

Production of Polyethylene Using Gas Fluidized Bed Reactor

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ABSTRACT

Polyethylene is the most common thermoplastic and used in a wide range of applications. There are various commercial technologies available to produce polyethylene. Gas fluidized bed polymerization is one of the later technology developed and is commonly employed in the production of linear-low density polyethylene (LLDPE) and high density polyethylene (HDPE). This paper reviews the historical development of fluidized bed polymerization technology as well as the development of catalyst from Ziegler-Natta catalyst to metallocene-based catalyst. A critical review of the challenges and opportunities from an operations view-point is presented.

Keywords: Fluidized bed reactor, metallocene, polyethylene, polymerization, Ziegler-Natta.

1 INTRODUCTION

Polyethylene is the most common thermoplastic and used in a wide range of applications. Polyethylene can be processed into various consumer products using processing techniques such as profile extrusion, film extrusion, injection molding, blow molding, rotomolding and etc. The wide application has continuously driven the demand for this thermoplastic. Scientists and engineers also continuously improved the polymerization techniques to improve polymer properties, increase production capacity and reduce the cost of material.

Polyethylene is produced using ethylene as a monomer. Ethylene is generally produced via steam cracking of crude oil derivatives. It is common to find a petrochemical complex where the refinery, cracker and polymer plant are located on a single site. This illustrates the high capital investment required to produce polyethylene although the final consumer product may be something very cheap and disposable. Hence, improving polymer production techniques with the objective to reduce manufacturing cost continues to be an area of research, development and process improvement.

2 GAS FLUIDIZED BED POLYMERIZATION PROCESSES

2.1 Earlier Technologies

The first commercial polyethylene was produced under very high pressure (~ 3,000 atm). This is a free radical reaction process which produces low-density polyethylene (LDPE) with narrow molecular weight distribution. The high operating pressure necessitates high capital investment (equipment to withstand the high pressure) and operating costs (power to compress reactants to the high operating pressure). Variants of this technology licensed by ExxonMobil Chemical Co. and Basell Polyolefins continue to be used today with a worldwide capacity of over 6 MMtpy. This technology is also used to produce ethylene vinyl acetate (EVA) which is generally used in high clarity shrink-wrap sheets.

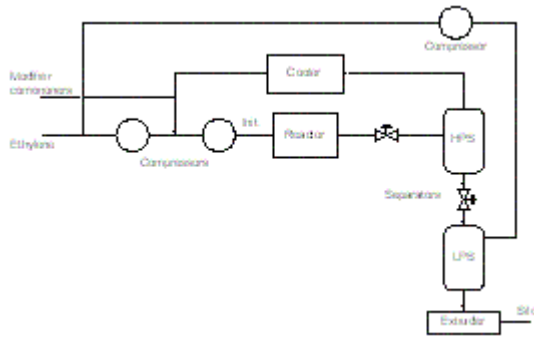


Figure 1: LDPE/EVA process, ExxonMobil Chemical Co. (*Hydrocarbon Processing, March 2003*)

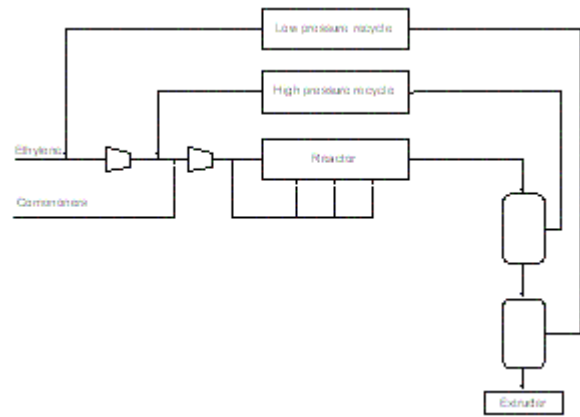


Figure 2: LDPE/EVA process, Basell Polyolefins (*Hydrocarbon Processing, March 2003*)

The subsequent technologies developed focused on achieving lower operating pressure. With the development of catalyst to allow coordination polymerization, slurry and solution phase reactors were invented. These reactors operate at a lower pressure compared to the earlier high-pressure free radical process. The slurry-phase “loop reactor” by Chevron Phillips Chemical Co. operates at 40 atm. Development for low pressure polymerization processes also started the use of comonomers such as 1-butene and 1-hexene to produce linear-low density polyethylene (LLDPE) and high density polyethylene (HDPE). The Chevron Phillips technology is used in eighty-six commercial LLDPE plants and account for 34% of worldwide capacity. Another variant of this technology by Mitsui Chemicals Inc., named *CX process* is used for production of HDPE and has a worldwide capacity of 4 MMtpy.

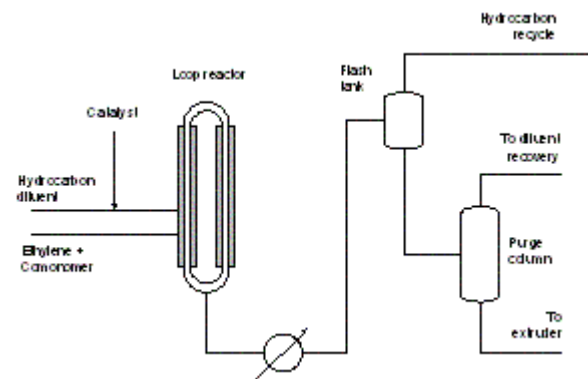


Figure 3: LPE process, Chevron Phillips Chemical Co., LP (*Hydrocarbon Processing, March 2003*)

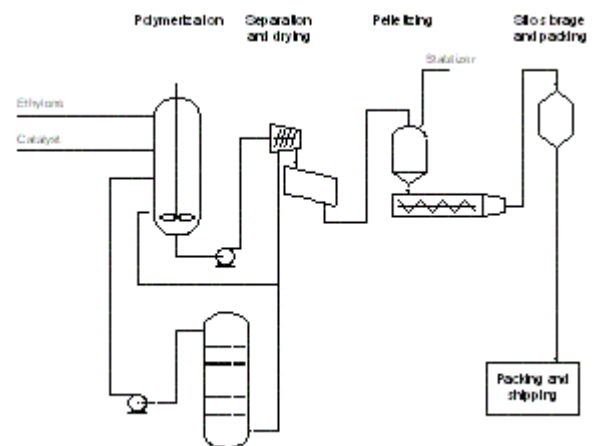


Figure 4: CX HDPE process, Mitsui Chemical Inc. (*Hydrocarbon Processing, March 2003*)

The following table summarizes polyethylene into 5 categories based on polymerization mechanism and reactor operating conditions.

Table 1: Polymerization Processes and Reactor Operating Conditions

	conventional high press. process	high-press. bulk process	solution polymn.	slurry polymn	gas phase polymn.
reactor type	tubular or autoclave	autoclave	CSTR	loop or CSTR	fluidized or stirred bed
reactor press., atm	1200 – 3000	600 – 800	~ 100	30 -35	30 - 35
temp, °C	130 – 350	200 – 300	140 – 200	85 – 110	80 – 100
polymn. mech.	free radical	coordination	coordination	coordination	Coordination
loci of polymn.	monomer phase	monomer phase	solvent	solid	solid
density, g/cm ³	0.910 – 0.930	0.910 – 0.955	0.910 – 0.970	0.930 – 0.970	0.910 – 0.970
melt index, g/10 min	0.10 - 100	0.80 - 100	0.50 - 105	< 0.01 – 80	< 0.01 – 200

2.2 Process Development

Gas fluidized bed polymerization reactors were invented in the 1950s. The major driving forces to this invention were to eliminate the need to remove the catalyst after reaction and to make the product in a form suitable for handling and storage. Distinguishing characteristic of gas phase polymerization is the system does not involve any liquid phase in the polymerization zone. Polymerization occurs at the interface between the solid catalyst and the polymer matrix, which is swollen with monomers during polymerization. The gas phase plays a role in the supply of monomers, mixing of polymer particles, and removal of reaction heat.

Dye (1962) [4] described one of the earlier reactors as three concentric superimposed vertical sections. Polymer particles were discharged through an extruder, which was connected to the bottom section of the reactor. The reactor was operated at 30 atm and 100°C. Goins (1960) [5] carried out ethylene copolymerization in a countercurrent fluidized bed reactor in presence of inert diluent gas. In this process, polymer particles are passed downward in the reactor and monomer mixed with diluent gas is passed counter-currently upward through a series of vertical fluidized bed reaction zones. The reaction zones can be controlled independently by taking off-gas from the last reaction zone, cooling it, and recycling portions of such off-gas to each of the reaction zones. Both patents (Dye, 1962; Goins, 1960) were assigned to Phillips Petroleum Company but were never applied commercially. Nevertheless, they formed the foundation idea of how a fluidized bed reaction process will be and subsequent commercialized processes are very similar to these earlier inventions.

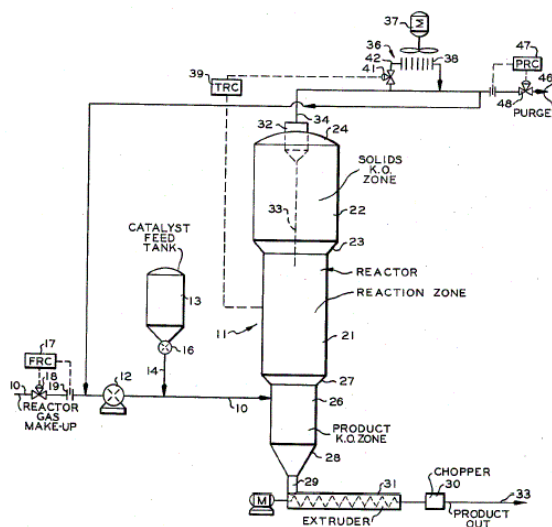


Figure 5: Fluidized bed reactor (Dye, 1962)

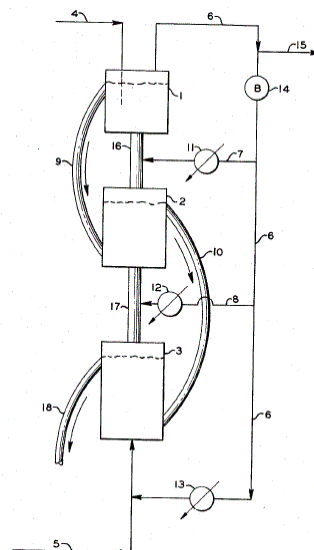


Figure 6: Fluidized bed reactor (Goins, 1960)

The first commercial gas phase polymerization plant using a fluidized bed reactor was constructed by Union Carbide in 1968 at Seadrift, Texas (Xie, 1994) [22]. This process was developed initially for HDPE production. The success of this novel technology led to the extension of the process to LLDPE and polypropylene (PP). The Union Carbide gas process is commonly known as the UNIPOL process and was described in several US Patents (Miller, 1977 [14]; Levine and Karol, 1977 [11]; Karol and Wu [10], 1978; Wagner et al., 1981 [20]; Jorgensen et al., 1982 [9]). The technology was later transferred to Dow Chemical Co. and finally to Univation Technologies, a joint-venture between Dow and ExxonMobil. Collectively, they have 96 reaction lines worldwide.

Another commercialized gas fluidized bed technology was developed by Naphtachimie in the 1970s. This technology was described in two US Patents (Dormenval, et al., 1975 [3]; Havas and Magin, 1976 [6]). The technology was transferred to BP Chemicals Ltd. after the Naphtachimie was amalgamated into the

latter. The original Naphachimie design was very similar to the Union Carbide design with exception of a pre-polymerization step. Monomers, catalysts and hydrogen were first activated in an n-heptane phase using a mechanically stirred vessel. The catalytically active solids or “pre-polymers” were decanted and subsequently fed to the fluidized bed reactor instead of solid catalyst as in the case of UNIPOL process. This major distinction was incorporated in the latter BP designs until the development of metallocene catalyst.

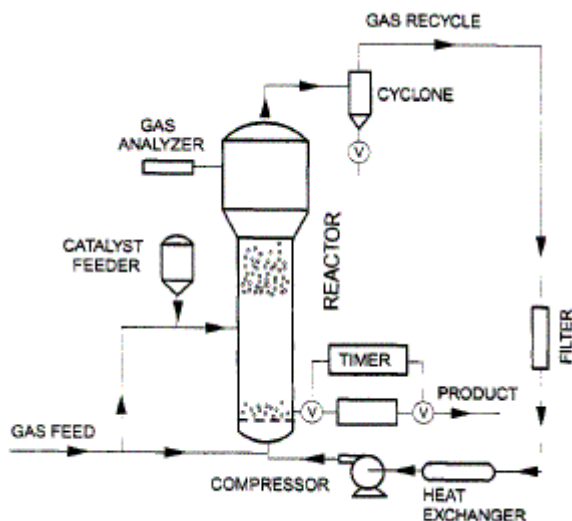


Figure 7: Union Carbide fluidized bed reactor (Miller 1977; Levine and Karol, 1977; Karol and Wu, 1978; Wagner et al., 1981; Jorgensen et al., 1982)

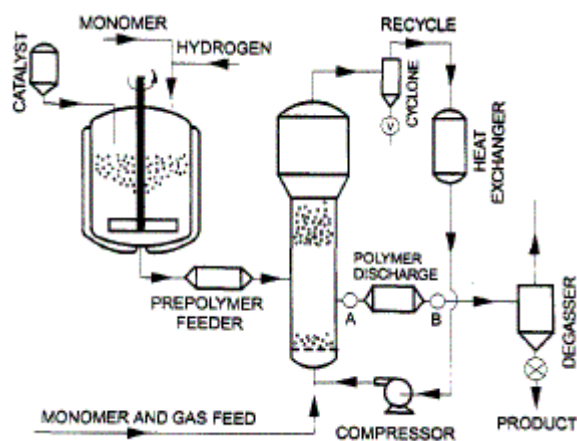


Figure 8 BP Chemicals fluidized bed reactor process (Dormenval et al, 1975; Havas and Magin, 1976; Havas and Lalanne-Magne, 1992)

Table 2 summarizes the similarities and differences between the Union Carbide and BP Chemicals fluidized bed reactor technologies. [Note that the later development of metallocene catalysts is not discussed here.]

Table 2: Fluidized Bed Reactors Processes and Operating Conditions

	Union Carbide	BP Chemicals
Reactor type	Fluidized bed	Stirred reactor and fluidized bed
Catalyst	Supported Ti, V and CrCO ₃ catalyst	Supported Ti and CrCO ₃ catalyst
Catalyst size, μm	30 - 250	~ 50 for prepolymer
Pressure, atm	20 - 30	15 - 25
Temperature, °C	75 - 110	70 - 115
Comonomer	1-butene or 1-hexene	1-butene or 1-hexene
MW control	H ₂	H ₂
MWD, $\overline{M}_w / \overline{M}_n$	4 - 30	6 - 20
Density, g/cm ³	0.91 - 0.97	0.91 - 0.96
Polymer particle size, μm	500 - 1300	300 - 1200

Since the successes of both Union Carbide and BP Chemicals processes, the fluidized bed reactor technology has been applied and improved in other proprietary polymerization processes. Notable examples are combination of slurry loop reactor and fluidized bed reactor in series for production of polyethylene and fluidized beds in series for production of polypropylene. These hybrid systems will be discussed in a later part of this paper.

2.3 Process Description

Both the Union Carbide and BP Chemicals technologies contain a reactor loop which consists of an expanded dome reactor vessel, a compressor and a cooler. The earlier designs adopted the cooler before the compressor configuration. This is to cool down the reacting gas mixture and hence, lowering the compression power required. The newer plants however adopted the cooler after compressor sequence.

Fouling of the cooler (polymer fines buildup in the exchanger tubes) often becomes the criteria of a shutdown; hence the reconfiguration allows longer service time between cooler cleaning. Putting the cooler downstream of the compressor also allows the comonomers (more notably 1-hexene) to condense partially in the cooler. This condensation phenomenon removes a lot of heat from the system and enables higher production rate. The cyclone shown in both the simplified flow diagrams has the function of removing polymer fines and reduces the fouling of the cooler or compressor blades. This equipment however is optional and is omitted in some newer plants built in the last decade. The following paragraphs are detailed description of the earlier configurations by Union Carbide and BP Chemicals.



Figure 9: Industrial scale UNIPOL reactor (Univation Technologies, 2004)

The fluidized bed reactor in a UNIPOL process consists of a reaction zone and a disengagement zone. The reaction zone has a height to diameter ratio of about 6-7.5. The disengagement zone has a diameter to height ratio of about 1-2. To maintain a viable fluidized bed, superficial flow through the bed is about 2-6 times the minimum flow required for fluidization. It is essential that the bed always contain polymer particles to prevent the formation of localized "hot spots" and to entrap and distribute the powdery catalyst. On startup, the reaction zone is charged with a base of polymer particles before gas flow is initiated. Monomer (ethylene gas) is fed to the compressor inlet, whereas the α -olefin comonomer (1-butene or 1-hexene) is added to the reactor inlet. The catalyst is stored in a catalyst feeder under a nitrogen blanket. Catalyst is injected into the bed at a rate equal to its consumption rate at 114 to 314 of the height of the bed. If co-catalyst (e.g., trialkyl aluminum) is required, it is fed separately to the reactor inlet. Catalyst concentration in the fluidized bed is essentially equal to the catalyst concentration in the product, namely on the order of about 0.005-0.50% of bed volume. Fluidization is achieved by a high rate of gas recycle to and through the bed, typically on the order of about 50 times the rate of feed of make-up gas. The pressure drop through the bed is typically on the order of 0.07 atm (1 psi). Make-up gas is fed to the bed at a rate equal to the rate at which polymer particles are withdrawn. A gas analyzer, positioned above the bed, determines the composition of the gas being recycled, and the make-up gas composition is adjusted accordingly to maintain an essentially steady-state gaseous composition within the reaction zone.

The gas which has not been consumed in the bed passes through the enlarged disengagement zone where entrained particles drop back into the bed. Particle entrainment is further reduced by a cyclone and a filter to avoid deposition of polymer on heat-transfer surfaces and compressor blades. Polymerization heat is removed by a heat exchanger before the recycle gas is compressed and returned to the reactor. The fluidized bed can maintain itself at an essentially constant temperature under steady-state conditions. To

increase heat removal capacity and productivity, UNIPOL reactors can be operated with an inlet gas temperature at the bottom of the fluidized bed which is below the dew point temperature of that gas. Recycle gas condenses in the external cooler, and the liquid droplets revaporize upon entry into the bed. It has been observed that droplets pass through the distributor as a mist and quickly wet the surface and pores of the polymer particles. The liquid vaporizes very quickly above the distributor. There is a dramatic change in the gas flow pattern in the gas feed region below the distributor. However, there is no apparent effect on bulk circulation patterns of bubbles and resin particles above the gas distributor.

The distribution plate at the bottom of a reactor plays an important role in the operation of the reactor. As the polymer particles are hot and possibly active, they must be prevented from settling to avoid agglomeration. Maintaining sufficient recycle and make-up gas flow rate through the distributor to achieve fluidization at the base of the bed is very important in fluidized bed polymerization reactor operation. The polymer particles are withdrawn close to the distributor through sequential operation of a pair of timed valves, defining a segregation zone. The reactor is operated at a temperature below the melting point of the polymer particles. For HDPE production, the operating temperature is 90-110°C. An operating temperature of about 90°C or lower is preferred for production of LLDPE, which contains about 15 mol % of one or more of the C₃ to C₆ α-olefins (Levine and Karol, 1977). The reaction zone and disengagement zone of the reactor are connected by a transition section having sloped walls. During polymerization, some fine particles from the disengagement zone fall onto the sloped walls of the transition section. These fine particles build up during reactor operation. Since the fine particles contain active catalyst, they further polymerize and form solid sheets which can grow until they block recycle gas flow or slide off the sloped walls into the polymerization zone. In the polymerization zone, the solid sheets block the flow of gas and cause fusion of the polymerization particles. Thus, large chunks of polymer can be formed which can block the entire polymerization zone unless the reactor is shut down and the sheets are removed.

The BP Chemicals gas phase process is a continuous two-stage polymerization process (Dormenval et al, 1975; Havas and Magin, 1976; Havas and Lalanne-Magne, 1992). This process uses a combination of a stirred tank reactor and a fluidized bed reactor in series. During conventional gas phase reactor operation, the catalyst and the cocatalyst may be brought into contact either prior to their introduction into the fluidized bed, or in the interior of the reactor. Whichever method is employed, the polymerization reaction always starts up very abruptly and attains a maximum rate soon after the catalyst system is introduced into the fluidized bed.

The initial phase of polymerization is where the risks of hot spots forming and grains bursting into fine particles are greatest. Hot spots may lead to formation of agglomerates and to settling of polymer inside the fluidized bed. Furthermore, during polymerization small variations in the feed rates of catalyst, monomer, and comonomer or in the withdrawal rate of polymer will also cause an unexpected increase in the quantity of heat evolved by the polymerization. If the heat cannot be removed efficiently, these small variations can cause hot spots in the reaction bed and formation of agglomerates by melting polymer. Such variations can therefore make it difficult to obtain a polymer of consistent quality, in particular, of constant molecular weight and particle size. These problems can be eliminated by adopting a prepolymerization stage.

Prepolymerization gives advantages in polymer particle size control and control of the catalyst activity in the fluidized bed reactor. Prepolymerization can be carried out in a liquid hydrocarbon medium or in a gas phase stirred reactor at temperatures from 40 to 115°C. Catalyst is introduced into the prereactor in the form of dry powder or in suspension in a liquid hydrocarbon. Prepolymerization is carried out to a conversion wherein the prepolymer contains 0.002-10 millimol of transition metal/g of polymer. The diameter of the prepolymer is in the range from 200 to 250 μm. Prepolymer is fed into the fluidized bed reactor through a metering feed device.

The fluidized bed reactor operates at a superficial velocity of approximately 0.5 m/s, 2-8 times the minimum fluidization velocity. To avoid induction time at startup, the prepolymer is treated with

triethylaluminum for polymerization with chromium oxide as catalyst. To create more porosity, the prepolymer is also treated with n-hexane to remove low molecular weight polymer (wax). Monomer, comonomer, hydrogen, and inert gas are fed through the bottom of the fluidized bed. Some comonomer and inert volatile hydrocarbon, such as isopentane, are introduced into the inlet line of the heat exchanger to avoid fine particles depositing on heat exchanger surfaces and compressor blades. The ratio of comonomer to monomer partial pressure is kept constant (normally 0.1-0.2) in the reactor. To avoid pressure fluctuations during polymer discharge, BP Chemicals developed a continuous discharge device consisting of two continuously rotating plug valves. These valves are connected with each other in such a way that the two valves do not open at the same time, rotating at a speed of about 0.5-1.0 rpm. The volume of the vessel between the valves is between 0.2% and 1% of the volume of the fluidized solid contained in the reactor.

2.4 Catalyst Development

Development of polymerization catalyst has attracted the participation of both academic and industrial laboratories. The wide application of polyethylene would not be possible without the thoughtful development of catalyst at the microstructure level. Catalysts were first developed with the objective to produce polymers at a low operating pressure. This objective is now shifted to engineer the desired properties of the final plastic product. Every polymer manufactured by coordination polymerization is essentially an engineered plastic which was developed meticulously to have the desired physical, chemical and mechanical properties.

Catalysts for ethylene polymerization are mostly heterogeneous, but some processes also use soluble catalysts. There are now four types of catalysts for ethylene polymerization: Ziegler-Natta, Phillips, metallocenes and late transition metal catalysts. Only the first three types are in use commercially, whereas the last is still in research and development stage.

Ziegler-Natta catalysts have many variations but are generally TiCl_4 supported on MgCl_2 , combined with a variety of electron donors and cocatalysts. Ziegler-Natta catalysts account for most of the polyethylene produced industrially. In operations, a trialkyl aluminum co-catalyst (typically triethyl aluminum) is added separately to the reactor feed. Figure 10 gives an illustration of how polyethylene is made using Ziegler-Natta catalysts in a fluidized bed reactor.

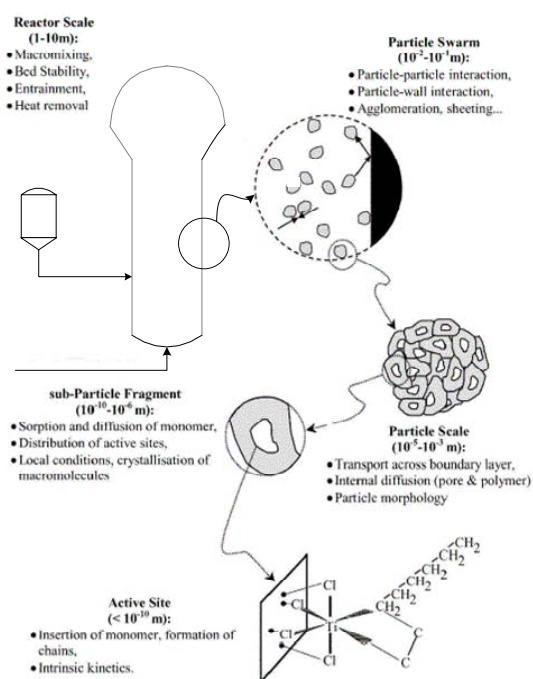


Figure 10: Ethylene polymerization using Ziegler-Natta catalyst

Phillips catalysts are mostly composed of chromium oxide supported on silica or silica/alumina. It is responsible for a considerable fraction of the HDPE produced. In operations, Phillips catalysts do not require separate addition of co-catalyst. It is however more exothermic and heat removal needs to be efficient.

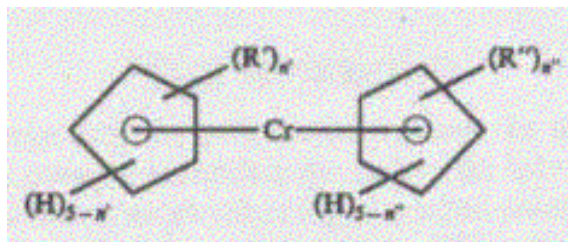


Figure 11: Inorganic oxide supported bis(cyclopentadienyl) chromium [II] (Karol et al., 1978)

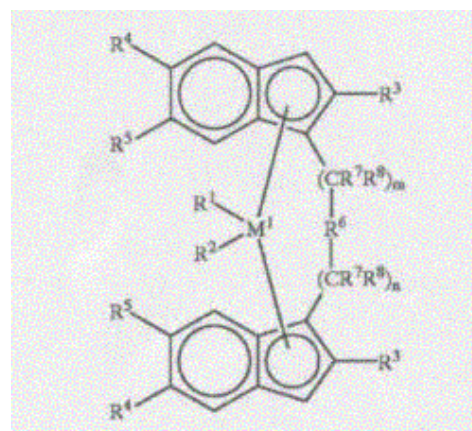


Figure 12: A metallocene structure (Winter et al., 2002) [21].

Metallocene catalysts are “sandwich” compounds of the type $B(L_1L_2)MX_2$, where a transition metal, M (most commonly zirconium or titanium), is sandwiched between two ligands, L_1 and L_2 (cyclopentadienyl, indenyl, Euorenyl, etc.), and bonded to two substituents, X (very commonly Cl atoms). The ligands can be connected by a bridge, B (ethyl, silyl, etc.). In some formulations (for instance, Dow Chemical’s constrained geometry catalysts), one of the bulky ligands is absent (half-sandwich compounds). The industrial use of metallocene catalysts is increasing rapidly due to their high activities, excellent polymer microstructural control, and easy implementation in existing Ziegler-Natta and Phillips processes.

The last class of ethylene polymerization catalysts is based on late transition metals. These catalysts are capable of producing polyethylene containing short-chain branches from the polymerization of ethylene alone [17].

2.5 Properties and Characteristics of Polyethylene

Two important properties in polymer production are density and melt flow index (MI). It is a commercial practice to classify polymer resin grades based on the two properties instead of implicit properties such as molecular weight and composition.

Polyethylene is generally divided into LDPE (0.91 – 0.93 g/ml) and HDPE (0.93 – 0.97 g/ml). LLDPE shares the same density range of LDPE but display many characteristics of HDPE. Density measurement is described by ASTM D-1505. Sample of polymer granules discharged from the reactor is converted into a plaque by conditioning for one hour at 120°C to approach equilibrium crystallinity. Density of the plaque is then measured using a density column. Sales specification of polymer resins are typically quoted to the third decimal value (in g/ml), hence a very tight control is required.

In general, the density of polyethylene decreases with an increase in branch numbers; the more branching, the lower the density. The crystallinity of PE decreases significantly with an increase in branch frequency and size. Hence, any physical properties related to crystallinity, such as stiffness and yield stress, will be affected by branching or chemical composition. Density decreases with an increase in molecular weight. This is because of the inhibition of crystallization by longer molecular chains. The basic relationships between polymer properties and density can be summarized in Figure 13.

MI is an interesting property that gives a clue on the chain length of the polymer and hence the molecular weight. Measurement of MI is described by ASTM D-1238. The apparatus and method is employed is very similar to viscosity measurement using a viscometer. MI can be translated into the units of viscosity. A polymer that exhibits a higher MI has a shorter polymer chain length.

Melt flow ratio (MFR) is the ratio of MI under different weight load as described by ASTM D-1238 (ratio of 440 psi melt index to 44 psi melt index). The MFR is a relative measure of the molecular weight distribution of a resin. This relationship between the MFR and molecular distribution is based on the phenomenon that polymers having a narrower molecular weight distribution are more Newtonian in melt flow behavior and thus, have flows which are less sensitive to shear. A polymer having a narrower molecular weight distribution have a lower MFR. Figure 14 summarizes general relationships between polymer properties and molecular weight.

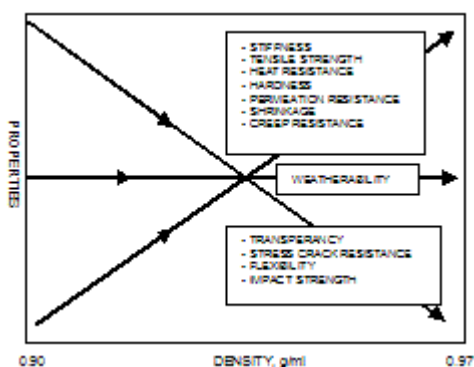


Figure 13: Relationship between polymer properties and resin density

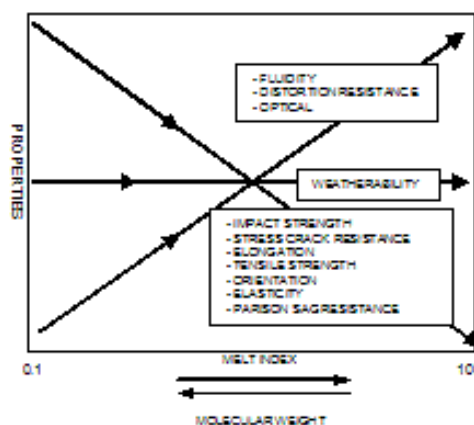


Figure 14: Relationship between polymer properties and resin molecular weight.

Table 3 illustrates how mechanical properties and processability of the polymer are affected by the polymer molecular structure we discussed earlier. Molecular weight and molecular weight distribution affects almost the mechanical properties and directly affects the processability of the polymer. The degree of branching and its distribution change the mechanical and chemical properties of a polymer.

Table 3: Relationship between molecular structure and properties of polyethylene [15]

		Molecular weight (M_w)	Molecular weight distribution	Branching chemicals	Degree of branching	Degree of branching distribution	Long chain branching (LCB)
Mechanical and chemical property	Transparency	o	o	o	o	o	
	Tensile strength	o	o	o	o	o	o
	Impact strength	o	o	o	o	o	o
	Rigidity				o	o	
	Heat resistance				o	o	
	Cold resistance	o	o	o	o	o	
	Chemical resistance	o	o	o	o	o	o
Processability	Heat seal	o	o	o	o	o	
	Bubble stability	o	o				o
	Draw-down	o	o				o
	Extrusion torque	o	o				o

3 REACTOR MODELING

3.1 Reaction Mechanisms

Ethylene polymerization can be envisioned as occurring at the interface between the solid catalyst and the polymer matrix, where the active centers are located. From gas-state monomer to solid-state polymer, ethylene experiences a dramatic physicochemical transition within a very short time. The polymerization environment changes with the composition of catalyst, polymerization process, reactant composition, reactor operating conditions, and extent of polymerization. Although intensive research activity has been focused on Ziegler-Natta catalyst systems since their discovery in the early 1950s, no definitive chemical reaction mechanisms have been developed to fully describe the kinetic behavior of ethylene homo/copolymerization, due to the complexity of the systems employed. Nevertheless, the key elementary reactions have been established, which include formation of active centers, insertion of monomer into the growing polymer chains, chain-transfer reactions, and catalyst deactivation. Most of the proposed mechanisms are based on information about polymerization rate, molecular weight and its distribution, polymer chain microstructure, and active center concentrations.

Since commercial production of LLDPE and HDPE consists of a copolymerization process, copolymerization mechanisms are required to understand kinetic behavior and polymer properties. If one assumes that all of the active centers perform the same reaction mechanisms, but with different reaction rates for each elementary reaction, then elementary reactions which are commonly adopted in modeling studies can be summarized as in Table 4, where C_p is the catalyst potential active center; P_0^* is the active center without polymer chain; $P_{m,n,i}^*$ is the active center with m units of monomer 1 and n units of monomer 2, with the third subscript i denoting the chain terminal monomer type bonded to the active center; $q_{m,n}$ is a dead polymer chain with a terminal double bond; and $q_{m,n}$ is a dead polymer chain without terminal double bond. For simplification of notation, no subscript is shown corresponding to the type of active center. The reactions shown in Table 3 should be considered to occur at each type of active center. The mechanisms in Table 4 are summarized based on Ti-based catalysts. Reaction mechanisms for chromium oxide based catalysts are a subset of those in Table 4.

Table 4: Summary of elementary reactions for ethylene and α -olefins co-polymerization [22]

Reaction	Description
Activation	
$C_p \xrightarrow{K_{as}} P_0^*$	Spontaneous activation
$C_p + [A] \xrightarrow{K_{aA}} P_0^*$	Activation by aluminum alkyl (A)
$C_p + [E] \xrightarrow{K_{aE}} P_0^*$	Activation by electron donor (E)
$C_p + [H_2] \xrightarrow{K_{aH}} P_0^*$	Activation by hydrogen (H_2)
$C_p + [M_1] \xrightarrow{K_{aM1}} P_0^* + [M_1]$	Activation by monomer 1 (M_1)
$C_p + [M_2] \xrightarrow{K_{aM2}} P_0^* + [M_2]$	Activation by monomer 2 (M_2)
Initiation	
$P_0^* + [M_1] \xrightarrow{K_{i1}} P_{1,0,1}^*$	Initiation of M_1 by normal active center
$P_0^* + [M_2] \xrightarrow{K_{i2}} P_{0,1,2}^*$	Initiation of M_2 by normal active center
$P_{H,0}^* + [M_1] \xrightarrow{K_{iH1}} P_{1,0,1}^*$	Initiation of M_1 by active center with H
$P_{H,0}^* + [M_2] \xrightarrow{K_{iH2}} P_{0,1,2}^*$	Initiation of M_2 by active center with H
$P_{A,0}^* + [M_1] \xrightarrow{K_{iA1}} P_{1,0,1}^*$	Initiation of M_1 by active center with A
$P_{A,0}^* + [M_2] \xrightarrow{K_{iA2}} P_{0,1,2}^*$	Initiation of M_2 by active center with A

$P_{E,0}^* + [M_1] \xrightarrow{K_{iE1}} P_{1,0,1}^*$	Initiation of M ₁ by active center with E
$P_{E,0}^* + [M_2] \xrightarrow{K_{iE2}} P_{0,1,2}^*$	Initiation of M ₂ by active center with E
Propagation	
$P_{m,n,1}^* + [M_1] \xrightarrow{K_{p11}} P_{m+1,n,1}^*$	Propagation of chain type 1 with M ₁
$P_{m,n,1}^* + [M_2] \xrightarrow{K_{p12}} P_{m,n+1,1}^*$	Propagation of chain type 1 with M ₂
$P_{m,n,2}^* + [M_1] \xrightarrow{K_{p21}} P_{m+1,n,2}^*$	Propagation of chain type 2 with M ₁
$P_{m,n,2}^* + [M_2] \xrightarrow{K_{p22}} P_{m,n+1,2}^*$	Propagation of chain type 2 with M ₂
Chain transfer	
$P_{m,n,i}^* \xrightarrow{K_{\beta pi}} P_0^* + q'_{m,n}$	Spontaneous chain transfer or β -elimination
$P_{m,n,i}^* + [H_2] \xrightarrow{K_{\beta H_2}} P_{H,0}^* + q'_{m,n}$	Chain transfer to hydrogen (H ₂)
$P_{m,n,i}^* + [A] \xrightarrow{K_{\beta A}} P_{A,0}^* + q'_{m,n}$	Chain transfer to aluminum alkyl (A)
$P_{m,n,i}^* + [E] \xrightarrow{K_{\beta E}} P_{E,0}^* + q'_{m,n}$	Chain transfer to electron donor (E)
$P_{m,n,i}^* + [M_1] \xrightarrow{K_{\beta M1}} P_{1,0,1}^* + q'_{m,n}$	Chain transfer to M ₁
$P_{m,n,i}^* + [M_2] \xrightarrow{K_{\beta M2}} P_{0,1,2}^* + q'_{m,n}$	Chain transfer to M ₂
Deactivation	
$P_{m,n,i}^* \xrightarrow{K_{dspi}} C_d + q_{m,n}$	Spontaneous deactivation
$P_{m,n,i}^* + [Z] \xrightarrow{K_{dZi}} C_d + q_{m,n}$	Deactivation by impurities or poison (Z)
$P_{m,n,i}^* + [A] \xrightarrow{K_{dAi}} C_d + q_{m,n}$	Deactivation by aluminum alkyl (A)
$P_{m,n,i}^* + [E] \xrightarrow{K_{dEi}} C_d + q_{m,n}$	Deactivation by electron donor (E)
$P_{m,n,i}^* + [H_2] \xrightarrow{K_{dH_2i}} C_d + q_{m,n}$	Deactivation by hydrogen (H ₂)
$P_{m,n,i}^* + [M_j] \xrightarrow{K_{dMji}} C_d + q_{m,n}$	Deactivation by monomers
Other possible reactions	
$P_{1,0,1}^* + q'_{r,s} \xrightarrow{K_{p1}^*} P_{r+1,s,1}^*$	Formation of short-chain branches
$P_{0,1,2}^* + q'_{r,s} \xrightarrow{K_{p2}^*} P_{r,s+1,2}^*$	Formation of short-chain branches
$P_{m,n,1}^* + q'_{r,s} \xrightarrow{K_{p1}^*} P_{m+r,n+s,1}^*$	Formation of long-chain branches (rare)
$P_{m,n,2}^* + q'_{r,s} \xrightarrow{K_{p2}^*} P_{m+r,n+s,2}^*$	Formation of long-chain branches (rare)

3.2 Mathematical Model

The multigrain model [13] gives a detailed description of phenomena taking place during polymerization with supported Ziegler–Natta and Phillips catalysts. The multigrain model takes into account the heterogeneous nature of the resulting polymer particle. Two levels of mass and heat transfer resistances were considered. The polymeric particle (called macroparticle or secondary particle) is formed by an agglomerate of microparticles or primary particles. Each microparticle consists of a fragment of the original catalyst particle, with all active sites on its external surface, surrounded by dead and living polymer chains (in fact, the microparticles are described by solid core models on a very small scale).

Monomer diffuses through the pores of the macroparticle, adsorbs on the layer of polymer surrounding the catalyst fragments in the microparticles, and diffuses through this layer to the active sites on the surface of the fragments, where polymerization finally takes. It is envisioned that the newly formed

polymer chains push the previously formed polymer layer, thus increasing the radius of the microparticles and consequently the size of the macroparticles. Electron microscopy studies confirm the formation of primary and secondary structures in polymerizations with Ziegler–Natta catalysts.

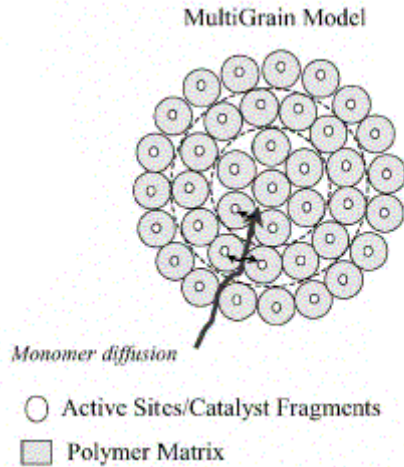


Figure 15: Schematic showing diffusion phenomenon in a multigrain model (McKenna and Soares, 2001)

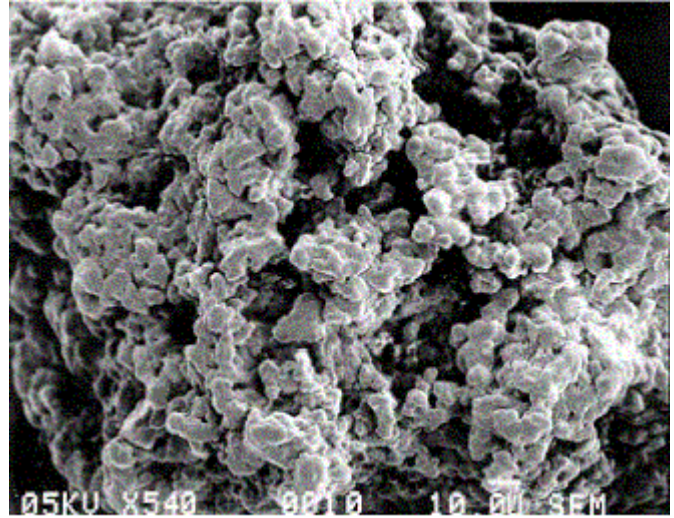


Figure 16: Micrograph of the surface of a prepolymer particle. The particle is clearly an assembly of smaller, spherical structures as described by the multigrain model (McKenna and Soares, 2001).

For the multigrain model, the radial profile of monomer concentration in the secondary particle (macroparticle) is described by the well-known diffusion-reaction equations in spherical co-ordinates:

$$\frac{\partial M_s}{\partial t} = \frac{1}{r_s^2} \frac{\partial}{\partial r_s} \left(D_{eff} r_s^2 \frac{\partial M_s}{\partial r_s} \right) - R_{pv} \quad (1)$$

$$\frac{\partial M_s}{\partial r_s} (r_s = 0, t) = 0 \quad (1a)$$

$$D_{eff} \frac{\partial M_s}{\partial r_s} (r_s = R_s, t) = k_s (M_b - M_s) \quad (1b)$$

$$M_s (r_s, t = 0) = M_{s0} \quad (1c)$$

where D_{eff} is the effective diffusivity of monomer in the macroparticle, k_s is the mass transfer coefficient in the external film, M_b is the bulk monomer concentration in the reactor, M_s and M_{s0} are the evolving and initial monomer concentrations in the macroparticle, respectively, R_{pv} is the volumetric rate of polymerization in the macroparticle, r_s is the radial position in the macroparticle, R_s is the radius of macroparticle, and t is the polymerization time. Note that R_{pv} is the average rate of polymerization at a given radial position in the macroparticle. In the multigrain model, it is supposed that the polymerization takes place only on the surface of the catalyst fragments in the primary particles (microparticles). It is this term that couples the models for the micro- and macroparticle.

The radial profile of monomer concentration in the microparticle is the same as that for the solid core model:

$$\frac{\partial M_p}{\partial t} = \frac{1}{r_p^2} \frac{\partial}{\partial r_p} \left(D_p r_p^2 \frac{\partial M_p}{\partial r_p} \right) \quad (2)$$

$$4\pi R_c^2 D_p \frac{\partial M_p}{\partial r_p}(r_p = R_c, t) = \frac{4}{3} \pi R_c^3 R_{pc} \quad (2a)$$

$$M_p(r_p = R_p, t) = M_{eq} \leq M_s \quad (2b)$$

$$M_p(r_p, t = 0) = M_{p0} \quad (2c)$$

where D_p is the effective diffusivity of monomer in the microparticle, M_{eq} is the equilibrium concentration of monomer in the interface between micro- and macroparticles, M_p is the monomer concentration in the microparticle, M_{p0} is the initial monomer concentration in the microparticle, R_{pc} is the rate of polymerization on the surface of the catalyst fragments, R_c is the radius of catalyst fragments in the microparticle, r_p is the radial position in the microparticle, and R_p is the radius of the microparticle. The rate of polymerization on the microparticles is generally given by

$$R_{pc} = k_p(t) C^*(t) [M]_{SA} \quad (3)$$

where R_{pc} is the rate of polymerization, k_p is the propagation rate constant, $C^*(t)$ is the time-dependent concentration of active sites on the surface of the microparticle, and $[M]_{SA}$ the concentration of monomer on the active site.

Most models have tried to relate the effective diffusivity, D_{eff} , to the value of the diffusivity of the component in question in the bulk phase of the reactor, D_b , using the expression commonly used for heterogeneous catalysts,

$$D_{eff} = \frac{D_b \varepsilon}{\tau} \quad (4)$$

where ε and τ are the porosity and tortuosity of the macroparticle, respectively. Note that due to particle fragmentation and growth, it is very likely that both τ and ε are functions of time and of radial position. This makes the estimation of these parameters a particularly difficult task. Given that adsorption and diffusion of monomer and other reactants can take place only in the amorphous fraction of a polymeric material, D_p needs to be corrected as a function of the crystallinity of the polymer matrix in the growing microparticles. If D_a stands for the diffusion of a given reactant in amorphous polymer, then D_p can be estimated according to the equation,

$$D_p = \frac{D_a}{\alpha\beta} \quad (5)$$

where α and β are correction factors to account for polymer crystallinity and chain immobilization of the amorphous fraction.

The multigrain model also includes analogous equations to calculate the radial temperature profile in the macroparticle,

$$\rho_p C_p \frac{\partial T_s}{\partial t} = \frac{1}{r_s^2} \frac{\partial}{\partial r_s} \left(k_e r_s^2 \frac{\partial T_s}{\partial r_s} \right) + (-\Delta H_p) R_{pv} \quad (6)$$

$$\frac{\partial T_s}{\partial r_s}(r_s = 0, t) = 0 \quad (6a)$$

$$k_e \frac{\partial T_s}{\partial r_s}(r_s = R_s, t) = h(T_b - T_s) \quad (6b)$$

$$T_s(r_s, t = 0) = T_{s0} \quad (6c)$$

where C_p is the heat capacity of the macroparticle, h is the film heat transfer coefficient, ΔH_p is the heat of polymerization, k_e is the effective heat conductivity in the macroparticle, T_b is the temperature of the continuous phase in the reactor, T_s is the temperature in the macroparticle, T_{s0} is the initial temperature in the macroparticle, and ρ_p is the density of the macroparticle.

Similarly, for the microparticles, the temperature profile is given by

$$\rho_p C_p \frac{\partial T_p}{\partial t} = \frac{1}{r_p^2} \frac{\partial}{\partial r_p} \left(k_e r_p^2 \frac{\partial T_p}{\partial r_p} \right) \quad (7)$$

$$-4\pi R_c^2 k_e \frac{\partial T_p}{\partial r_p}(r_p = R_c, t) = (-\Delta H_p) \frac{4}{3} \pi R_c^3 r_c \quad (7a)$$

$$T_p(r_p = R_p, t) = T_s \quad (7b)$$

$$T_p(r_p, t = 0) = T_{p0} \quad (7c)$$

where T_{p0} is the initial temperature in the microparticle. Equations for intraparticle monomer concentration and temperature radial profiles for the polymer flow model are similar to the ones for the macroparticles of the multigrain model. It is either assumed that the mass transfer resistance at the level of the microparticles is negligible or that it can be accounted for indirectly in the effective diffusivity D_{eff} , so that one can use Eq. (3) with a monomer concentration in equilibrium with the concentration of the macroparticle to calculate the radial variation of the polymerization rate. The multigrain model is certainly the most studied expansion model for polymerization of olefins with supported Ziegler–Natta catalysts. It has been used extensively to predict heat and mass transfer resistances for homo- and copolymerization of ethylene, propylene, and higher α -olefins, in slurry and gas-phase reactors.

3.3 Melt Flow Index and Density Control Model

The models proposed above are used in design of polymerization reactors and developing new polymer grades. In industrial-scale production, different models are needed for real-time control using properties measurable explicitly or analytically in a relatively short period of time. For this reason, density and melt flow index (MI) are controlled at the polymerization reaction stage.

Density is a relative measure on degree of branching. The branching mechanism as discussed earlier is a chain transfer step which requires the presence of a comonomer molecule. In an industrial reactor, the ratio of comonomer to ethylene is a manipulated parameter to control density. To achieve a higher density, the ratio is reduced and less comonomer is added.

The melt flow index (MI) is a relative measure of the polymer chain length. Referring to the reaction mechanism, this is controlled by the termination step which requires either a monomer or a hydrogen molecule. In an industrial reactor, the ratio of hydrogen to ethylene is a manipulated parameter to control the MI. To achieve a higher MI, the ratio is increased and more hydrogen is fed to the reactor.

Some mathematical models have been developed to relate density and MI to the two feed ratios. These correlations combined reaction kinetics with empirical parameters and serve as good guidelines to startup a reactor or transition to a different resin grade. The following equation developed by McAuley and MacGregor (1991) [12] illustrates how the instantaneous MI is estimated and related to the feed ratio as well as the reactor temperature.

$$\ln(MI_i) = 3.5 \ln \left\{ k_0 + k_1 \frac{[H_2]}{[C_2]} + k_2 \frac{[C_3]}{[C_2]} + k_3 \frac{[C_4]}{[C_2]} + k_4 \frac{[R]}{[C_2]} \right\} + k_5 \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (8)$$

where, MI_i is the instantaneous MI; H_2 , C_2 , C_3 and C_4 are concentration of hydrogen, ethylene, propylene and 1-butene respectively; R is concentration of higher α -olefin comonomer and T is the reactor temperature.

Typically, during a startup or product grade transition, the comonomer to ethylene ratio is first adjusted to achieve the desired density before trying control the MI. The primary reason is because polymer density must be controlled to sustain the fluidization in the reactor. A sharp increase in density can result the polymer granules becoming too heavy and lose fluidization. The secondary reason is density is also a function of molecular weight. As MI is adjusted, density may change slightly. Depending on the final value, the comonomer to ethylene ratio can be fine tuned to achieve the desired density without affecting the MI.

4 CHALLENGES AND OPPORTUNITIES

Three decades have passed since the Union Carbide and BP built the earlier fluidized bed reactors. Although many reaction lines have since been built, some inherent features of the process remain as a challenge for an engineering breakthrough. Some of these challenges have even caused manufacturers to choose alternative processes despite higher capital investment and/or utilities costs. In this section we shall discuss some of these challenges and opportunities for process improvement.

4.1 Minimize off-specification product during grade changeover

One of the greater attractions of the fluidized bed reactor technology is the ability to produce polymers with a wide range of density and melt flow index combination. This attraction is severely undermined by the production loss involved in transition between resin grades. It will be ideal to switch between grades “seamlessly” without any off-specification product while maintaining the production rate. In practice, grade specifications rarely overlap, hence generating off-specification products during transition. The production rate is also sacrificed to minimize these off-specification products, which can only be sold for a small fraction of the prime grade resins. Grade transitions pose quality and capacity utilization challenges.

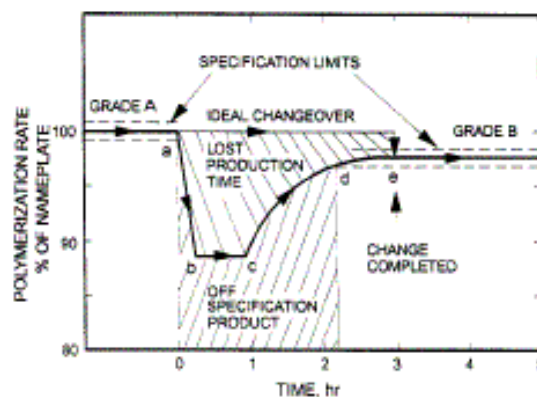


Figure 17: Grade changeover scheme for ethylene polymerization

The root cause of this problem is the fluidization nature of the reactor. Unlike certain slurry and solution reactor configurations, the reaction in a fluidized bed reactor cannot be terminated during transition. There must always be polymer granules fluidized in the reactor, which necessitates catalysts to be fed continuously. An easy way to overcome this problem is to develop polymer grades that have overlapping

specifications. Having too many product grades make it difficult to market the products and hence is seldom practiced.

4.2 Heat removal control

The greatest challenge to the operators is the heat removal control. Polymerization is a very exothermic reaction and it is essential to keep the reactor temperature constant. The challenge is greater if the cooler is fouled and heat transfer is poor. If localized “hot spot” occurs, the fluidization pattern is modified. The hot spot becomes a nucleus for polymerization at a much rapid rate. The granules can fuse into a sheet or chunk. This sheet or chunk is too heavy to be suspended and will fall down to the gas distributor. It can block the gas feed causing the reactor to lose fluidization and cease heat removal. Worst case scenario is losing fluidization totally and all gases in the reactor convert into a single polymer chunk. This has occurred in practice and the unit needs to be shut down. The polymer chunk was slowly cut into smaller pieces before removing from the reactor.

One of the protection system employed is to reduce the polymerization rate by injecting some poison into the reactor when temperature rises above the control limit. Usually carbon monoxide is injected in small doses to prevent temperature excursion. If a chunk is detected, carbon monoxide is injected in a large dose to terminate the reaction totally.

Heat removal capability also limits the production capacity. This means an existing production line cannot be debottlenecked easily without large capital investment. One method to overcome this challenge led to the development of the “condensed mode” operation. This mode of operation as discussed earlier involves using large amount of 1-hexene comonomer which will condense in the cooler and vaporizes at the gas feed distributor. This action removes a large amount of heat and enables higher production rate. The scarcity of 1-hexene supply in some regions however limits the usefulness of this novel method.

4.3 Removal of reaction poisons

The gas fluidized bed process is very sensitive to poisons. Acetylene, carbon monoxide and carbon dioxide are by-products of the pyrolysis process to make ethylene. These by-products in minute levels are able to reduce the polymerization rate significantly. It is surprising that the high pressure and slurry processes are not affected by these poisons.

To ensure the ethylene feed is free of the poisons, the supply has to be purified using a series of adsorption beds. A typical purification train will have a palladium bed to remove acetylene, a copper oxide bed to remove carbon monoxide, a copper bed to remove oxygen and molecular sieves to remove moisture. For the same reason, comonomers also require a purification step. Comonomers are usually degassed using a stripper column and dried using molecular sieve. The purification train poses a capital investment cost and operating costs that is not incurred in other processes.

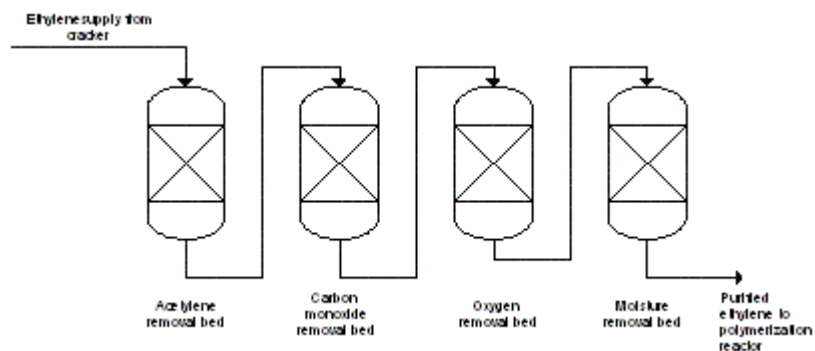


Figure 18: Ethylene purification train

4.4 Static Control

When polyethylene granules are fluidized within the reactor, they also rub with each other during their random collision. This rubbing action generates static electricity. When two granules with dissimilar electrical charges meet, they are attractive to each other and fuse into a larger granule. Left uncontrolled, this can also form a nucleus for rapid polymerization similar to the hot spot phenomenon. This problem is also unique to fluidized bed process.

In an industrial reactor, probes are added at different locations of the reactor to measure electrical potential. Under normal situation, the static voltage reading will vary close to neutral state. For some catalyst grade, the potential may swing towards positive or negative voltage. To control the static voltage, a small dose of water or methanol (simple polar molecules) is injected into the reactor. This helps to neutralize the static voltage.

4.5 Gel formation

Gels are polyethylene granules that are very hard and dense. They are after effects of localized hot spots or temperature excursions but did not grow big enough to form a chunk. Gel can either remain as part of the fluidized phase or stick to the walls of the reactor. Either way, they will finally come out as part of product. The problem with these gels is that they do not melt under the normal extrusion temperature either during pelletizing or extruded into the final product. They pose a major problem to film blowing grade resins. The gels are visible on the blown film and may burst the film bubble.

When gels are detected in the product, the reactor needs to be shut down for mechanical cleaning. Gel formation is a common operations phenomenon, causes unplanned production outage and further reduces the capacity utilization.

4.6 Film clarity

All grades of polyethylene produced using the fluidized bed reactor processes are co-polymers of ethylene with α -olefins (usually 1-butene or 1-hexene). Films made from these co-polymers lose out in film clarity compared to the homopolymers LDPE made using the free radical high pressure process. There is a continuous demand for high clarity LDPE film especially for food packaging (e.g. bread packaging) and films made from co-polymers loses out in this market.

This is one of the areas of improvement in the last few years. Special metallocene catalysts are formulated to improve the clarity of the film. Some of these metallocenes are already commercialized [19]. The successful development of late transition metal catalysts will enable manufacturers to produce homopolymers using the fluidized bed reactor process. The commercialization of such catalyst however is projected to be only in 2010 as development is still restricted to laboratory-scale experiments.

5 HYBRID TECHNOLOGIES

Hybrid technologies development is another area of active research and development. Utilizing the principles of fluidized bed reactor, the process has been expanded to production of a wider range of polyethylene and extended to production of polypropylene. Two commercial processes of such nature are reviewed here.

5.1 Combination of Loop Reactor and Fluidized Bed Reactor [8]

The *Spherilene* gas-phase technology was developed by Basell Polyolefins to produce very low density polyethylene (VLDPE), LLDPE as well as HDPE. The process uses a single Ziegler-Natta titanium-based

catalyst family. The process has a loop reactor and two fluidized bed reactors in series. Catalyst components are mixed and fed directly to the loop reactor for pre-polymerization. This step exploits the catalyst system potential in terms of morphology and mileage.

Product density is controlled from less than 0.9 g/ml (VLDPE) to more than 0.96 g/ml (HDPE). MI capability ranges from 0.01 to > 100 g/ 10 min. Because of the two fluidized bed reactors setup, this technology is able to produce bimodal grades (MI, density) and specialty polymers based on new molecular models. For example, terpolymer grades which have better properties compared to conventional 1-butene LLDPE/VLDPE and hexene “quattropolymer” to replace hexene based LLDPE. LDPE replacement grades for clarity and shrink film applications have also been developed. There are 8 plants using this technology and a combined capacity of 1.8 MMtpy.

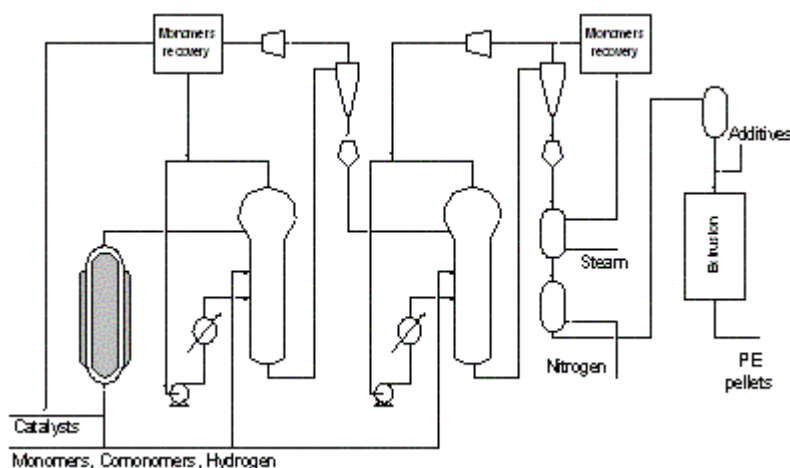


Figure 19: Spherilene gas-phase technology (Hydrocarbon Processing, 2003)

5.2 Fluidized Bed Reactors in Series [8]

The UNIPOL PP process was developed by Dow Chemical to produce homopolymers, random copolymer and impact copolymer polypropylene. A wide range of polypropylene is made in a gas phase fluidized bed reactor using proprietary catalysts. Melt flow index, isotactic level and molecular weight distribution are controlled by utilizing the proper catalyst, adjusting operating conditions and adding molecular weight control agent. Random copolymers are produced by adding ethylene or 1-butene. Ethylene addition to a second reactor in series is used to produce the rubber phase of impact copolymers.

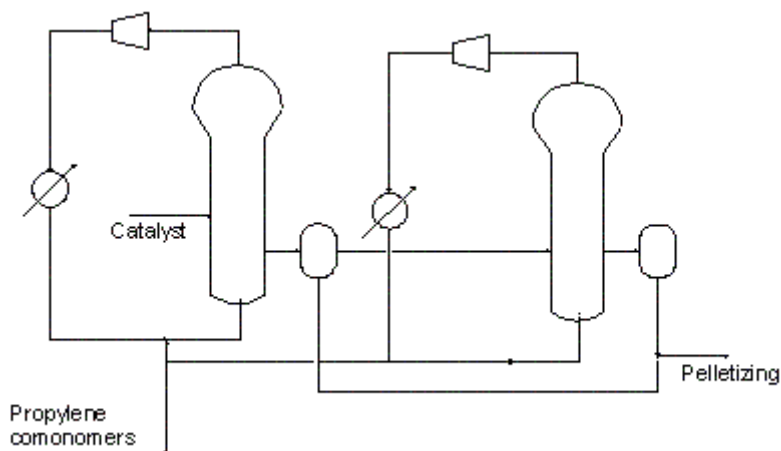


Figure 20: Dow Chemical Co. UNIPOL PP technology (Hydrocarbon Processing, 2003)

Homopolymers can be produced with MI from less than 0.1 to 3,000 g/ 10 mins and isotactic content up to 99%. Random copolymers can be produced with up to 12% ethylene or up to 21% 1-butene. Impact copolymers can be polymerized with a good stiffness to impact balance. More than 30 reaction lines are in operation. Total worldwide production is over 5 MMtpy.

6 CONCLUSIONS

Polyethylene is the most common thermoplastic and used in a wide range of applications. There are various commercial technologies available to produce polyethylene. Gas fluidized bed polymerization is one of the later technology developed and is commonly employed in the production of linear-low density polyethylene (LLDPE) and high density polyethylene (HDPE). The early fluidized bed reactor technology was developed independently by Phillips Petroleum, Union Carbide and Naphtachimie. Commercial fluidized bed PE technology is now licensed by Univation Technologies and BP Chemicals. There are three types of commercial catalysts, namely Ziegler-Natta catalyst, Phillips catalyst and metallocene catalyst. A fourth type of catalyst based on late transition metal is still in the research and development phase. Polymerization mechanism is made up of a series of reactions. Multigrain model was presented to describe the reaction process mathematically. Mechanical properties and processability is affected by molecular weight distribution and the degree of branching. In production process, this is measured as melt flow index and density. Some operational challenges were presented to highlight the limitations of the process. Some new polymerization processes are hybrid processes which borrowed the principles of fluidized bed reactors for polyethylene production.

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