

Control of molecular weight distribution of polyethylene in gas-phase fluidized bed reactors

Mohammad Al-haj Ali[†], Emadadeen Ali AbdelHamid Ajbar, and Khalid Alhumaizi

Department of Chemical Engineering, King Saud University, P.O.Box 800, Riyadh 11421, Saudi Arabia
(Received 9 May 2009 • accepted 8 August 2009)

Abstract—This paper presents a feasibility study of the broadening of polyethylene molecular weight distribution produced using a multisite Ziegler-Natta catalyst in a fluidized-bed reactor. A nonlinear model predictive control algorithm, applied to a validated model of the reactor, is used for the on-line control of the *entire* molecular weight distribution of the produced polymer. Control of a target chain-length distribution is achieved by selecting a collection of points in the distribution and using them as set points for the control algorithm. An on-line Kalman filter is used to incorporate infrequent and delayed off-line molecular weight measurements. Through simulation the control algorithm is evaluated, under tracking conditions as well as plant-model mismatch. The results demonstrate that the control algorithm can regulate the entire molecular weight distribution with minimum steady state error. However, the efficiency of this approach is highly dependent on the dynamics of hydrogen inside the reactor.

Key words: Molecular Weight Distribution, Nonlinear Model Predictive Control, Polymerization Reactor Control, Polyethylene, Fluidized-bed Reactor

INTRODUCTION

Polymers are important industrial products with a wide range of applications. The physical and chemical properties of a polymer generally determine its areas of use. Among such characteristics is the molecular weight distribution (MWD), which is considered as one of the fundamental properties of the polymer. The monitoring and control of MWD is therefore important during industrial production. Significant research has been carried out in the literature in the modeling, control and monitoring of polymerization reactors. Excellent reviews can be found, for instance, in references [1-4]. In Table 1 we have summarized some key research contributions in the field. When considering the studies that focus on polyolefins, a number of useful observations could be made from this table. First, it can be noted that most of the available studies in the literature use the weight average molecular weight (M_w) to describe polymer MWD. The molecular weight can be obtained either from gel permeation chromatography (GPC), melt index or intrinsic viscosity measurements, in addition to polydispersity index (PDI). On the other hand, only few researchers used the entire molecular weight distribution in their control studies. The use of M_w and PDI to describe polymer quality is helpful; however, sometimes it is more useful to describe polymer quality by using the entire molecular weight distribution. For instance, in some polymer applications such as paints and paper coatings, it is required to specify the weight distribution accurately [3,5]. Furthermore, the use of molecular weight average can be misleading when the distribution shows bimodalities and/or if it has high molecular weight tails. Moreover, although polydispersity is a useful and convenient measure of the width of polymer molecular weight distribution, the polydispersity value itself does

not contain enough information about a complete differential molecular weight distribution. It is possible that polymers of different chain length distribution can have the same polydispersity value but exhibit significantly different end-use properties. There is therefore a strong incentive to develop control strategies that can handle the complete distribution, and not only pre-specified parameters. The second observation that could be made from Table 1 is that most of the work that was carried out in controlling the entire MWD of the produced polyolefins used a mixture of different metallocenes [6-13] or a hybrid catalyst of Ziegler-Natta and metallocene catalysts in a one stage process [14-16]. The use of a single reactor to produce the desired polymer is a cost-efficient alternative. However, for each polymer grade a sophisticated catalyst has to be developed in order to adjust the amount, the molecular weight distribution, the comonomer incorporation, and the comonomer distribution of both fractions formed in the polymerization reaction. Moreover, the mixture of different catalysts may lead to complex undesirable catalyst interactions and non-reproducible catalyst behavior due to the high variability of the polymerization rate of each catalyst [11,17]. For these reasons, this method is still in the research stage and it may take some time before it can be implemented in industry. It should be noted that different polyolefins grades are currently produced in the industry using reactor cascades, where each reactor is operated at different polymerization conditions (usually hydrogen concentration). This technology is commonly used with Ziegler-Natta catalysts. It has the advantage that only one optimized catalyst is required for the production of various grades. The desired molecular weight distribution and comonomer distribution are designed by the process. However, this method is characterized with high operational costs [23], and the overall process has a low throughput since two serial processes are used [24].

An alternative approach that could be used to control the entire molecular weight distribution may lie in the introduction of varia-

[†]To whom correspondence should be addressed.
E-mail: alhajali@ksu.edu.sa

Table 1. Papers on controlling polymerization reactors

Paper	MON	RT	WN	MV	CV	CS
Al-haj Ali et al. [40]	P	CSTR	S	CTA/JT	MI/C	NLMBC
Atasoy et al. [41]	AN	CSTR	S	CTA	MW	NN PC & NN NARMA-L2
Dunnebie et al. [42]	NM	Plant	S	M/T/C/RM	C/V	EKF/MPC
Kiparssides et al. [43]	MMA	BAT	S	T	NA/WA/MWD/C	PI-PID/EKF
Vicente et al. [44]	S/BA	BAT	S/E	M/C/CTA	MWD/CC	NLMBC
Wang et al. [45]	E	-	S	H/M/C	MI/PR/TP	NLMPC/EKF
Ogawa et al. [46]	E	CSTR	S/E	M/C	MI	CC/OLIS
Ali et al. [47]	E	FBR	S	C/RSM	C/T	NLMPC
Crowley and Choi [48,49]	MMA	BAT	S/E	T	MWD	EKF/MPC
Echevarria et al. [50]	S	BAT	S/E	CTA/M	MWD	NLMBC
Pladis and Kiparssides [51]	E	Autoclave	S	IFR	C/MI	SQDMC

MON: MONomer (Ethylene, Propylene, Methyl MethAcrylate, Styrene, n-Butyl Acrylate, Not Mentioned)

RT: Reactor Type (Continuous Stirred Tank Reactor, BATch, Fluidized Bed Reactor)

WN: Work Nature (Simulation, Experimental)

MV: Manipulated Variables (Hydrogen, Monomer, CoMonomer, Catalyst feed (or Concentration), Temperature, Chain Transfer Agent, Initiator Flow Rate, Recycle Monomer, Jacket Temperature)

CV: Controlled Variables (Melt Index, Number Average molecular weight, Weight Average molecular weight, Molecular Weight Distribution, Conversion, Copolymer Composition, Production Rate, Temperature, Viscosity, Total Pressure, Ratio of Superficial velocity to Minimum fluidization velocity)

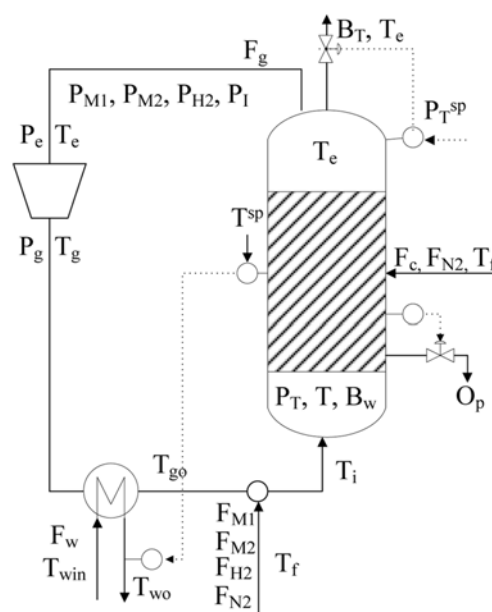
CS: Control Structure (Neural Network, Predictive Control, Nonlinear Auto Regressive Moving Average, Extended Kalman Filter, Proportional-Integral, Proportional-Integral-Derivative, Nonlinear Model-Based, Cascade Control, Online Inferential Scheme, Supervisory Quadratic Dynamic Matrix Controller)

tions in the polymerization conditions, usually in a periodic way, in a single polymerization reactor. The periodic operation of continuous chemical reactors is known to improve the performance of the reacting system [19] and can allow better control of the molecular weight distribution in a single reactor [20-22]. The objective of this work is to carry out a feasibility study to investigate whether the distribution of polyethylene, produced in a *single* fluidized bed reactor, could be broadened through variations of different inlet feeds to the reactor using nonlinear model predictive control (NLMPC) strategy. The “broadening” in this work has to do with the *entire* molecular weight distribution of the produced polymer instead of using only the polydispersity index. To control the whole distribution using NLMPC, a number of representative points in the distribution are selected and used as set points to the controller.

PROCESS MODEL

In fluidized-bed polyethylene reactors the copolymerization of ethylene and -olefin monomers is carried out using a multi-site Ziegler-Natta catalyst. It is assumed that the catalyst consists of three different types of active sites. Each active site produces polymer with molecular weight distribution that can be described by Schulz-Flory distribution. The polyethylene reactor process is depicted in Fig. 1. The process model was developed by McAuley et al. [25] and is given below. This model was chosen because its kinetic parameters were validated against plant data [25]. The various states and parameters of the model are defined in the nomenclature.

$$V_g \frac{dC_{M1}}{dt} = F_{M1} - x_{M1}B_i - R_{M1} \quad (1)$$

**Fig. 1. Schematic of the polyethylene reactor.**

$$V_g \frac{dC_{M2}}{dt} = F_{M2} - x_{M2}B_i - R_{M2} \quad (2)$$

$$V_g \frac{dC_H}{dt} = F_H - x_HB_i - R_H \quad (3)$$

$$V_g \frac{dC_N}{dt} = F_N - x_NB_i \quad (4)$$

$$\frac{dY_c}{dt} = F_c a_c - k_d Y_c - O_p Y_c / B_w \quad (5)$$

$$(M_r C_{p_r} + B_w C_{p_p}) \frac{dT}{dt} = HF + HG - HR - HT - HP \quad (6)$$

$$M_w C_{p_w} \frac{dT_g}{dt} = F_g C_{p_g} (T_{gi} - T_g) + F_w C_{p_w} (T_{wi} - T_{wo}) \quad (7)$$

$$P_i = (C_{M1} + C_{M2} + C_H + C_N) RT \quad (8)$$

$$T_{gi} = \left(\frac{P_i}{P_i + \Delta P} \right) T \quad (9)$$

$$F_w C_{p_w} (T_{wi} - T_{wo}) = 0.5 UA [(T_{wo} + T_{wi}) - (T_{gi} + T_g)] \quad (10)$$

where

$$HF = (F_{M1} C_{p_{M1}} + F_{M2} C_{p_{M2}} + F_H C_{p_H} + F_N C_{p_N}) (T_f - T_{ref}) \quad (11)$$

$$HG = F_g C_{p_g} (T_g - T_{ref}) \quad (12)$$

$$HT = (F_g + B_w) C_{p_g} (T - T_{ref}) \quad (13)$$

$$HP = O_p C_{p_p} (T - T_{ref}) \quad (14)$$

$$HR = M_w R_{M1} \Delta H_r \quad (15)$$

$$O_p = M_{w1} R_{M1} + M_{w2} R_{M2} \quad (16)$$

$$R_{M1} = C_{M1} Y_c k_{p1} e^{-\frac{E}{R} (1/T - 1/T_{ref})} \quad (17)$$

$$R_{M2} = C_{M2} Y_c k_{p2} e^{-\frac{E}{R} (1/T - 1/T_{ref})} \quad (18)$$

$$C_{p_g} = \sum x_i C_{p_i} \quad (19)$$

The model equations listed above are slightly modified from those given by McAuley et al. [25]. For simplicity, the energy balance around the cooler considers the dynamic of the recycle temperature explicitly instead of the heat removal used by McAuley et al. [25]. In due course, the cooling process is modeled as a well mixed system. The thermal effect of the recycle compressor is also included in this model. Note that the partial pressure of the reactants can be calculated directly from the reactant concentrations using the ideal gas law. The steady state operating conditions for the plant are given in Tables 2 and 3. These operating conditions were found by optimization and were discussed elsewhere [26].

1. Molecular Weight Distribution Model

The instantaneous molecular weight distribution for each type

of active sites can be described by Flory-Schulz exponential function [27]:

$$y_j^d = j \cdot q^2 \cdot \exp(-j \cdot q) \quad (20)$$

The overall distribution of the produced polymer can be calculated by the weighted sum of the three distributions as given below:

$$y_{j,ins} = \sum_{i=1}^3 w_i \cdot (y_j^d)_i \quad (21)$$

where $y_{j,ins}$ is the overall instantaneous molecular weight distribution, and w_i is the mass fraction of each site. The molecular weight distribution of the polymer accumulated in the reactor after a certain polymerization time can be calculated using the following equation:

$$\frac{dy_j}{dt} = \frac{O_p \cdot (y_{j,ins} - y_j)}{B_w} \quad (21)$$

Finally, the GPC reading of the MWD is calculated by the following equation:

$$GPC = j \cdot y_j \cdot \ln(10) \quad (22)$$

In the above equations, j is the number of repeating units and q is the chain termination probability. It is defined as the sum of chain-termination rates over the chain propagation rate:

$$q = \frac{k_{tm} + k_{th} X}{k_{tm} + k_{th} X + k_p} \quad (23)$$

X denotes the molar ratio of hydrogen to monomer inside the reactor. This ratio is a crucial parameter to adjust the value of q and consequently the molecular weight distribution, as it is discussed in the results section.

THE ON-LINE NLMPC ALGORITHM

In this work, the structure of the MPC version developed by Ali and Zafriou [28] that utilizes directly the nonlinear model for output prediction is used. A usual MPC formulation solves the following on-line optimization:

$$\min_{\Delta u(t_0), \dots, \Delta u(t_0+M-1)} \sum_{i=1}^P \|f(y(t_{k+i}) - R(t_{k+i}))\|^2 + \sum_{i=1}^M \|\Delta u(t_{k+i-1})\|^2 \quad (24)$$

subject to

Table 2. Steady state operating condition

C_{M1}	297.06 mole/m ³	F_{M1}	131.13 mole/s	Y_c	5.849 mole	T_g	324.7 K
C_{M2}	116.17 mole/m ³	F_{M2}	3.51 mole/s	T	82.7 °C	T_{wo}	308 K
C_H	105.78 mole/m ³	F_H	1.6 mole/s	B_i	10.39 mole/s	T_{wi}	293 K
C_N	166.23 mole/m ³	F_N	2.52 mole/s	F_w	3.11×10^4 mole/s	F_c	2.0 kg/hr

Table 3. Process parameters

B_w	70×10^7 g	ΔH_r	-894 cal/g	k_{p1}	85 L/mole·s	C_{p_H}	7.7 cal/mole·K
C_{p_p}	0.85 cal/g·K	k_d	0 L/s	k_{p2}	3 L/mole·s	$C_{p_{M1}}$	11 cal/mole·K
E	9,000 cal/mole	$M_r C_{p_r}$	1,400 kcal/K	T_f	293 K	C_{p_N}	6.9 cal/mole·K
V_g	500 m ³	F_g	8,500 mole/s	ΔP	3 atm	$C_{p_{M2}}$	24 cal/mole·K
T_{ref}	360 K	UA	1.263×10^5 cal/s·K	a_c	0.548 mole/kg	C_{p_w}	18 cal/mole·K

$$A^T \Delta U(t_k) \leq b \quad (25)$$

For nonlinear MPC, the predicted output, y over the prediction horizon P is obtained by the numerical integration of:

$$\frac{dx}{dt} = f(x, u, t) \quad (26)$$

$$y = g(x) \quad (27)$$

from t_k up to t_{k+P} where x and y represent the states and the output of the model, respectively. The symbol $\|\cdot\|$ denotes the Euclidean norm, k is the sampling instant, Γ and Λ are diagonal weight matrices and $R = [r(k+1) \cdots r(k+P)]^T$ is a vector of the desired output trajectory. $\Delta U(t_k) = [\Delta u(t_k) \cdots \Delta u(t_{k+M-1})]^T$ is a vector of M future changes of the manipulated variable vector u that are to be determined by the on-line optimization. The control horizon (M) and the prediction horizon (P) are used to adjust the speed of the response and hence to stabilize the feedback behavior. Γ is usually used for trade-off between different controlled outputs. The input move suppression, Λ , on the other hand, is used to penalize different inputs and thus to stabilize the feedback response. The objective function (Eq. (24)) is solved on-line to determine the optimum value of $\Delta U(t_k)$. Only the current value of Δu , which is the first element of $\Delta U(t_k)$, is implemented on the plant. At the next sampling instant, the whole procedure is repeated.

To compensate for modeling error and eliminate steady state offset, a regular feedback is incorporated on the output predictions, $y(t_{k+1})$ through an additive disturbance term. Therefore, the output prediction is corrected by adding to it the disturbance estimates. The latter is set equal to the difference between plant and model outputs at present time k as follows:

$$d(k) = y_p(k) - y(k) \quad (28)$$

The disturbance estimate, d is assumed constant over the prediction horizon due to the lack of an explicit means of predicting the disturbance. However, for severe modeling errors, or open-loop unstable processes the regular feedback is not enough to improve the NLMCP response. Hence, state or parameter estimation is necessary to enhance the NLMPC performance in the face of model-plant mismatch. In this work, Kalman filtering (KF) will be incorporated to correct the model state and, thus, to address the robustness issue. Utilization of the NLMPC with KF requires adjusting an additional parameter, σ . More details on the integration of KF with the NLMCP algorithm are given elsewhere [28]. In addition to state estimation by KF, the predicted output will be also corrected by the additive disturbance estimates of Eq. (28).

The main objective of the use of the NLMPC is to control the MWD. It is also necessary to maintain acceptable polymer production rate. Process stability is another important issue which is handled through regulating the total gas pressure and the bed temperature. These two controlled objectives are satisfied using two separate PI control loops. The design and tuning parameters of these loops are given elsewhere [26].

RESULTS AND DISCUSSION

1. Open-loop Analysis

It is well-known that, for conventional transition-metal catalysts,

the specific hydrogen to monomer ratio (X) is manipulated to control the polymer molecular weight. In this paper, different polymer grades are characterized by the corresponding entire molecular weight distribution. When a certain MWD is required, the situation is quite difficult because it requires "mixing" different polymer grades during polymer synthesis. This can be achieved, for instance, by disturbing the polymerization process through moving between two operating conditions for the ratio (X) within certain time duration, i.e., cyclic operation. Because the hydrogen consumption rate for Ziegler-Natta catalyst is low, changing polymer molecular weight distribution is a very slow process, due to the long time it takes for the excess hydrogen to wash out. To accelerate the transition times, two of the strategies used industrially for gas-phase polymerization reactors, namely vent flow increase and manipulated variables over-

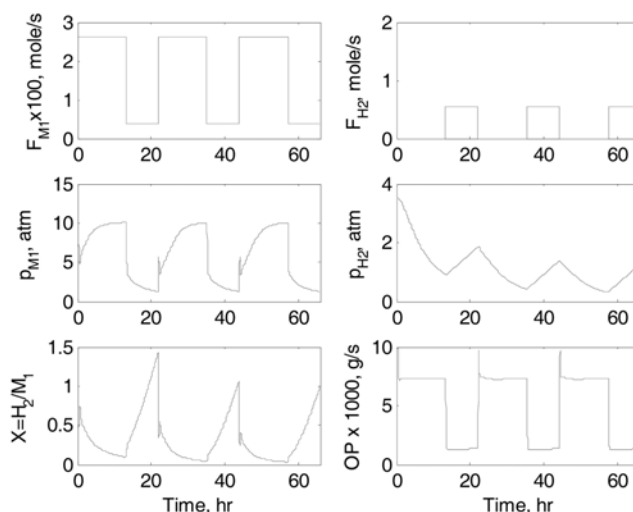


Fig. 2. Input and output sequences for high Mw operating condition.

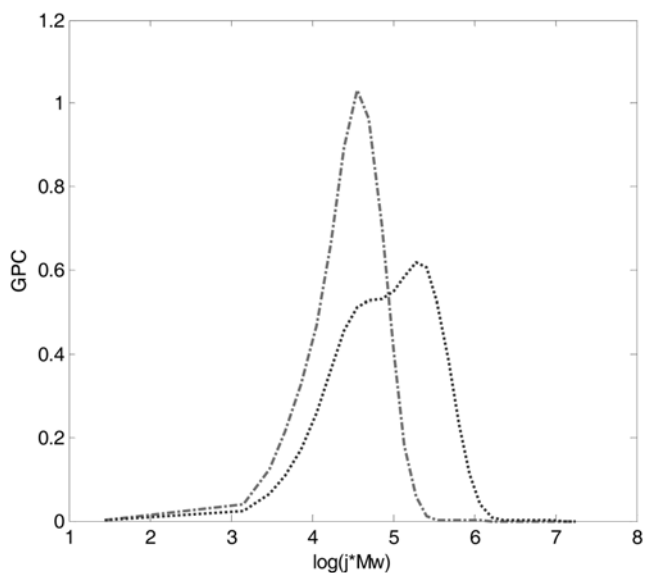


Fig. 3. Molecular weight distribution for input sequence shown in Fig. 2; dash-dot: MWD at initial operating condition, dotted line: MWD at the end of simulation.

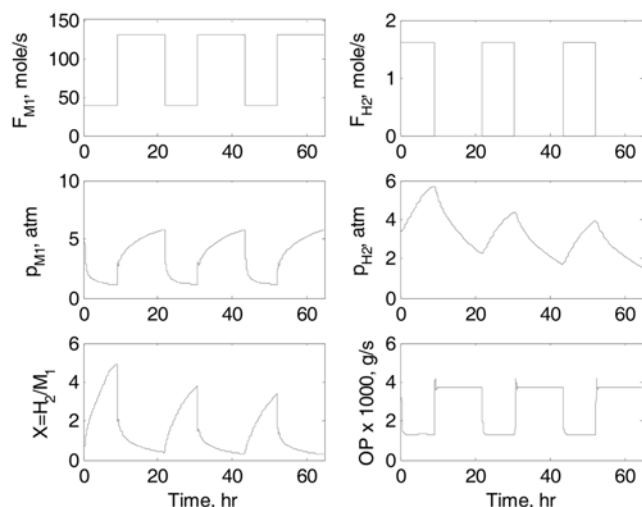


Fig. 4. Input and output sequences for low Mw operating condition.

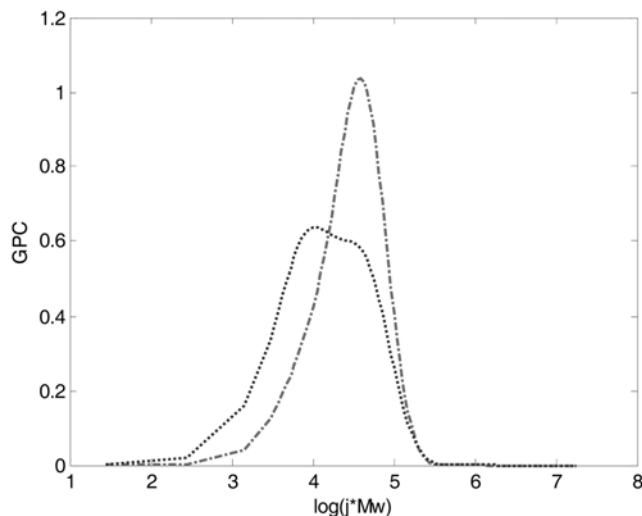


Fig. 5. Molecular weight distribution for input sequence shown in Fig. 4; dash-dot: MWD at initial operating condition, Dashed: MWD at the end of simulation.

shoot [29,30], are used here.

The process is firstly simulated in open-loop mode for periodic operation in the inlet flow rate of hydrogen and monomer. The results are shown in Figs. 2-5. The input sequences in Fig. 2 are designed such that it moves the process towards lower X and consequently higher M_w . The same period is used for hydrogen and monomer feed flow rates, but the pulse width is not the same. Pulse durations and widths are determined by trial-and-error to obtain the broad MWD shown in Fig. 3. The magnitude of the input sequence is set to specific limits. For example, the monomer flow rate is constrained between 40 and 260 mole/s, while the hydrogen flow rate is bounded between 0 and 0.5 mole/s. High upper limit for monomer and low upper limit for hydrogen is chosen to produce minimal X . The lower limit for monomer is set slightly higher than zero to maintain a reasonable production rate. The periodic changes in X result in a broadened MWD as shown by Fig. 3. The use of periodic

operation produces different polymer grades. These grades are blended at the molecular scale which is a lauded advantage of this approach.

It should be noted that in batch reactors, polymer distribution can be broadened by changing hydrogen concentration inside the reactor once [31]. However, this is not sufficient when dealing with continuous reactors. In fact, the broadening of the distribution can only be achieved by varying X periodically during the polymerization reaction. The implementation of periodic operation improves process performance and product properties and this has been the subject of many experimental and theoretical studies [17,20,32-37].

Figs. 4 and 5 show simulations for the case for higher X value. Once again, the duration of the up and down step changes in the feed flow rates is determined by iterations. The magnitude of the input sequence is set to specific limits. For example, the monomer flow rate is limited between 40 and 131 mole/s, while the hydrogen flow rate between 0 and 1.6 mole/s. Low upper limit for monomer and high upper limit for hydrogen were chosen to produce large variations in X . As shown in Fig. 5, a wide MWD is obtained. Obviously, lower average production rate is obtained in this case. Attempts to increase the lower limit of F_{M1} for the sake of higher average production rate are found to distort the shape of the MWD.

It should be mentioned that varying hydrogen flow rate solely can adjust X ; however, hydrogen partial pressure inside the reactor has slow dynamics. This requires an input cycle with long pulse period to affect the MWD. Therefore, varying both monomer and hydrogen flow rates was adopted to speed up the time response of X . For this reason and because the process has wide residence time distribution, designing the duration of the two halves of the input cycle is crucial as mentioned earlier.

2. Closed-loop Analysis

It is worth mentioning that obtaining input trajectories that provide desired MWD is a difficult task since the final polymer quality is sensitive to the value of X and to the mass of the produced polymer. In this sense, maintaining the desired MWD during process operation is even more challenging. In the presence of model-plant mismatch and/or when unmeasured disturbances enter the plant, the situation becomes more complex. For this purpose, we will test the effectiveness of nonlinear model predictive control to handle this

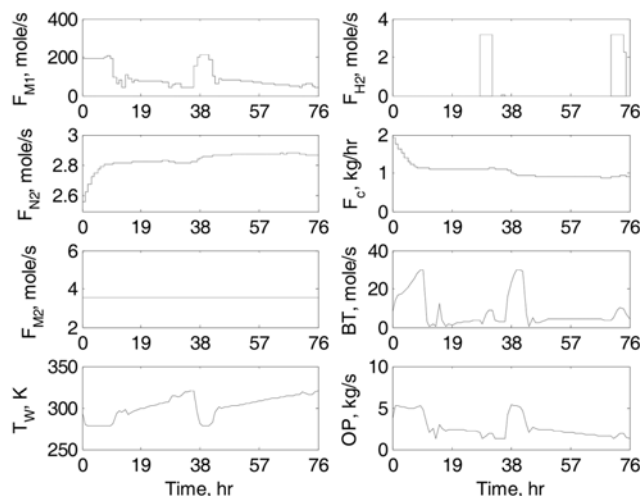


Fig. 6. Manipulated variable response using NLMPC.

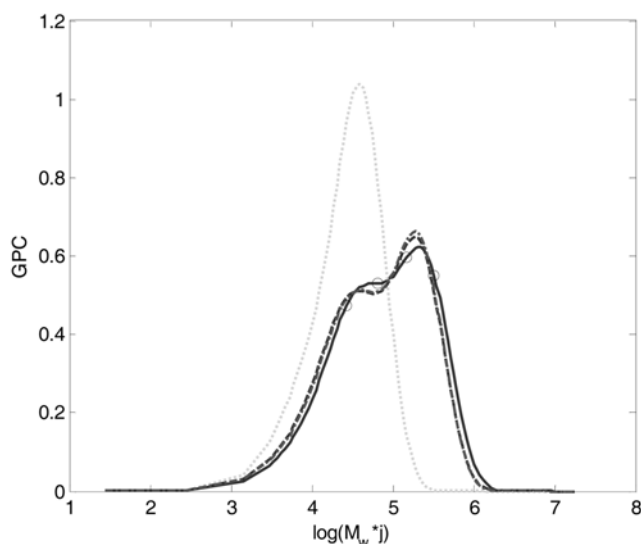


Fig. 7. MWD using NLMPC, dotted: initial condition, solid: target, dashed: controlled output initially; dash-dot: controlled output at the end of simulation.

issue. The control objective here is to produce and maintain broad polyethylene with well-defined MWD starting from narrow distribution. The results of closed loop simulations are shown in Figs. 6 and 7. Four manipulated variables, which are the monomer, hydrogen, nitrogen and catalyst flow rates, are used. The weighting factors for these inputs are $\lambda=[0 \ 0 \ 20 \ 50]$. Four controlled variables, which represent specific points in the target MWD, are considered as shown by the dots in Fig. 7. The weighting factors for all outputs are given by the same value of $\Gamma=[1 \ 1 \ 1] \times 100$. The lower limit for the manipulated variables is set to zero and the upper limit is set to twice their nominal values. The MWD target function contains 103 points, but only four points were selected as controlled outputs to reduce the computation effort required by the NLMPC calculations. The input horizon (M) and output horizon (P) are taken equal to 1 and 4, respectively. A sampling time of 1 hr is used. Usually the GPC measurements are available at low frequency. Advanced measurement sensors that can provide measurements in the order of minutes are available but are costly [38,39].

Fig. 7 demonstrates the ability of NLMPC to maintain the new set point for the polymer distribution with minor distortion in the distribution function. More interesting is the response of the manipulated variables shown in Fig. 6. The response of the manipulated variables is in the form of periodic functions. Long prediction and moving horizon capability of NLMPC helped the controller to understand the dynamic nature of the process to an extent that it produced cyclic input sequences. Moreover, Fig. 6 shows how the bleed flow rate (BT) and the cooling water inlet temperature (T_w) are varied by separate PI controllers to maintain the total pressure at 20 atm and the reactor temperature at 82 °C. Note that the manipulated variables used by NLMPC are plotted in discrete form because the NLMPC works in discrete time fashion.

Next we test the closed loop algorithm for targeting a different MWD. In this case, six points on the GPC curve are taken as the controlled variables with their weights fixed at $\Gamma=[1 \ 100 \ 100 \ 200 \ 100 \ 50] \times 10^2$. The lower limit of F_{M1} is set to 40 mole/s to keep high

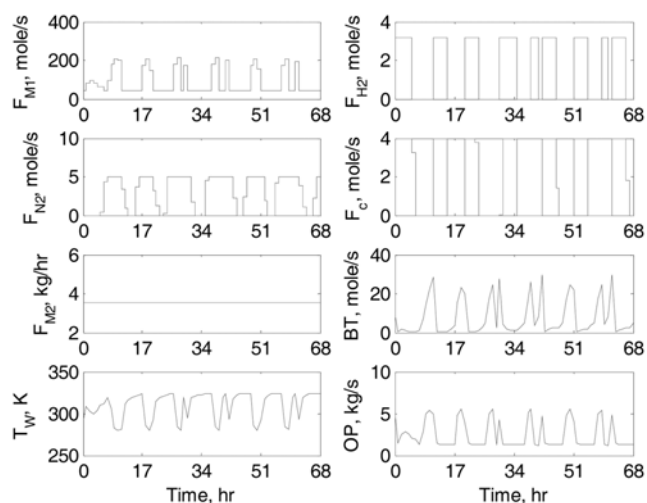


Fig. 8. Manipulated Variables response using NLMPC.

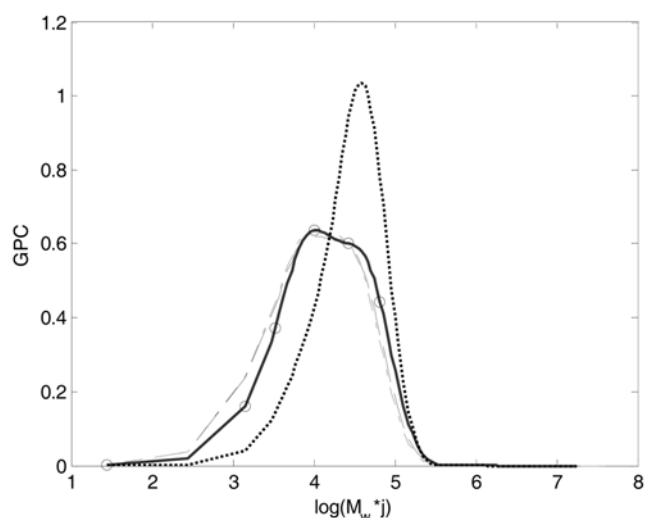


Fig. 9. MWD using NLMPC, dotted: initial condition, solid: target, dashed: controlled output initially; dash-dot: controlled output at the end of simulation.

monomer concentration in the reactor. The values of the rest of the parameters remain the same as before. The simulation results are shown in Figs. 8-9. Evidently, the nonlinear controller managed to generate suitable periodic input sequences that produce MWD close to the desired one as shown in Fig. 9. The MWD suffered from minor distortion; however, exact match of the target function is not necessary, especially when we know that the relative error in GPC measurements is around 10%. In this case, higher values of X require lower F_{M1} which reduces the production rate. The small production rate is obvious from Fig. 8. To improve the production rate, the latter is incorporated as a controlled variable in the NLMPC algorithm. In this case, the production rate is incorporated as an additional output into the NLMPC algorithm. Setting its corresponding weight to, for instance, $\gamma=0.1$, the controller managed to increase the polymer production to 2.86 kg/s but with notable variations in the MWD. Results are not shown here for space limitations. Increasing further the weight of the controlled output will increase the production rate

but the MWD will depart away from the desired set point. Our investigation revealed the existence of trade-offs between the production rate and broadening the MWD. Widening the distribution requires pronounced changes in hydrogen concentration inside the reactor. Increasing hydrogen concentration is achieved by feeding more hydrogen to the reactor, this reduces ethylene polymerization rate and as a consequence reduces the overall production rate. Whereas, reducing hydrogen concentration is achieved by opening the vent [30] that allows hydrogen in the reactor to escape, causing hydrogen concentration to fall quickly. Such reduction in the concentration affects positively the production rate. It should be noted that large fluctuations in bleeding flow rate are common in the industry. One way to reduce these fluctuations is by increasing the pressure set-point inside the reactor.

The previous simulations were carried out assuming a perfect

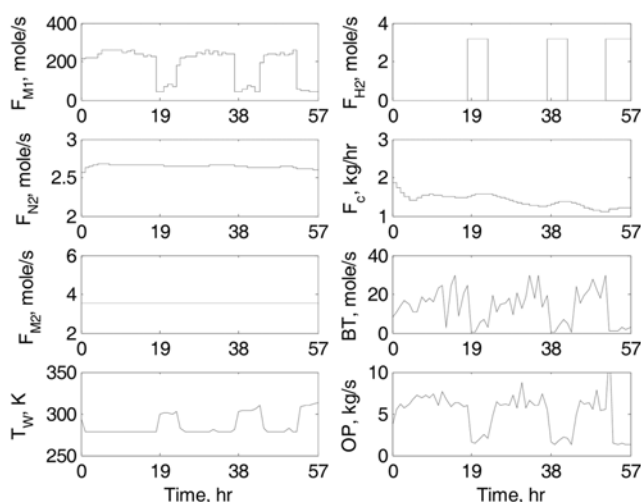


Fig. 10. Manipulated variable response using NLMPC in the presence of 20% error in catalyst activation and reaction rate constant.

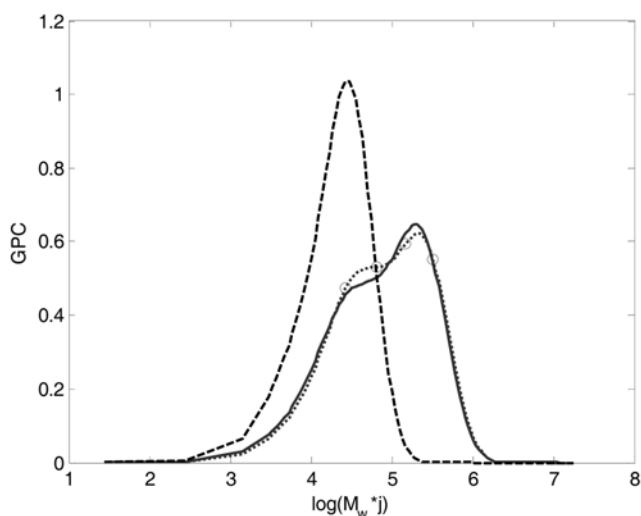


Fig. 11. MWD using NLMPC in the presence of 20% error in catalyst activation and reaction rate constant, dashed: initial condition, solid: target, dotted: controlled output.

model. However, this is not always true in real practice. To test the robustness of NLMPC to handle modeling errors, the simulation of targeting higher molecular weight is repeated with -20% error in the reaction rate constant and catalyst activity. The results are shown in Figs. 10-11. To further investigate the influence of model uncertainty on the control performance, additional $+15\%$ error on the bed mass, B_w , is injected into the model. The inaccuracy in the bed mass is expected to directly influence the dynamic of the cumulative molecular weight distribution. The outcome of running NLMPC under this situation is illustrated in Figs. 12-13. It is evident that NLMPC was able to keep good control performance despite minor loss in the performance. The simple additive disturbance estimates were sufficient to help the NLMPC overcome the influence of the model uncertainty.

It is worth mentioning that the controller performance could be

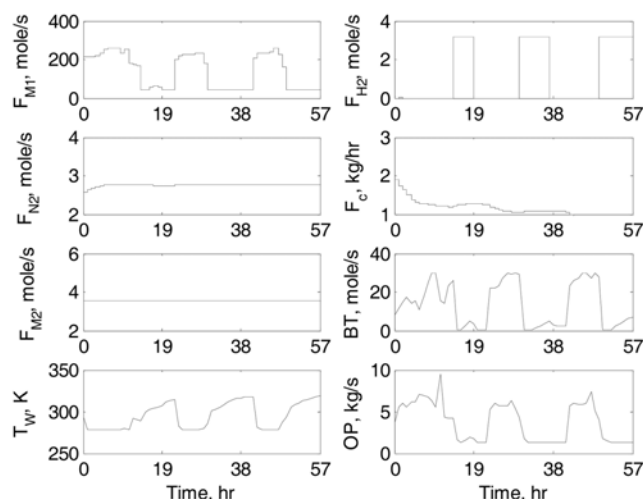


Fig. 12. Manipulated variable response using NLMPC in the presence of -20% error in catalyst activation and reaction rate constant and $+15\%$ error in bed mass.

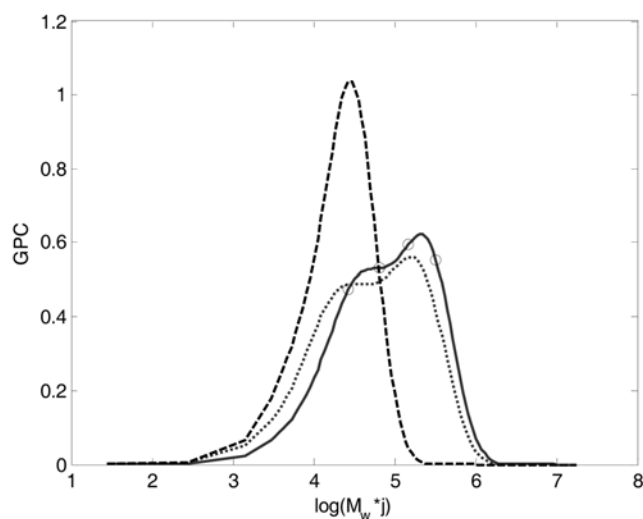


Fig. 13. MWD using NLMPC in the presence of -20% error in catalyst activation and reaction rate constant and $+15\%$ error in bed mass, dashed: initial condition, solid: target, dotted: controlled output.

improved more if the dynamics of hydrogen is faster. Since hydrogen is not consumed in the reactor and large fluctuations in hydrogen concentration are required to broaden polymer distribution, improving controller performance would not be an easy task. This challenge can be solved by using either a catalyst that is highly-sensitive to hydrogen as metallocenes or a hydrogen consuming agent. The first approach depends on implementing a relatively new catalyst that is not widely used industrially [18]. The second approach still needs more investigation to prove its applicability for the studied process. Finally, it should be noted that venting is usually used to reduce hydrogen concentration, as described above; however, venting reactor contents is not an economical choice because monomer also escapes from the reactor. Nonetheless, no other choices are available.

CONCLUSIONS

A *feasibility* study was performed to investigate the possibility of using on-line MWD control technique to broaden polyethylene molecular weight distribution, in a fluidized-bed polymerization reactor, by changing the operating conditions inside the reactor. This strategy used a detailed polymerization process model and Kalman filter to correct model states. An NLMPC controller was designed to control polymer MWD and polymerization process productivity. For the calculation of the MWD, selected points in the polymer distribution curve were used as set points for the controller that manipulates monomer, hydrogen, nitrogen and catalyst feed rates. To test the feasibility of the proposed MWD control technique, simulations were carried out for ethylene gas-phase polymerization using conventional Ziegler-Natta catalyst. The simulations suggest that the proposed control strategy can be a useful technique for broadening the MWD of polymer in continuous polymerization processes *provided that* hydrogen can be efficiently removed from the reactor.

ACKNOWLEDGMENT

The financial support from Saudi Basic Industries Company (SABIC), grant number 7/429, is greatly appreciated.

NOMENCLATURE

A : constant matrix for linear constraints
 a_c : active site concentration [mole/kg]
b : vector of upper and lower bounds for the linear constraints
 B_w : mass of the polymer in the bed [gm]
 B_T : bleed flow rate [mole/s]
 C_{M1}, C_{M2}, C_N, C_H : concentration monomer, co-monomer, nitrogen, and hydrogen [mole/m³]
 $Cp_{M1}, Cp_{M2}, Cp_H, Cp_N$: heat capacity of monomer, co-monomer, hydrogen and nitrogen [cal/mole K]
 Cp_g, Cp_w : heat capacity of recycle gas and water [cal/mole K]
 Cp_p : heat capacity of polymer [cal/g K]
E : activation energy for propagation [cal/mole]
 F_c : catalyst flow rate [kg/s]
 F_w, F_g : cooling water and recycle flow rate [mole/s]
 F_{M1}, F_{M2}, F_N, F_H : monomer, co-monomer, nitrogen and hydrogen flow rate [mole/s]
HF, HG, HP : sensible heat of fresh feed, recycle gas and product

[cal/s]
HR : enthalpy generated from ethylene polymerization [cal/s]
 k_d : deactivation rate constant [1/s]
 k_{p1}, k_{p2} : propagation rate constant for monomer and co-monomer [L/mole s]
 k_{th} : reaction rate constant for chain transfer to hydrogen [m³/mol s]
 Kp : propagation reaction rate constant [m³/mole s]
 k_{tm} : reaction rate constant for chain transfer to monomer [m³/mol s]
M, M_p : control horizon, constant matrix
 M_w : water holdup in the heat exchanger [mole]
 M_r, Cp_r : thermal capacitance of the reaction vessel [kcal/K]
Op : polymer outlet rate [kg/s]
P : prediction horizon
 P_t : total pressure, atmosphere
 P_{M1}, P_{M2}, P_N, P_H : partial pressure of monomer, co-monomer, nitrogen and hydrogen [atm]
q : chain termination probability
R : ideal Gas constant, atm m³/K mole also vector of set points
 R_{M1}, R_{M2}, R_H : consumption rate of monomer, co-monomer, and hydrogen [m³/mole s]
T, T_f, T_{ref} : bed, feed and reference temperature [°C]
 T_{g1}, T_g : temperature of recycle stream before and after cooling [°C]
 T_{w1}, T_{w2} : cooling water temperature before and after cooling [°C]
t : time [s]
UA : overall heat transfer coefficient multiplied by the heat transfer area [cal/s K]
 V_g : gas holdup in the reactor [m³]
x : vector of states
 x_{M1}, x_{M2}, x_N, x_H : mole fraction of monomer, co-monomer, nitrogen and hydrogen
X : hydrogen to monomer ratio
Y, Y_p : vector of future outputs over n and P, respectively
 Y_c : number of moles of catalyst site [mole]
y, y_p : vector of model outputs, and of plant outputs
 y_j, y_j^d : cumulative and instantaneous molecular weight distribution

Greek Letters

Δu : vector of manipulated variables
 ΔU : vector of M-future manipulated variables
 ΔH_r : heat of reaction [cal/g]
 Λ : input weight
 Γ : output weight
 σ : tuning parameter for Kalman filtering

REFERENCES

1. G. E. Elicabe and G. R. Meira, *Polym. Eng. Sci.*, **28**(3), 121 (1988).
2. M. Embirucu, E. L. Lima and J. C. Pinto, *Polym. Eng. Sci.*, **36**(4), 433 (1996).
3. J. P. Congalidis and J. R. Richards, *Polym. Eng. Sci.*, **6**, 71 (1998).
4. J. R. Richards and J. P. Congalidis, *Comput. Chem. Eng.*, **30**, 1447 (2006).
5. C. Sayer, G. Arzamendi, J. M. Asua, E. L. Lima and J. C. Pinto, *Comput. Chem. Eng.*, **25**, 839 (2001).
6. R. E. Murray and S. Mawson, *Olefin polymerization catalyst sys-*

- tem, USA (2001).
7. D. R. Loveday and D. H. McConville, *Mixed catalyst compounds, catalyst system and their use in a polymerization process* (2001).
8. D. Beigzadeh, J. B. P. Soares and A. Hamielec, *J. Appl. Polymer Sci.*, **71**, 1753 (1998).
9. K. Heiland and W. Kaminsky, *Makromolekulare Chemie-Macromolecular Chemistry and Physics*, **193**(3), 601 (1992).
10. J. D. Kim, J. B. P. Soares and G. L. Rempel, *Macromolecular Rapid Communications*, **19**, 197 (1998).
11. L. D'Agnillo, J. B. P. Soares and A. Penlidis, *Polymer International*, **47**, 351 (1998).
12. G. Ondery, *Chem. Eng.*, New York, **111**(12), 15 (2004).
13. C. Chatzidoukas, V. Kanellopoulos and C. Kiparssides, *Macromolecular Theory and Simulation*, **16**, 755 (2007).
14. H. S. Cho, J. S. Chung and W. Y. Lee, *Journal of Molecular Catalysis A: Chemical*, **159**, 203 (2000).
15. E. S. Shamshoum, H. Chen and L. Margarito, *Ziegler-natta catalyst with metallocene for olefin polymerization*, US Patent 6653254 (2003).
16. T. E. Nowlin, S. D. Schregenberger, P. P. Shirodkar and G. O. Tsien, *Process for controlling the MWD of a broad or bimodal resin in a single reactor*, US Patent 6653254 (2002).
17. M. Nele and J. C. Pinto, *Journal of Applied Polymer Science*, **77**, 437 (2000).
18. P. Galli and G. Vecellio, *Polymer Science*, **26**, 1287 (2001).
19. A. Stankiewicz and M. Kuczynski, *Chem. Eng. Process.*, **34**, 367 (1995).
20. W. H. Ray, *Ind. Eng. Chem. Process Des. Dev.*, **7**(3), 422 (1968).
21. G. R. Meira, *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry*, **20**(2), 207 (1981).
22. R. S. Schiffrino, *Process for polyolefin production using short residence time reactors*, USA (1995).
23. J. B. P. Soares and A. Penlidis, *Measurement, mathematical modeling and control of distribution of molecular weight, chemical composition and long-chain branching of polyolefins made with metallocene catalysts*, in *metallocene-based polyolefins: Preparation, properties and technology*, J. Scheirs and W. Kaminsky, Eds., Johan Wiley (2000).
24. G. Debras and J. Dath, *Production of polyethylene having a bimodal molecular weight distribution*, Fina Research, S. A., Feluy: USA (2001).
25. K. B. McAuley, D. A. McDonald and P. J. McLellan, *AIChE J.*, **41**, 868 (1995).
26. E. M. Ali, K. Al-Humaizi, and A. Ajbar, *Ind. Eng. Chem. Res.*, **42**, 2349 (2003).
27. Y. V. Kissin, F. M. Mirabella and C. C. Meverden, *J. Appl. Polymer Sci.*, **43**, 4351 (2005).
28. E. M. Ali and E. Zafiriou, *Journal of Process Control*, **3**, 97 (1993).
29. J. A. Debling, C. Han, F. Kuipers, J. VerBurg, J. J. Zacca and W. H. Ray, *AIChE J.*, **40**, 506 (1994).
30. D. P. Lo and W. H. Ray, *Ind. Eng. Chem. Res.*, **45**, 993 (2006).
31. M. Al-haj Ali, *Modeling and control of molecular weight distribution in a liquid-phase polypropylene reactor*, Twente University, Enschede (2006).
32. N. M. Al-Bastaki and A. Abbas, *Sep. Sci. Technol.*, **33**(16), 2531 (1998).
33. J. Wang, *Journal of Chemical Physics*, **119**(7), 3626 (2003).
34. P. L. Silveston and J. Hanika, *Can. J. Chem. Eng.*, **82**(6), 1105 (2004).
35. K. Chmiel, A. Konieczny, M. Palica and A. B. Jarzebski, *Chem. Eng. Sci.*, **60**, 2845 (2005).
36. G. R. Meira, A. F. Johnson and J. Ramsay, *Polymerization Reactors and Processes*, 254 (1979).
37. M. Al-haj Ali, J. Stroomer, B. Betlem, G. Weickert and B. Roffel, *J. Appl. Polymer Sci.*, **108**, 2446 (2008).
38. O. Kammona, E. G. Chatzi and C. Kiparssides, *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics*, **C39**, 57 (1999).
39. J. R. Leiza and J. C. Pinto, *Control of polymerization reactors*, in *polymer reaction engineering*, J. M. Asua, Ed., Blackwell Publishing Ltd, Oxford, 329 (2007).
40. M. Al-haj Ali, B. Betlem, G. Weickert and B. Roffel, *Chemical Engineering and Processing Journal*, **46**, 554 (2007).
41. I. Atasoy, M. Yuceer, E. O. Ulker and R. Berber, *Chem. Eng. Technol.*, **30**(11), 1525 (2007).
42. G. Dunnebie, D. V. Hessen, J. V. Kadam, K. Klatt and M. Schlegel, *Chem. Eng. Technol.*, **28**(2), 575 (2005).
43. C. Kiparssides, P. Seferlis, F. Mourikas and A. J. Morris, *Ind. Eng. Chem. Res.*, **41**, 6120 (2002).
44. M. Vicente, J. R. Leiza and J. M. Asua, *AIChE J.*, **47**(7), 1594 (2001).
45. Y. Wang, H. Seki, S. Ohyama, K. Aksumatsu, M. Ogawa and M. Ohshima, *Comput. Chem. Eng.*, **24**, 1555 (2000).
46. M. Ogawa, M. Ohshima, F. Watanabe, K. Morinaga and I. Hashimoto, *Quality inferential control of an industrial high density polyethylene processes*, in *IFAC world congress meeting*, San Francisco, USA (1999).
47. E. M. Ali, A. E. Abasaeed and S. M. Al-Zahrani, *Ind. Eng. Chem. Res.*, **37**, 3414 (1998).
48. T. J. Crowley and H. K. Choi, *Ind. Eng. Chem. Res.*, **36**, 3676 (1997).
49. T. J. Crowley and H. K. Choi, *Chem. Eng. Sci.*, **53**(15), 2769 (1998).
50. A. Echevarria, J. R. Leiza, J. de la Cal and J. M. Asua, *AIChE J.*, **44**(7), 1667 (1998).
51. P. Pladis and C. Kiparssides, *Supervisory control of high pressure LDPE reactors*, in *IFAC dynamics and control of process systems*, Corfu, Greece (1998).