
Manufacturing Efficiencies From Metallocene Catalysis In Gas-Phase Polyethylene Production

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MANUFACTURING EFFICIENCIES FROM METALLOCENE CATALYSIS IN GAS-PHASE POLYETHYLENE PRODUCTION

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ABSTRACT

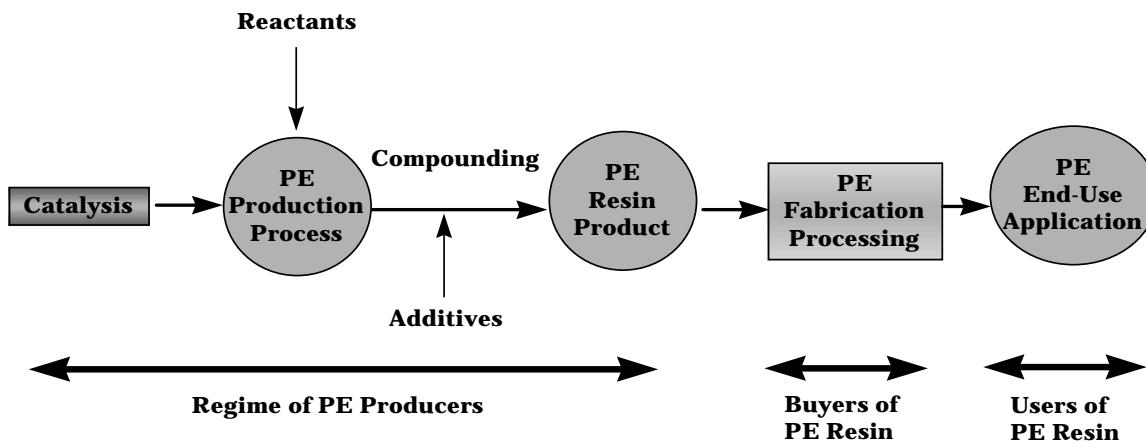
Metallocene catalysis is a rich and fertile technology with major implications for the polyolefins industry. It is a very broad technology. Much industry symposia discussion has focused on the importance of this technology as a vehicle to new and better products. Metallocene catalyst systems also bring important process benefits to gas-phase polyethylene production. High catalyst activity, signature kinetic profile/process response characteristics, and control of polymer molecular architecture, together, can be leveraged to enhance manufacturing efficiencies with the

UNIPOL® PE Process. Specific metallocene catalyst systems provide a cascade of process technology benefits to UNIPOL PE manufacture.

INTRODUCTION

Catalysis sits far upstream in the technology flow of producing and using polyethylene resins. In this framework, shown in **Figure 1**, metallocene catalysts control the stochastic processes of assembling monomers and comonomers into polymers of distributed structure and tailored performance. The reaction system, its process

FIGURE 1. CONCEPT SCHEMATIC-TECHNOLOGY FLOW IN PRODUCING AND USING POLYETHYLENE



engineering and operating protocols, defines the efficiency of this polymer assembly and the production dynamics of resin manufacture.

Metallocene chemistry is a powerful molecular engineering tool for polyethylene product development. It is this embodiment of metallocene technology, the product implications of the chemistry, which has dominated industry symposia discussion and defined the emphasis for much R&D effort. Product development with this tool is now moving from a specialty niche applications focus into the core of volume PE production and the arena of commodity markets and applications. In the application of metallocene technology to the manufacture of resins with broad product functionality for the volume PE marketplace, economic considerations and manufacturing efficiencies become important drivers of technology development. To win in this commercial arena, metallocene catalyst capability must be integrated with an efficient, cost effective, PE production process.

The UNIPOL[®] PE Process is the world's premier gas-phase PE production technology, now used around the world by Union Carbide, its joint ventures and 47 licensees in 74 reactor lines with an operating capacity of more than 9 million TPY. By 2000, 90 reactors will be producing more than 12 million TPY. UNIPOL PE process technology combines the lowest capital and operating costs with a record of proven reliability and safety in PE production.

Exxon Chemical and Union Carbide have formed a joint venture company, Univation Technologies, to develop, market, and license advanced production and process technologies for the manufacture of performance and economic-advantaged polyethylenes. The new venture is a technology and licensing company committed to driving technology renewal in the polyethylene industry. A focus of Univation Technologies is to accelerate the pace of commercial development and broaden the global reach of metallocene technology applied to volume PE manufacture.

Process aspects of catalyst performance are critical considerations in the development of commercial catalysts to address the manufacturing complexities and practicalities of volume PE production in world scale plants. Both Exxon Chemical and Union Carbide have developed customized metallocene catalyst systems specifically for the operating regime of the UNIPOL Process for PE manufacture. Metallocene catalyst chemistries, custom fit to the reaction process, advance and broaden further the operational scope and product capabilities of the UNIPOL PE Process.

With the formation of Univation Technologies, EXXPOL[®] metallocene catalyst systems (now including complementary UCC metallocene technology) and capacity-enhancing Super Condensed Mode Technology (SCM-T) become fully leveraged with UNIPOL process technology.

EXXPOL[®] Metallocene Catalyst Systems

There are a very large number of metallocene catalyst systems. **Table 1** lists categories of metallocene precursors. The various metallocene catalysts exhibit a wide range of kinetic behaviors and process response characteristics.

Table 1. CATEGORIES OF METALLOCENE CATALYSTS

Bis Cp Systems

- Unbridged
- Bridged
 - Si, C₂, Other
- Symmetric, Asymmetric
- Halogen, Non-Halogen Ligands

Mono Cp Systems

- Unbridged
- Bridged
- Alkyl, Non-Alkyl Ligands

Transition Metals

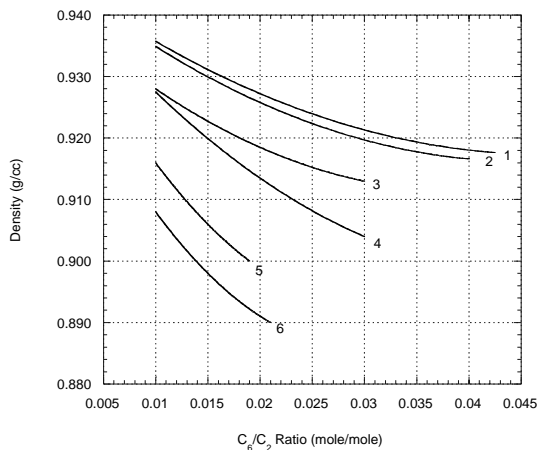
- Ti
- Zr
- Hf

Activation Systems

- Alumoxanes
- Non-Coordinating Anions

Metallocene ligand structure, metal center, and activation chemistry define the electronic and steric environment of the catalyst system, which, in turn, establish the catalyst's regulation of the stochastic processes of monomer/comonomer insertion and chain transfer chemistries. "Electronics and sterics" also define catalyst kinetic profiles, e.g., activation and decay characteristics which determine catalyst productivity, and catalyst kinetic response to temperature and reactant concentrations. **Figure 2** shows the differing copolymerization responses for a range of metallocenes.

Figure 2. COPOLYMERIZATION BEHAVIOR FOR SELECTED METALLOCENE CATALYSTS



Resin density is plotted vs C_6/C_2 ratio for metallocenes of different structure. **Figure 3** shows the differing chain transfer responses to H_2 for a range of metallocene systems. **Figure 4** shows the very different gas-phase polymerization profiles of three metallocene systems which make very similar polyethylenes.

UNIPOL® PE Process - Basics

A UNIPOL® Process overview schematic is shown in **Figure 5**. Growing polymer particles are fluidized by a recycle gas stream of

monomer, comonomer, hydrogen, nitrogen and inert condensing agent such as hexane or isopentane. The "cycle" gas flow provides monomer and comonomer for polymerization, agitates the bed, and also removes the heat of polymerization. The cycle gas exits the top of the reactor and is then compressed and cooled before being fed into the bottom of the fluidized bed.

Figure 3. CHAIN-TRANSFER-TO-HYDROGEN RESPONSE FOR SELECTED METALLOCENE CATALYSTS

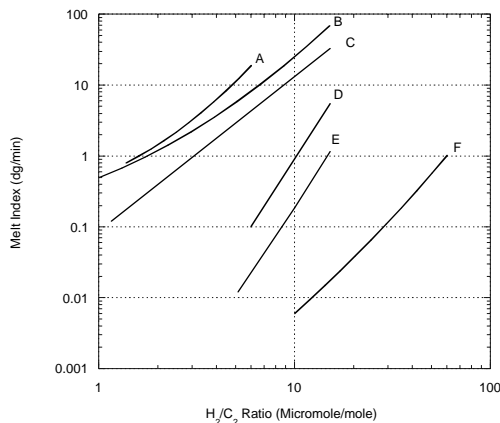
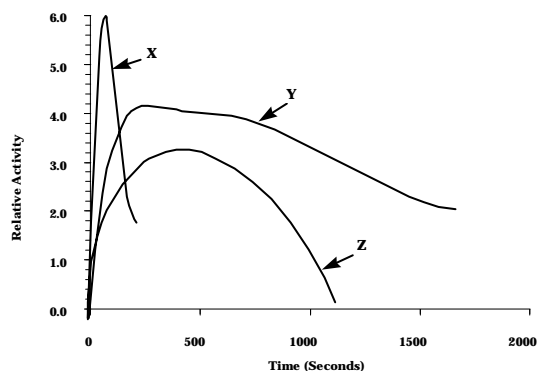
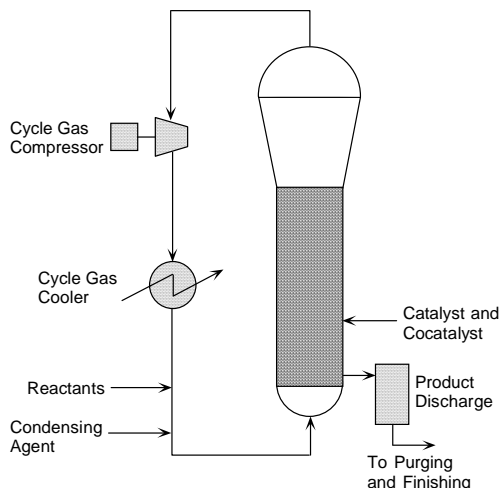


Figure 4. GAS-PHASE POLYMERIZATION KINETIC PROFILES FOR SELECTED METALLOCENE CATALYSTS



**Figure 5. PROCESS SCHEMATIC-UNIPOL®
GAS-PHASE REACTOR SYSTEM**



Olefin polymerization is a very exothermic reaction. Reaction system production rate is limited by heat removal from the cycle gas in the cooler. For fixed engineering design, heat removal is governed by the heat capacity, dew point, and temperature of the cycle gas.

EXXPOL®/UNIPOL® - Catalyst/Process/Product Synergies

In the gas-phase fluid bed UNIPOL® PE Process, catalysis, process, and product technology interact with mutual interdependency to determine process operability and manufacturing efficiencies. Much Exxon Chemical⁽¹⁾ and Union Carbide R&D effort has been directed at manipulating catalyst behavior to address UNIPOL reaction process considerations.

Benefits of Efficient Comonomer Incorporation

Certain metallocene catalysts exhibit exceptional copolymerization capability. Catalyst “electronics and sterics” govern the relative rates at which monomer and comonomer are added to the growing chain.

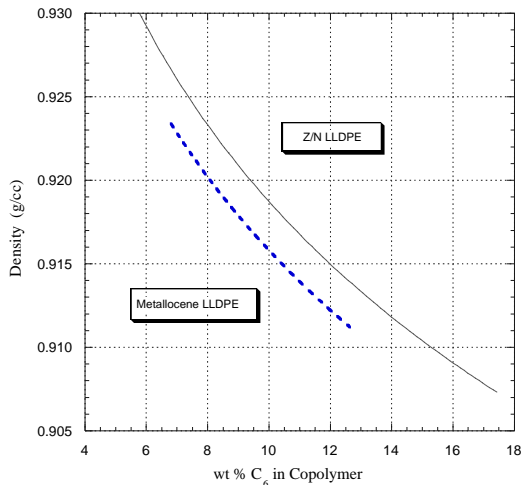
Table 2 compares the hexene to ethylene ratio in the gas phase required by various catalysts to produce LLDPE at 0.920 resin density. Some metallocene catalysts require significantly less comonomer in the reactor than Z/N or chrome based catalysts to produce resins of a given density. Reduced comonomer levels in the gas composition leads to less comonomer dissolved in the resin, in turn, improving process efficiency because less comonomer is lost in product discharge and recovery.

**Table 2. GAS-PHASE COMONOMER RATIO
REQUIRED TO ACHIEVE 0.920 DENSITY
FOR SELECTED CATALYSTS**

Catalyst	C₆/C₂ Ratio
Bridged Metallocene	0.005
Unbridged Metallocene	0.02
Mono-Cp Metallocene	0.03
Chromium Oxide	0.03
Vanadium	0.06
Mg/Titanium	0.12

Certain metallocene catalysts lead to completely random copolymerization which produces resins with inter- and intramolecular compositional homogeneity. In contrast, multi-site catalysts like Z/N systems produce compositionally heterogeneous resins where some chains can have high levels of comonomer and other molecules have little. Non homogeneous composition distribution in C₂/alpha olefin copolymers, in effect, wastes some comonomer in depressing resin density. **Figure 6** compares the efficiency of hexene in lowering LLDPE resin density with a specific single site metallocene catalyst vs a multi-site Z/N catalyst system. In this case, the mLLDPE contained approximately 10-15 wt% less hexene at a given density than the comparable Z/N LLDPE.

Figure 6. DENSITY DEPRESSING EFFICIENCY OF COMONOMER IN METALLOCENE AND Z/N BASED POLYETHYLENES



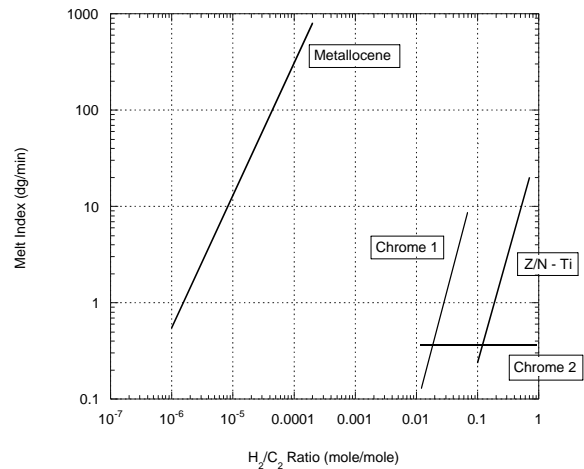
The combination of less dissolved comonomer in the resin and more homogeneous incorporation (absence of low molecular weight extractable fraction) dramatically reduces resin stickiness in the reaction and conveying processes, allowing increased reactor operating temperature. These factors also allow increased condensing level in the reactor, leading to further process efficiencies which will be discussed in a subsequent section.

Benefits of Improved Hydrogen Chain Transfer

Chain transfer to hydrogen is extremely efficient with metallocene catalysts. Typical film and molding LLDPEs can be produced with significantly less hydrogen in the reactor than is used for certain Z/N catalysts, resulting in several process and product benefits. **Figure 7** compares the hydrogen response in the gas phase of various catalysts in producing C_2/C_6 LLDPE.

High melt index mLLDPEs can be made with improved efficiencies because of decreased hydrogen requirements. With certain metallocene catalysts, polymer molecular weight can be

Figure 7. MELT INDEX RESPONSE TO HYDROGEN FOR SELECTED CATALYST FAMILIES



varied over a wide range with easy adjustments in reactor hydrogen concentration. Transitions from high to low MI resins with certain Z/N catalysts require removal of high hydrogen concentrations. These transitions can require flaring cycle gas, resulting in lost monomer and comonomer. Reduced hydrogen levels in the reactor will reduce monomer/comonomer loss in transition and recovery, resulting in improved process efficiencies.

Reaction production rates can be increased with metallocene catalysts because hydrogen in the cycle gas is replaced with materials with higher heat capacities. Hydrogen can constitute approximately five molar percent of the cycle gas at typical Z/N conditions for a 1-MI film product. Reduction of hydrogen from five to 0.01 percent with certain metallocene catalysts allows addition of five percent isopentane while maintaining reactor pressure. The overall gas heat capacity increases 10%, which can translate to a 10% increase in the maximum production rate (assumes no dew point limitation). This does not include the more important benefit of condensed mode operation, to be discussed below.

Improved Condensed Mode Operation

Metallocene catalysts allow UNIPOL[®] operation with increased cycle gas heat capacity. Because metallocene catalysts require much less hexene and hydrogen than Z/N systems to produce a given LLDPE, more ethylene and isopentane can be added to the gas mix. Higher ethylene partial pressure improves catalyst productivity. Increased isopentane increases overall gas heat capacity, thus increasing the heat removal capability of the fluidizing gas.

Heat removal in non-condensing systems is proportional to the temperature difference between the cooling water inlet and the reactor. As the reactor temperature increases, the production rate can be increased. Metallocene catalyzed resins can be produced at higher reactor temperatures than Z/N based resins because they are less prone to stickiness and agglomeration.

The reactor dew point is important to the amount of heat removal in the reactor. The gas dew point must be kept below the temperature in the fluidized bed or liquid accumulation can occur. In condensed mode operation, higher-boiling components in the cycle gas condense in the heat exchanger when the gas temperature falls below its dew point. The cycle gas and condensed liquids are fed to the bottom of the reactor where the liquids evaporate, removing heat via the latent heat of vaporization. Thus, condensed mode provides a dramatic improvement in heat removal capacity.

High levels of higher alpha-olefin (HAO) comonomers, hexene or octene, and/or induced condensing agents such as hexane or isopentane can limit production by exacerbating resin stickiness problems. For Z/N catalysts, the higher hexene concentrations required to achieve a given resin density combined with the intrinsic compositional heterogeneity of the product restrict total condensation level due to particle agglomeration. With metallocene catalysts, reduced hexene level in the gas for a given density and the narrow composition distribution of the resin mean the

total condensing amount can be increased to a higher limit before resin stickiness causes particle agglomeration. A higher level of condensing, more heat removal, and more reactor capacity are the result. The percentage of the cycle gas which condenses can reach beyond 30%, and the production rate can be increased proportionately.

Enhanced Long Chain Branching in the Gas Phase

Long chain branching in polyethylene resins has long been associated with improved processing in film fabrication, and some molding and extrusion applications. The shear thinning characteristics of branched polymers result in reduced die pressures and motor loads, while improved bubble stability results from the higher melt strengths associated with branched polymers.

In transition metal catalyzed ethylene polymerization, chain termination via beta-hydride elimination can lead to polymer chains with terminal vinyl groups. Long chain-branched polymers are produced when these macro-monomers are reincorporated into growing polymer chains. This long chain branching mechanism has long been known as a pathway to low level LCB formation with chromium-oxide catalysts.⁽²⁾ CrOx catalysts show little or no chain transfer to hydrogen and produce polyethylenes with significant levels of vinyl unsaturation. Certain metallocene catalysts also produce vinyl terminated chains which can be reincorporated as long chain branches, which are readily incorporated in gas-phase PE polymerization.^(3,4)

The facile production of long-chain branched polymers in a gas-solid polymerization process may at first seem counter-intuitive, however, the restricted mobility of recently-produced vinyl end-groups in the vicinity of an actively polymerizing site favors reincorporation of macro-monomer, provided the electronic and steric characteristics of the catalyst are favorable.

Summary

Metallocene catalysis brings important process technology benefits to gas-phase polyethylene production that can be utilized to enhance manufacturing efficiencies with the UNIPOL® PE Process. With specific metallocene catalyst systems, high catalyst activities, unique process response characteristics, and control of polymer molecular architecture can be combined synergistically in the UNIPOL process for improved manufacturing efficiencies.

Acknowledgments

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