

## Prediction and quality control of the melt index during production of high-density polyethylene

Eun Ho Lee, Tae Young Kim, and Yeong Koo Yeo<sup>†</sup>

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

(Received 11 June 2007 • accepted 16 January 2008)

**Abstract**—In polyolefin processes the melt index (MI) is the most important control variable indicating product quality. Because of the difficulty in the on-line measurement of MI, a lot of MI estimation and correlation methods have been proposed. In this work a new dynamic MI estimation scheme is developed based on system identification techniques. The empirical MI estimation equation proposed in the present study is derived from the 1<sup>st</sup>-order dynamic models. Effectiveness of the present estimation scheme was illustrated by numerical simulations based on plant operation data including grade change operations in high density polyethylene (HDPE) processes. From the comparisons with other estimation methods it was found that the proposed estimation scheme showed better performance in MI predictions. The virtual sensor model developed based on the estimation scheme was combined with the virtual on-line analyzer (VOA) to give a quality control system to be implemented in the actual HDPE plant. From the application of the present control system, significant reduction of transition time and the amount of off-spec during grade changes was achieved.

Key words: Polyethylene, Melt Index, Dynamic Model, Grade Change, Quality Control

### INTRODUCTION

Demand for petrochemical products with high quality and low price is greatly increasing, especially in modern high density polyethylene (HDPE) markets. Consumers' requirements have become increasingly sophisticated and strict for new HDPE products. In HDPE production operations the melt index (MI) is the most important control variable indicating product quality. To meet the various and stringent requirements for HDPE products such as MI, it is imperative to maintain uniformity of HDPE properties during grade change operations. However, long settling time for each grade and large overshoots as well as large amount of off-specification products prohibit achievement of efficient grade transitions in actual plant operations. It is very difficult to measure MI on-line during plant operations. Thus, it is a usual practice to estimate MI values in terms of measurable key variables such as temperature, pressure, feed rates of each reactants, etc.

So far a large number of MI estimation and correlation methods have been proposed. The estimation method presented by McAuley and MacGregor [1,2] is based on the logarithm of the linear combination of flow rates of each component. To take into account unmeasured impurities or disturbances, they employed a constant term that is updated iteratively. In the estimation model proposed by Ohshima [3] an additional term representing temperature is included. In contrast to taking the logarithm of the linear combination as in the model by McAuley and MacGregor [1,2], they take linear combinations on the logarithms of each variable. It is relatively easy to estimate the effects of reactants at steady-state operation from their model. Oh [4] developed an off-line Excel-based program for estimating polymer properties. They proposed an empirical prediction model for estimation of instantaneous MI.

Although the MI estimation methods proposed so far have shown good prediction results, application of those MI models for the construction of operation control systems or direct utilization of those methods in the actual operations has not been reported.

In the present study dynamic models to estimate cumulative MI for HDPE process are developed. In particular, we first identify four or five key variables followed by derivation of dynamic cumulative MI prediction models. In particular, MI prediction models for each unit of the HDPE plant are developed. The models developed in this study can easily be transformed to instantaneous MI prediction models. Results of estimations by present models are compared with those obtained by existing prediction models as well as with measured data. The dynamic MI models developed in the present study were combined with the virtual on-line analyzer (VOA) to give a quality control system. The quality control scheme was used in the plant operation after some test trials. Results of application showed improved control performance compared to classical operation strategies.

### PROCESS DESCRIPTION

The HDPE plant at LG petrochemicals (LGPC) consists of two processes where the polymerization reaction occurs. Fig. 1 shows a typical slurry polymerization process for the production of HDPE considered in the present study. Two polymerization reactors are involved in each process. The polymerization reaction is highly exothermic with reaction heat of about 1,000 kcal per 1 kg ethylene. Thus, it is required to provide internal cooling coils and appropriate external cooling systems which remove about 80% of polymerization heat. Ethylene, comonomer (1-butene or higher  $\alpha$ -olefin), hydrogen, catalyst, activator and hexane as well as continuously recycled mother liquid are fed into reactors as reactants. About 90-95% of reactor volume is occupied by reaction slurry. As the reaction pressure builds up, the polyethylene slurry is transported to subsequent process equipment and the level in the reactor is main-

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: ykyeo@hanyang.ac.kr

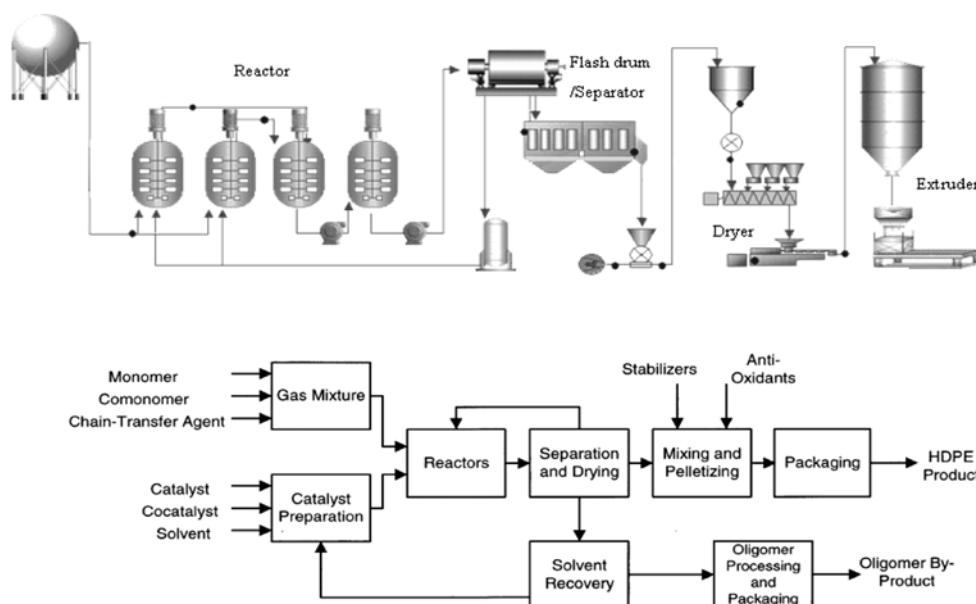


Fig. 1. A schematic of slurry polymerization process for the production of HDPE.

tained within a permissible range. Cake containing diluents is obtained from the separation of the reaction slurry in the centrifugal separator followed by removal of diluents by hot nitrogen gas in the dryer. Then appropriate additives are added according to final uses. Pelletization is performed in water. Dried pellets are transferred to homogenizer and cooled.

## MI ESTIMATION MODELS

### 1. Instantaneous MI Models

McAuley and MacGregor [1,5] proposed an inferential system for the on-line prediction of MI of low density polyethylene (LDPE) produced in the UNIPOL fluidized-bed reactor. They employed two models: (1) an instantaneous polymer property model that describes the relationship between process variables and the current polymer property; and (2) a cumulative property model that describes the relationship between the instantaneous and cumulative polymer properties in the reactor. The instantaneous MI model can be represented as

$$\ln(MI_i) = 3.5 \ln \left\{ k_0 + k_1 \frac{[H_2]}{[C_2]} + k_2 \frac{[C_3]}{[C_2]} + k_3 \frac{[C_4]}{[C_2]} + k_4 \frac{[R]}{[C_2]} \right\} + k_2 \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (1)$$

where the subscript  $i$  denotes the  $i$ -th reactor, MI is the instantaneous MI,  $k_j$  ( $j=0, 1, \dots, 5$ ) denotes parameters,  $T_0$  is the reference temperature,  $T$  is the temperature of the reactor, and  $[H_2]$  and  $[C_2]$  are the concentrations of hydrogen and ethylene, respectively. The corresponding cumulative MI model is given by

$$\frac{d(MI_c(t)^{-0.286})}{dt} = \frac{1}{\tau(t)} MI_i(t)^{-0.286} - \frac{1}{\tau(t)} MI_c(t)^{-0.286} \quad (2)$$

where  $MI_c$  and  $MI_i$  denote MIs of cumulative polymer and instantaneous polymer, respectively [1,3].

Oh [4] presented an empirical instantaneous MI estimation model that predicts instantaneous properties of polymer. The ratio of the amount of feeds instead of concentrations of each component is used in this model, which is given by

$$\log(MI_{inst,i}) = \alpha + a_0 \log(T)_i + a_1 \log \left( \frac{[H_2]}{[C_2]} \right)_i + a_2 FC_3 C_{2,i} + a_3 FC_4 C_{2,i} \quad (3)$$

Ohshima et al. [3,7] suggested an instantaneous MI estimation model based on the assumption that reaction time is much shorter than the residence time in the reactor and the typical polymer structure is similar with each other [6]. Their model is a linear combination of concentration ratios of each reactants and logarithm of catalyst and temperature terms and is represented as

$$\log(MI_i) = \beta + \alpha_1 \frac{[H_2]}{[C_2]} + \alpha_2 \frac{[C_3]}{[C_2]} + \alpha_3 \frac{[C_4]}{[C_2]} + \alpha_4 \log[R] + \alpha_5 \log(T) \quad (4)$$

Again the corresponding cumulative MI model can be given by

$$\frac{d \log(MI_c(t))}{dt} = \frac{1}{\tau_i(t)} \log(MI_i(t)) - \frac{1}{\tau_i(t)} \log(MI_c(t)) \quad (5)$$

where  $\tau_i$  represents the residence time of polymer in the reactor. Table 1 shows key scaled parameters used in Eq. (1), (3) and (5).

Cumulative MI models for each process unit except the extruder are given by

Table 1. Scaled parameters used in the MI estimation models

| Parameter  | Scaled value [-] | Equation |
|------------|------------------|----------|
| $k_1$      | 0.0726           | (1)      |
| $k_3$      | 0.3298           | (1)      |
| $\alpha_1$ | 2.2              | (3), (5) |
| $\alpha_2$ | 0.6              | (3), (5) |
| $\alpha_5$ | 1.1              | (3), (5) |

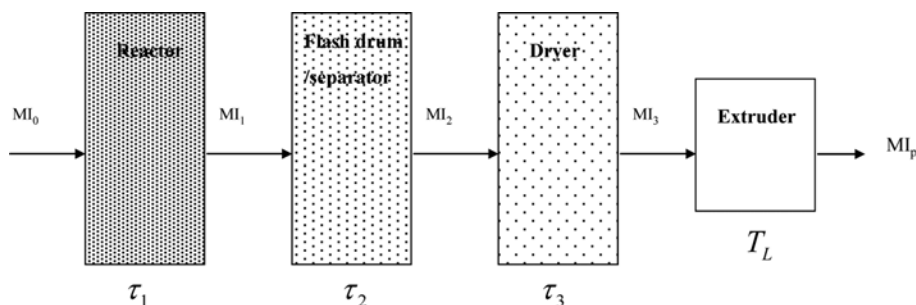


Fig. 2. Four sequential process units with time delays.

$$\frac{d \log(MI_q(t))}{dt} = \frac{1}{\tau_q(t)} \log(MI_{q-1}(t)) - \frac{1}{\tau_q(t)} \log(MI_q(t))$$

( $q=1, 2$  and  $3$ ) (6)

By assuming time delay of  $T_L$ , the extruder can be represented as

$$\log(MI_q(t)) = \log(MI_3(t - T_L))$$

(7)

All of the four units (reactor, flash drum/separator, dryer and extruder) described above are shown in Fig. 2, where each unit is denoted by

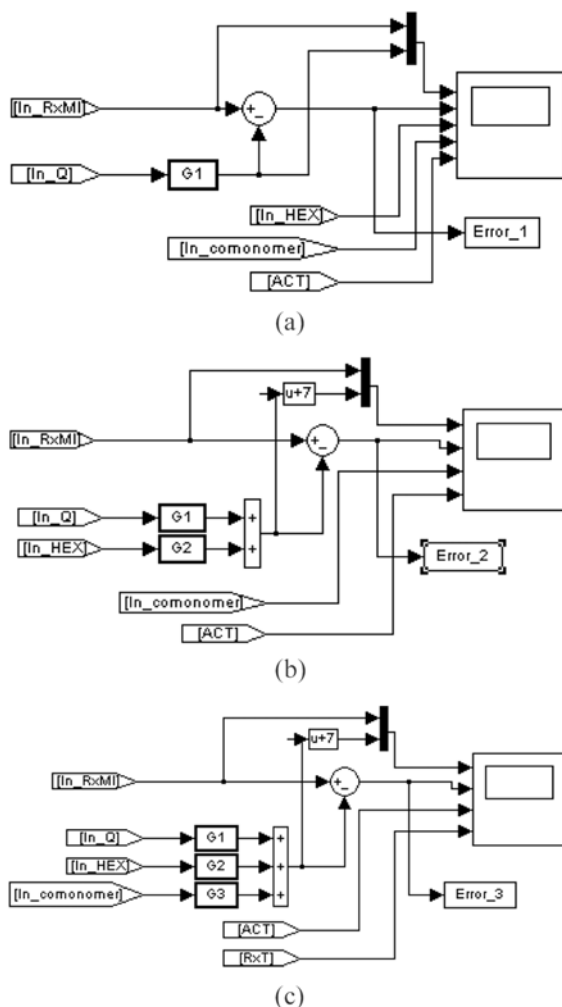


Fig. 3. Simulink configurations to identify dynamic MI models: (a) Step 2; (b) Step 5; (c) Step 7.

1, 2, 3 and 4. In Fig. 2,  $MI_q$  is the MI of polymer produced at unit  $q$ ,  $MI_0$  is the instantaneous MI produced in the reactor and  $MI_p$  is the MI of polymer powder.

## 2. Dynamic MI Models

Plant models are commonly identified by performing a step or a pulse test on key variables. But these tests can hardly be done on plants under operation because of high cost and safety. Operating data can be effectively used to obtain plant models, and various closed-loop identification techniques have been proposed so far. But in this work we employ a simple and efficient scheme based on the operating data accumulated during certain operation periods to get cumulative MI models. Fig. 3 shows the Simulink configuration to identify dynamic MI models. The procedure can be summarized as the following:

**Step 1)** Choose dominant input variables by which certain output variables are influenced most. The system is assumed to be linear time invariant.  $Q$  was selected as the first input variable the logarithm of which is incorporated in the model.

**Step 2)** Apply plant data to the model to get modeling error (Error 1) (see Fig. 3(a)).

**Step 3)** The second input variable is the one which exerts the strongest influence on Error 1. HEX was chosen as the second input variable, the logarithm of which is incorporated in the model. In this work HEX consists of pure hexane (HDH) fed into the reactor and recycled hexane (HMH).

**Step 4)** Find the 1<sup>st</sup>-order models relating  $\ln(\text{HEX})$  and Error 1.

**Step 5)** Again apply plant data to the resulting models to get modeling error (Error 2) (see Fig. 3(b)).

**Step 6)** Choose the input variable which exerts the strongest influence on the Error 2. In this work the amount of the comonomer was chosen as the third input variable. As in the previous steps find models which relate the third input variable and Error 2.

**Step 7)** Find Error 3 (see Fig. 3(c)).

**Step 8)** Repeat above procedures until 1<sup>st</sup>-order models are identified for all the input variables. The desired cumulative MI model is given by the combination of all the models obtained so far.

The resulting model (model 1) which takes into account the amount of activator feed (ACT) can be written as

$$y = G_1 u_1 + G_2 u_2 + G_3 u_3 + G_4 u_4$$

(8)

where

$$u_1 = \ln(Q), u_2 = \ln(\text{HDH/ETH} + \text{HMH/ETH}),$$

$$u_3 = \ln(\text{comonomer/ETH} + 0.01), u_4 = \text{RxT}$$

(9)

and  $y$  denotes  $\ln(MI)$ .  $G_i$  ( $i=1, 2, 3, 4$ ) are 1st-order models given by

$$\begin{aligned} G_1 &= \frac{2.5887}{29.143s+1}, & G_2 &= \frac{-2.5913}{165.68s+1}, & G_3 &= \frac{0.9891}{81.55s+1}, \\ G_4 &= \frac{0.1}{46.945s+1}, \end{aligned} \quad (10)$$

If we include  $RxT$  (Reactor temperature) in model 1 we have

$$y = G_1 u_1 + G_2 u_2 + G_3 u_3 + G_4 u_4 + G_5 u_5 \quad (11)$$

where

$$\begin{aligned} u_1 &= \ln(Q), & u_2 &= \ln(HDH/ETH + HMH/ETH), \\ u_3 &= \ln(\text{comonomer}/ETH + 0.01), & u_4 &= ACT, & u_5 &= RxT \end{aligned} \quad (12)$$

$$G_1 = \frac{2.5887}{29.143s+1}, \quad G_2 = \frac{-2.5913}{165.68s+1}, \quad G_3 = \frac{0.9891}{81.55s+1},$$

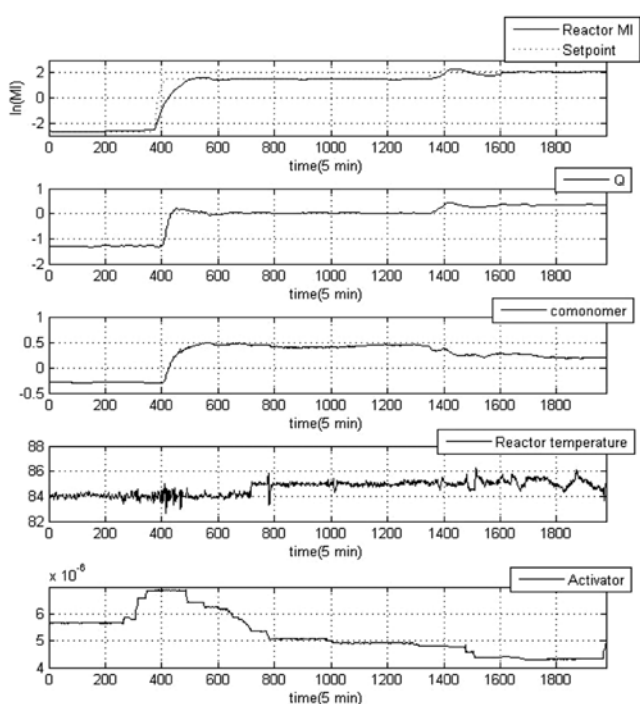


Fig. 4. Trends of key operation variables: Case A.

$$G_4 = \frac{145.81}{184.07s+1}, \quad G_5 = \frac{0.1}{46.945s+1}, \quad (13)$$

### 3. Application of MI Models

Results of computations based on each MI models were compared with measured data. Table 1 summarizes key scaled parameters used in existing models (Eq. (1), (3) and (5)). In this work we considered two typical operation cases. Trends of key operation variables for each operation case are shown in Figs. 4 and 5. Values of  $k_0$ ,  $\alpha$  and  $\beta$  used in the operations for estimation of MI based on the present dynamic model during grade transitions are shown in Fig. 6. As we can see from the figure, the ratio of hydrogen to ethylene ( $Q$ ) mostly affects MI in both cases. Fig. 7 represents predicted MI based on the cumulative MI model for each process unit. Measured MIs of polymer powder were compared with those predicted based on the dynamic prediction model proposed in the present study. The measured time delay of each unit was  $\tau_1=2(h)$ ,  $\tau_2=$

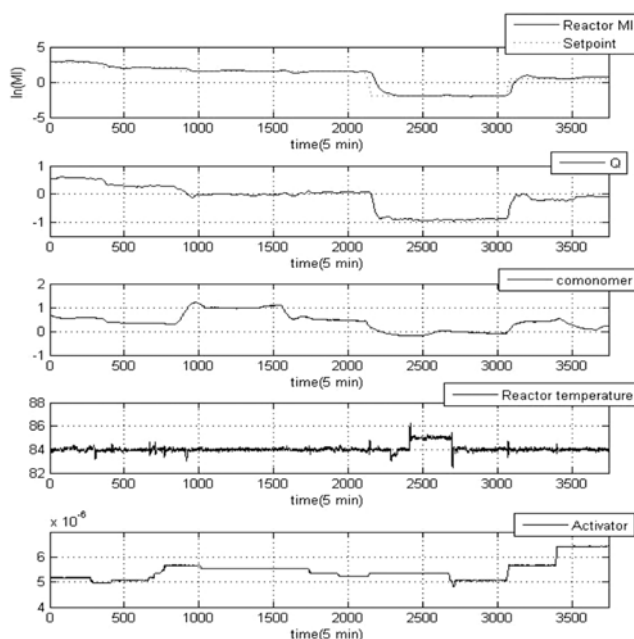
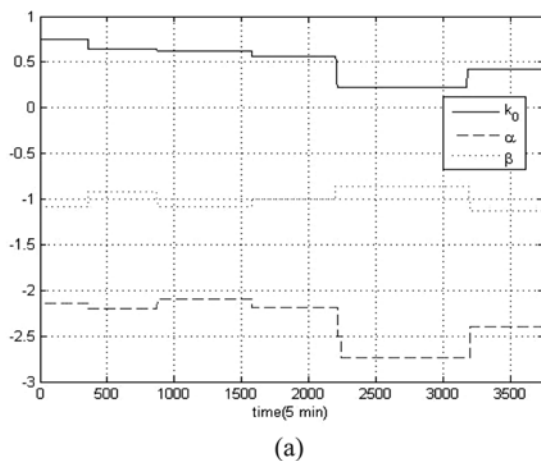
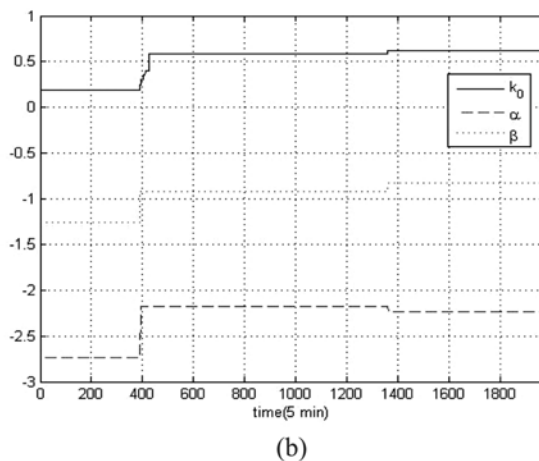


Fig. 5. Trends of key operation variables: Case B.



(a)



(b)

Fig. 6. Values of  $k_0$ ,  $\alpha$  and  $\beta$  used in MI models during grade change operations: (a) Case A, (b) Case B.



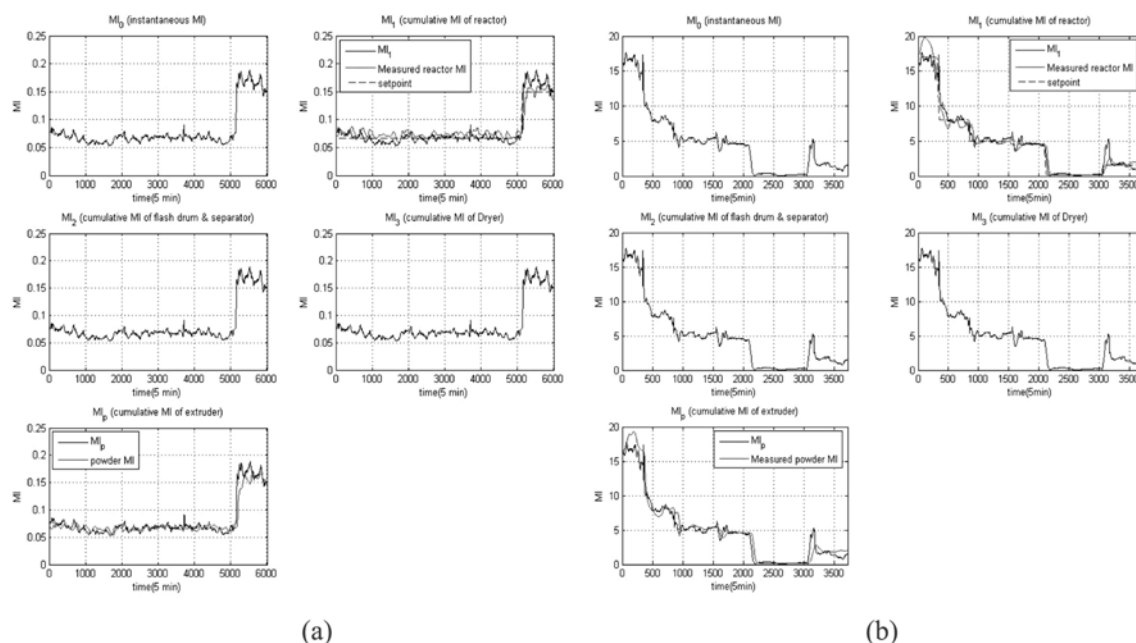


Fig. 7. Comparison of MIs between measured values and estimated values based on the cumulative MI model for each process unit.

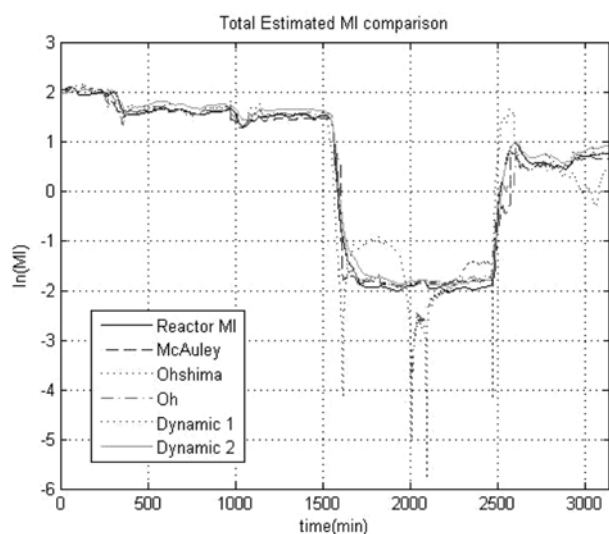


Fig. 8. Performance of MI estimation models: Case A.

0.6(h),  $\tau_3=0.4167$ (h) and  $T_L=0.9$ (h).

Fig. 8 and Fig. 9 show the performance of MI prediction models described in this paper. As we can see from the figures, the estimated MI values based on existing MI models show oscillations or stiff peaks during grade changes. For both operation cases, we can see that model 1 and model 2 proposed in the present study show better tracking performance than existing MI models.

Fig. 10 and Fig. 11 highlight estimation errors of each model shown in Figs. 8 and 9. Table 2 shows ISEs for each estimation model. From Figs. 10 and 11 and Table 2, we can see the effectiveness of the proposed models 1 and 2. Fig. 12 shows predicted values of MI based on the present models 1 and 2 compared to measured MI values. We can see the excellent prediction performance of the proposed models 1 and 2.

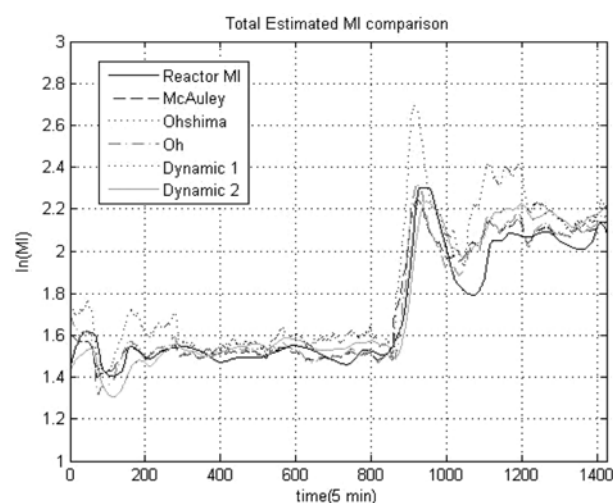


Fig. 9. Performance of MI estimation models: Case B.

#### 4. HDPE Quality Control

Fig. 13 shows the strategy for MI Quality to be applied in HDPE plant of LG Petrochemicals, Inc. The whole operation procedure can be divided into normal operation and grade change operation. VOA (virtual on-line analysis) displays values of predicted MIs to operators. During normal operation a control system consisting of VOA, MI and Q controllers is employed to make MI match with the target MI of corresponding grade. A sequence control system based on SOP (standard operation procedure) is to be used during grade change operation so that grade transition is achieved according to the operation sequences. VOA, Q and MI controllers and sequence control steps by SOP as well as user program modules are stored in the server computer used in control. Fig. 14 shows a grade change control strategy with start and interruption points of VOA, Q and MI controllers and sequence control. In order to shorten the

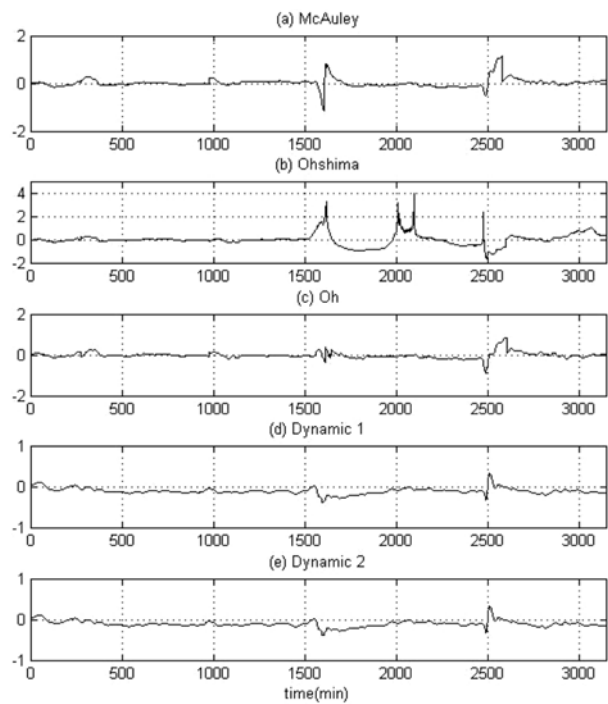


Fig. 10. Estimation errors of each estimation model (Case A): (a) McAuley (b) Ohshima; (c) Oh; (d) Model 1; (e) Model 2.

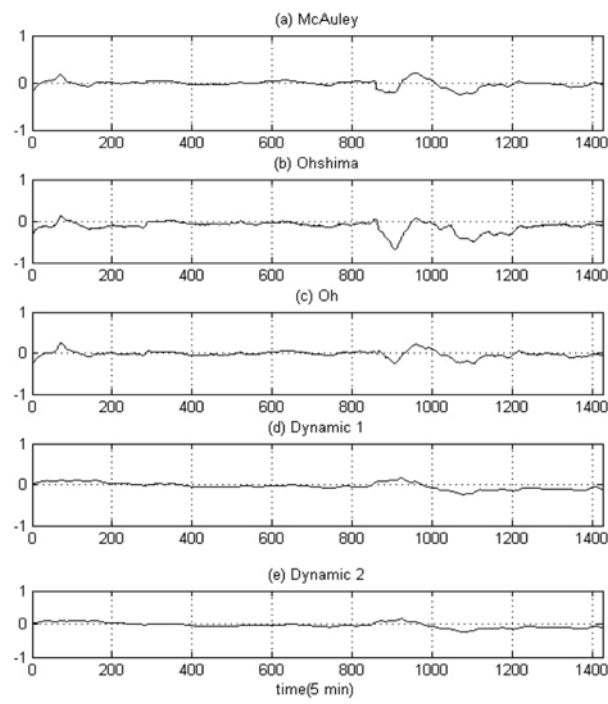


Fig. 11. Estimation errors of each estimation model (Case B): (a) McAuley (b) Ohshima; (c) Oh; (d) Model 1; (e) Model 2.

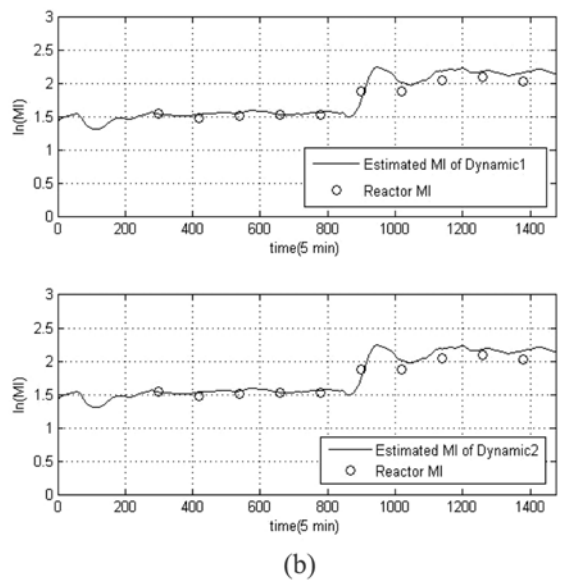
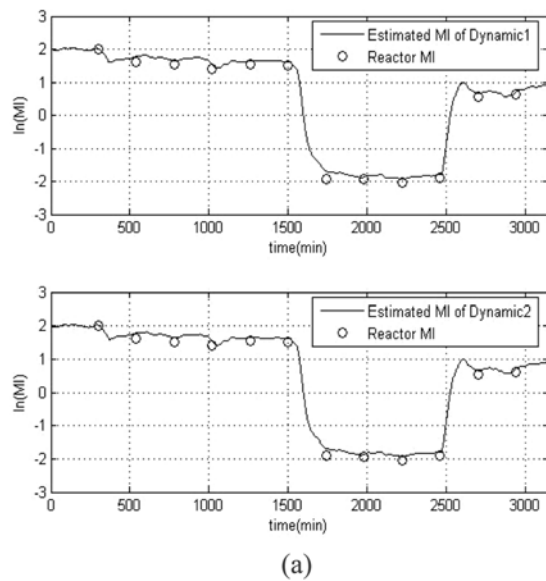


Fig. 12. Predicted values of MI based on the present model 1 and 2 compared to measured MI values: (a) Case A, (b) Case B.

transition interval, Q should display an undershoot (Fig. 14(a)) when the grade change occurs from high grade to low grade. However, when the grade change occurs from low grade to high grade, Q should display an overshoot (Fig. 14(b)).

The change of MI is initiated by the change of hydrogen/ethylene ratio within the reactor, i.e., the change in flow rate of hydrogen. Typical sampling time to measure MI during grade change is 2 hours, while the usual sampling time for normal operation is 4 hours. The SOP on which the sequence control system is based should include

Table 2. ISEs in various estimation models

| Model     | ISE     |          |
|-----------|---------|----------|
|           | CASE A  | CASE B   |
| McAuley   | 34.5202 | 111.8766 |
| Ohshima   | 76.3055 | 918.8001 |
| Oh        | 45.4063 | 75.9788  |
| Dynamic 1 | 38.7394 | 55.4794  |
| Dynamic 2 | 39.0247 | 22.0317  |

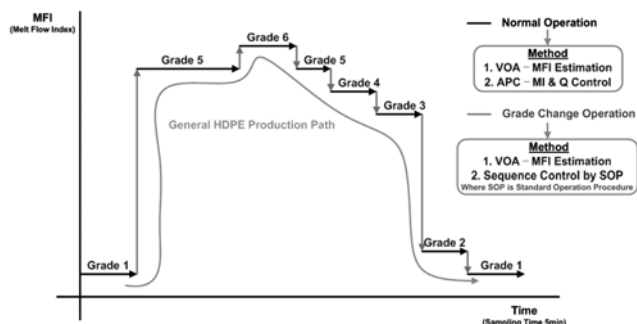


Fig. 13. LGPC HDPE plant quality control concept.

operational heuristics. Fig. 15 represents typical controlled variables and manipulated variables to maintain the quality specification of HDPE products.

Values of MI are mainly controlled by the amount of hydrogen in the reactor. More specifically, MI is manipulated by the ratio of partial pressure of hydrogen to that of ethylene. Concentrations of hydrogen and ethylene can be measured by analyzing the gaseous phase in the reactor. If there are fluctuations in process variables such as temperature, gaseous feed and concentration of activators, we cannot rely on the manipulation of hydrogen to control MI. Fig. 16 shows a basic control concept for MI.

The MI control system developed in the present study based on the concept depicted in Fig. 16 is shown in Fig. 17. The control procedure can be summarized as follows:

- (1) Predict MI by VOA.
- (2) Adjust predicted values by VOA bias update system based on the difference between predicted MI and measured MI.
- (3) Change Q Target (setpoint) by MI Controller.
- (4) Change setpoints for CAT (catalyst) and HYD (hydrogen).

The update procedure used in the VOA bias update system is summarized in Fig. 18. This procedure is activated only when the difference between predicted MFI and measured MFI crosses a cer-

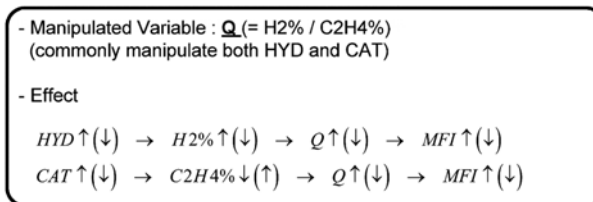


Fig. 15. MI control specification.

tain threshold set by operators.

VOA was designed based on the assumption of time-invariant system. But the polymerization process is in fact a typical time-variant system because of the change of process dynamics due to the accumulation of scale in the reactor, the heat exchanger and other process equipment. Change of dynamics causes variation in MI since reaction conditions for the polymerization are changed. The VOA bias update system developed in the present study compensates for discrepancies and fluctuations in predicted and measured MFI values. Fig. 19 shows the configuration of the MI controller. The target value of the MI supplied by DCS system and the estimated MI value from VOA are fed into the MI controller. Eq. (11) was used as an MI estimation model. The target value of Q computed by the MI controller is transferred to the Q controller. Fig. 20 shows a schematic of the Q Controller. The Q model given by Eq. (14) can be identified by the similar procedure used to get the dynamic MI model.

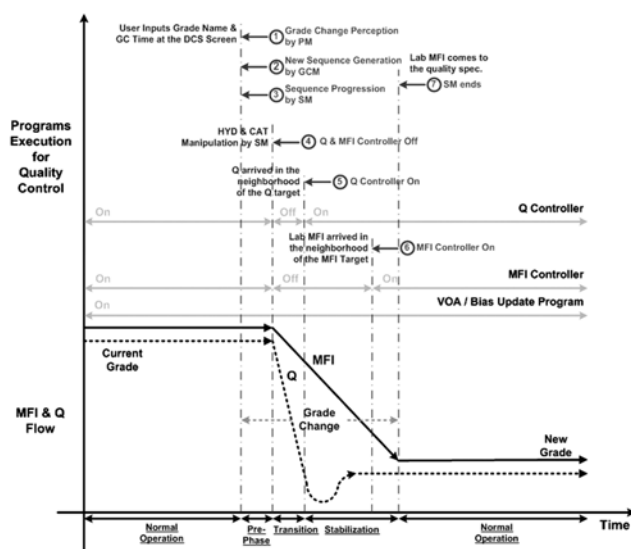
$$y = G_1 u_1 + G_2 u_2 + G_3 u_3 \quad (14)$$

where

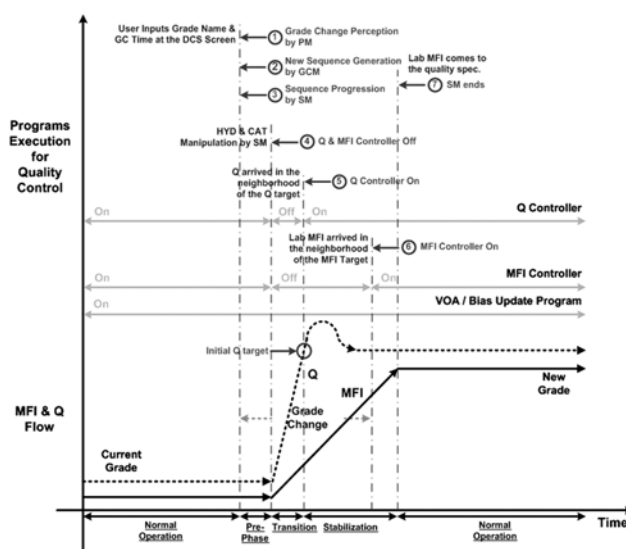
$$y = Q, u_1 = CAT, u_2 = HYD, u_3 = ETH \quad (15)$$

$$G_1 = \frac{0.02264}{49.99s+1} e^{-14.752s}, \quad G_2 = \frac{0.011848}{50s+1} e^{-31.89s},$$

$$G_3 = \frac{-0.000152229}{58.725s+1} e^{-12.6465s} \quad (16)$$



(a) Grade change (MI: high → low).



(b) Grade change (MI: low → high).

Fig. 14. Grade change control strategy.

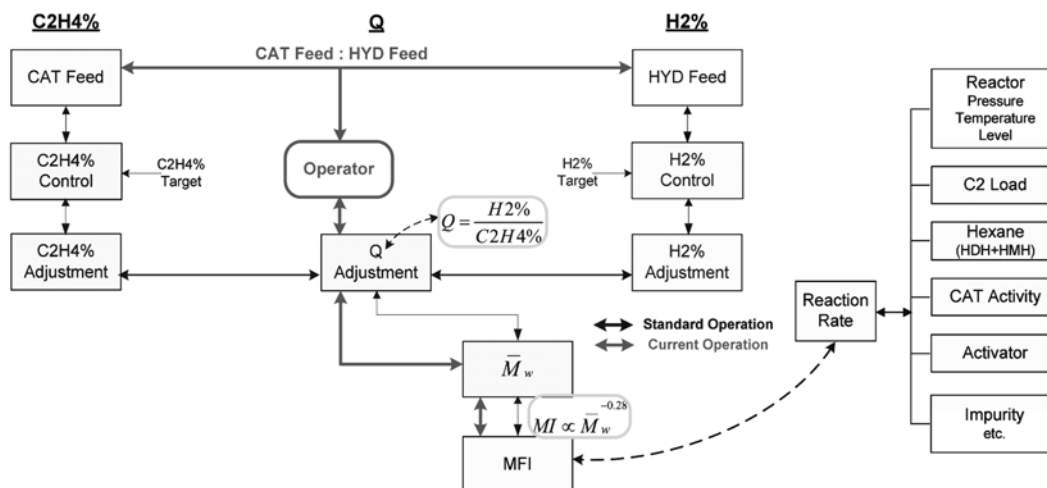


Fig. 16. Basic MI control concept.

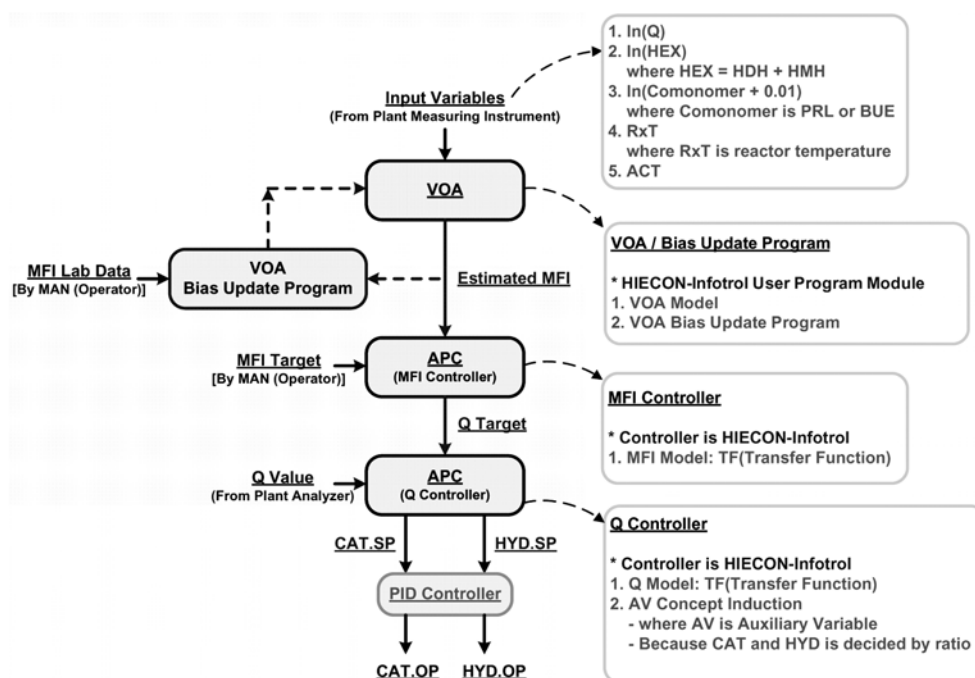


Fig. 17. Overview of MI control system.

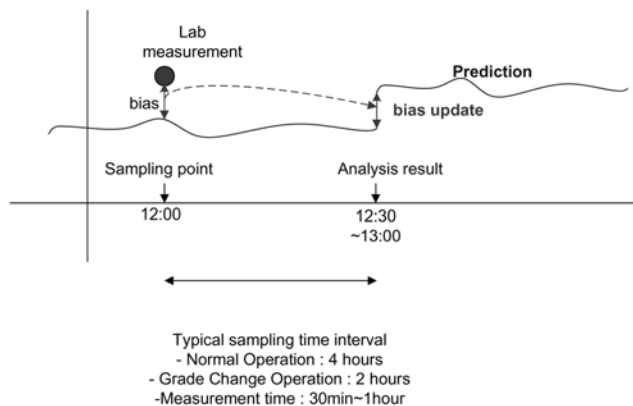


Fig. 18. Concept of the bias update system.

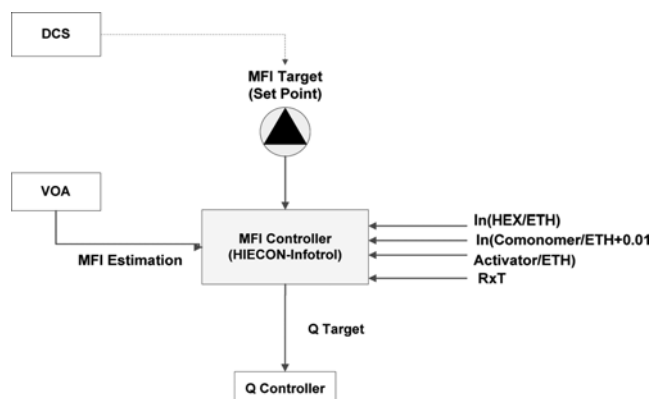


Fig. 19. A schematic of the MI controller.



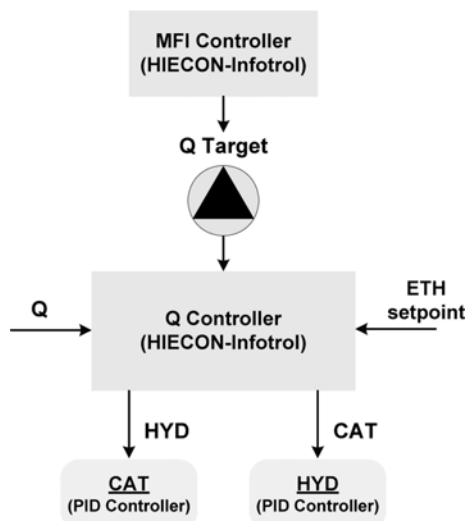


Fig. 20. A schematic of the Q controller.

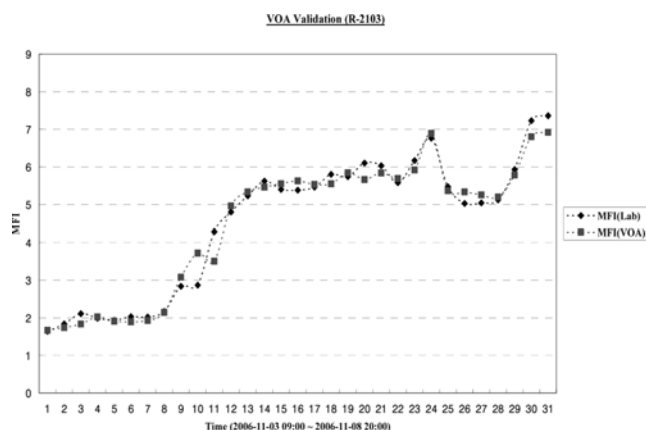


Fig. 21. Predicted MI values compared to measured MI values (R-2103).

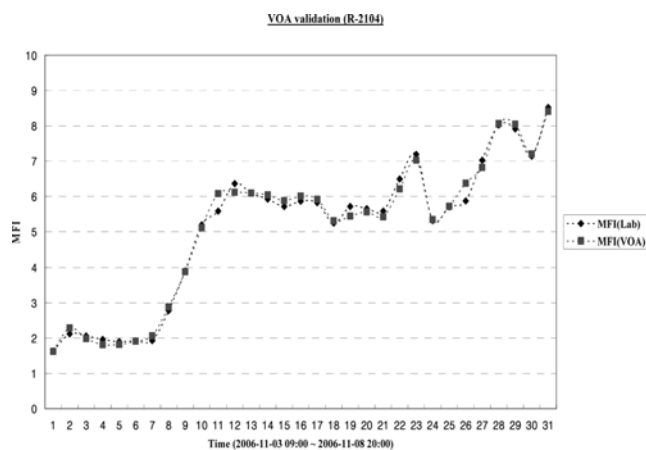


Fig. 22. Predicted MI values compared to measured MI values (R-2104).

Figs. 21 and 22 show predicted MI values compared to those measured in operations using R-2103 and R-2104, respectively. As we

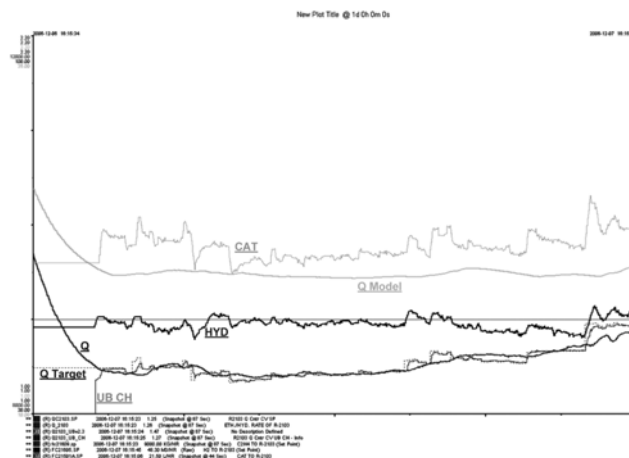


Fig. 23. Application results of the quality control system (R-2103).

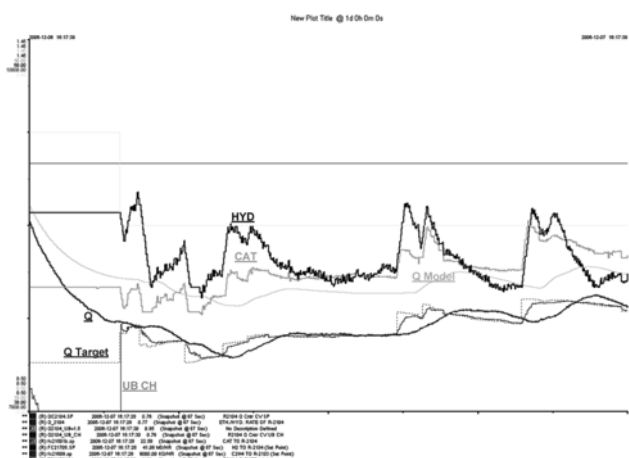


Fig. 24. Application results of the quality control system (R-2104 (1)).

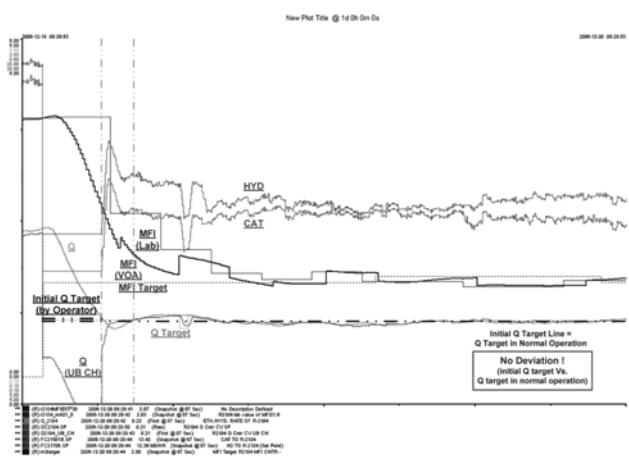


Fig. 25. Application results of the quality control system (R-2104 (2)).

can see, the predicted MFI values track the measured MFI very well. This fact validates the use of the prediction models developed in the present study for the quality control system.

Results of application of the quality control system developed in the present study are shown in Figs. 23, 24 and 25. The quality control system was implemented at the HDPE plant in LG Petrochemicals, Inc. The Q target predicted by the Q model is fed into the Q controller. The stability and reliability of the Q target are guaranteed by the effectiveness of the prediction model illustrated in Figs 21 and 22. The Q controller, in turn, sends target values for HYD and CAT to corresponding sub-controllers. As can be seen in Fig. 23-25, UB CH (Control Horizon) values show excellent tracking performance to the Q target.

## CONCLUSIONS

In this study dynamic models to estimate cumulative MI for HDPE process are developed. We first identify key variables followed by derivation of dynamic cumulative MI prediction models. The models developed in this study can easily be transformed to instantaneous MI prediction models. For each selected input variable a 1<sup>st</sup>-order model without time delay was identified and combined to give dynamic cumulative MI models. In order to illustrate the effectiveness of the present estimation model, numerical simulations were performed and results were compared with plant operation data. From the comparison with existing estimation methods, it was found that the present estimation schemes showed excellent performance in predictions.

A quality control system was developed based on the prediction models developed in the present study. The control system was implemented in the actual HDPE plant. Operation results showed excellent control performance. In particular, the amount of the off-spec during the transition was reduced from 140.29 tons to 94.5 tons (decrease of 48.45%). The transition time during grade changes was reduced from 9.2 hours to 6.3 hours (decrease of 31.52%). Moreover, the frequency of the DCS operations was decreased up to 90%.

## ACKNOWLEDGMENTS

This work was partly sponsored by the Infotrol Technology Co., Ltd. The authors wish to thank them for their support.

## NOMENCLATURE

$a_0, a_1, a_2, a_3$  : coefficients in the instantaneous MI model of Sang Joon Oh [-]  
 ACT : amount of cocatalyst or activator feed [L/h]  
 $[C_2], [C_3], [C_4]$  : concentration of ethylene, propylene and 1-butene [kg/h]  
 CAT : concentration of catalyst feed [mmol/h]

ETH : amount of ethylene feed [kg/h]  
 $FC_3C_2$  : feed rate ratio of propylene to ethylene [-]  
 $FC_4C_2$  : feed rate ratio of 1-butene to ethylene [-]  
 HDH : amount of pure hexane feed to reactor [kg/h]  
 HEX : amount of hexane feed [kg/h]  
 HMH : amount of recycled hexane feed to reactor [kg/h]  
 HYD : amount of hydrogen feed [Nm<sup>3</sup>/h]  
 $[H_2]$  : concentration of hydrogen [m<sup>3</sup>/h]  
 $i$  : subscript indicating an instantaneous melt index [-]  
 MI : melt flow index (MFI), weight of molten polymer produced during a 10-min period under certain condition [g/10 min]  
 $MI_0$  : instantaneous MI produced in the reactor [g/10 min]  
 $MI_c$  : cumulative MI [g/10 min]  
 $MI_i, MI_{inst}$  : Instantaneous MI [g/10 min]  
 $MI_p$  : cumulative MI of powder [g/10 min]  
 $MI_q$  : MI of the estimated polymer at the q th unit [g/10 min]  
 Q : ratio of hydrogen to ethylene [-]  
 $[R]$  : concentration of cocatalyst (activator) [L/h]  
 RxT : reactor temperature [°]  
 RxMI : measured MI of reactor [g/10 min]  
 T : reactor temperature [K]  
 $T_0$  : reference temperature [K]  
 $T_L$  : dead time of extruder [h]

## Greek Letters

$\alpha$  : coefficient in the instantaneous MI model of Sang Joon Oh [-]  
 $\beta, \alpha_1 \dots \alpha_5$  : parameters in instantaneous melt index of M. Oshima Eq. [-]  
 $k_0, k_1 \dots k_5$  : parameters in instantaneous melt index model of K. B. McAuley Eq. [-]  
 $\tau_1, \tau_2, \tau_3$  : residence time of reactor, flash drum & separator and dryer [h]

## REFERENCES

1. K. B. McAuley and J. F. MacGregor, *AIChE J.*, **37**, 825 (1991).
2. K. B. McAuley and J. F. MacGregor, *AIChE J.*, **38**, 1564 (1992).
3. M. Ogawa, M. Ohshima, K. Morinaga and F. Watanabe, *Journal of Process Control*, **9**, 51 (1999).
4. S. J. Oh, J. S. Lee and S. W. Park, *Ind. Eng. Chem. Res.*, **44**, 8 (2005).
5. K. B. McAuley and J. F. MacGregor, *AIChE J.*, **39**, 855 (1993).
6. M. Ohshima and M. Tanigaki, *Journal of Process Control*, **10**, 135 (2000).
7. F. Watanabe, M. Ogawa, M. Ohshima and I. Hashimoto, *AIChE J.*, **149** (1993).