Dynamic Modeling of Product Grade Transitions for Olefin Polymerization Processes

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Most olefin polymerization processes produce a wide range of resin grades to suit market demand. Determining the transition policy between these grades is an important consideration that can affect process economics and safety. In this article, we compare several grade transition strategies and the relative performance of solution, slurry, bulk and gas-phase processes for the production of polypropylene, linear low-density polyethylene, high-density polyethylene and ethylene-propylene rubber. It is shown that the most important parameters that determine the grade transition performance of a process are reactor design, residence time, runtime per grade and residence time distribution of the polymer, gas and/or solution phases. Slow hydrogen dynamics severely retard grade changes involving increases in product molecular weight. The simulation results are obtained by using the dynamic simulation package "POLYRED" developed at the University of Wisconsin-Madison.

Introduction

Commercially produced polyolefins encompass major commodity polymers used for a variety of applications such as injection and blow molded, film, pipe and tubing products as well as some specialty polymers. Polyolefin products have been produced for nearly half a century with current total world capacity of approximately 40 million tons per year. Annual worldwide growth is foreseen to be 3–5% making polyolefin production technology a very active area of research.

A wide variety of polyolefin products, ranging from polyethylene and polypropylene homopolymer to ethylene propylene diene monomer (EPDM), may be produced in a number of catalytic processes including slurry, solution, bulk, and gas-phase media. The choice of process, however, depends on such factors as the nature of the product and its properties, catalyst type, production capacity, environmental effects, and the number of product grades to be produced. Regardless of the selected process, it is generally required that a range of different product grades is produced in the same plant to meet market demand. Typical run lengths can vary from less than one day to several weeks per grade, depending on the process, product, and grade schedule.

In formulating the production strategy, a balance must be found among such factors as market demand, inventory costs, operational costs, and plant stability. As demand fluctuates, the production schedule is adjusted to meet market requirements and to avoid stockout penalties, while minimizing inventory levels. Furthermore, the production schedule must reflect the fact that a significant cost penalty is incurred when switching between product grades. Accordingly, the production of the plant's product slate will be carried out in the most economical sequence (Picaseno-Gamiz and Sullivan, 1988). Owing to the variety of grades produced in a plant and the transition frequency, optimizing the transition between two different grades within the production schedule is of considerable economic interest. During a grade transition, the off-spec product produced must be sold at a discounted price and valuable production is lost during this time.

In this article, we will use the dynamic simulation package POLYRED (Ray, 1989; Ramanathan and Ray, 1991) to compare grade transition strategies and performance for the most common processes used for polyolefin production. The study will encompass the production of polypropylene (homopolymer, impact grade) linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and ethylene-propylene rubber (EPR) in a variety of processes including solution, slurry, liquid pool, and gas-phase reactors. The goal is to

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provide information on the relative natural advantages and disadvantages of each process and to compare various strategies for a given process.

In this work, we have only studied the reactor sequence and have not simulated the downstream separation and pelletization processing steps. However, these downstream processes are assumed not to provide serious recycle disturbances and thus do not influence the reactor behavior. For the gas-phase processes, these downstream steps should be relatively simple and fast, and the reactor dynamics clearly determine the grade transition. By contrast, for solution processes these downstream steps have more significant time constants than the reactor and strongly affect the grade transition transients. For slurry and liquid pool processes, the reactor behavior still dominates the grade transitions even though the downstream steps can have significant time constants. These points should be kept in mind while interpreting the results to follow.

Defining the Grade Transition Problem

Motivation for efficient grade transitions

Sinclair (1987) has noted three basic aspects of a grade change that determine cost penalties. First, there is often a reduction in plant output during a grade transition to maintain safe operating conditions. For example, in the high-pressure free radical polymerization of ethylene to LDPE, a grade change at normal production capacity (reaction rate) can result in reactor temperature or pressure runaway. The second cost issue relates to the off-spec product produced during the grade transition that must be sold for a lower price than the regular product within specification. Finally, economic costs are incurred due to the maintenance of product inventories, which are necessary to ensure sufficient supplies of each grade while the reactor is producing other grades of the product slate.

Examples of the penalties for producing off-spec material are given by Sinclair (1987). Table 1 shows these costs for LLDPE.

Obviously a reduction in off-spec product can result in a significant reduction in the total production cost of the product illustrating the need for efficient transitions between reactor grades. This is particularly true of processes with large reactor residence times and short production runs.

McAuley and MacGregor (1992) have studied the optimization of grade transitions for linear low-density polyethylene in a commercial fluidized-bed reactor. They conclude that any optimization strategy must consider the economic conditions of the market. During periods of high market demand, it may be preferable to reduce the grade transition time as much as possible. In periods of low market demand, however, a policy which produces less off-specification material at the expense of a longer transition time may be preferred.

Table 1. Cost Penalties for LLDPE Off-Spec Production*

Item	¢/kg
Monomer inefficiencies	0.44
Total maintenance	0.57
Operating labor	1.28
Plant overhead	1.46
Total utilities	1.92
Grade change penalties	2.20
Other fixed costs	1.24

* Adapted from Sinclair (1987).

Important factors affecting grade transitions

It is generally accepted that conducting a grade transition in any polymerization plant is a complex process in which plant personnel such as operators play a key role (Sinclair, 1987). Often, many plant variables will be changed simultaneously, either stepwise or according to a special predefined strategy. The objective is to:

- Conduct the grade transition as swiftly as possible
- Minimize off-spec production.

The impact of some important variables on the grade transition is shown in Table 2.

In conducting a grade transition, one must note that the reactor has inherent inventory in the gas, polymer bed and solution phases. One or more of these may be rate-limiting factors. A strategy that involves a rapid grade transition will involve changing the reactor conditions as quickly as possible. To reduce the transition time several different strategies can be applied. For example, overshootng the reactor concentration of monomer, hydrogen or inert is well known and applied in industry. Deinventorying the reactor contents can also improve the speed of the grade transition.

Product that is present in the reactor will be naturally mixed with off-spec product produced during the transition. This off-spec product cannot be recycled and can only be blended in small volumes with on-spec product. Deinventorying the on-spec polymer product prior to adjusting reactor conditions can lead to off-spec reductions and some savings in transition time. This strategy has been practiced in some fluidized-bed operations. Reducing the polymerization rate during the grade transition also helps; however, this leads to increases in the total grade transition time.

Different processes all respond differently to each of the strategies. Characteristics such as mean residence time, residence time distribution, reactor medium, presence of inerts and reactor inventory are important issues.

Polyolefin processes considered

As indicated above, we consider grade transitions for a variety of polyolefin processes. Tables 3–5 and Figures 1–6 provide the details on the processes and simulation conditions used in this study. To compare different polyolefin processes it is necessary to define the basis regarding production rate, residence time, reactor conditions, and so on. Since our goal is to compare different processes, the polymerization kinetics are identical for similar processes and catalysts, producing the same product. For example, the kinetics used for gas-phase production of polypropylene homopolymer and impact co-

Table 2. Effect of Process Variables on Grade Transitions

Product Properties	Reaction Rate	Plant Operation
Comonomer conc.	Catalyst feed	Product discharge
Hydrogen conc.	Temperature	Polymer inventory
	Pressure	Equipment limitations
	Monomer conc.	

Table 3. Conditions for Polypropylene Homopolymerization + Copolymerization

Process	Bulk (Liquid Pool)		Multistage Gas Phase		
Example Licensors	Himont/Mitsui*		Union Carbide/BP**	BASF/ICI/USI†	AMOCO/Chisso‡
Reactors	Loop/Stirred Tank + Fluidized Bed Low Recycle	High Recycle	Fluidized Bed + Fluidized Bed	Vertical Stirred Bed + Vertical Stirred Bed	Horizontal Stirred Bed + Horizontal Stirred Bed
Diluent (or Solvent)	Liquid Monomer	Liquid Monomer	Nitrogen	—	—
Polymer Yield (g/g cat)	$TiCl_4/MgCl_2$ ~11,000	$TiCl_4/MgCl_2$ ~14,000	$TiCl_4/MgCl_2$ ~17,000	$TiCl_4/MgCl_2$ ~17,000	$TiCl_4/MgCl_2$ ~22,000
Bed Volume					
Stage 1 (m^3)	2×50	2×50	60	32	32
Stage 2 (m^3)	22	30	40	24	32
Diseng. (m^3)	20	27	30		
Temp. (°C)					
Stage 1	70	70	70	70	70
Stage 2	80	80	80	80	80
Pres. (atm)					
Stage 1	35	35	25	25	25
Stage 2	20	20	20	20	20
Res. Time (h)	1.6+0.9+0.6	1.6+0.9+0.6	1.10+0.75	1.10+0.70	1.20+0.80
PP (ton/h)	10.7	13.4	12.5	12.5	16.2
HIPP (ton/h)	13.7	17.1	16.0	16.0	21.0

*Di Drusco and Rinaldi (1984); Simonazzi et al. (1991); Galli and Ali (1987); Miller (1987); Brockmeier (1983); Weintritt and Burdett (1989).

**Hussein and Nemzek (1989); Choi and Ray (1985); Goodenbour et al. (1989).

†Ross and Bowles (1985); BASF Report (1986); Choi and Ray (1988).

‡Brockmeier (1991); Caracotsios (1992); Brockmeier and Koizumi (1991); Brockmeier (1983).

polymer are the same. They were chosen to correspond to activities and residence times of industrial catalyst systems as reported in the literature. Also typical values for temperature and pressure are chosen from published industrial plant data. For the liquid pool polypropylene process in Table 3, high- and low-recycle conditions are noted. High-recycle conditions are used in the normal-grade transitions whereas lower recycle conditions are used for faster-grade transitions.

Dynamic Simulation Package POLYRED

The grade transition simulations were performed with the latest version of POLYRED, a CAD package for polymerization processes developed by the University of Wisconsin Polymerization Reaction Engineering Laboratory. The package is capable of both steady-state and dynamic simulation of process flowsheets and allows the estimation of process model

Table 4. Conditions for LLDPE and EP-Rubber Polymerization

Process	Single-Stage Gas Phase	Solution Process	Single-Stage Gas Phase
Example Licensors	Union Carbide/BP*	Dow/DuPont/DSM**	Union Carbide†
Reactors	Fluidized Bed	Stirred Tank	Fluidized Bed
Product	LLDPE	LLDPE	EPR
Comonomer	Butene-1	Butene-1	Propylene
Diluent (or solvent)	Nitrogen	Iso-octane	Nitrogen
Polymer Yield (g/g cat)	$TiCl_4/MgCl_2$ ~20,000	$TiCl_4/MgCl_2$ ~1,500	VCl_3 ~500
Bed Volume			
Stage 1 (m^3)	85	15	33.5
Diseng. (m^3)	85		33.5
Temp. (°C)			
Stage 1	70	180	30
Pres. (atm)			
Stage 1	22	21.7	20.4
Res. Time (h)	2.1	0.083	4.6
LLDPE/EPR (ton/h)	12.6	10.4	5.25

*Jenkins et al. (1985); Noshay et al. (1984).

**Forsman (1972).

†Rifi et al. (1990); Rhee et al. (1991).

Table 5. Conditions for High-Density Polyethylene Polymerization

Process	Single-Stage Gas Phase	Slurry	
Example Licensors	Union Carbide*	Phillips**	
Reactors	Fluidized Bed	Loop Reactor	
		High Recycle	Low Recycle
Comonomer	Butene-1	Butene-1	Butene-1
Diluent (or solvent)	Nitrogen	Iso-butane	Iso-butane
Polymer	CrO_2/Silica	CrO_2/Silica	CrO_2/Silica
Yield (g/g cat)	~10,000	~15,000	~15,000
Bed Volume			
Stage 1 (m^3)	85	30	30
Diseng. (m^3)	85		
Temp. (°C)			
Stage 1	100	100	100
Pres. (atm)			
Stage 1	30	30	30
Res. Time (h)	3	1.0	1.0
HDPE (ton/h)	8.6	12.1	12.2

* Noshay et al. (1984)
** Short (1983)

parameters from experimental data (Ray, 1989; Ramanathan and Ray, 1991). While steady-state simulation programs are used routinely in the petrochemical industry, dynamic simulation packages are relatively new. Furthermore, simulation packages for polymerization chemistries are rare because available general process simulation programs do not have the necessary features to adequately address the modeling issues unique to polymer systems (Ramanathan et al., 1992). These issues include a detailed description of reaction kinetics, polymer physical properties, polymer component characterization, phase equilibrium and polymerization reactor modeling.

The structure of POLYRED consists of a CAD environment and libraries of process units herein referred to as "Modules." The CAD environment consists of "System Programs," "Numerical Drivers," and "Libraries" for file manipulation, I/O and pull down menus. The system programs contain programs for flowsheet construction, specification of simulation data, and a graphics plotter for both 2- and 3-dimensional profiles. A convenient shell program allows the user to access all of the system programs and to select and run example simulations within the CAD environment, without having to enter commands from the command line. Further scripting features allow program execution in batch mode.

Within the POLYRED environment, common industrial processes are easily constructed from a library of reactor modules (such as continuous stirred tank, fluidized bed, and loop) as well as nonreactor units (splitters, mixers and separators).

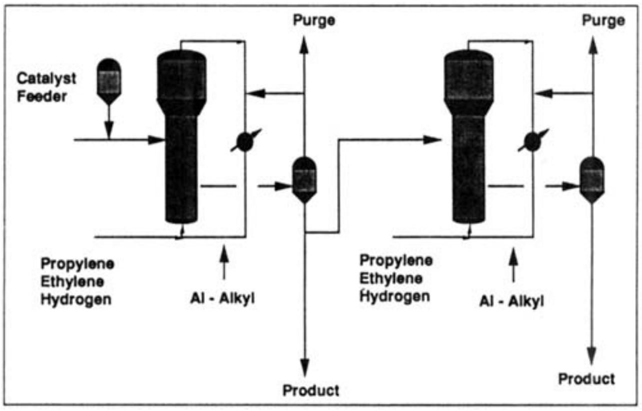

Figure 2. Union Carbide UNIPOL process.

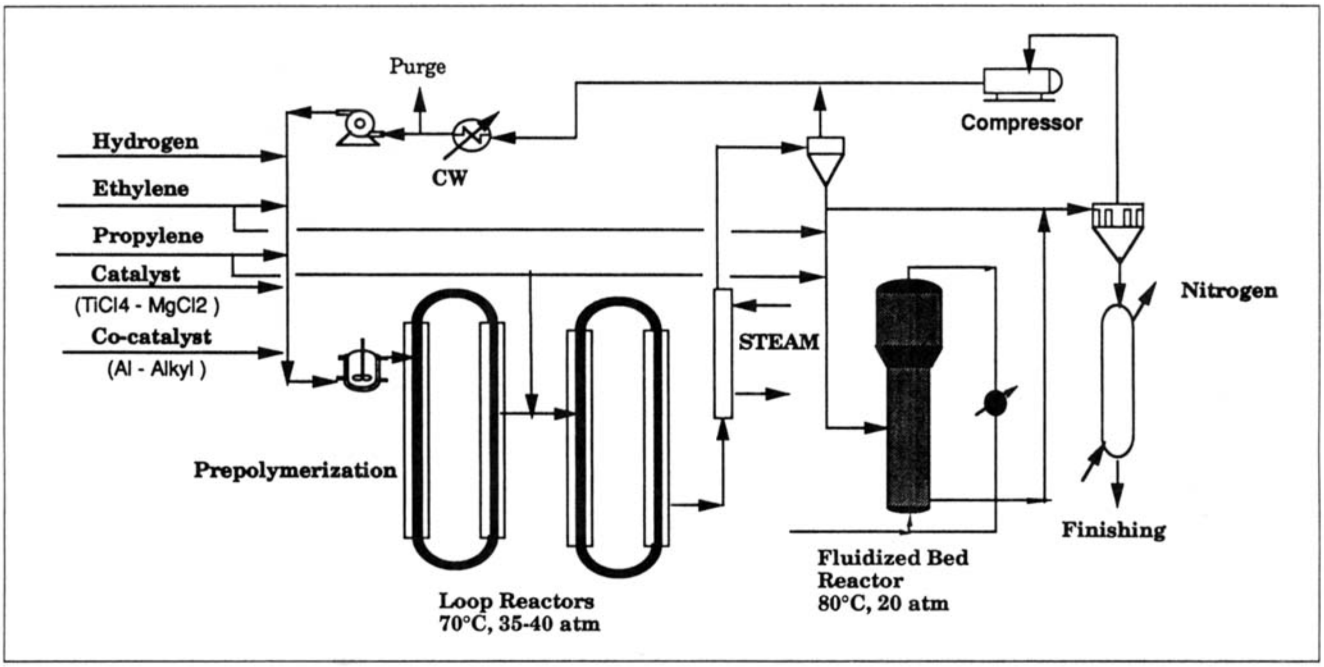

Figure 1. Himont spheripol process.

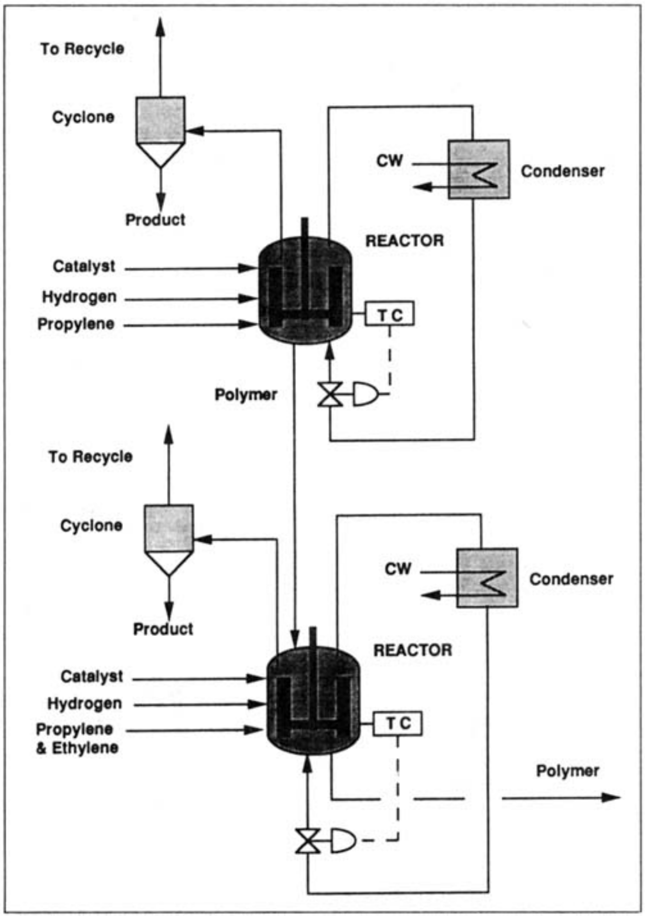

Figure 3. BASF gas-phase vertical stirred bed process.

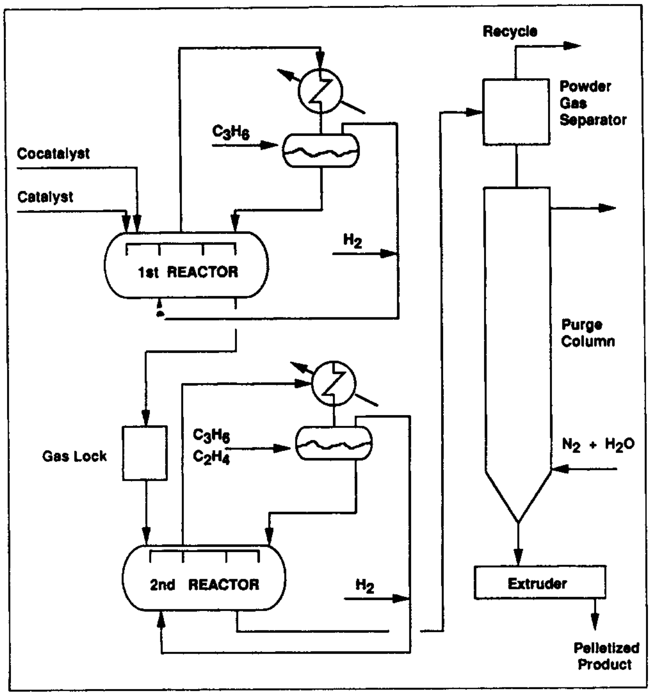

Figure 4. AMOCO/Chisso gas-phase horizontal stirred bed process.

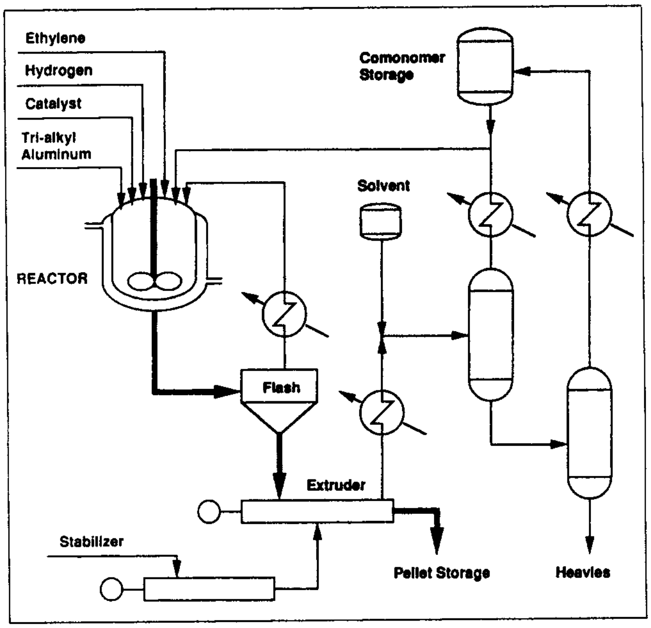

Figure 5. Solution process (Dow, DuPont, DSM).

The modules libraries are grouped by chemistry and currently include the following kinetics:

- Condensation
- Ionic
- Free radical
- Group transfer
- Transition-metal catalyzed

A major advantage of POLYRED is that the user is never required to write computer code. The graphical-menu-based CAD environment of POLYRED allows construction of detailed flowsheets in minutes without coding. Then, simulation can be carried out using POLYRED's pull-down menu features and dynamic simulation display screens.

Although POLYRED can be used to study process dynamics and grade transitions for the wide variety of polymerization chemistries noted above, the remainder of this article will focus on the "Transition-Metal Catalyzed" chemistry for olefin polymerization.

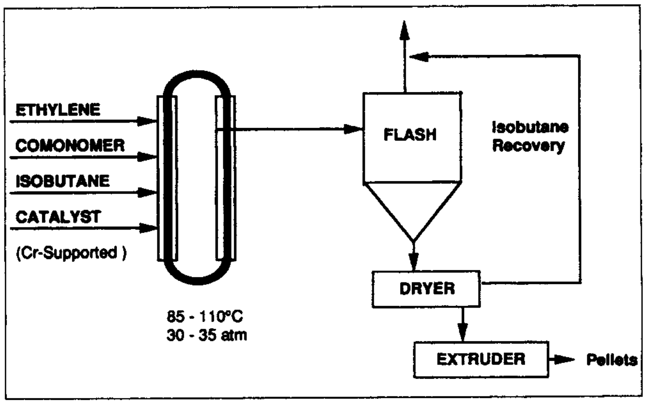

Figure 6. Phillips slurry process.

Table 6. POLYRED Modules for Transition-Metal Catalyzed Olefin Polymerization

Module Name	Description
CZN-CSBR	Polymerization in a Continuous Stirred Bed Reactor
CZN-FBR	Polymerization in a Fluidized Bed Reactor
CZN-LOOP	Polymerization in a Loop Reactor
CZN-TANK	Polymerization in a Continuous Stirred Tank Reactor
CZN-SOL-GAS	Solution to Gas Steady-State Flash Vessel
CZN-GAS-SOL	Gas to Solution Steady-State Condenser/ Separator Vessel
CZN-MIXER	Solution Steady-State Stream Mixer
CZN-DMIXER	Solution Dynamic Stream Mixer
CZN-SPLITTER	Solution Steady-State Separator Vessel
CZN-DSPLITTER	Solution Dynamic Separator Vessel

Modules for transition-metal catalyzed olefin polymerization

POLYRED contains a wide variety of process modules for transition-metal catalyzed olefin polymerization, as shown in Table 6. The large selection gives the user the flexibility to configure process flowsheets for most industrial olefin polymerization processes and to compare the dynamics of competitive processes. Modules are available for the polymerization of olefins in both gas-phase and solution/slurry conditions.

Modules CZN-LOOP and CZN-TANK describe the dynamics of solution/slurry polymerization in a loop and continuous stirred-tank reactor, respectively. CZN-LOOP simulates a liquid-full loop reactor with an axial pump to impel the reaction mixture. The reactor is modeled as two tube sections with axial dispersion and the assumption of a pseudo-homogeneous fluid (Zacca and Ray, 1993). A cooling jacket for the removal of the heat of polymerization is provided, but the reactor may also be operated as adiabatic or isothermal. To solve the resulting set of partial differential equations, the method of orthogonal collocation is used. In the case of CZN-TANK, pseudo-homogeneous batch, semibatch, underflow and overflow CSTRs may be simulated.

CZN-CSBR and CZN-FBR simulate gas dispersion reactors (continuous stirred bed (Choi and Ray, 1988) and fluidized bed (Choi and Ray, 1985), respectively) that contain a mixture of both gaseous and solid components. Material balances are performed on the components present in both the gas and solid polymer phases. For the fluidized bed reactor, CZN-FBR, a disengagement zone with user-specified volume is also considered. Optional controllers for bed level, temperature, and pressure can be selected for these reactors. The controllers may be single-loop PID, steady-state perfect control, or no control action. Setpoints for the control variables, as well as the PID controller parameters, may be time-varying. Pressure is controlled by monomer feed to the reactor. Temperature is controlled by adjusting the liquefaction of the recycle gas (CZN-CSBR) or the recycle temperature (CZN-FBR). Bed level is controlled by product removal rate. Controllers for hydrogen and composition have also been implemented.

In all of the modules, the presence of a diluent or solvent may be specified and hydrogen may be present. Up to three monomers may be used. A wide variety of the process variables may be manipulated at any time during the simulation to study the impact of disturbances on the process. Generally these include, but are not limited to, input streams, heat-transfer coefficients, and output streams.

Flowsheet construction

Construction of the simulated processes involves the following steps:

- Selection of the process modules and specification of connectivity
- Configuration of the flowsheet for the desired numerical driver (dynamic simulation, parameter estimation, and so on)
- Specification of kinetic parameters, simulation conditions.

Processes involving a train of reactors in series for the production of layered products are easily constructed by specifying the connection from the outlet of the upstream reactor to the inlet of the downstream reactor. Splitter and mixer units may be added where there is a need to remove some components or add intermediate feeds. Combination flowsheets where polymerization occurs in different media such as solution and gas reactors were constructed by using the connection programs CZN-SOL-GAS and CZN-GAS-SOL. Here, the media can be condensed or vaporized, diluent or noncondensables removed, and the stream may be heated or cooled prior to injection into the next reactor. For example, the Himont process for impact polypropylene consists of propylene polymerization in two loop reactors in series followed by ethylene-propylene copolymerization in a fluidized bed. The liquid monomer is flashed between the second-loop and fluidized-bed reactor. The flowsheet for this process was created by combining CZN-LOOP + CZN-LOOP + CZN-SPLITTER + CZN-SOL-GAS + CZN-FBR in series.

The resulting set of nonlinear ODEs and algebraic equations that describe the process flowsheet are processed and integrated by the time integration driver, TNTEG. This time integration driver is based on SPDASSL, a modified version of the differential-algebraic equation solver DDASSL (Petzold, 1983) that takes advantage of sparsity in the Jacobian matrix.

TNTEG allows the specification of disturbances and dynamic display of output variables. Disturbances may be in the form of step inputs, ramps, pulses, sine waves or alternatively a user-constructed data file. By using this convenient feature, changes from one grade to another are easily simulated.

Kinetic scheme

A comprehensive kinetic model is available for transition-metal catalyzed olefin polymerization as shown in Table 7. The kinetic scheme allows the use of up to four types of active sites and three monomers (Hutchinson et al., 1992). For the examples shown here, only a subset of the available kinetic mechanisms has been utilized (shaded dots) and only one active site has been chosen. All kinetic rate coefficients are based on the concentration of sorbed species at the catalyst site (Hutchinson and Ray, 1990).

Grade Transition Simulations

In this section, the grade transition behavior of commercial processes for polypropylene, EPR, LLDPE and HDPE production are presented. We focus on the reactor sequence and

Table 7. General POLYRED Kinetic Scheme for Transition Metal-Catalyzed Olefin Polymerization

	Site Activation	Chain Initiation	Chain Propagation	Chain Transfer	Site Transform	Site Deactivation
Hydrogen	○			●	○	○
Cocatalyst	●			○	○	○
Donor	○			○	○	○
Monomer	●	●	●	○		○
Solvent				○	○	
CTA				●		
Inhibitor					○	○
Byproduct						○
Spontaneous	●			○	○	●

the properties of the polymer exiting the last reactor. As discussed earlier, downstream parts of the process (such as polymer separation and pelletization), which also contribute something to the grade transition time, have not been simulated here.

Strategies employed

For each process, different grade transition strategies are compared. These are selected either because they are used in industrial practice or because they would seem to offer practical advantages. Obviously, a great variety of strategies could have been evaluated (and, indeed, POLYRED allows these to be quickly simulated); however, we chose what we considered the most appropriate strategies for the basis of comparison. The details of these strategies are given in Table 8. There are other more detailed strategies employed by industry, but we have not attempted to simulate every detailed transition strategy that is specific to a certain process. Such specific information is difficult to obtain and is often confidential.

Polypropylene processes

In this section, the grade transition behavior of processes for the production of polypropylene homopolymer and impact copolymer are considered. The processes chosen for study are shown in Table 3 and Figures 1-4. These represent some of the most commercially significant processes for propylene polymerization. For the gas-phase processes, the catalysts used in the simulations are based on reported yields and production

Table 8. Definition of Grade-Transition Strategies

	Strategy	Description
A	Base	• Step inputs of hydrogen feed rate and monomer feed composition to final values.
B	Quick Venting	• Step inputs of hydrogen feed rate and monomer feed composition to final values. • Open the gas vent valve of the reactor during the first 10 min of the grade change to change the composition of the reactor gas phase as quickly as possible. The flow rate of the venting is proportional to the size of the gas inventory in the reactor.
C	Bed De-inventorying	• Step inputs of monomer feed composition to final values. • During first 10 min discharge approximately 50% of the reactor bed. Then, stop product withdrawal to slowly build up the bed volume to its initial value. When bed level is close to the final value, turn on PI control of the bed level.
D	Quick Venting + Overshoot	• Vent reactor during first 10 min of grade change as in strategy B. • During the period of reactor venting, adjust the monomer composition and hydrogen feed rates to overshoot final desired values. After the venting ends, adjust these feed rates to the final desired levels in a stepwise fashion. This procedure helps speed the change in gas-phase composition.
E	Quick Venting + Overshoot + Bed De-inventorying	• Vent reactor during first 10 min of grade change as in strategy B. • Overshoot the monomer and hydrogen feed rates during the first 10 min as in strategy D. • Deinventory the bed as in strategy C.
F	Overshoot + Bed De-inventorying	• Overshoot the monomer and hydrogen feed rates during the first 10 min as in strategy D. • Deinventory the bed as in strategy C.
G	Quick Venting + Overshoot + Nitrogen overshoot	• Vent reactor during first 10 min of grade change as in strategy B. • Overshoot the monomer and hydrogen feed rates during the first 10 min as in strategy D. • During approximately one residence time, adjust nitrogen feed rate to overshoot final desired values. This procedure helps speed the change in gas-phase composition. In particular, since monomer feed is used to control reactor pressure, it can initially overshoot desired composition if nitrogen is not increased to compensate.
H	Loop Low Recycle	• Step inputs of monomer and hydrogen feed rates to final values. • Reduce recycle rate in loop reactor to narrow the residence time distribution.
J	Solution Low Recycle	• Reduce recycle rate of the process. • Overshoot the hydrogen feed rate and reduce the comonomer feed during the first 100 s of the grade transition.

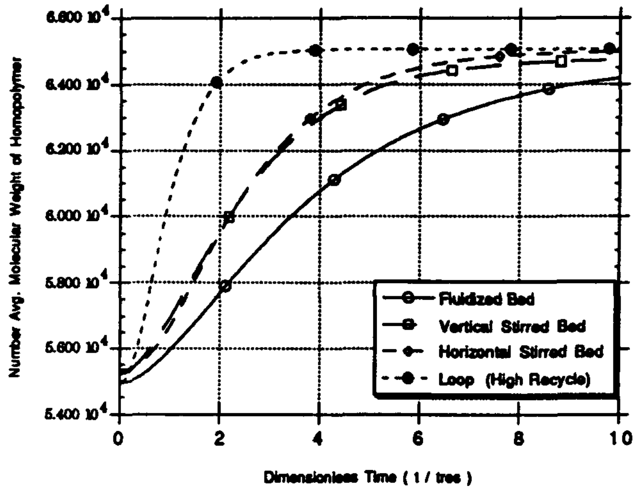

Figure 7. Grade change in molecular weight of polypropylene homopolymer, strategy A.

rates (Brockmeier, 1991; Caracotsios, 1992; Byck et al., 1987; Hussein and Nemzek, 1989; Ross and Bowles, 1985; BASF Report, 1986; Weintritt and Burdett, 1989), with a supported Titanium Ziegler-Natta catalyst. For the liquid pool processes, a lower activity catalyst characteristic of these processes is used (Di Drusco and Rinaldi, 1984; Simonazzi et al., 1991; Galli and Ali, 1987; Miller, 1987; Brockmeier, 1983). Residence times, conversions, and productivities are representative of industrial conditions.

Polypropylene homopolymer production is considered in four different types of processes:

- *Gas-phase fluidized bed* (such as UCC/Shell) (Hussein and Nemzek, 1989; Weintritt and Burdett, 1989; Choi and Ray, 1985; Goodenbour et al., 1989)
- *Gas-phase vertical stirred bed* (such as BASF/ICI/Quantum) (Ross and Bowles, 1985; BASF Report, 1986; Choi and Ray, 1988)
- *Gas-phase horizontal stirred bed* (such as AMOCO/Chisso) (Brockmeier, 1991; Caracotsios, 1992; Brockmeier and Koizumi, 1991; Brockmeier, 1983)
- *Liquid pool loop* (such as Himont) or CSTR (such as Mitsui) with two reactors in series (Di Drusco and Rinaldi, 1984; Simonazzi et al., 1991; Galli and Ali, 1987; Miller, 1987; Brockmeier, 1983).

The AMOCO horizontal stirred bed reactor is simulated as four CSBRs in series with a uniform gas composition. Similarly, the AMOCO/Chisso impact copolymer process consists of two units, each of which is modeled as four CSBRs as above.

The grade change consists of an increase in number average molecular weight (decrease in Melt Index) from approximately 55,000 to 65,000, corresponding to the production of a stiffer product. Two strategies are considered:

- *Gas-phase reactors*: strategy A, base; strategy B, quick venting
- *Loop reactor*: strategy A, base for loop (high recycle); strategy H, loop low recycle

Strategy A consists of simply adjusting the feed rate of hydrogen in a stepwise fashion, and no special efforts are made to flush hydrogen from the system. Results are shown in Figures 7 and 8. Note that the time axis is normalized by the process mean residence time. On this basis, it is clear that the liquid pool process responds more quickly than the gas-phase processes because the hydrogen level responds most quickly (cf. Figure 8). This is a result of two factors. First, there are two liquid pool reactors in series, thus providing a narrower residence time distribution for the hydrogen than in the other reactors. Secondly, the relatively large gas inventory in the gas-phase reactors coupled with the low outflow rate of hydrogen (by consumption and withdrawal) results in a large hydrogen residence time in the reactor during the transition.

The result that both the horizontal stirred bed and vertical stirred bed respond similarly is due to the fact that the hydrogen concentration responds very slowly, dominating the grade transition, even though the powder beds have different residence time distributions. Thus, the gas-phase reactors (even AMOCO horizontal stirred-bed) have one effective CSTR for the gas phase. The fluidized bed reactor performance is worse in this base case because of the large gas inventory in the disengagement zone.

Figures 9 and 10 illustrate the results of strategies B and H,

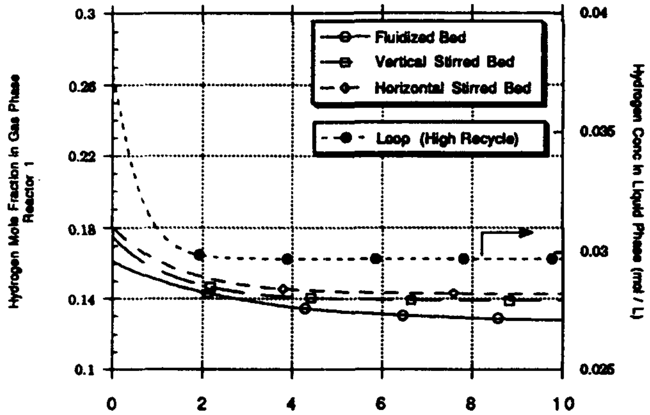

Figure 8. Reactor hydrogen concentration for polypropylene homopolymer, strategy A.

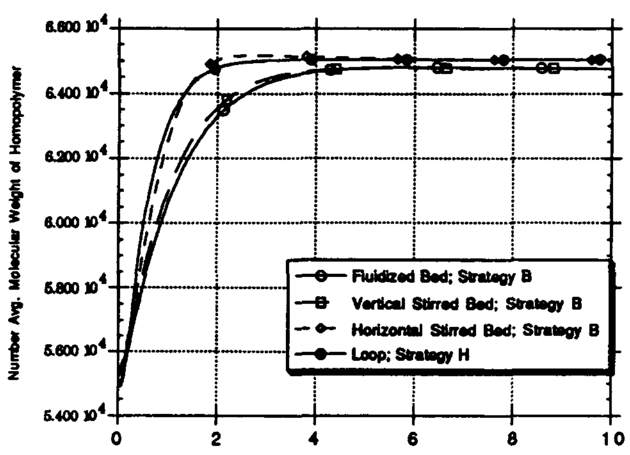

Figure 9. Grade change in molecular weight of polypropylene homopolymer.

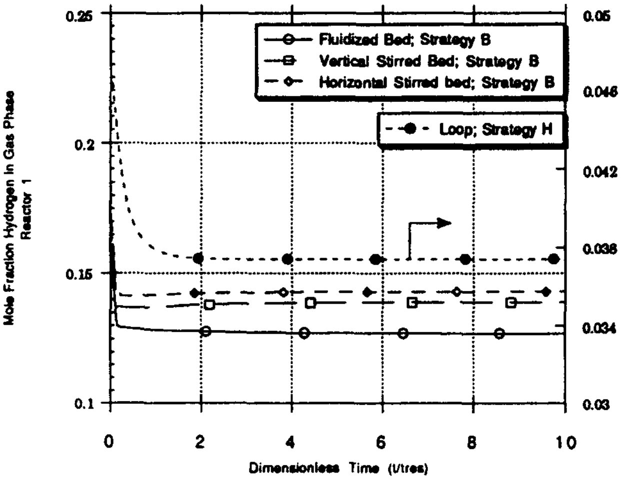

Figure 10. Reactor hydrogen concentration for polypropylene homopolymer.

when special procedures are taken to quickly reduce the hydrogen level in the reactor during the grade transition. For the liquid pool loop process, the loop circulation rate was reduced to narrow the residence time distribution. For the gas-phase reactors, a gas blowdown at the start of the grade transition was employed to quickly reduce the hydrogen level. When the dominating effects of hydrogen are removed, the natural residence time distributions of different processes become more evident. The loop and horizontal stirred bed reactor respond more quickly than the fluidized bed and vertical stirred bed reactors, as a result of their narrower residence time distribution.

Figures 11 and 12 summarize the results of the grade transitions, where the off-spec product as a percentage of total production of the grade is shown. Note that each of the processes has a different residence time, which must be considered when comparing the different processes. Figure 11 compares the results when each process operates for 50 residence times before beginning the grade transition. An alternate basis using equal production campaigns with somewhat different production times is shown in Figure 12. The campaign in Figure 11 emphasizes the advantage of processes with a narrow residence time distribution without regard to the magnitude of the mean residence time. Thus, processes such as the low recycle loop and horizontal stirred bed reactor produce less off-spec product when the comparison is on a fixed number of residence times. By contrast, the basis for comparison used in Figure 12 (equal production rates) allows the influence of mean residence time to be felt. Thus, the loop reactor which has the largest overall residence time (cf. Table 3) has the largest off-spec losses. In all cases, the quick venting strategy (Strategy B) greatly reduced the off-spec losses for the gas-phase reactors.

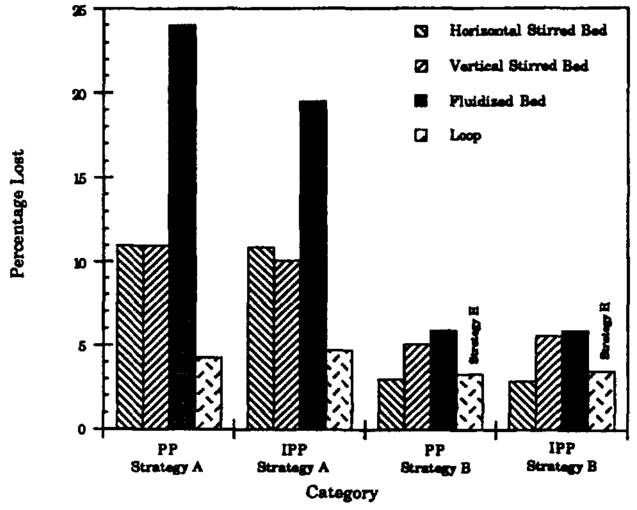

Figure 11. Percent off-spec product based on 50 times residence time for PP and 30 times residence time for HIPP (±500 M_n).

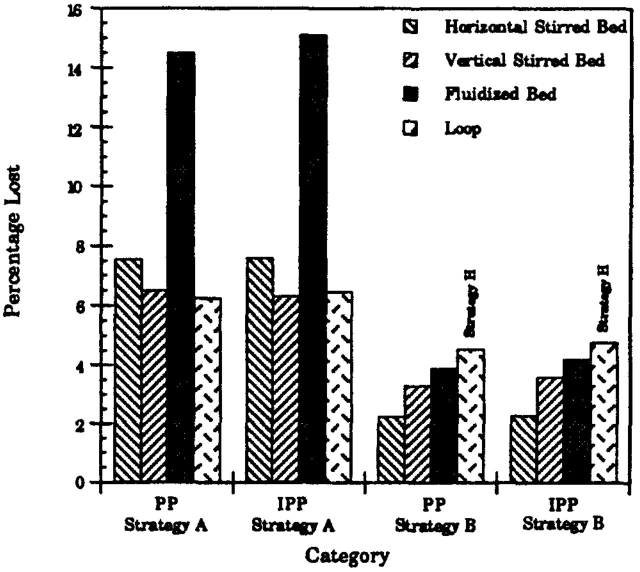

Figure 12. Percent off-spec product based on 1,000 ton of product within specification.

All processes are scaled to production level of 12.5 ton/h PP and 16 ton/h IPP.

Impact polypropylene is prepared in a multistage cascade of reactors. In the first stage, the homopolymer product is the

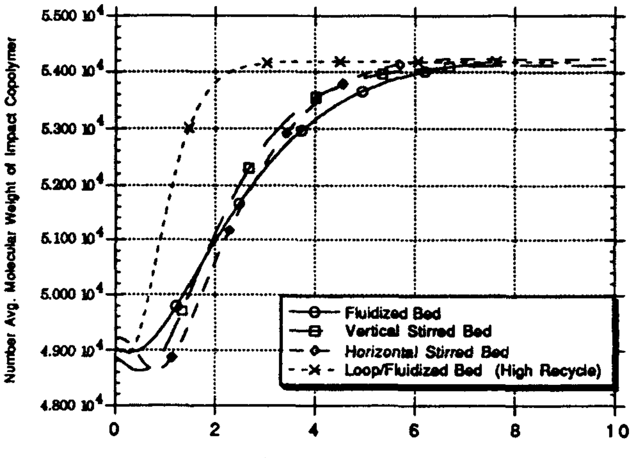

Figure 13. Grade change in molecular weight of polypropylene copolymer, strategy A.

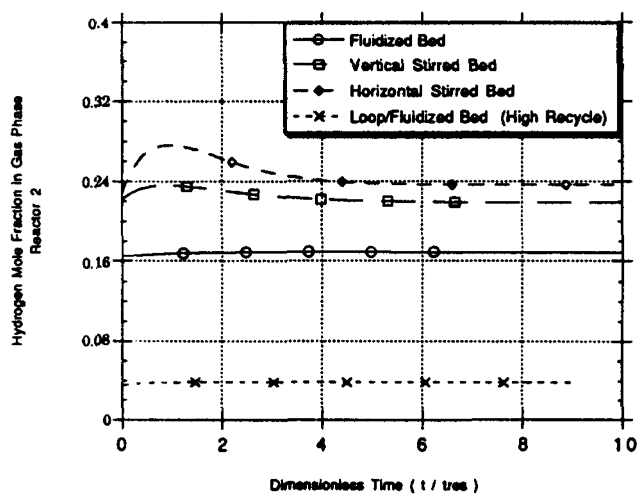

Figure 14. Reactor hydrogen concentration for polypropylene copolymer, strategy A.

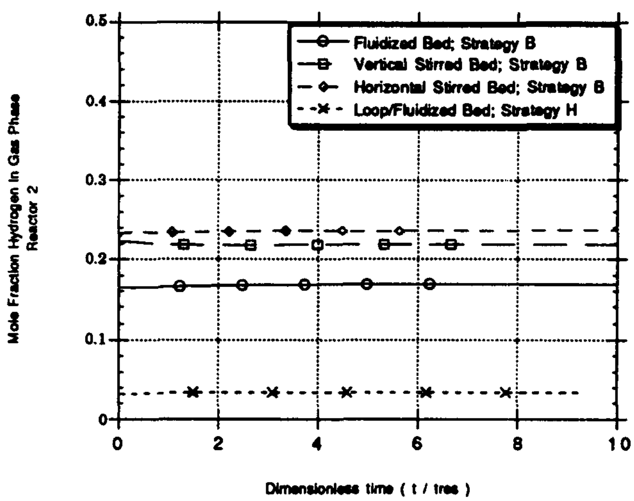

Figure 16. Reactor hydrogen concentration for polypropylene copolymer.

same as previously considered. In the second stage, EP Rubber is produced with the composition and content in Table 3. Grade transitions are presented in Figures 13-16 for the step input case (strategy A) and quick venting (strategy B) for the gas-phase reactors and low recycle (strategy H) for the loop. The grade transition corresponds to the same increase in molecular weight of the homopolymer with identical content and composition of EP Rubber, thus producing a stiffer product. Without taking special precautions to remove hydrogen in the first reactor, the effect on the composite molecular weight of the impact copolymer is similar to the homopolymer case. Here, off-spec product carried over from the first reactor has an effect on the product in the second reactor.

Linear low-density polyethylene

In this section, the grade transition of two different processes for the production of linear low-density polyethylene are considered:

- *Solution* (such as Dow/DuPont) (Forsman, 1972)
- *Gas-phase fluidized bed* (such as UCC/BP) (Jenkins et al., 1985; Noshay et al., 1984)

The process schematics are shown in Figures 2 and 5, and conditions used for the simulations are summarized in Table 4. Note that only one reactor is used in the Union Carbide fluidized bed process, and the solution process contains a significant recycle stream. The catalyst used for these processes is a third-generation Ziegler-Natta catalyst for ethylene polymerization such as $TiCl_4/MgCl_2$. Although, in general, different comonomers can be used for the production of ethylene copolymers, we only consider butene-1 as the comonomer in this study.

The grade change consists of an increase in density from approximately 920 to 935 kg/m^3 and a decrease in number average molecular weight from approximately 25,000 to 15,000. This requires an adaption of both comonomer and hydrogen concentration simultaneously. This transition is somewhat easier because we are adding hydrogen rather than trying to remove it.

For the gas-phase fluidized bed four different strategies are considered:

- *Strategy A*: base
- *Strategy D*: quick venting + overshoot
- *Strategy E*: quick venting + overshoot + bed deinventorying
- *Strategy F*: overshoot + bed deinventorying

Figures 17 and 18 show the transition of the density and the number average molecular weight. For the fluidized bed, venting is considered in this case to adapt the monomer to comonomer ratio as fast as possible. In Figure 17 the advantage of venting on the density transition is shown. It is obvious that even in the base case the density transition is reasonably fast compared to the molecular weight transition. Since this ratio is not really transition time determining, venting is not a required nor recommended strategy. Figure 18 shows that strategies D, E and F show a faster response for the transition of the molecular weight because of faster adaption of the monomer to hydrogen ratio. It is clear that strategy F gives the fastest response because hydrogen can be fed rapidly to reach

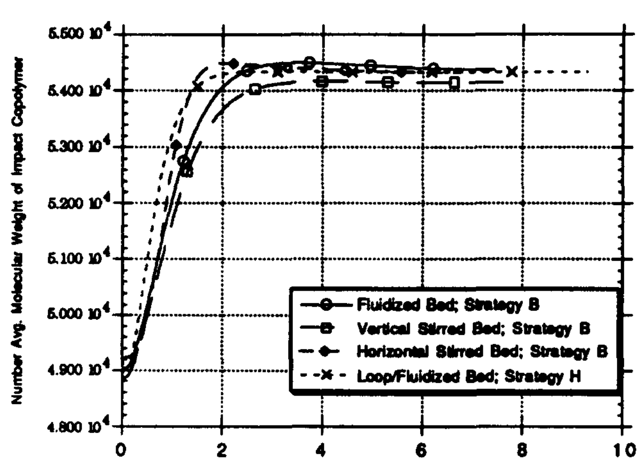

Figure 15. Grade change in molecular weight of polypropylene copolymer.

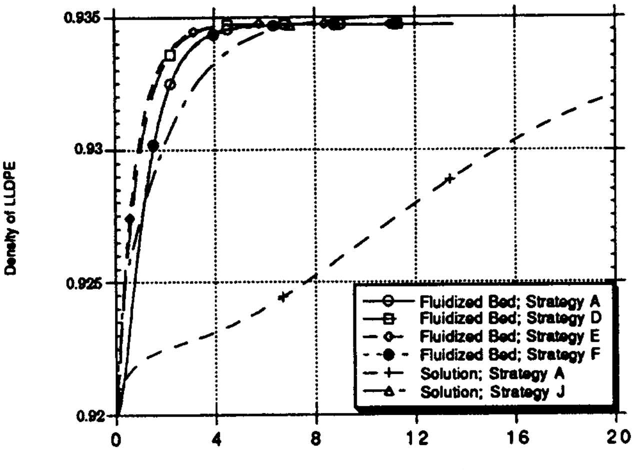

Figure 17. Grade change in density of LLDPE for both fluidized bed and solution process.

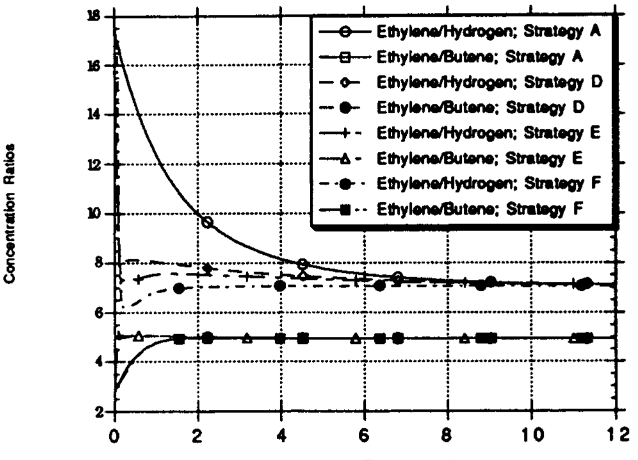

Figure 19. Concentration ratios during grade transition for fluidized bed gas phase.

the proper final level without imparting any disturbances caused by venting such as in strategies D and E. The gas-phase compositions during the transients are shown in Figure 19.

Figure 20 shows the advantage of deinventorying the polymer bed just before the grade transition. The savings in off-spec percentage with strategy D is not more than 15% from the base case, whereas the savings with strategy F is nearly 50%. This emphasizes the importance of residence time distribution and polymer holdup on the off-spec produced.

There is another advantage in deinventorying the bed. Because there is often a significant amount of diluent, monomer and hydrogen present in the voids and sorbed into the polymer (particularly for heavier components), deinventorying the bed can help speed up the composition changes during the grade transition.

For the solution process, two different strategies are considered:

- *Strategy A*: base
- *Strategy J*: lower recycle + overshoot

It can be seen from Figures 17 and 18 that the base case transition for the solution process is very slow in terms of the number of residence times required. The reason for this is that most of the comonomer which exits the reactor is flashed in the separator and recycled back to the reactor in order to obtain a high polymer weight fraction in the heavy fraction leaving the separator.

The grade transition can be sped up by reducing the amount of recycled monomer and comonomer thereby decreasing the weight fraction of polymer in the product stream. This strategy relies on downstream processing to handle the increase in the amount of solvent and monomers that have to be removed. The change in recycle rate appears to have no effect on the polymer properties or production rate. Therefore, this change can take place before the grade transition is started as was done in this simulation.

At the start of the transition itself, an overshoot strategy was used for the first 100 seconds. The hydrogen concentration was increased to twice the value that was needed for the new steady state, and the comonomer was not fed at all. After 100 s, the feed stream was set to the concentrations for the new product steady state. The benefit of the overshoot strategy is

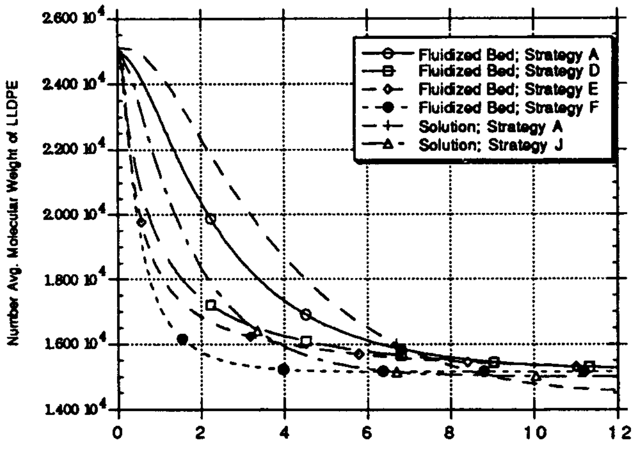

Figure 18. Grade change in molecular weight of LLDPE for both fluidized bed and solution process.

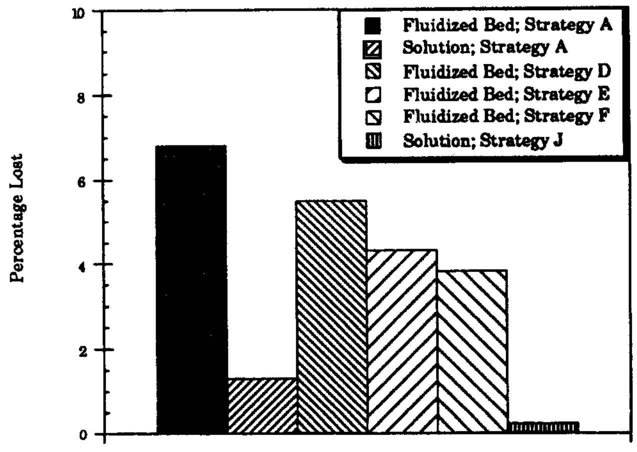

Figure 20. Percent off-spec product based on 2,000 ton of product within specification (±500 M_n).

Scaled to a production level of 12.6 ton/h for both processes.

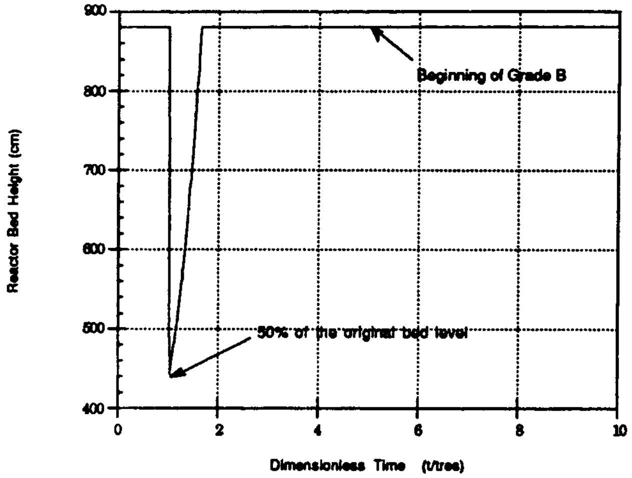

Figure 21. Change in reactor bed height during rapid polymer inventory discharge for EPR fluidized bed process.

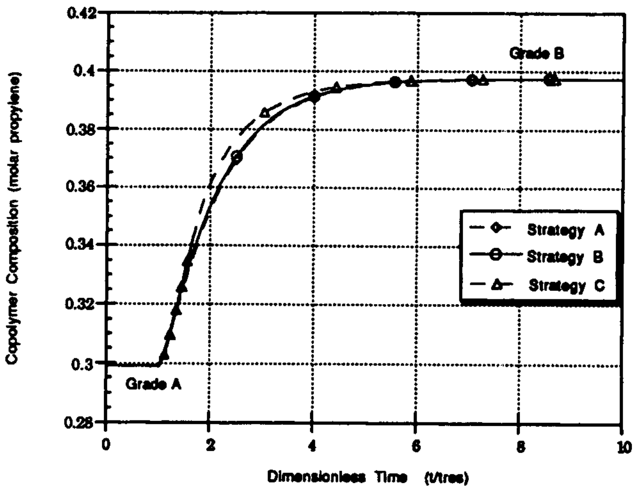

Figure 23. Grade change in copolymer composition for EPR fluidized bed process.

evident in the polymer density, Figure 17. The density changes rapidly at first and then slows when comonomer is introduced into the feed stream again.

Figure 20 shows the benefit of reducing the recycle rate. The amount of off-spec product is reduced by 83%. Figure 20 also shows the great advantage of the short residence time solution process over the much longer residence time fluidized bed. Even in the base case, the solution process creates much less off-spec product than the best fluidized bed transition.

Ethylene-propylene rubber

Grade transitions for EPR production are considered in a gas-phase fluidized bed with conditions in Table 4, (Rifi et al., 1990; Rhee et al., 1991). The catalyst used for this process is assumed to be a modern vanadium catalyst. A grade change in which the propylene content of the polymer changes from 30 to 40 mol% is carried out. Three different policies are considered:

- *Strategy A*: base
- *Strategy B*: quick venting
- *Strategy C*: bed deinventorying

The details of the deinventorying strategy are shown in Figures 21 and 22. The simulation results in Figures 23 and 24 show that all policies result in a rapid change in the gas-phase monomer concentration (cf. Figure 24), so that the speed of the grade transition is about the same for each strategy. This is due in part to the fact that monomer feed is used to control pressure in the reactor. For strategies A and B, the off-spec product losses (based on operation for 50 residence times before beginning the grade transition) are 8.7%. The bed reduction strategy C has the advantage that it recovers 50% of the bed volume consisting of grade A material, and thus the total off-spec product produced is about 25% less than with the other two strategies.

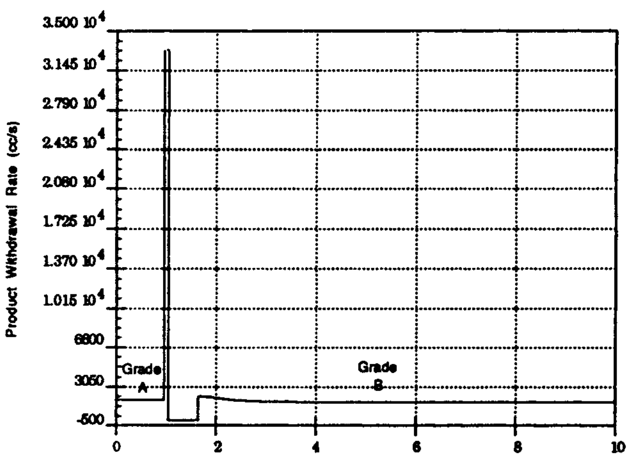

Figure 22. Discharge profile for the rapid polymer bed discharge for EPR fluidized bed process.

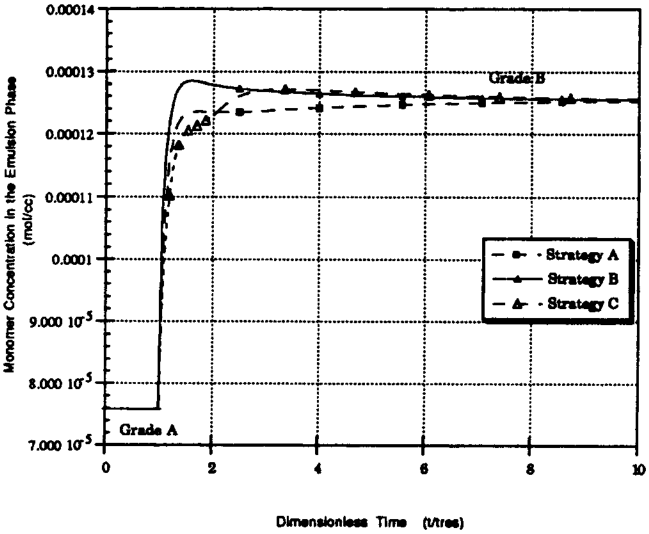

Figure 24. Monomer concentration profiles during grade transition of EPR in a fluidized bed process.

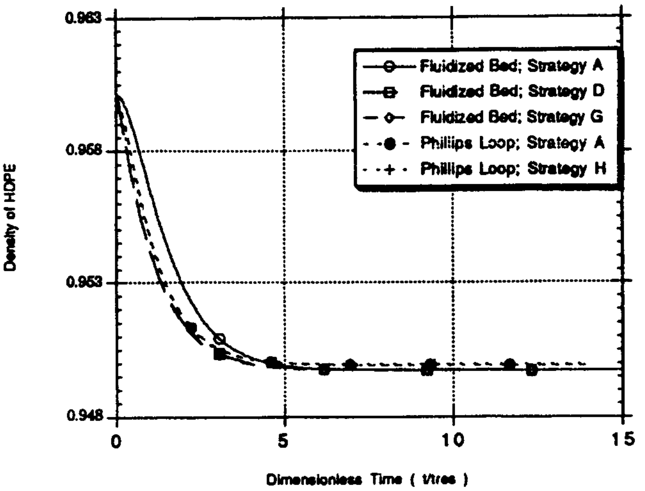

Figure 25. Grade change in density of HDPE for both fluidized bed and slurry loop process.

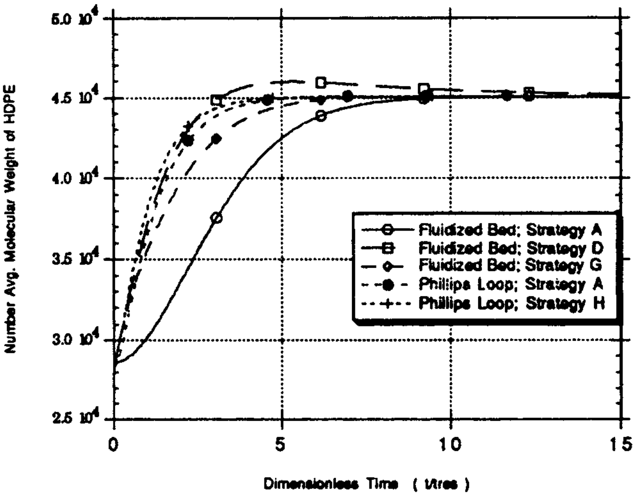

Figure 26. Grade change in molecular weight of HDPE for both fluidized bed and slurry loop process.

High-density polyethylene

In this section, the grade transition of two different processes for the production of high-density polyethylene with a small amount of butene-1 comonomer are considered in the following processes:

- Gas-phase fluidized bed (such as UCC)
- Liquid slurry loop (such as Phillips)

For both processes, a chromium-based catalyst is assumed and the conditions used for the simulation are given in Table 5. The process schematics are shown in Figures 2 and 6. Again note that only one fluidized bed reactor and one loop reactor are used for the two processes, respectively.

We consider a grade change consisting of an increase in number average molecular weight from approximately 28,500 to 45,000 and a decrease of density from approximately 960 to 950 kg/m^3. As for the linear low-density polyethylene case, both comonomer and hydrogen concentration must be adjusted to carry out this grade transition. In actual practice with some HDPE catalysts, the H_2 response is not strong enough to achieve the desired grade transitions so that the reactor temperature is changed as well during a transition. In these examples, however, the H_2 response was assumed adequate and the reactor temperature was maintained constant.

Strategies considered for the fluidized bed include:

- *Strategy A*: base
- *Strategy D*: quick venting + overshoot
- *Strategy G*: quick venting + overshoot + nitrogen overshoot

For the slurry loop:

- *Strategy A*: base
- *Strategy H*: loop low recycle

Figures 25 and 26 illustrate the transition for density and number average molecular weight. For the density, no significant differences are shown by using different strategies. This is due to the fact that both monomer and comonomer are significantly consumed by reaction so that the monomer to comonomer ratio adapts very quickly without special measures. The transition in number average molecular weight shows some sizable differences for different strategies. The base fluidized-bed strategy shows a very slow grade transition because of the large gas inventory in the disengagement zone. Because the consumption of hydrogen is very low, the only way for a fast adaption of the hydrogen level is by flushing hydrogen from the system. This is illustrated both in strategies D and G.

Strategy D for the fluidized bed as shown in Figure 26 includes venting of the reactor during the first 10 minutes to flush the hydrogen from the system as fast as possible. Simultaneously, an overshoot of comonomer is fed in this same period of time to reach the proper butene-1 concentration in the reactor. In this case, we see a rapid transition to the new level for the number average molecular weight because the required ethylene to hydrogen ratio in the gas is achieved rather rapidly. However, the number average molecular weight is slightly overshooting and settles slowly to the new level. This is a result of the ethylene concentration profile during this grade transition. Because of venting the reactor and the fact that the pressure is controlled by the fresh ethylene feed, the ethylene concentration increases in the beginning and decreases very slowly because no extra efforts are made to hasten the decrease of the ethylene concentration to the new level (see Figure 27). To prevent this behavior an oversupply of nitrogen can be fed to the reactor during a certain time. The result of this is shown in Figure 26 for the nitrogen strategy. In Figures 27 and 28, the concentration profiles of ethylene and nitrogen are shown for the three different strategies. One has to bear in mind that the nitrogen strategy is not optimized and a further decrease of off-spec product may be realized with further optimization.

For the slurry loop process, the transition of the number average molecular weight is already reasonably fast without any special efforts. Because there is no gaseous hydrogen inventory in the reactor, the ethylene to hydrogen ratio responds nearly as fast as the ethylene to butene-1 ratio. It is possible to decrease the grade transition time by lowering the recycle ratio in the loop in order to narrow the residence time distri-

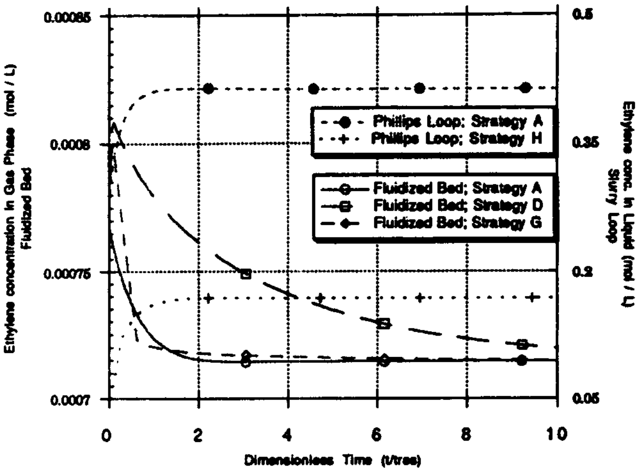

Figure 27. Ethylene concentration profiles during grade transition of HDPE in fluidized bed and Phillips loop.

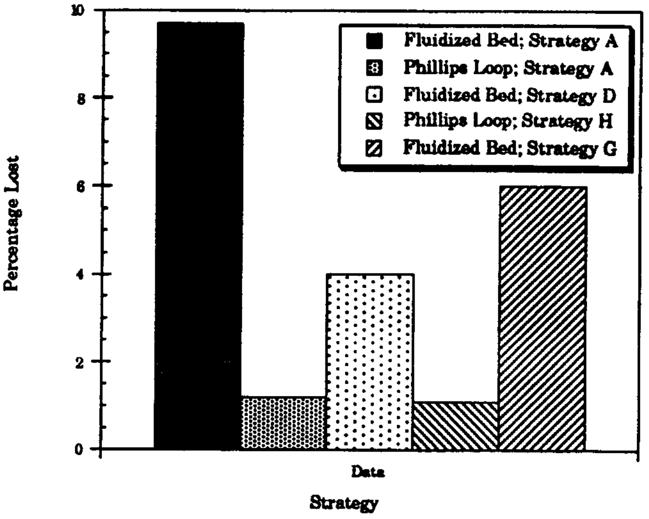

Figure 29. Percent off-spec product based on 2,000 ton of product within specification.

Scaled to a production capacity for both processes of 12.1 ton/h (±1,000 M_n).

bution (strategy H). One has to bear in mind, however, that the residence time for the fluidized bed will be approximately three times the residence time of the slurry loop.

Because the time scale in the figures is normalized by the mean residence time of different processes, the transition in molecular weight for the fast transitions of the slurry loop and the fluidized bed appear very close. However, the influence of the mean residence time is expressed in the off-spec material, as shown in Figure 29. Here it is clear that the off-spec for the fluidized bed will be approximately three times as high as the off-spec for the slurry loop. This emphasizes that the loop is more suitable for product slates with shorter run lengths than the fluidized bed.

Summary

Two important objectives for conducting efficient grade transitions are discussed in this article: minimizing the transient time between reactor grades and minimizing the production of off-spec product. Scheduling of the product slate and optimizing the run lengths of each grade are decisions that must consider prevailing economic factors in addition to process concerns. Optimization at this level is beyond the scope of this article.

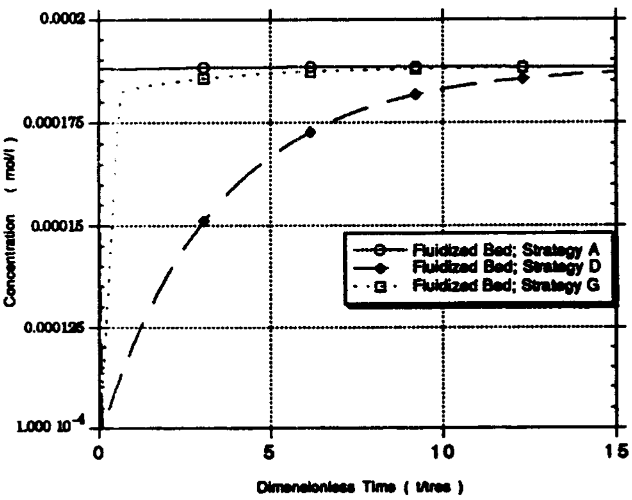

Figure 28. Nitrogen concentration profiles during grade transition of HDPE in fluidized bed.

The most important parameters that determine the grade transition performance of a process are reactor design, residence time, runtime per batch, and residence time distribution of the polymer, gas and/or solution phase. A reactor configuration that approximates plug flow will naturally achieve efficient transitions between grades. The loop reactor illustrates this effect at low recycle rates. The importance of the residence time distribution in all of the reactor phases has been illustrated. For example, the AMOCO/Chisso horizontal stirred bed reactor has a residence time distribution closer to plug flow for the polymer particle phase. However, the gas phase is expected to act as a fully backmixed CSTR, for the BASF vertical stirred bed reactor. To make use of the narrow polymer-phase residence time distribution in the AMOCO/Chisso reactor, additional efforts are necessary to eliminate the gas-phase RTD as the transition-determining step. Increasing product molecular weight has been used to illustrate this concept. One such option described here is by rapidly venting the reactor gas to reduce the hydrogen level. Practically implementing such a scheme must consider factors such as environmental (venting/flaring), economic (monomer cost) and process (capacity). It should be noted that the converse transition (decreasing molecular weight) does not present the same challenges, since this strategy involves increasing the hydrogen level in the reactor.

Difference in process residence time leads to different runtime and product slate strategies. The Phillips loop reactor for the production of HDPE has a lower residence time than the UCC fluidized bed reactor, making the Phillips process more suitable for smaller campaigns per product. However, the fluidized bed process has the flexibility of deinventorying the polymer bed prior to commencing the grade, thereby resulting in additional savings in off-spec product. This strategy has been practiced by some fluidized bed operators and can reduce the off-spec by over 25%. It is not known if a similar strategy is in use in the horizontal and vertical stirred bed technology.

One must always bear in mind that all processes contain inherent and unique constraints that cannot be adequately addressed here. For instance, undersized equipment, lack of instrumentation, and venting capacity may limit implementation of a venting strategy for molecular weight control. Additionally, such complex grade changes may be difficult to coordinate or control. As polymerization processes become more integrated through the use of central computer control, grade transition strategies that were once too logistically onerous may become realistic.

It has been shown that POLYRED is a valuable tool for studying grade transition strategies for polyolefin processes. These studies provide important insight into process operation limitations and suggest process design and control changes to minimize the production of off-spec product or grade transition time.

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