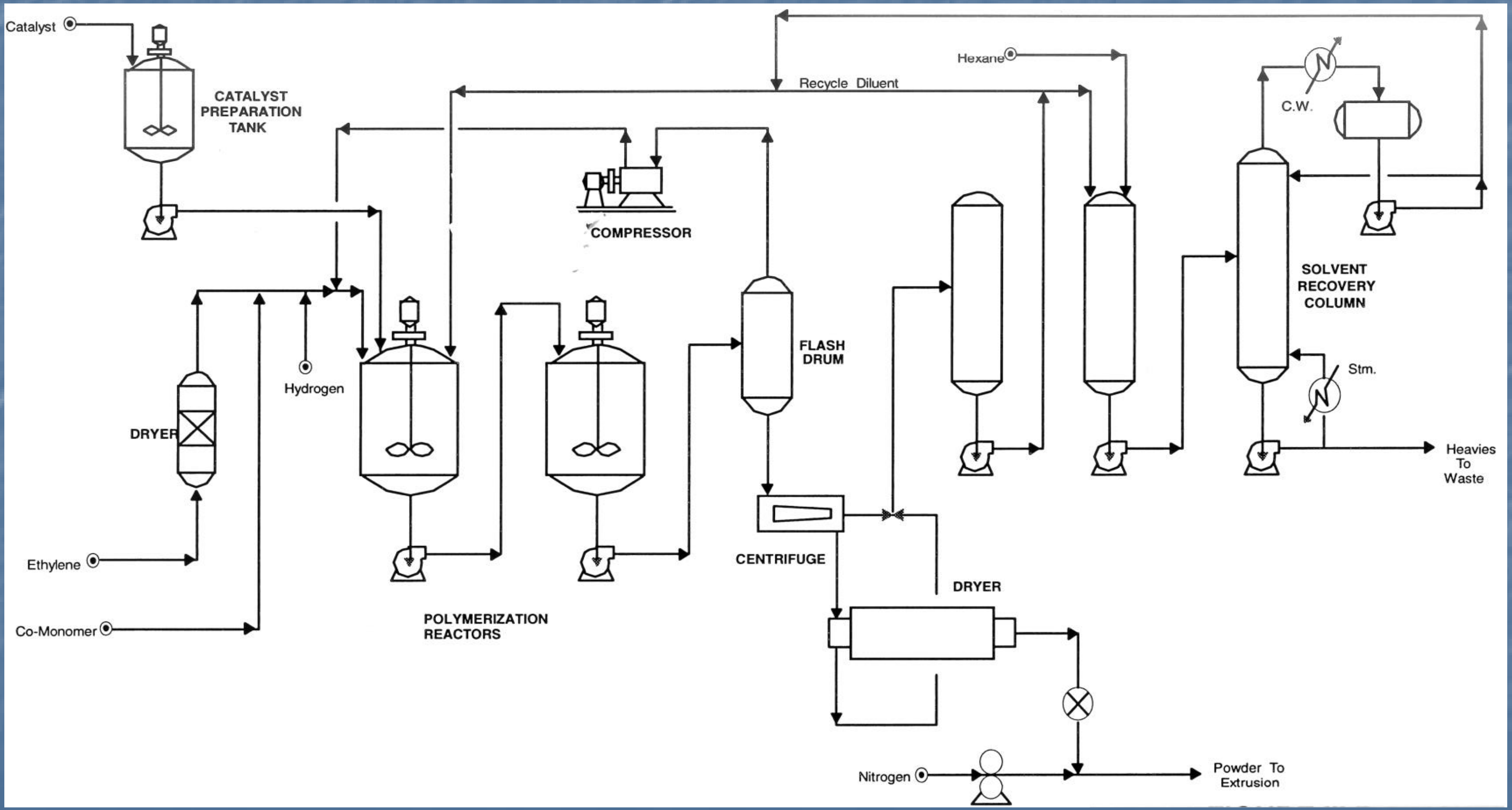


Phillips Process at TVK

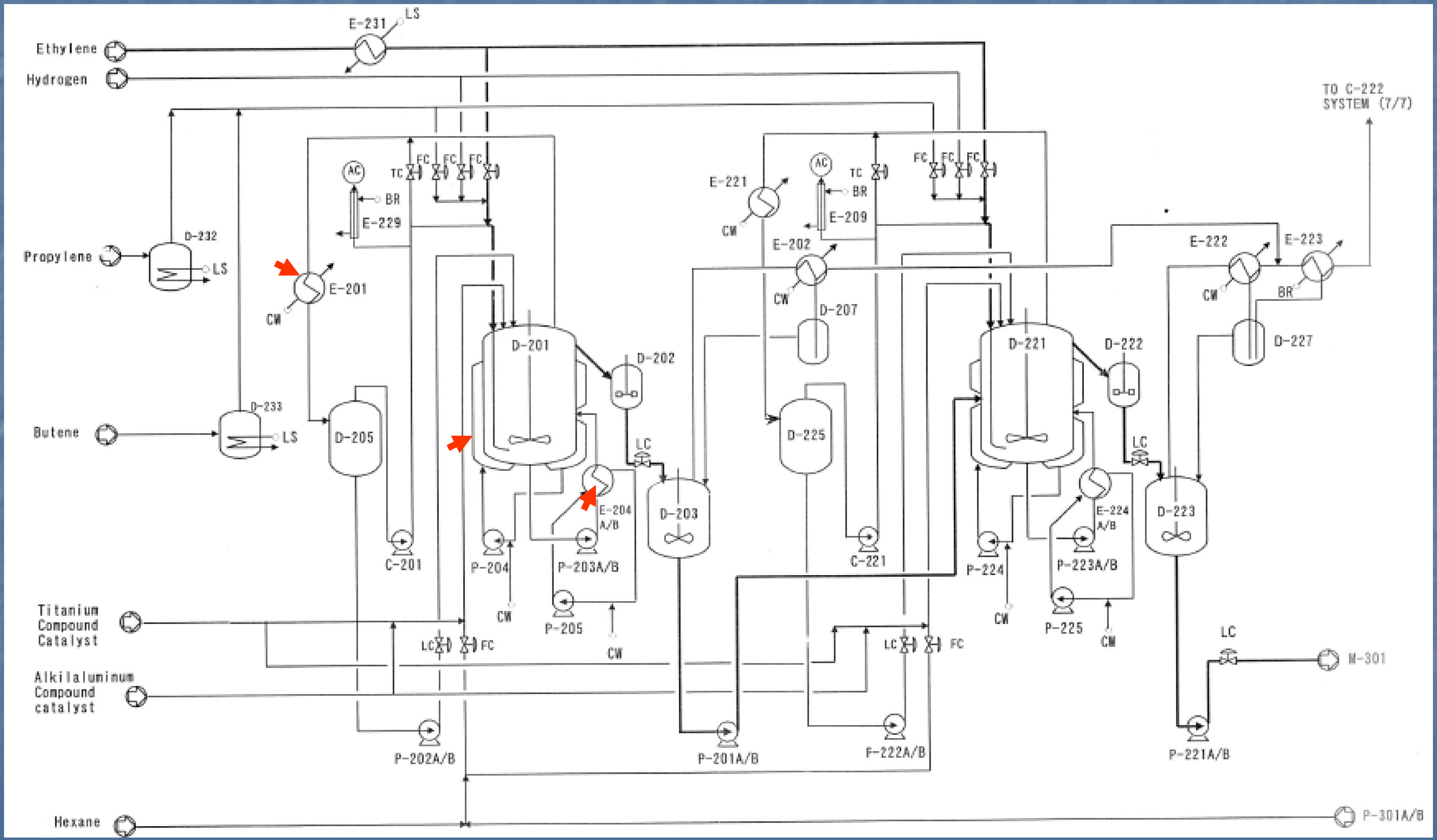
Additivation and Pelletizing



Slurry Process
CSTR- Cascade Stirred Reactor



Slurry Process – CSRT
Reactor and Surroundings



Slurry Process - CSTR
Process Characteristics

- Catalyst: Ziegler, (metallocene)
- 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

    $[H_2]/[Et]\uparrow$ MI $\uparrow$
  - Chromium catalyst: T, [Et], $[H_2]$

    T $\uparrow$ MI $\uparrow$

    $[Et]\uparrow$ MI $\downarrow$

    $[H_2]\uparrow$ MI $\uparrow$
- Density

  [comonomer] $\uparrow$ 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

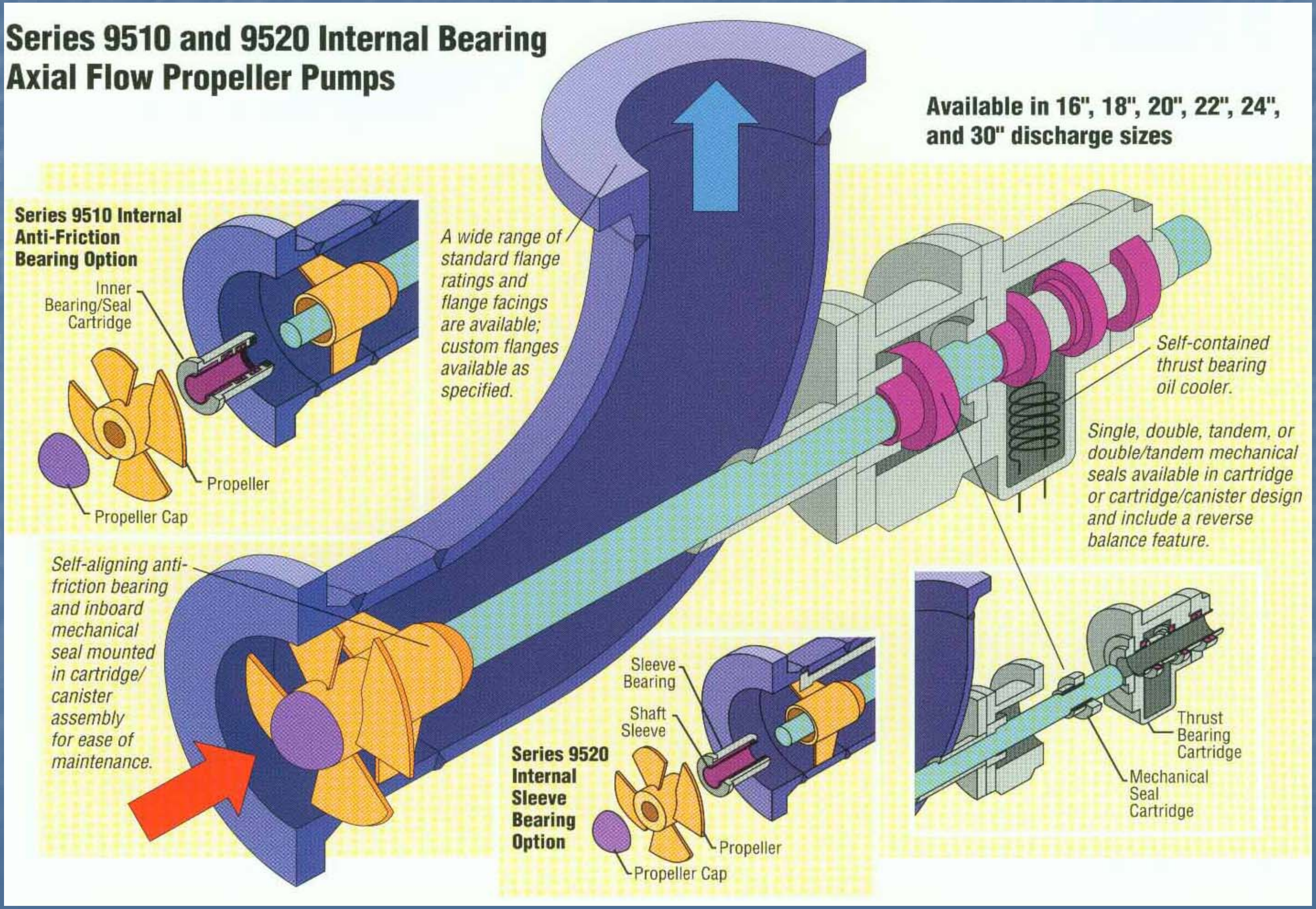
Key Equipment

- Reactors
  - Loop with axial circulating pump
  - Gas phase
- Decanter centrifuge – in CSTR only
- Extrusion line

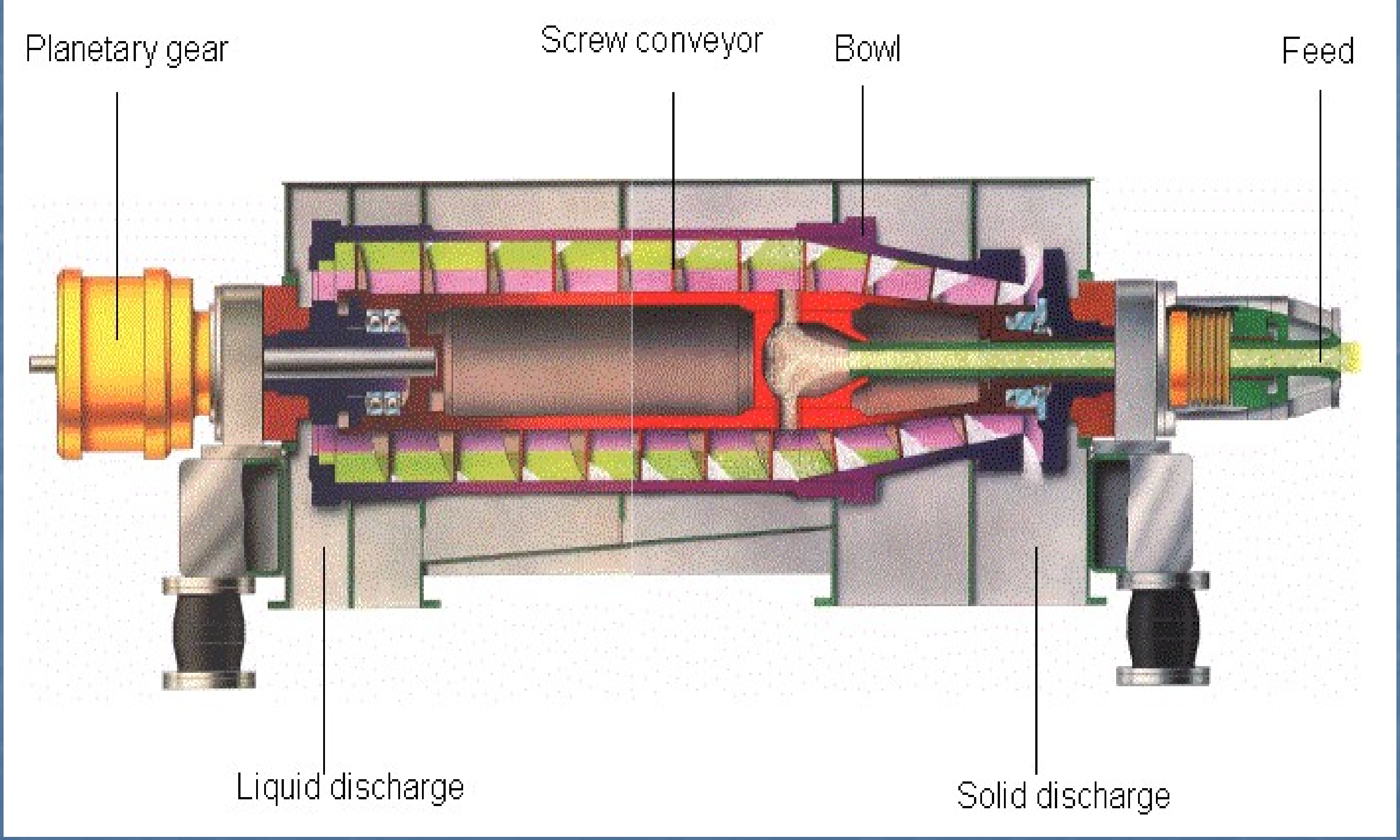
Reactors

- 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

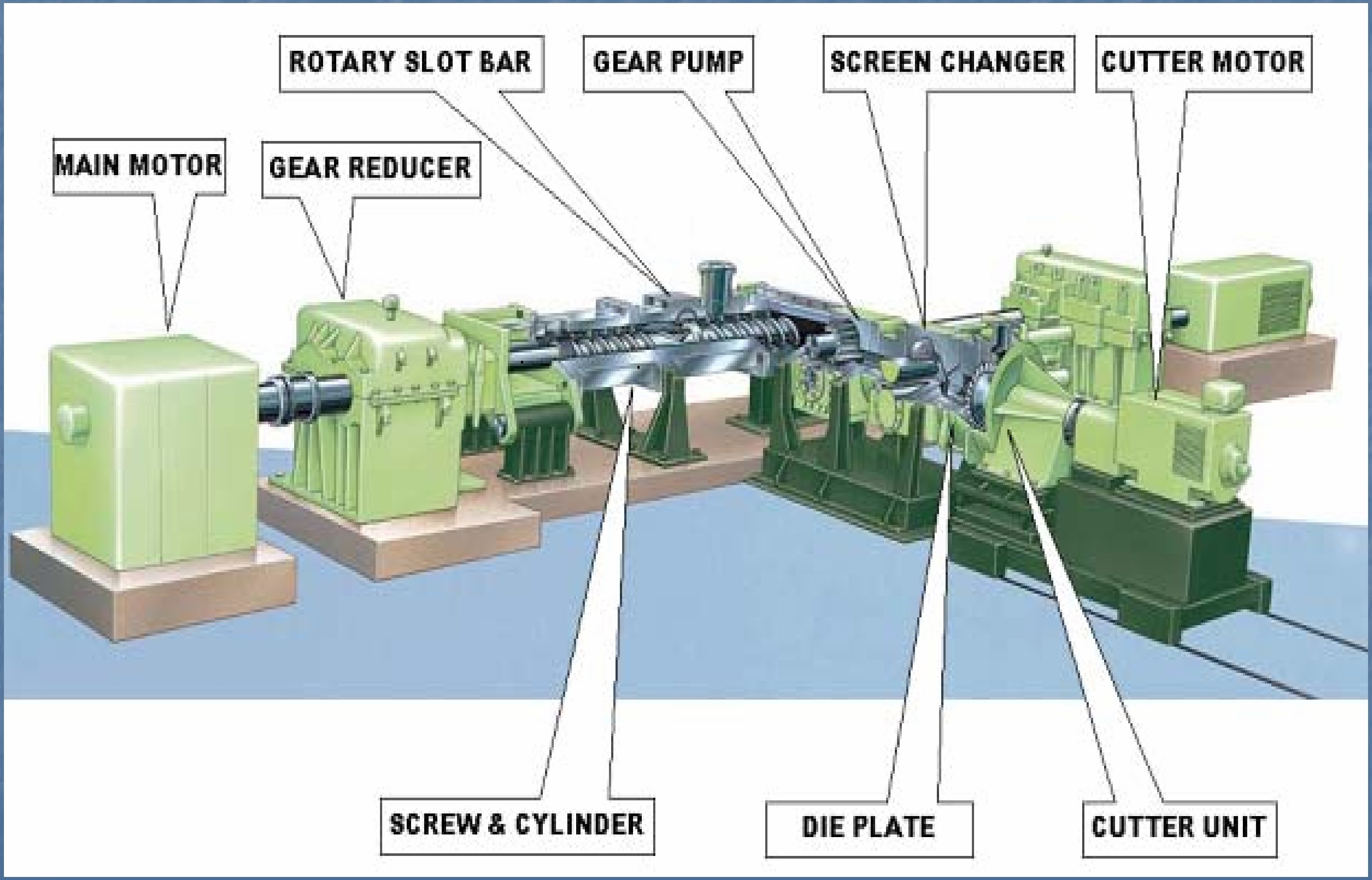
Loop Reactor Circulating Pump



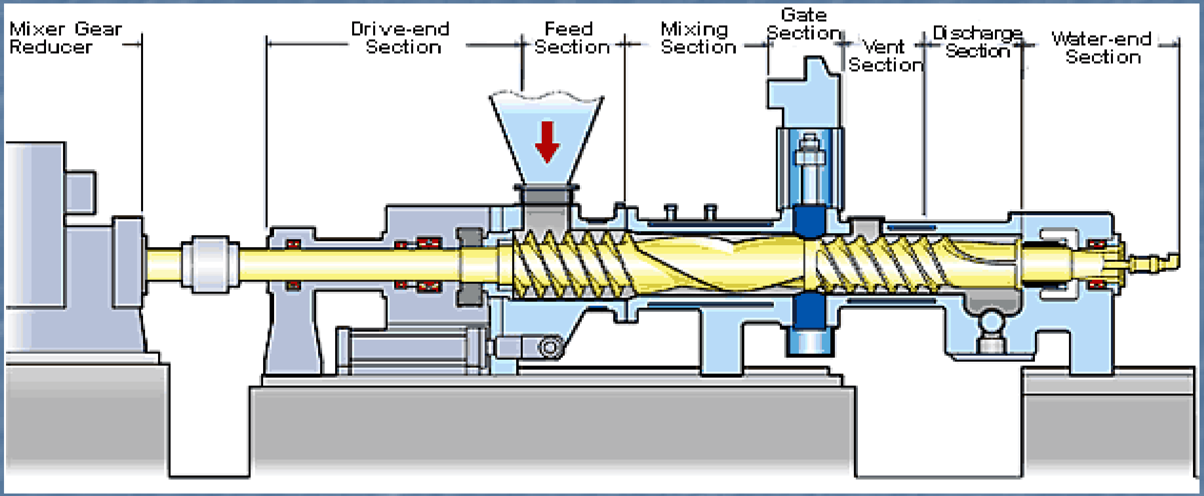
Decanter Centrifuge

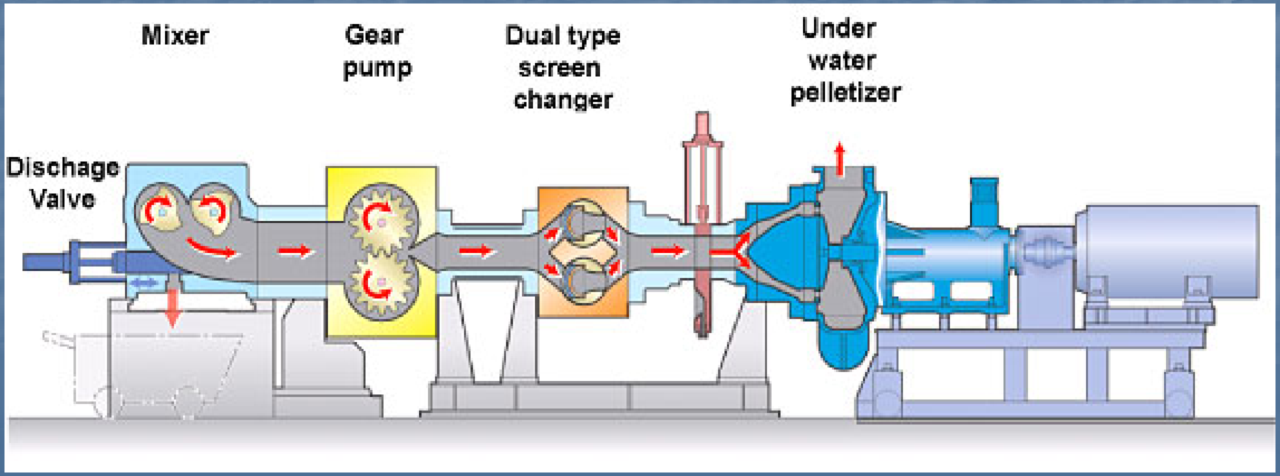


CMP Extrusion Line Arrangement

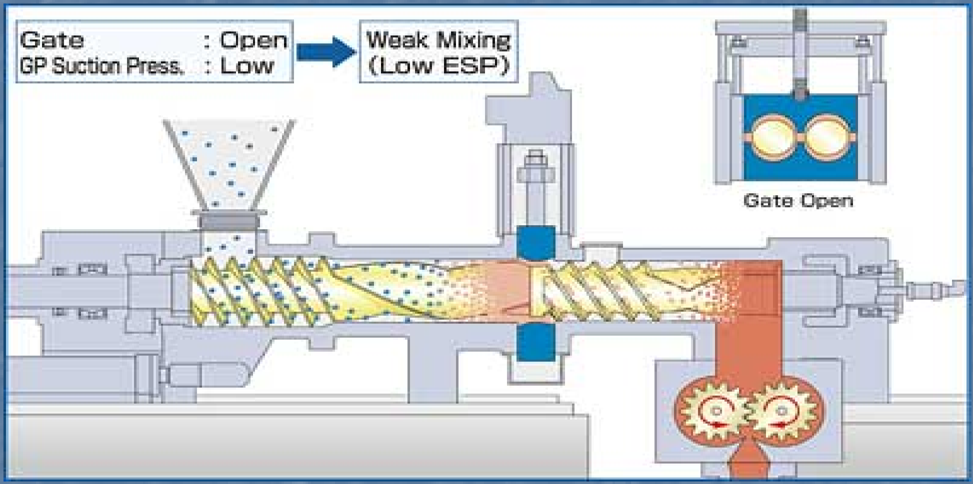


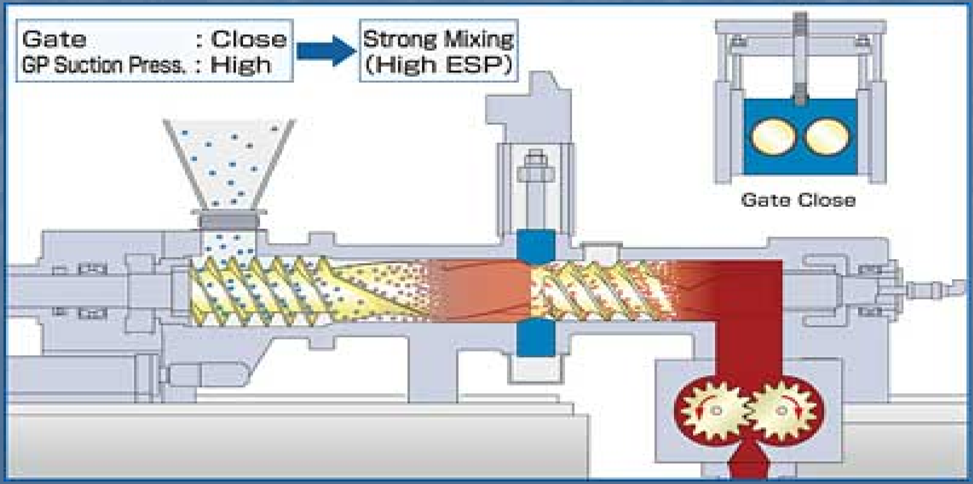
CMP Elements





Mixing in CMP



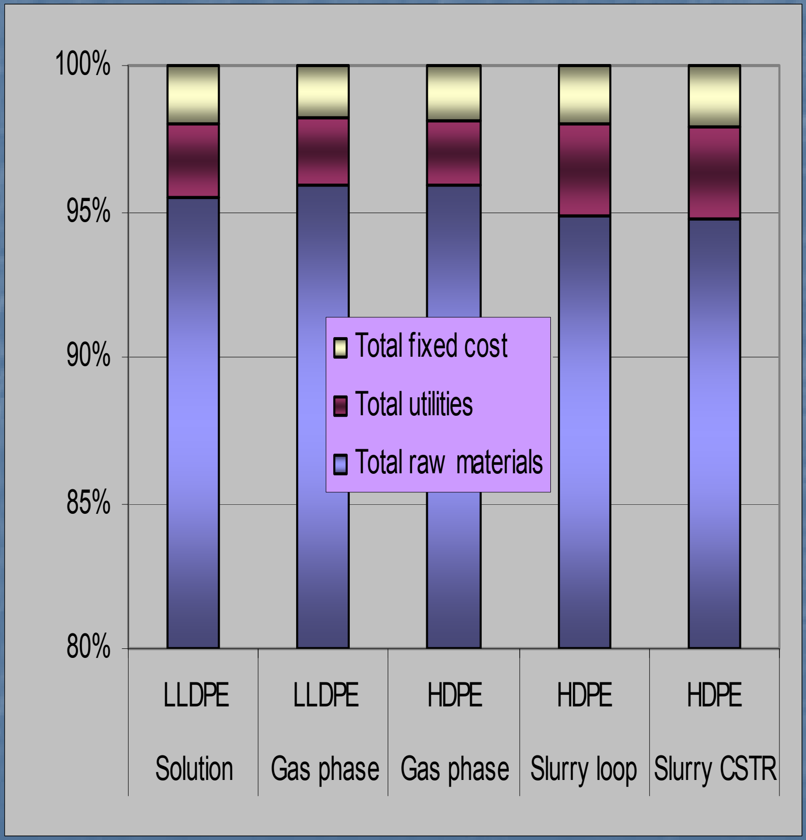


Investment Cost
Basis: USGC 2008Q1; 400 kt

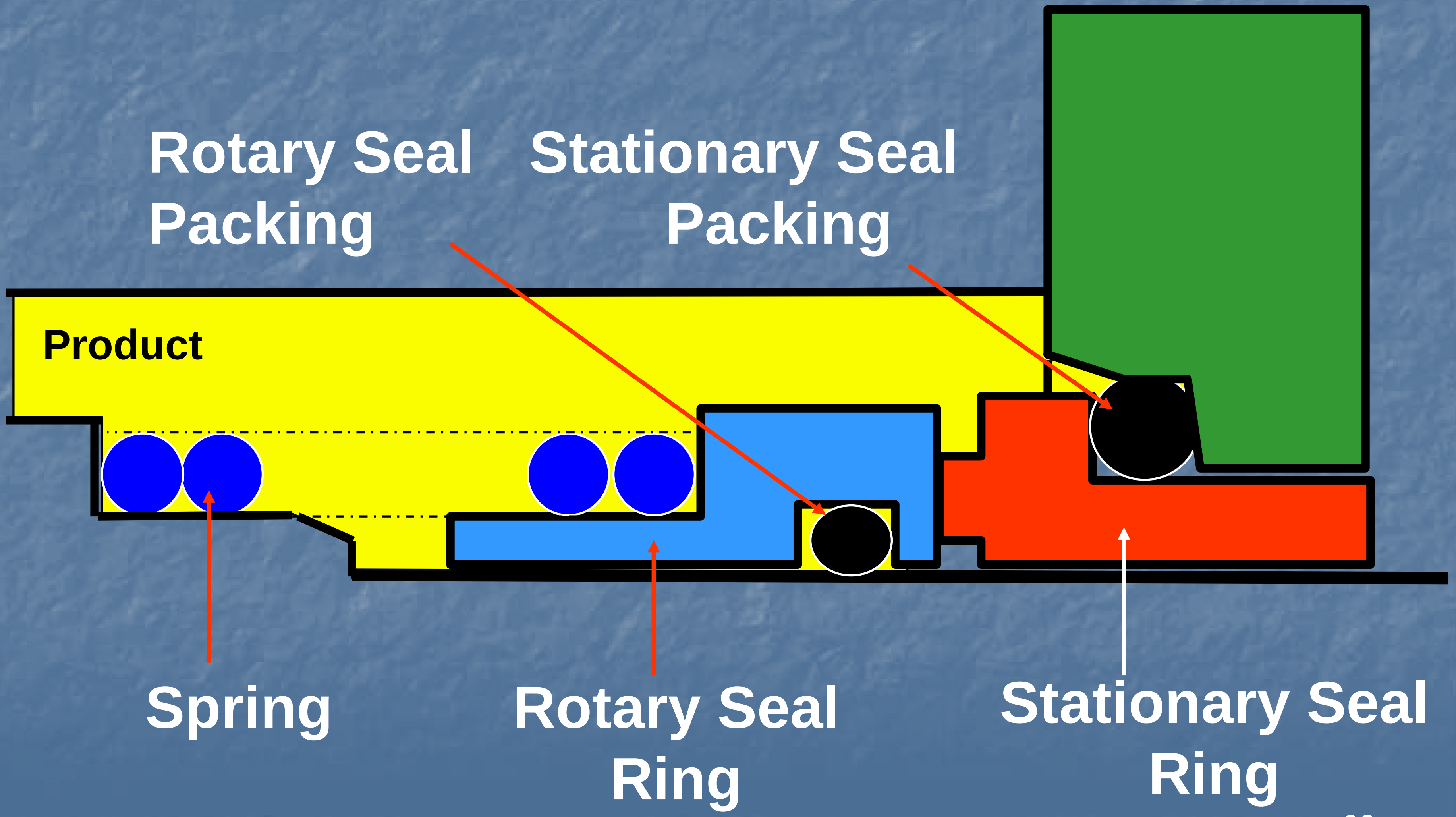
Technology	Solution	Gas phase	Gas phase	Slurry loop	Slurry CSTR
Product	LLDPE	LLDPE	HDPE	HDPE	HDPE
			million USD		
ISBL	126,4	93,8	94,7	114,1	126,8
OSBL	115,3	102,6	102,7	113,7	116,4
Other project cost	131,3	116,5	114,2	123,9	127,3
Total investment	373	312,9	311,6	351,7	370,5
Specific investment, USD/t	*933*	*782*	*779*	*879*	*926*

Cost of Production
Basis: USGC 2008Q1; 400 kt

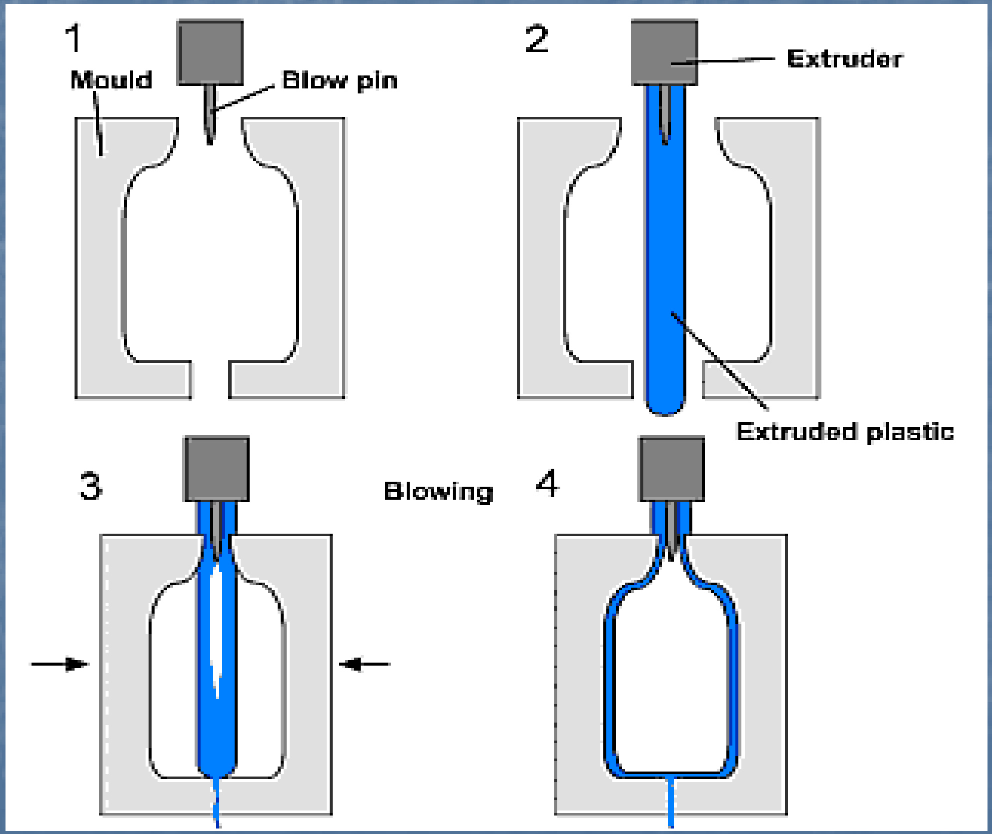
Technology	Solution	Gas phase	Gas phase	Slurry loop	Slurry CSTR
Product	LLDPE	LLDPE	HDPE	HDPE	HDPE
			USD/t		
Ethylene	1223	1222	1326	1324	1334
Comonomer	176	159	25	24	25
Catalysts&Chemicals	47	14	27	42	22
Additives	13	15	18	18	18
Total raw materials	*1459*	*1410*	*1396*	*1408*	*1399*
Power	15	22	25	30	26
Steam	16	2	2	6	13
Other utilities	8	10	6	11	8
Total utilities	*39*	*34*	*33*	*47*	*47*
Variable cost	*1498*	*1444*	*1429*	*1455*	*1446*
Direct cash cost	14	12	12	14	14
Allocated cash cost	17	15	15	16	17
Total fixed cost	*31*	*27*	*27*	*30*	*31*
Total cash cost	*1529*	*1471*	*1456*	*1485*	*1477*



Appendix: Typical Mechanical Seal



Appendix: Blow Moulding



Appendix: Pipe Extrusion