OPTIMAL GRADE TRANSITIONS FOR POLYETHYLENE REACTORS

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Abstract: In fluidized-bed gas-phase polymerization reactors, several grades of polyethylene are produced in the same equipment by changing the operating conditions. Transitions between the different grades are rather slow and results in production of a considerable amount of off-specification polymer. In this paper, the problems of minimizing the transition time and the amount of off-spec material are considered. It is shown that, in most cases, both the optimal steady-state operation and the optimal grade transitions are determined by operational and process constraints.

Keywords: Polymerization, Polyethylene, Grade transition, Dynamic optimization.

1. INTRODUCTION

Polyethylene is widely used today in a multitude of products and is produced continuously in gas-phase fluidized-bed reactors (Choi and Ray, 1985). The variety of polyethylene products call for the production of various polymer grades, which can be accomplished by changing the operating conditions of the reactor. Often, a considerable amount of off-specification polymer is produced during grade transitions (Debling *et al.*, 1994). The goal of this work is to analyze and characterize the grade transition problem from the point of view of minimizing the transition time or the amount of off-spec polymer.

The grade transition problem has been studied extensively. Debling *et al.* (1994) tested different grade transition operations using the simulation package POLYRED. McAuley and MacGregor (1992) and Wang *et al.* (2000) calculated optimal grade transition strategies in a gas-phase fluidized-bed reactor by applying the control vector parameterization (CVP) method to approximate each manipulated variable profile by a series of ramps. Takeda and Ray (1999) also used the CVP method to find optimal grade transitions for a slurry-phase loop reactor. However, in all of the aforementioned works, the cost function that is optimized corresponds to the integral squared error from a pre-defined transition trajectory and not to an economic objective. In this work, the optimal grade transition problem will be formulated using either the transition time or the amount of off-spec material as the economic objective function. Another important aspect will be to interpret the various intervals that constitute the optimal solution in terms of the objectives and the constraints of the optimization problem.

The paper is organized as follows. Section 2 provides a brief description of the process and a simplified mathematical model. In Section 3, various grades are defined and the steady-state operating points that maximize production are computed. In Section 4, the optimal grade transition problem is cast into a dynamic optimization framework, and the optimization results are discussed. Finally, conclusions are drawn in Section 5.

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2. PROCESS DESCRIPTION

In this study, the polymerization of ethylene in a fluidized-bed reactor with a heterogeneous Ziegler-Natta catalyst is considered (Choi and Ray, 1985; Kiparissides, 1996). A schematic diagram of the reactor system is shown in Figure 1. Ethylene, hydrogen, nitrogen (inert), and catalyst are fed continuously to the reactor. The gas phase consisting of ethylene, hydrogen and nitrogen provides the fluidization of the polymer bed and transports heat out of the reactor through a recycling system. A compressor pumps the recycle gases through a heat exchanger and back into the bottom of the reactor. The fresh feeds are mixed with the recycle stream before entering the reactor. The single pass conversion of ethylene in the reactor is usually low ($1-4\%$) and hence the recycle stream is much larger than the inflow of fresh feeds. Excessive pressure and impurities are removed from the system in a bleed stream at the top of the reactor. Fluidized polymer product is removed from the base of the reactor through a discharge valve. The rate at which the product is removed is adjusted by a bed-level controller that keeps the bed level or, equivalently, the polymer mass in the reactor at the desired set point.

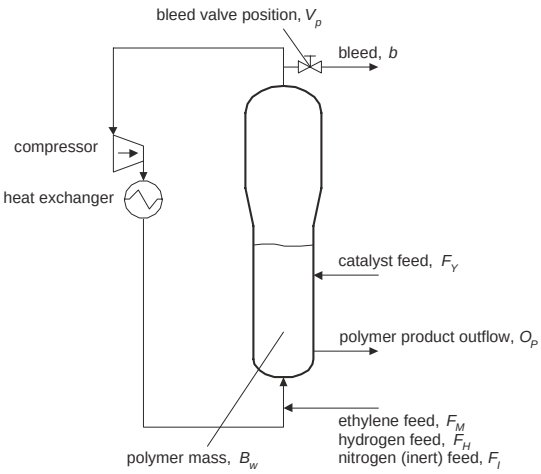

Fig. 1. Gas-phase polyethylene reactor.

A simplified first-principles model (McAuley *et al.*, 1995; McAuley and MacGregor, 1991) of a fluidized-bed polyethylene reactor can be derived under the following assumptions: (i) The gas and solid phases in the fluidized bed are well mixed; (ii) The temperature in the reactor is uniform and perfectly controlled at its set point; (iii) The time lag associated with the recycle flow through the heat exchanger and recycle lines can be neglected; (iv) The feed rates and valve positions can be changed instantaneously. The balance equations read:

$$V_g \frac{d[H_2]}{dt} = \frac{F_H}{m_{wH}} - b[H_2] \tag{1}$$

$$V_g \frac{d[I]}{dt} = \frac{F_I}{m_{wI}} - b[I] \tag{2}$$

$$V_g \frac{d[M]}{dt} = \frac{F_M}{m_{wM}} - b[M] - k_p Y[M] \tag{3}$$

$$\frac{dY}{dt} = F_Y - \frac{O_p Y}{B_w} - k_d Y - k_f [H_2] Y + \frac{k_h k_f B_w [H_2] Y}{k_h B_w + k_p m_{wM} Y} \tag{4}$$

$$\frac{dB_w}{dt} = k_p [M] Y m_{wM} - O_p \tag{5}$$

where $[H_2]$, $[I]$ and $[M]$ are the molar concentrations of hydrogen, nitrogen (inert) and monomer, respectively. Y is the number of moles of active catalyst sites in the bed. F_H, F_I, F_M and F_Y are the fresh feeds of hydrogen, nitrogen, ethylene and catalyst, respectively. b is the pressure-dependent volumetric bleed rate at the top of the reactor, and V_g the volume of the gas phase. B_w denotes the polymer mass in the reactor bed, and O_p is the outflow rate of polymer product from the reactor. m_{wi} are the molecular weights of the different species, $i = \{H, I, M\}$. k_p is the reaction propagation constant, k_h the ethylene site reactivation constant, k_d and k_f the deactivation constants for the catalyst and hydrogen sites, respectively.

The pressure-dependent bleed rate is set via the bleed valve position, V_p:

$$P = ([M] + [H_2] + [I])\, RT \quad [atm] \tag{6}$$

$$b = \frac{RT}{P} V_p C_v \sqrt{P - P_v} \quad [m^3/h] \tag{7}$$

where P is the pressure of the gas phase in the reactor, T the temperature, C_v the valve coefficient, and R the gas constant.

The specification of polyolefin products is often characterized in terms of the melt index number, i.e. the amount of melted polymer that can be squeezed through a standard orifice in 10 minutes. It is an inverse measurement of viscosity that depends on the molecular-weight distribution, temperature, and the shear rate. The instantaneous and cumulative melt indices, MI_i and MI_c, are calculated as:

$$MI_i = k_T \left(k_1 + k_2 \frac{[H_2]}{[M]} \right)^{3.5} \tag{8}$$

$$\frac{d\left(MI_c^{-\frac{1}{3.5}}\right)}{dt} = \frac{1}{\tau} \left(MI_i^{-\frac{1}{3.5}} - MI_c^{-\frac{1}{3.5}} \right) \tag{9}$$

where $\tau = \frac{B_w}{k_p [M] Y m_{wM}}$ is the solid-phase residence time and thus the time constant for the cumulative melt index MI_c. k_T is the chain transfer rate

constant, and k_1 and k_2 are melt index constants. The distinction between the instantaneous and cumulative melt indices is necessary since the polymer chains are produced very quickly compared to the residence time of the polymer in the reactor. The numerical values of the model parameters and the operating conditions used in this study are given in Table 1.

Parameter	**Value**
$C_v(atm^{-0.5}kmol/h)$	27
k_1	0.4
k_2	0.33
$k_d(h^{-1})$	0
$k_f(m^3/kmolh)$	316.8
$k_h(m^3/kmolh)$	3600
$k_p(m^3/kmolh)$	306000
k_T	0.166
$m_{wM}(kg/kmol)$	28.05
$m_{wH}(kg/kmol)$	2.016
$m_{wI}(kg/kmol)$	28.00
$R(atm\ m^3/kmolK)$	0.0821
$P_v(atm)$	17
$T(K)$	360
$V_g(m^3)$	500

Table 1. Model parameters and operating conditions.

3. STATIC OPTIMIZATION OF GRADES

During steady-state production of polyethylene, the goal is to maximize the outflow rate of polymer while meeting operational and safety requirements. The optimization problem can be formulated mathematically as follows:

$$\begin{aligned} \max_{F_i, O_p, V_p} \quad & O_p \qquad (10) \\ s.t. \quad & \text{r.h.s of equations (1)-(5)} = 0 \\ & \text{equations (6)-(9)} \\ & MI_c = MI_{c,ref} \\ & B_w = B_{w,ref} \\ & P_{\min} \leq P \leq P_{\max} \\ & F_{i,\min} \leq F_i \leq F_{i,\max}\ , i \in \{H, I, M, Y\} \\ & V_{p,\min} \leq V_p \leq V_{p,\max} \\ & O_{p,\min} \leq O_p \leq O_{p,\max} \end{aligned}$$

The optimal operating conditions for two grades (A and B) are shown in Table 2 along with the values of the upper and lower bounds used in Problem (10). Though, in principle, V_p can be manipulated between 0 and 1, industrially it is preferable to have a non-zero bleed at steady state to handle impurities. So, $V_{p,\min} = 0.5$ is used here.

Clearly, increasing F_M increases the production of polyethylene, and thus F_M is maximum. The pressure is on its lower bound so as to minimize the waste of monomer through the bleed, which fixes F_I. F_Y is maximum to increase productivity, F_H is determined from the melt index requirement, O_p is set to keep the polymer mass at its reference value, and the bleed rate V_p is minimum. Thus, the six decision variables are determined by six active constraints, an indication that the objective function exhibits no curvature.

4. DYNAMIC OPTIMIZATION OF GRADE TRANSITIONS

4.1 *Grade Belt*

Before addressing the dynamic optimization problem, it is important to introduce the concept of a grade belt. In practice, it is common to specify a polyethylene grade as a range of acceptable values around the desired nominal value. This range corresponds to a grade belt for the cumulative melt index: $(1-\gamma)MI_{c,ref} \leq MI_c \leq (1+\gamma)MI_{c,ref}$, with γ a specified parameter (here, $\gamma = 0.2$).

The time at which MI_c enters the desired grade belt is denoted by t_{belt}. Through the definition of the sign function s:

$$s = \begin{cases} 1 & \text{for increasing } MI_c,\ A \rightarrow B \\ -1 & \text{for decreasing } MI_c,\ B \rightarrow A \end{cases} \qquad (11)$$

t_{belt} is defined as the time for which

$$MI_c(t_{belt}) = (1 - s\gamma)\, MI_{c,ref} \qquad (12)$$

4.2 *Formulation of the Optimization Problem*

The optimization is carried out under the following constraints:

- Reactor operation must satisfy safety and operational requirements. In contrast to the static optimization problem, the polymer mass is allowed to vary within bounds.
- The instantaneous melt index should not go past the exterior limit of the grade belt, $sMI_i(t) < s(1+s\gamma)MI_{c,ref}$.

The optimization of two different objective functions is considered:

(1) Minimization of the time needed to get to the grade belt, i.e. $J_{time} = t_{belt}$.
(2) Minimization of the amount of off-spec material during grade transition, i.e. $J_{off} = \int_0^{t_{belt}} O_p dt$.

It is common practice not to manipulate the monomer and inert feed rates. Thus, throughout the transition, F_M is kept at its upper bound and F_I at its final steady-state value. Among the other decision variables, two sets of inputs are considered:

	Lower Bound	**A**	**B**	Upper Bound	Active Constraint
$MI_{c,ref}$ $(g/10min)$		0.009	0.09		
$B_{w,ref}$ $(10^3 kg)$		70	70		
P (atm)	20	20	20	25	
F_H (kg/h)	0	1.1	15	70	$MI_{c,ref}$
F_I (kg/h)	0	495	281	500	$P_{\min}$
F_M $(10^3 kg/h)$	0	30	30	30	$F_{M,\max}$
F_Y $(10^{-3} kmol/h)$	0	10	10	10	$F_{Y,\max}$
V_p	0.5	0.5	0.5	1	$V_{p,\min}$
O_p $(10^3 kg/h)$	21	29.86	29.84	39	$B_{w,ref}$

Table 2. Optimal operating conditions and active constraints for grades A and B, as well as upper and lower bounds used in Problem (10).

(1) $\mathcal{U}_{feed} = \{F_Y, F_H\}$ - only the feed rates are manipulated,
(2) $\mathcal{U}_{all} = \{F_Y, F_H, O_p, V_p\}$ - the outflow and bleed rates are also adjusted.

The four problems $\Big((J_{time}, \mathcal{U}_{feed}),\ (J_{off}, \mathcal{U}_{feed}),\ (J_{time}, \mathcal{U}_{all}),\ (J_{off}, \mathcal{U}_{all})\Big)$ are studied for both transitions $A \to B$ and $B \to A$. The optimization problems can be stated mathematically as follows:

$$\begin{aligned} \min_{u(t), t_{belt}} \quad & J_{time} \text{ or } J_{off} \qquad (13) \\ s.t. \quad & (1) - (9) \\ & MI_c(t_{belt}) = (1 - s\gamma)\, MI_{c,ref} \\ & sMI_i(t) \le s(1 + s\gamma)\, MI_{c,ref} \\ & u_{\min} \le u(t) \le u_{\max}\ , u \in \mathcal{U}_{feed} \text{ or } \mathcal{U}_{all} \\ & P_{\min} \le P(t) \le P_{\max} \\ & B_{w,\min} \le B_w(t) \le B_{w,\max} \end{aligned}$$

Parameter	**Min**	**Max**
$B_w (10^3 kg)$	56	84
V_p	0	1

Table 3. Additional bounds used in the dynamic optimization.

The bounds are given in Tables 2 and 3. Only the problem of reaching the grade belt is detailed here. Once the system is inside the grade belt, though the material that is produced is acceptable, the solution is not necessarily optimal in terms of the production rate. Further transition to the optimal operating point via tracking is required, but this is not addressed in this paper.

4.3 *Optimization Results*

The numerical approach is described elsewhere (Gisnas, 2002) and is not given here.

Solution with $\mathcal{U}_{feed} = \{F_Y, F_H\}$

For the input set $\mathcal{U}_{feed}$, the optimal solutions are identical for both objective functions J_{time} and J_{off}. The structure of the solution for the two transitions is discussed next:

- *Transition $A \to B$:* As shown in Figure 2, the optimal solution consists of two intervals. Initially, both the hydrogen and catalyst feed rates are maximum to increase $[H_2]$ and thus MI_i as quickly as possible (8). Once MI_i reaches the upper limit of the grade belt, F_H is reduced to keep MI_i on that limit until MI_c is inside the grade belt.
- *Transition $B \to A$:* The optimal solution in this case also consists of two intervals (Figure 3). Initially, the hydrogen and catalyst feed rates are minimum to decrease $[H_2]$ and the consumption of monomer, respectively, thereby allowing MI_i to decrease rapidly. This, however, increases $[M]$ and with it also the pressure. Once the pressure limit is reached, catalyst is added to promote the reaction, thereby decreasing $[M]$ and keeping the pressure at its limit.

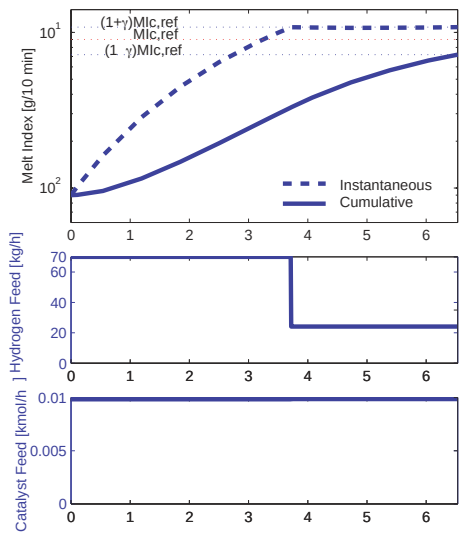

Fig. 2. Optimal profiles for the transition $A \to B$ with the input set $\mathcal{U}_{feed} = \{F_Y, F_H\}$

Solution with $\mathcal{U}_{all} = \{F_Y, F_H, O_p, V_p\}$

For the input set $\mathcal{U}_{all}$, the optimal solution is the same for both objective functions, except for the outflow rate O_p in the transition $A \to B$. The structure of the solution for the two transitions is discussed next:

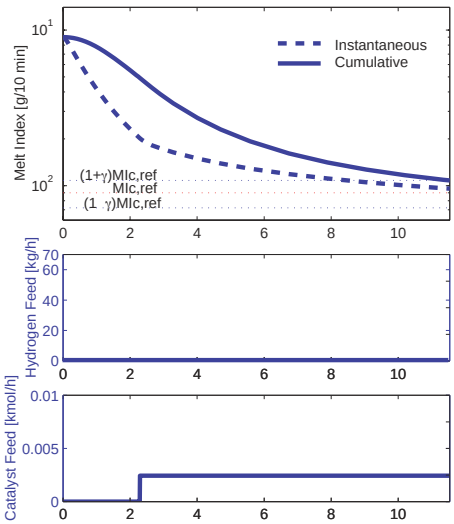

Fig. 3. Optimal profiles for the transition $B \rightarrow A$ with the input set $\mathcal{U}_{feed} = \{F_Y, F_H\}$

- *Transition $A \rightarrow B$:* With the objective function J_{time}, the optimal policy has four intervals (Figure 4). Initially, F_H and F_Y are maximum and the bleed valve is completely closed. At the same time, O_p is maximum to reduce the polymer mass in the reactor as quickly as possible. Once B_w has reached its lower limit, O_p is adjusted to keep it there. The third interval starts when the pressure reaches its upper limit. The bleed valve is then opened to about 60% to keep the pressure there. Eventually, MI_i reaches the upper limit of the grade belt. A reduction of F_H is then necessary to keep MI_i on that limit. Also, the bleed valve opens completely.

  When J_{off} is optimized, the only difference is that the polymer mass is not reduced to its minimum, but to some intermediate compromise-seeking value. The reason for this will be discussed later.
- *Transition $B \rightarrow A$:* As shown in Figure 5, only three intervals are needed. For all three, the bleed valve is fully open and F_H is turned off to reduce $[H_2]$ as quickly as possible. F_Y is set to zero initially in order to reduce MI_i. Furthermore, O_p is maximum to reduce the polymer mass. Once B_w has reached its lower limit, O_p is adjusted to keep it there. The third interval starts when the pressure reaches its upper limit. The pressure is kept there by increasing F_Y.

  In this case, the optimal transitions using J_{time} and J_{off} are identical.

A compromise-seeking interval exists for the manipulated variable O_p in the transition $A \rightarrow B$ when the objective function J_{off} is used. This can be explained as follows. Increasing O_p has two opposing effects on J_{off}: (i) A smaller polymer mass results in a shorter solid-phase residence time and thus quicker transition and less off-spec material; (ii) Removing off-spec material from the reactor to reduce B_w corresponds to a wasted opportunity. If that material had not been removed, it could have been mixed with better quality polymer to produce useful product. A compromise between these two effects is sought through some intermediate value of B_w and a corresponding value of O_p in the $A \rightarrow B$ transition. In the $B \rightarrow A$ transition, however, since the reduction in transition time dominates the loss of material, this compromise does not exist.

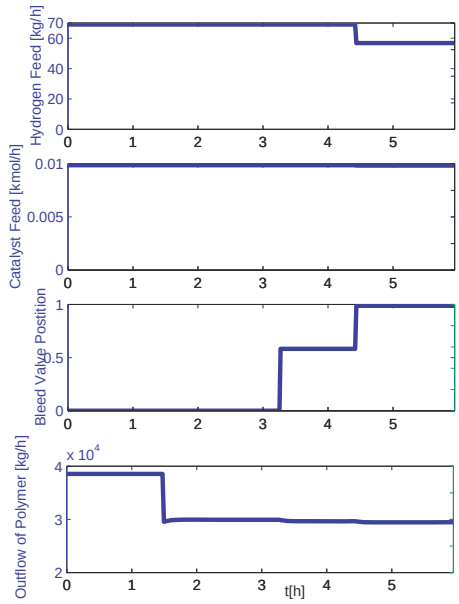

Fig. 4. Optimal profiles for the transition $A \rightarrow B$ with the input set $\mathcal{U}_{all} = \{F_Y, F_H, O_p, V_p\}$

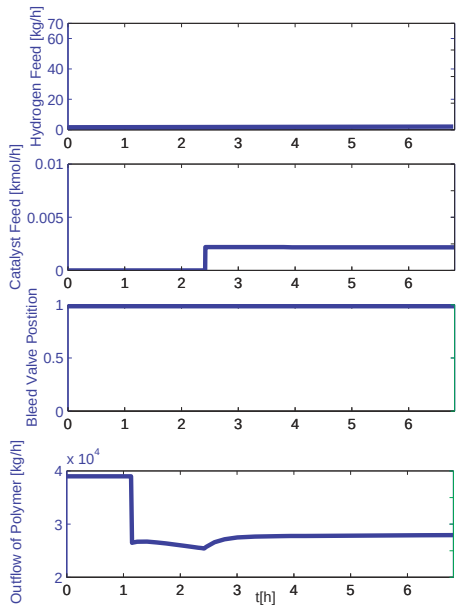

Fig. 5. Optimal profiles for transition $B \rightarrow A$ with the input set $\mathcal{U}_{all} = \{F_Y, F_H, O_p, V_p\}$

4.4 *Summary of the Results*

The results for the transitions $A \rightarrow B$ and $B \rightarrow A$ are summarized in Tables 4 and 5, respectively. For all policies, the times to reach the grade belt and the amounts of off-spec material are compared.

$\mathcal{U}_{feed}$ does a fairly good job for the $A \rightarrow B$ transition. Including V_p and O_p as additional manipulated variables reduces the transition time t_{belt} by less than 10% and the off-spec material by only 2-3%. Also, a comparison of $(J_{time}, \mathcal{U}_{all})$ and $(J_{off}, \mathcal{U}_{all})$ shows that the compromise-seeking value of O_p improves the amount of off-spec material only marginally (by about 1%).

On the other hand, optimization using $\mathcal{U}_{feed}$ does not result in a satisfactory $B \rightarrow A$ transition. This is because there is no simple way of quickly eliminating the hydrogen when only flow rates are used. Thus, opening the bleed valve helps significantly. The improvement using $\mathcal{U}_{all}$ is therefore more than 40% in both transition time and amount of off-spec material.

Policy	$\mathbf{t_{belt}}$	$\int_0^{t_{belt}} \mathbf{O_p dt}$
$(J_{time}, \mathcal{U}_{feed})$	6.53 h	194 $10^3 kg$
$(J_{off}, \mathcal{U}_{feed})$	6.53 h	194 $10^3 kg$
$(J_{time}, \mathcal{U}_{all})$	5.95 h	190 $10^3 kg$
$(J_{off}, \mathcal{U}_{all})$	6.05 h	188 $10^3 kg$

Table 4. Comparison of optimal transition policies for the transition $A \rightarrow B$.

Policy	$\mathbf{t_{belt}}$	$\int_0^{t_{belt}} \mathbf{O_p dt}$
$(J_{time}, \mathcal{U}_{feed})$	11.54 h	333 $10^3 kg$
$(J_{off}, \mathcal{U}_{feed})$	11.54 h	333 $10^3 kg$
$(J_{time}, \mathcal{U}_{all})$	6.81 h	200 $10^3 kg$
$(J_{off}, \mathcal{U}_{all})$	6.81 h	200 $10^3 kg$

Table 5. Comparison of optimal transition policies for the transition $B \rightarrow A$.

5. CONCLUSIONS

Using a tendency model for a gas-phase fluidized-bed reactor, it was possible to show that the optimal steady-state operating conditions are determined by constraints related to the grade specification, the amount of polymer and the pressure in the reactor, and the valve sizes.

Similarly, the optimal grade transition problem is completely determined by process constraints, except for one decision variable in one case (the production rate seeks a compromise when the melt index is increased while trying to minimize the amount of off-spec material). In all other cases, the optimal transition corresponds to a bang-bang type solution.

The next step is to study how this qualitative knowledge about optimal grade transitions can be used for on-line implementation. The effect of model uncertainty and disturbances need to be considered. If concentration measurements in the gas-phase are available, a control scheme that tracks the active constraints using simple feedback control is a promising way to carry out grade transitions (Srinivasan *et al.*, 2003).

ACKNOWLEDGEMENTS

The authors wish to thank Dr. M. Hillestad, Cybernetica AS, Trondheim, Norway, and Dr. T. McKenna, ESCPE-Lyon, France, for their inputs regarding the problem formulation.

6. REFERENCES

Choi, K. Y. and W. H. Ray (1985). The dynamic behaviour of fluidized bed reactors for solid catalysed gas-phase olefin polymerization. *Chem. Eng. Sci.* **40**, 2261–2279.

Debling, J. A., G. C. Han, F. Kuijpers, J. Verburg, J. Zacca and W. H. Ray (1994). Dynamic modeling of product grade transitions for olefin polymerization processes. *AIChE J.* **40**(3), 506–520.

Gisnas, A. (2002). *Optimal grade transitions for polyethylene reactors.* Diploma project, Department of Engineering Cybernetics, Norwegian University of Science and Technology.

Kiparissides, C. (1996). Polymerization reactor modeling: A review of recent developments and future directions. *Chem. Eng. Sci.* **51**(10), 1637–1659.

McAuley, K. B. and J. F. MacGregor (1991). On-line inference of polymer properties in an industrial polyethylene reactor. *AIChE J.* **37**(6), 825–835.

McAuley, K. B. and J. F. MacGregor (1992). Optimal grade transitions in a gas-phase polyethylene reactor. *AIChE J.* **38**(10), 1564–1576.

McAuley, K. B., D. A. Macdonald and J. F. MacGregor (1995). Effects of operating conditions on stability of gas-phase polyethylene reactors. *AIChE J.* **41**(4), 868–879.

Srinivasan, B., D. Bonvin, E. Visser and S. Palanki (2003). Dynamic optimization of batch processes: II. Role of measurements in handling uncertainty. *Comp. Chem. Eng.* **27**, 27–44.

Takeda, M. and W. H. Ray (1999). Optimal grade transition strategies for multistage polyolefin reactors. *AIChE J.* **45**(8), 1776–1793.

Wang, Y., S. Seki, S. Ohyama, K. Akamatsu, M. Ogawa and M. Ohshima (2000). Optimal grade transition control for polymerization reactors. *Comp. Chem. Eng.* **24**, 1555–1561.