NEW INNOVATIONS DRIVE GAS PHASE PE TECHNOLOGY

Dr. Ian Burdett, Univation Technologies LLC, presents new innovations driving gas phase PE technology leadership.

The gas phase, fluidised bed technology has been one of the principal process approaches for catalytic polymerisation to produce polyethylene (PE) since the 1980s. A leading provider of this technology for the manufacture of PE is Univation Technologies, LLC, (Univation), a joint venture of a subsidiary of The Dow Chemical Company and ExxonMobil Chemical Company. Univation is the exclusive licensor of the UNIPOL™ PE Process. In Univation, catalyst developments, especially in the area of metallocenes and 'engineered' catalysts for products with a bimodal molecular weight distribution, have driven significant process advances to fully capture the commercial potential of these catalyst systems. Coupled with this have been many process technology advances in areas such as production capacity per unit reactor volume, monomer utilisation, process control and instrumentation.

Process description

A schematic of the UNIPOL PE fluidised bed process is shown in Figure 1.[1, 2] Catalyst is fed into the cylindrical lower section of the fluidised bed vessel. Reaction occurs within the catalyst particles, which become growing polymer particles. In essence, each activated catalyst particle acts as a separate microreactor. There is no need to separate catalyst from final product. Cycle gas containing monomer reactants passes upward through the fluidised bed, providing the medium for heat transfer and fluidisation. Above the reaction section, there is an expanded section in which particles having a terminal velocity higher than the gas velocity disengage from the cycle gas stream. After leaving the reactor, cycle gas passes through a compressor and one or more heat exchangers to remove the heat of polymerisation before it returns to the bottom of the reaction zone. In the UNIPOL PE process no cyclone is required for entrained particles. There is generally a gas distribution plate immediately below the reaction section. Because these reactors operate at a pressure of typically 1×10^6 - 4×10^6 Pa and to achieve high reactant efficiency, a technically advanced discharge system is used to remove granular product intermittently from the reactor. A key

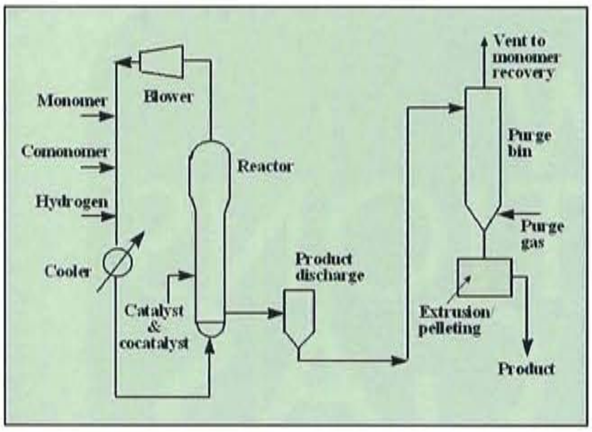
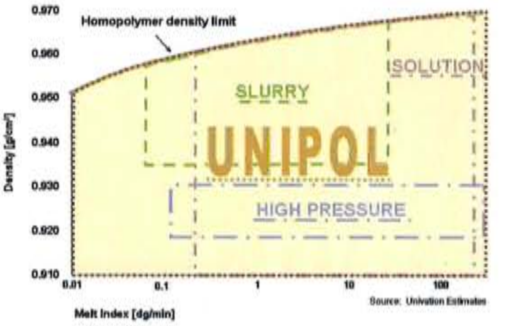


Figure 1. UNIPOL process for PE.



Source: Univation Estimates

The UNIPOL PE process is capable of covering the entire density-melt index range, other processes have limitations

Figure 2. Versatility of the UNIPOL PE process.

process design requirement is a vent recovery system that recovers the hydrocarbons released during polymer product discharge and which is contained in a stream from post reactor polymer purging. Standard compression and cooling systems easily recover the bulk of the hydrocarbons (reactants and induced condensing agent) for direct recycle to the reactor. The non condensable stream is flared with no catalytic oxidiser required. Overall hydrocarbon losses from the system are very small, making recycle integration into olefin crackers (if at same plant site) unnecessary as well as uneconomical.

Process flexibility: single reactor platform, multiple product opportunities

The fluidised bed process for PE can make the entire range of linear low density polyethylene (LLDPE) and high density (HDPE) products by utilising different catalyst systems (Figure 2). Other PE processes, such as solution, slurry and high pressure, have a variety of constraints, which limit their product capabilities and force specialisation to narrower product windows.

Through the use of multiple catalyst families and the ability to operate over wide variations of gas composition and reactor temperatures, it is possible, as previously shown in Figure 2, to produce grades for essentially all polyethylene applications. The Ziegler-Natta catalyst family has become the industry benchmark for manufacturing products for LLDPE film, injection moulding (LLDPE and HDPE) and rotational moulding applications using the gas phase PE process. Chrome catalysts are also used to manufacture products for a wide range of blow moulding, HDPE film and pipe applications. The Univation family of UCAT™ catalysts includes the complete range of Ziegler-Natta and chrome alternatives for servicing a broad range of application needs.

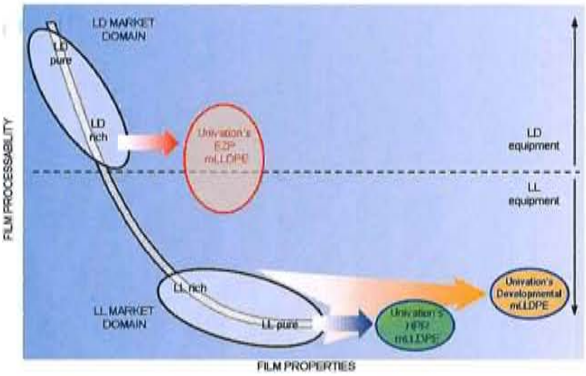


Figure 3. Polyethylene processability versus properties map.

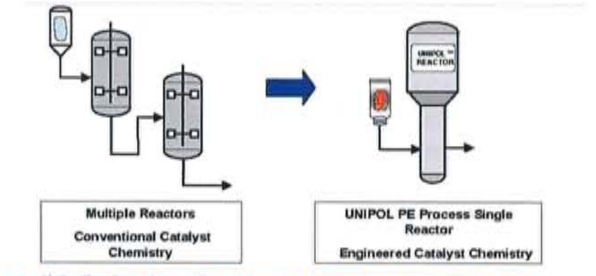
The inclusion of metallocene catalyst systems, such as Univation's XCAT™ HPR and XCAT™ EZP, has extended the product range of LLDPE beyond the capabilities of conventional Ziegler-Natta based systems. Products having much superior toughness, excellent optics and fabrication processing approaching that of high pressure low density resin (LDPE) are achievable with these systems (Figure 3).

The manufacture of bimodal products typically requires the use of multiple reactor technology. Univation Technologies' recent development of 'engineered' PRODIGY™ bimodal catalyst systems breaks this paradigm by providing the ability to produce bimodal resins using a single reactor UNIPOL PE Process platform. This advancement eliminates the need for the series reactor configuration needed for conventional approaches to bimodal product manufacture, thus reducing investment costs for the core facility by approximately 30% (Figure 4).[3] A single reactor environment is easier to control and operability is inherently improved. Both catalyst components are intimately mixed on the same catalyst particle and high and low molecular weight components grow simultaneously in one reactor for inherently better product quality. Further product extensions from these engineered catalysts allow the manufacture of products that can be used for PE-100 pipe, HPDE film and blow moulding products with a bimodal molecular weight distribution.

The flexibility of the UNIPOL PE gas phase process combined with the inherent advantages of the fluidised bed gas phase process provide the capability to produce a broad product mix of general purpose commodity grades and higher value specialty grades all within the simplicity of a single reactor system.

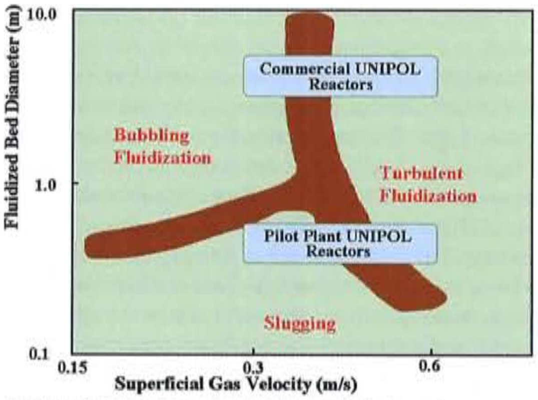
Transition technologies

A wide variety of products can be made by transitions within and between catalyst types. To transition to different grades within a catalyst family requires adjustment to new steady state process conditions, which is readily accomplished by proprietary advanced process control



Univation has chosen the engineered catalyst route with single reactor economics

Figure 4. Single reactor bHDPE via engineered catalyst chemistry.



- Commercial reactors operate in or near turbulent fluidization regime.
- Scale-up effects are minor because of the turbulent regime.
- Flow regime can be affected by varying operating parameters and reactor geometry.

Figure 5. Fluidisation regime and scaleup.

systems. Such transitions are known as 'running' transitions with generally little or no loss in production rate. The economics of transitions are such that it is important to minimise the loss of resin production and the quantity of off grade produced. Univation has used process control strategies and optimised product wheels (and in some cases resin trim back systems) to achieve essentially little or no off grade within catalyst transitions.

To transition between different catalyst types, Univation, in its process, is also able to execute 'running' transitions, involving steps in which the production rate is only briefly reduced. For example, the Ziegler-Natta to chrome catalyst switch is a running transition. However, certain catalyst families are incompatible requiring removal of the current polymer bed in the reactor and replacement by a so called 'seed bed' generally stored in a silo. Univation has technology and procedures to rapidly discharge and replace bed material with a pre-dried 'seed bed' thereby minimising downtime. Such technology is low cost and rapidly repays investment in reduction of production delays. Other gas phase technologies, with larger resin particles presumably by inclusion of a prepolymerisation step, can grow a bed in an empty reactor. However, such an operation is uneconomical since it takes substantially longer and results in more lost production. It is also more susceptible to operating problems as the reaction continues in a polymer bed well below the optimum polymer bed height at the junction of 'straight' side and the expanded section. Additionally, operation of the fluidised bed reactor with substantially larger particles can lead to the need for more costly higher gas recycle velocities to ensure that the bed is well mixed.

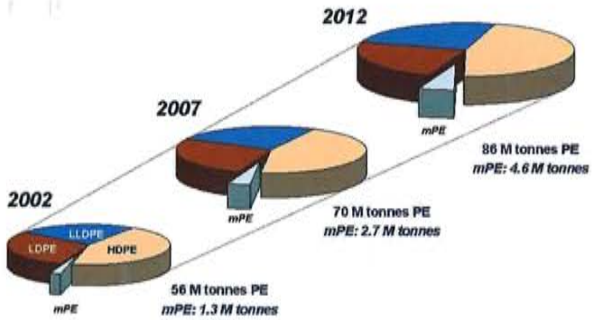


Figure 6. Metallocene product (mPE) worldwide volume growth. Source: Nexant Chem Systems, POPS 2006, millions of t.

Contamination of the new product to be made with previous production grades or residual activity of the previous catalyst is often raised as a concern. This previous catalyst is chemically deactivated so product contamination is solely related to the degree of difference in the new product grade from the previous product grade. Such concerns are easily solved by proper sequencing of products in the production wheel and typically require little or no special cleaning between grades except in unusual circumstances such as very gel sensitive products. All polyethylene processes can occasionally experience so called 'black spec' contamination, which occurs in post reaction systems and is normally due to product additive problems and extruder misoperation.

Many UNIPOL PE process licensees operate two or more reaction systems allowing them to optimise their product wheels and minimise inter catalyst transitions.

Heat removal advances: drive reactor production capacity

Fluidised bed reactors have characteristics which make them an excellent choice for polymerisation processes, which have large exothermic heat releases. However, they differ significantly from other fluidisation applications. Major differences include above ambient operating pressure, strong inter particle forces including electrostatics, sticky particles, and deep beds. These reactors are unique in the sense that they operate within a few degrees of the polymer sintering point. Such differences imply special challenges in the design, scaleup and operation of the polymerisation reactors. In particular, information about hydrodynamic parameters such as flow regime, particle classification, bubble characteristics and mixing pattern are necessary for the modelling, scaleup and operation of polyolefin fluidised bed reactors.[2] One advantage in this scaleup development is that commercial reactors operate in the turbulent fluidisation regime in which reactor diameter for a given recycle gas velocity is not a significant variable (Figure 5).

Another advantage of UNIPOL PE fluidised bed reactors is the ability to have single reactor systems producing 600 000 tpy or more. This is achieved by combination of three factors:

- The ability to design and operate large fluidised bed reaction systems.

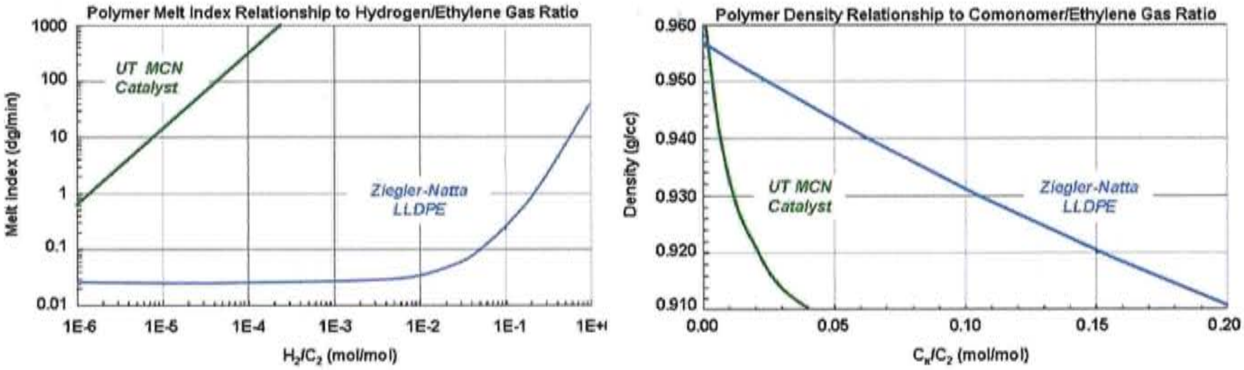


Figure 7. Catalyst response to hydrogen and co-monomer gas concentrations.

- The utilisation of patented condensing and super condensing mode technology.
- The successful use of advanced metallocene catalysts for a broad mix of product grades.

It is important to understand the specifics of how the exothermic heat of reaction is removed and design conditions are determined. The more heat that can be removed, the higher the achievable production rate. The recycle gas velocity has to be sufficient to keep the bed well mixed in turbulent fluidisation; it is not set based on overall heat removal requirements. Sufficient mixing in all regions of the bed is what prevents over heating of polymer particles and agglomeration. All the heat generated in the bed has to be removed by the recycling flow. In most gas phase polymerisation fluidised bed processes, the heat removal is constrained by the need to keep the recirculating gas from condensing in the external cooler to form liquid droplets. In such a situation, heat removal is limited to sensible heat of the gas.

$$\triangle H_R \cdot \text{(production rate)} = M_g \cdot C_{Pg} (T_{g\,\text{bed exit}} - T_{g\,\text{bed inlet}})$$

This can be increased by the addition of inert hydrocarbons such as propane, which will increase gas density and its heat capacity (although it makes separation of components difficult in post reactor recovery systems). In technology offered by Univation, the gas is partially condensed in the external cooler, resulting in a gas stream in which fine liquid droplets are carried back into the polymer bed.[4, 5] Such droplets rapidly evaporate near the distribution plate on re-entry to the reactor. Removal of the no-condensing constraint dramatically increases the heat removal capability of the recirculating fluid because of the addition of latent cooling on the condensed portion of the recirculating stream.

$$\triangle H_R \cdot P_R = M_g \cdot C_{Pg} (T_{g\,\text{bed exit}} - T_{g\,\text{bed inlet}}) + M_g \cdot X_C \cdot \triangle H_{vap}$$

This proprietary advance can increase heat removal by more than five fold when applied at high levels of condensing.[6, 7] This technology is known as Super Condensed Mode Technology and is licensed exclusively through Univation for the UNIPOL PE process.

For gas compositions in which condensation would not occur in the external cooler (such as in making high density products with essentially no co-monomer present), it is possible to add a condensable inert such as isopentane or hexane to force condensation and achieve the production rate benefits. Lower molecular weight condensing agents such as propane or butane are also feasible, but add significant cost due to the need to design and operate at higher pressures to achieve condensation.

Although condensing mode clearly increases the possible production rate, another variable that has to be considered is polymer sintering, which is a function of reactor temperature, co-monomer and inert condensing agent gas concentrations and polymer properties (primarily density). It is not possible to operate beyond these sintering limits, although as discussed in the next section, the use of metallocene catalysts for LLDPE products have substantial advantages in being far less constrained by such limits.

The metallocene catalyst process advantage

The ability to commercially use metallocene catalysts in a gas phase fluidised bed provides some significant product and process advantages. The product advantages over Ziegler-Natta catalysed products have been well publicised. However, the characteristics of metallocene catalysts have also provided the opportunity for improved process efficiency, particularly in higher production capacity for LLDPE copolymer grades. The four primary metallocene catalyst attributes (as compared to Ziegler-Natta catalysts) that change the production capacity for such grades are vastly improved hydrogen response, better co-monomer incorporation, narrow molecular weight distribution and narrow composition distribution. These catalyst attributes create an entirely different reactor environment. This allows the use of condensing and super condensing mode for these LLDPE grades with butene, and hexene. This advantage has now been exploited by Univation licensees to produce large volumes of high value polyethylene products (Figure 6).[9, 10]

To technically understand how this benefit arises requires consideration of the impact of metallocene catalysts on heat removal and polymer particle 'sintering' in the reaction bed and Figure 7 explains this. Metallocene catalysts require on the order of a hundred times lower hydrogen concentration in the gas phase for equivalent polymer molecular weight as compared to Ziegler-Natta catalysts. In addition, if hexene is the co-monomer its concentration in the gas phase can be less than 50% of concentration of hexene required for Ziegler-Natta grades of equivalent density. The lower hydrogen and hexene concentrations allow substantially more condensing agent, such as isopentane, to be present in the gas phase in the reactor. This increases the gas density, which means more weight of gas at a given velocity is being recycled and raises the dew point temperature so more of the recycle stream is condensed. This increases the production rate due the positive interaction of these factors on the overall heat balance as shown above.

Further, the more uniform composition distribution of co-monomer across the molecular weight range and to a lesser extent the narrower molecular weight distribution results in a polymer with a narrow range of melting temperature. This modifies the melting curve of the polymer so that a smaller fraction of amorphous or 'melted' polymer exists at a given temperature. These results substantially reduce the 'sintering' limit versus equivalent Ziegler-Natta products and allow higher reactor temperature operation and even higher induced condensing agent levels in the gas phase. These process and product differences from conditions allowable for Ziegler-Natta catalysts further increase production capacity.

Figure 8 shows the impact of catalyst choice and reactor operating mode on production capacity. If a base capacity of one unit is assumed for the Ziegler-Natta catalyst with hexene co-monomer operating in non condensing mode, the production capacity advantage of operating in condensing mode with metallocene catalysts is clearly apparent. This level of advantage can substantially reduce investment costs for a given capacity on new plants or provide strong economic incentive to retrofit existing plants for condensing mode operation with metallocene catalysts.

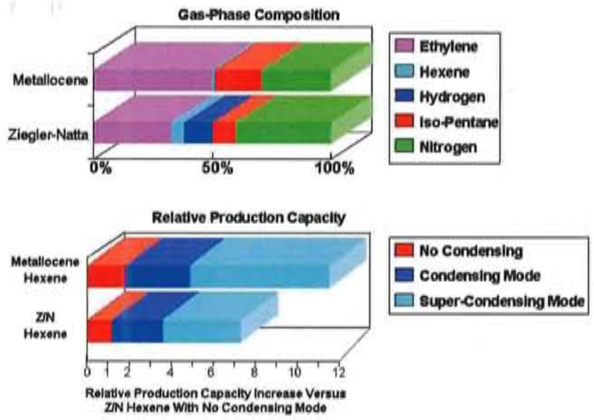


Figure 8. Metallocene catalyst and condensing mode impact on production rate.

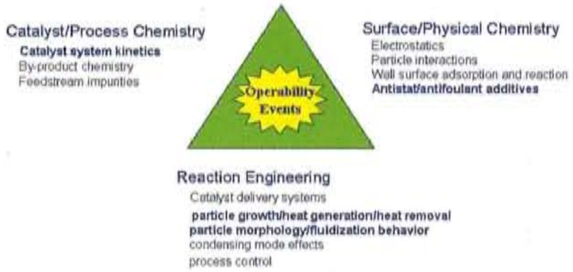


Figure 9. The operability triangle.

Operational excellence

During the initial commercialisation of metallocene catalysts in the mid 1990s, many operational challenges were faced. However, as demonstrated by the large volume of metallocene catalysed products produced commercially from the UNIPOL PE process, these challenges can be overcome by fundamental understanding of the causes of operational instability (such as formation of polymer wall sheets) and the use of technologies developed from this understanding.

The primary operational concern is the formation of polymer sheets on either the vertical reactor wall or in the expanded section dome. (This is a relatively fast phenomenon as opposed to long term gradual polymer fouling.) This polymer sheeting occurs when attractive forces hold masses of resin together under conditions where heat transfer is inadequate to remove enough heat of polymerisation to keep particles from melting and fusing. For this to occur, a combination of three distinct elements is required (Figure 9).

- Catalysts with kinetics, which maintain high reactivity beyond polymer sintering temperatures.
- Meso scale heat generation rate and lack of sufficient bed mixing to prevent polymer particle temperatures from rising above sintering point.
- Local or long range attractive forces (generally from surface effects or electrostatics).

In the time scale of polymer sheet formation, kinetics are rarely a factor since few polymerisation catalysts decay in reactivity fast enough as particle temperature rises to prevent polymer melting if the other two criteria are met.

To the contrary, most metallocene catalysts have overall apparent high activation energies and accelerate in rate as the temperature rises. Prepolymerisation of catalysts prior to feeding into the primary reactor, although minimising high initial catalyst particle reaction rates, will not prevent the sheeting phenomena since all three criteria are still very viable.

Also, poor reactor design or incorrect operating conditions can result in regions of inadequate particle mixing and insufficient heat transfer from particle to gas. Local reactor temperatures will not remain at intended bulk reactor operating temperature under such circumstances.

Lastly, the physical and chemical nature of the surface of the polymer particles and the reactor wall is a key requirement. When fluidising dielectric materials in the presence of metal walls and internals, triboelectric charging occurs that can be of a magnitude to cause particles to attach to each other and to the reactor wall.[11] This triboelectric charging is bipolar in nature so that significant overall static charges can be developed. Alternatively, operation at boundaries of polymer sintering due to polymer properties and absorption of co-monomers and higher molecular weight inerts can cause interparticle sintering and wall adhesion.

The above discussion may be perceived negatively, but in actuality the understanding of these phenomena at Univation has driven technical solutions which, when applied commercially, have made operational instabilities very rare events. This reliability has made the UNIPOL PE process much less susceptible to operating failures versus other polyethylene process technologies.

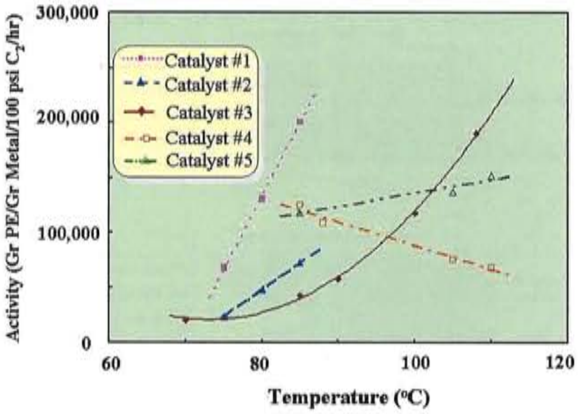


Figure 10. Activities of various PE catalysts as function of temperature.

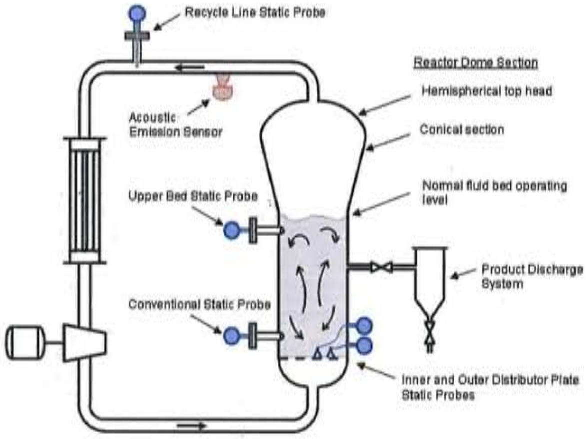


Figure 11. Advanced instrument configuration in a pilot plant.

So how is it done?

First, reactor design and operating parameters must be such that the fluidised bed is well mixed and reaction heat is effectively transferred to the circulating gas flow. Reactor and recycle system design must prevent significant particle entrainment and avoid any stagnant zones in piping or equipment in which accumulation of resin could occur. The next issue to address is catalyst kinetics. In essentially all circumstances, if the catalyst will form a separate and distinct fluidisable particle, fluidised bed systems such as UNIPOL PE will operate successfully regardless of catalyst kinetics (Figure 10).[12] Very high catalyst activity is not a restriction for use. Catalyst chemistry, supporting technologies and regulation of particle growth to achieve this polymer particle are the key variables.

The third requirement addresses surface chemistry phenomena and can be technically challenging. As discussed, electrostatic charging of resin and catalyst particles can occur. A number of factors such as catalyst type, polymer properties, areas of frictional charge generation and wall chemistry influence the magnitude of such charges. Univation has technical capabilities to limit likelihood of electrostatic charging and, if it occurs, to measure, regulate and neutralise such charge generation. Particle sintering can also be effectively controlled from knowledge and control of polymer properties and operating conditions.

Enhanced commercial performance from technology integration

The discussion above addresses some specific operability technologies, but to achieve high quality, high value commercial performance requires an advanced integrated approach to rational design and operation. Many of the specific elements of this are proprietary and/or patented. For Univation, it is clear that a proven design and control system, with well developed operational procedures, can deliver high performance metrics in production rate, product quality and aim grade percentage, monomer and co-monomer efficiency, environmental standards, and transition effectiveness. These metrics can be substantially improved by utilisation of more sophisticated technologies. Advanced process control systems, such as PREMIER Services APC+™, offer features such as resin property control, production rate maximisation and automated transitions. Univation's technology derives from model based coordinated control which integrates specific process understanding into the control applications. Recent developments focus on process reliability both from equipment and process control system operation and knowledge of fundamental expectations of process operation in the fluidised bed. To accomplish the latter requires specific proprietary instruments and sensors, which can detect variables such as local wall temperatures, polymer bed height, level of particle mixing in localised areas, local particle electrostatic charges and particle entrainment rates. Devices, such as fast responding skin thermocouples and pressure sensors, electrostatic probes and acoustic sensors, can provide, when coupled with process understanding and statistical tools (or so called 'signal processing methods'), reliable assessments of the status of process operation which can then initiate the necessary process control responses. Collectively these elements represent a 'health' monitor of the state of the process. A developmental system shows an example instrument configuration and the ability of such instruments to detect process instability (Figures 11 and 12).[13]

Conclusion

Manufacturers of polyethylene resin have historically relied on multiple technology and process platforms to develop the broad product capabilities needed to meet the changing needs of the marketplace. The flexibility of the UNIPOL PE process combined with the inherent advantages of the fluidised bed gas phase technology provide the capability to produce a diversified mix of general purpose and higher value specialty grades all within the simplicity of a single reactor system and technology platform. Process technology advances in the fields of design, operating modes; advanced instrumentation and model based process control have extended Univation's technology leadership and enabled full commercial potential of metallocene catalysts.

Univation's continued emphasis on research and development in catalyst technology, process improvements and instrumentation will continue to increase the capability of the UNIPOL PE process and keep it at the forefront in providing polyethylene resin solutions for market applications.

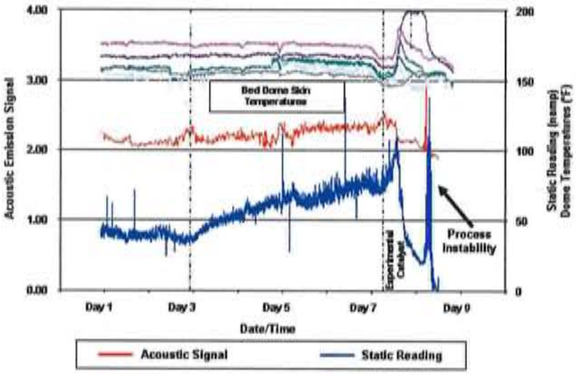


Figure 12. Advanced instrument signal responses to process instability.

Symbols

C_{Pg}: specific heat of gas.

$\triangle H_R$: heat of polymerisation reaction per unit mass.

$\triangle H_{vap}$: latent heat of vaporisation per unit mass.

M_g: gas circulation rate, mass per unit time.

P_R: polymer production rate, mass per unit time.

$T_{g\ bed\ exit}$: temperature of gas at bed exit.

$T_{g\ bed\ inlet}$: temperature of gas at bed inlet.

X_C: fraction of total gas flow condensed in cooler.

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