Korean J. Chem. Eng., **27**(6), 1669-1674 (2010)
DOI: 10.1007/s11814-010-0290-8

Development of polyethylene melt index inferential model

Tae Young Kim and Yeong Koo Yeo†

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
(*Received 26 January 2010 • accepted 8 March 2010*)

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 large number of MI estimation and correlation methods have been proposed. In this work, we propose a new MI predicting model in which the reaction heat term in existing prediction models is replaced by temperature. The proposed model is compared with other prediction models as well as operating data to evaluate MI predicting performance. The present model shows least predicting errors compared to existing models.

Key words: Polymerization Reactor, Polyethylene, Melt Index Prediction, Reaction Heat

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 usual practice to estimate MI values in terms of measurable key variables such as temperature, pressure, feed rates of each reactants, etc.

So far many 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 which 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 et al. [4] developed an off-line Excel-based program for estimating polymer properties. They proposed an empirical prediction model for estimation of instantaneous MI.

The prediction models suggested so far involve a reaction heat term which is difficult to meausre. In this work, we propose a new MI predicting model in which the reaction heat term in existing prediction models is replaced by temperature. The proposed model is compared with other prediction models as well as operating data to evaluate MI predicting performance.

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

PROCESS DESCRIPTION

The HDPE plant at LG petrochemicals (LGPC) consists of two processes (K1 and K2) where the polymerization reaction occurs. The 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, 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 maintained within the permissible range. In the K1 polymerization process two reactors are operated in parallel mode, while reactors of the K2 process are operated in series mode. The K2 process is mainly used for the production of HDPE with wide molecular weight distribution. The operation pressure range of K1 process is 8-10 kg/cm^2 and that of K2 process is 2-4 kg/cm^2. The reaction temperature is in the range of 74-85 °C. Fig. 1 illustrates schematic of a polymerization reactor.

DEVELOPMENT OF MI ESTIMATION MODEL

For relatively low shear rate, the viscosity η is dependent on the molecular weight of the polymer being considered:

$$\eta \propto \overline{M}_W \tag{1}$$

The melt index (MI) is inversely proportional to the low shear viscosity. Thus MI can be represented in terms of $\overline{M}_W$ as given by:

$$MI = \beta\left(\frac{1}{\overline{M}_W}\right)^{\alpha} \tag{2}$$

where α and β are coefficients dependent upon the polymer being considered. Gas-phase Ziegler-Natta olefin copolymerization is controlled by reaction rather than by diffusion [6]. The broad molecu-

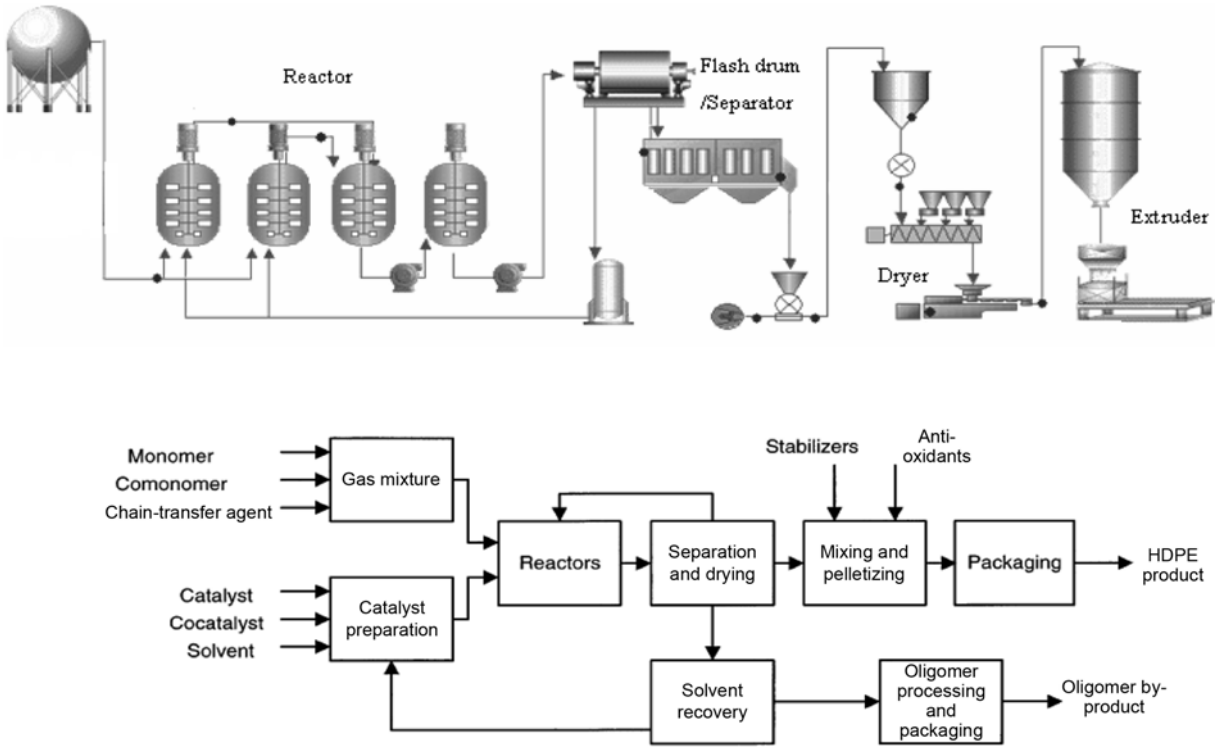

Fig. 1. Schematic of slurry polymerization process for the production of HDPE.

lar weight and compositional distributions that have been observed for these systems result from multiple types of active sites on the catalyst [7]. In this case, the growing polymer chain is terminated exclusively by the chain transfer and deactivated reacting sites. For the polymer created at each position type, the instantaneous molecular arrangement is Flory-Schultz and the molecular distribution equivalent to the most possible arrangement is equal to 2 [8]. Thus, for active sites, the instantaneous $\overline{M}_W$ and average molecular weight $\overline{M}_n$ can be related as

$$\overline{M}_W = 2\overline{M}_n \tag{3}$$

Therefore, the MI of the polymer produced instantaneously at the active sites is relevant to r_n and the average degree of instantaneous polymerization can be represented by

$$MI \propto \left[\frac{1}{r_n}\right]^{\alpha} \tag{4}$$

r_n is defined as the ratio of the growth rate of living polymer R_p to the production rate of dead chain R_{tr}:

$$r_n = \frac{R_p}{R_{tr}} \tag{5}$$

In fact, R_{tr} denotes the chain transfer combined with the site deactivation.

$$R_{tr} = R_c + R_d \tag{6}$$

$$R_p = k_p C_M C_p \tag{7}$$

$$R_c = (k_{cH}C_H + k_{cM}C_M + k_{cAT}C_{AT} + k_{cSp})C_p \tag{8}$$

$$R_d = (k_{dH}C_H + k_{dM}C_M + k_{dAT}C_{AT} + k_{dX}C_X + k_{dSp})C_p \tag{9}$$

where C_H, C_M, C_{AT}, C_X, and C_p represent concentrations of molecular weight regulator, monomer, co-catalyst, foreign substance and active growth ring in the reactor, respectively, and k_p is the rate con-

Table 1. Kinetic mechanism of Ziegler-Natta catalyst polymerization

Type	Reaction	Kinetic equations
Site activation		
By co-catalyst	$C_p + A \rightarrow P_0^k + B$	$R_{aA}^k = k_{aA}^k C_p A$
By monomers	$C_p + M_i \rightarrow P_0^k + M_i$	$R_{aM_i}^k = k_{aM_1}^k C_p M_i$
Spontaneous	$C_p \rightarrow P_0^k$	$R_{aSp}^k = k_{aSp}^k C_p$
Chain initiation	$P_0^k + M_i \rightarrow P_{1,i}^k$	$R_{ii}^k = k_{ii}^k P_0^k M_i$
Propagation	$P_{n,j}^k + M_i \rightarrow P_{n+1,i}^k$	$R_{pji}^k = k_{pji}^k p_{n,j}^k M_i$
Chain transfer		
To hydrogen	$P_{n,i}^k + H_2 \rightarrow P_0^k + D_n^k$	$R_{cHi}^k = k_{cHi}^k P_{n,i}^k H_2$
To co-catalyst	$P_{n,i}^k + A \rightarrow P_0^k + D_n^k$	$P_{cAi}^k = k_{cAi}^k P_{n,i}^k A$
To monomers	$P_{n,j}^k + M_i \rightarrow P_{1,i}^k + D_n^k$	$R_{cMji}^k = k_{cMji}^k P_n^k M_i$
Site deactivation		
By hydrogen	$P_{n,i}^k + H_2 \rightarrow C_d + D_n^k$	$R_{dHi}^k = k_{dH}^k P_{n,i}^k H$
	$R_0^k + H_2 \rightarrow C_d$	$R_{dH0}^k = k_{dH}^k P_0^k H_2$
By co-catalyst	$P_{n,i}^k + A \rightarrow C_d + D_n^k$	$R_{dAi}^k = k_{dA}^k P_{n,i}^k A$
	$R_0^k + A \rightarrow C_d$	$R_{dA0}^k = k_{dA}^k P_0^k A$
By monomer	$P_{n,i}^k + M_i \rightarrow C_d + D_n^k$	$R_{dMji}^k = k_{dMi}^k P_{n,j}^k M_i$
	$P_0^k + M_i \rightarrow C_d$	$R_{dM0i}^k = k_{dMi}^k P_0^k M_i$
Spontaneous	$P_{n,i}^k \rightarrow C_d + D_n^k$	$R_{dSpi}^k = k_{dSp}^k P_{n,i}^k$
	$P_0^k \rightarrow C_d$	$R_{dSp0}^k = k_{dSp}^k P_{n,0}^k$
Forward inhibition	$P_0^k + H_2 \rightarrow C_p^{i,k}$	$R_{fi}^k = k_{fi}^k P_0^k H_2$
Reverse inhibition	$C_p \rightarrow P_0^k + H_2$	$R_{ri}^k = k_{ri}^k C_p^{i,k}$

stant of the reaction ring growth. k_{cH}, k_{cM}, k_{cAT}, k_{cSP} are rate constants in the chain transfer for molecular weight regulator, monomer, co-catalyst and spontaneous transfer, respectively. k_{dH}, k_{dM}, k_{dAT}, k_{dX}, k_{dSP} are rate constants at deactivated sites for hydrogen, monomer, co-catalyst, foreign substance and spontaneous termination, respectively. Table 1 shows the kinetic mechanism employed in this work [9].

Substitution of Eqs. (7)-(9) into Eq. (5) gives

$$r_n = \frac{R_p}{R_{tr}} = \frac{R_p}{R_t + R_d} = \frac{k_p C_M}{(k_{cH}+k_{dH})C_H + (k_{cM}+k_{dM})C_M + (k_{cAT}+k_{dAT})C_{AT} + k_{dX}C_{dX} + k_{cSP} + k_{dSP}} \quad (10)$$

The above result can be rearranged as the relation between MI and reaction kinetics to give:

$$MI \propto \beta \left\{ \left(\frac{k_{cH}+k_{dH}}{k_p}\right)\left(\frac{C_H}{C_M}\right) + \left(\frac{k_{cM}+k_{dM}}{k_p}\right) + \left(\frac{k_{cAT}+k_{dAT}}{k_p}\right)\left(\frac{C_{AT}}{C_M}\right) + \left(\frac{k_{dX}}{k_p}\right)\left(\frac{C_{dX}}{C_M}\right) + \left(\frac{k_{cSP}+k_{dSP}}{k_p}\right)\left(\frac{1}{C_M}\right) \right\}^{\alpha} \quad (11)$$

Eq. (11) can be simplified as

$$MI \propto \beta \left\{ k_1\left(\frac{C_H}{C_M}\right) + k_2 + k_3\left(\frac{C_{AT}}{C_M}\right) + k_4\left(\frac{C_{dX}}{C_M}\right) + k_5\left(\frac{1}{C_M}\right) \right\}^{\alpha} \quad (12)$$

The effect of temperature on the MI can be characterized by considering the Arrhenius relation given by

$$k_{tr}(T) = k_{tr}(T_0)\exp\left(-\frac{Ea_{tr}}{RT}\left\{\frac{1}{T} - \frac{1}{T_0}\right\}\right) \quad (13)$$

where k_{tr} is the rate constant for the chain transfer reaction and T_0 is a reference temperature. The ratio of k_{tr} to k_p is given by

$$\frac{k_{tr}(T)}{k_p(T)} = \frac{k_{tr}(T)}{k_p(T)}\exp\left(\frac{-Ea_{tr}+Ea_p}{RT}\left\{\frac{1}{T} - \frac{1}{T_0}\right\}\right) \quad (14)$$

where is the activation energy for chain growth. Substitution of Eq. (14) into Eq. (12) gives

$$\ln(MI) \propto \frac{k_6}{T} - \frac{k_6}{T_0} + \alpha \ln\left\{ k_1\left(\frac{C_H}{C_M}\right) + k_2 + k_3\left(\frac{C_{AT}}{C_M}\right) + k_4\left(\frac{C_{dX}}{C_M}\right) + k_5\left(\frac{1}{C_M}\right) \right\} \quad (15)$$

From Eq. (15) we can see that MI is affected by concentrations of molecular weight regulator, monomer, co-catalyst, foreign substance, reaction temperature and catalyst properties. Construction of the MI estimation model based on these elements requires some assumptions including:

· Polymerization time is very short compared to the residence time of polymer in the reactor.

· The molecular structure and physical properties of the polymer produced in short time are consistent.

· The molecular structure of the polymer produced is determined by the technical operating conditions of polymerization.

Exact identification of kinetic parameters for each reaction is very difficult due to the complicated polymerization reaction structure of the ethylene. Moreover, the activity of the catalyst may differ at each reaction cycle. The activity of the catalyst may also be deteriorated by the existence of foreign substance such as moisture, oxygen and carbon monoxide in the feed stream. Detection of such unwanted substance is very difficult during operation, which makes the accurate measurement of MI very difficult. For these reasons, the MI estimation model given by Eq. (15) is not suitable for practical application.

Increase of the ratio C_{dX}/C_M indicates abundance of impurities which may deteriorate catalyst activity followed by decrease of the ethylene conversion. Lower ethylene conversion causes a decrease in the amount of reaction heat. On the other hand, if the polymerization rate increases due to higher reaction temperature, the rate of the ethylene conversion shows substantial increase followed by increase of reaction heat. In short, the amount of reaction heat represents degree of the polymerization. In fact, the reaction heat represents the effects of concentrations of unmeasurable impurities and catalyst activity on MI. Based on this observation, Jin proposed an instantaneous MI model including the effect of the reaction heat [10] given by:

$$\ln(MI) = b_0 + b_1\ln\left(\frac{C_H}{C_M}\right) + b_2\ln\left(\frac{C_{AT}}{C_M}\right) - b_3\ln(H_r) \quad (16)$$

Here b_0, b_1, b_2, b_3 are model parameters to be determined. In an actual operation, it is very hard to measure the reaction heat. Therefore, in this work, we propose a new MI estimation model which incorporates the reaction temperature instead of the inclusion of the reaction heat. The new model can be represented as:

$$\ln(MI) = c_0 + c_1\ln\left(\frac{C_H}{C_M}\right) + c_2\ln\left(\frac{C_{AT}}{C_M}\right) - c_3\left(\frac{1}{T}\right) \quad (17)$$

where c_0, c_1, c_2, c_3 are model coefficients to be determined empirically. For determination of these coefficients, operation data are plug into Eq. (17) to give a linear system in the form of Ax=b where A, b, and x are given by

$$A = \begin{bmatrix} 1 & \ln\left(\frac{C_H}{C_M}\right)_1 & \ln\left(\frac{C_{AT}}{C_M}\right)_1 & -\frac{1}{T_1} \\ 1 & \ln\left(\frac{C_H}{C_M}\right)_2 & \ln\left(\frac{C_{AT}}{C_M}\right)_2 & -\frac{1}{T_2} \\ \vdots & \vdots & \vdots & \vdots \\ 1 & \ln\left(\frac{C_H}{C_M}\right)_n & \ln\left(\frac{C_{AT}}{C_M}\right)_n & -\frac{1}{T_n} \end{bmatrix}, \quad x = \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \end{bmatrix},$$

$$b = \begin{bmatrix} \ln(MI)_1 \\ \ln(MI)_2 \\ \vdots \\ \ln(MI)_n \end{bmatrix} \quad (18)$$

We need operation data for each grade because the model coefficients are dependent upon the product grade. Table 2 shows values of the model coefficients based on recent operation data.

The cumulative MI model for the proposed MI model is given by:

$$\frac{d\ln(MI_c)}{dt} = \frac{1}{\tau}\ln(MI_i) - \frac{1}{\tau}\ln(MI_c) \quad (19)$$

where MI_c, MI_i are cumulative MI and instantaneous MI, respectively, and τ is the residence time in solid state.

Table 2. Scaled parameters required for the inference scheme

Parameter	Scaled value [-]
c_0	2.75
c_1	0.3
c_2	2.4
c_3	480

MI ESTIMATION MODELS

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

$$\ln(MI_i) = 3.5\ln\left\{k_0 + k_1\frac{[H_2]}{[C_2]} + k_2\frac{[C_3]}{[C_2]} + k_3\frac{[C_4]}{[C_2]} + k_4\frac{[R]}{[C_2]}\right\} + k_5\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (20)$$

where the subscript i denotes the i-th reactor, MI is the instantaneous MI, k_j (j=0, 1, …, 5) parameters, 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

$$\frac{d(MI_c(t)^{-0.286})}{dt} = \frac{1}{\tau(t)}MI_i(t)^{-0.286} - \frac{1}{\tau(t)}MI_c(t)^{-0.286} \quad (21)$$

where MI_c and MI_i denote MI of cumulative polymer and instantaneous polymer, respectively [1,2].

Ohshima [3] 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 types [1]. Their model is a linear combination of concentration ratios of each reactants and logarithm of catalyst and temperature term.

$$\log(MI_i) = \gamma + \alpha_1\frac{[H_2]}{[C_2]} + \alpha_2\frac{[C_3]}{[C_2]} + \alpha_3\frac{[C_4]}{[C_2]} + \alpha_4\log[R] + \alpha_5\log(T) \quad (22)$$

Again the corresponding cumulative MI model is given by

$$\frac{d\log(MI_c(t))}{dt} = \frac{1}{\tau_1(t)}\log(MI_i(t)) - \frac{1}{\tau_1(t)}\log(MI_c(t)) \quad (23)$$

where τ_1 represents the residence time of polymer in the reactor.

Oh [4] presented an empirical instantaneous MI estimation model which predicts instantaneous properties of polymer. They use the ratio of the amount of feeds instead of concentrations of each component. Their model is given by

$$\log(MI_{inst,i}) = \theta + a_0\log(T)_i + a_1\log\left(\frac{[H_2]}{[C_2]}\right)_i + a_2FC_3C_{2,i} + a_3FC_4C_{2,i} \quad (24)$$

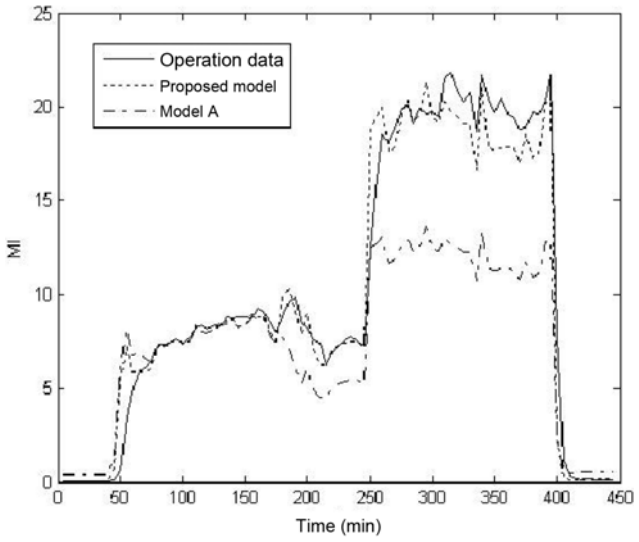

Fig. 2. Comparison of measured MI and predicted MI.

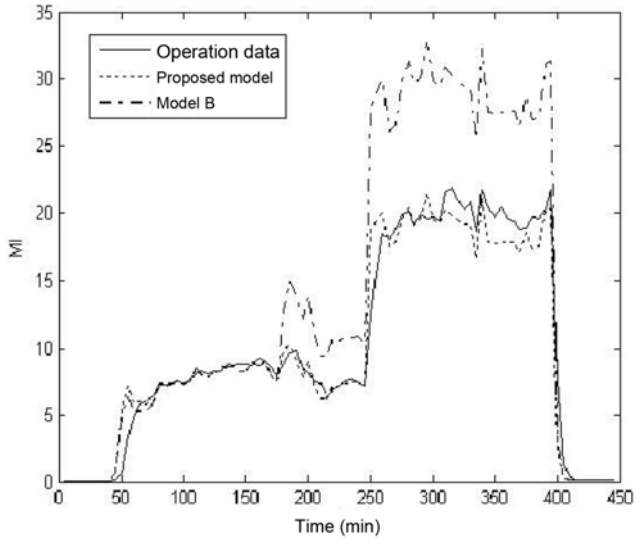

Fig. 3. Comparison of measured MI and predicted MI.

To demonstrate the validity of the present model, we compare the prediction performance of each of the existing model described above and of the present model based on the operation data. MI cannot be measured on-line, and the MI value is determined by analyzing samples every two hours in the operation.

Fig. 2 shows the results of MI estimation by Model A as well as those by the MI model presented in this study. As we can see, the proposed model exhibits fewer estimation errors compared to Model A. In Fig. 3, we compare our model with Model B. Again, we can see that the estimation performance of the proposed model is better than that of Model B. Fig. 4 represents the results of MI estimation by Model C as well as those by the proposed model in this study. As we can see, the proposed model again exhibits fewer estimation errors compared to Model C. The prediction performances of the four models can also be quantitatively assessed from Table 3, which lists the root-mean-squared errors (RMSEs) between the measured and predicted values of the melt index defined as:

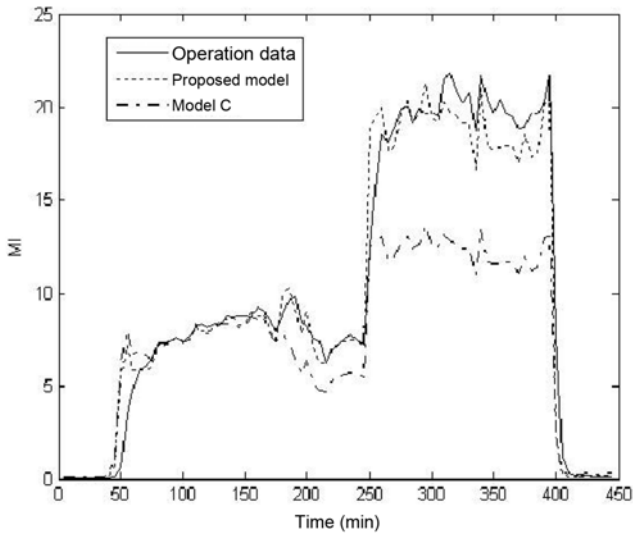

Fig. 4. Comparison of measured MI and predicted MI.

Table 3. RSMEs for the models for melt index

Model	RMSE for the testing data sets
Model A	1.65
Model B	1.93
Model C	1.65
Proposed model	0.46

$$\mathrm{RMSE}=\sqrt{\sum_{i=1}^{n}(\hat{y}_i-y_i)/n} \tag{25}$$

In short, the MI prediction model proposed in this work shows better performance than other existing models and gives little discrepancy between measured data and prediction results.

CONCLUSION

We have proposed a new MI predicting model in which the reaction heat term in existing prediction models is replaced by temperature. For the purpose of comparison, we choose among other models three MI estimation models known to be successful so far. The estimation performance of the proposed model is compared with that of each chosen model as well as operating data obtained from HDPE plant. The present model shows least predicting errors compared to existing models.

ACKNOWLEDGEMENTS

This work is the outcome of a Manpower Development Program for Energy supported by the Ministry of Knowledge and Economy (MKE).

NOMENCLATURE

MI : melt flow index (MFI), weight of molten polymer produced during a 10-min period under certain condition [g/10 min]
MI_i : instantaneous MI produced in the reactor [g/10 min]
MI_c : cumulative MI [g/10 min]
$\overline{M}_W$: weight average molecular weight
$\overline{M}_n$: number average molecular weight
R_p : rate of propagation of living polymer chains
R_{tr} : rate of production of dead polymer chains
R_c : rate of production of chain transfer
R_d : rate of production of site deactivation
k_p : rate constant of propagation
k_H : rate constant of 1-butane/propylene
k_M : rate constant of monomer
k_{AT} : rate constant of co-catalyst
k_X : rate constant of impurity
k_{SP} : rate constant of spontaneous
k_{tr} : rate constant of dead polymer chains
C_H : concentration of 1-butane/propylene
C_M : concentration of monomer
C_{AT} : concentration of co-catalyst
C_X : concentration of impurity
C_{SP} : concentration of spontaneous
C_P : mole of active sites in the reactor
T : reactor temperature [K]
T_0 : reference temperature [K]
H_r : heat of reaction
$[C_i]$: concentration (i=2: ethylene, i=3: 1-butene i=4: higher alpha-olefin) [kg/h]
$[H_2]$: concentration of hydrogen [m^3/h]
[R] : concentration of cocatalyst (activator) [L/h]
FC_3C_2 : feed rate ratio of propylene to Ethylene [-]
FC_4C_2 : feed rate ratio of 1-butene to Ethylene [-]
$a_0 \ldots a_3$: coefficients in the instantaneous MI model of Sang Joon Oh Eq. [-]
$k_0, k_1 \ldots k_5$: parameters in instantaneous melt index of K.B.McAuley Eq. [-]
$b_0 \ldots b_3$: parameters in instantaneous melt index model of Xuelan Jin Eq. [-]
$c_0 \ldots c_3$: parameters in instantaneous melt index of Proposed Eq. [-]

Greek Symbols

η : viscosity of a polymer melt at low shear rates
β : coefficients dependent upon the polymer
τ_i : residence time (i=1: reactor, i=2: flash drum, i=3: separator and dryer)[h]
θ : coefficients in the instantaneous MI model of Sang Joon Oh Eq. [-]
γ : parameters in instantaneous melt index model of M.Ohshima Eq. [-]
$\alpha_1 \ldots \alpha_5$: parameters in instantaneous melt index model of M.Ohshima Eq. [-]

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