Macromol. Symp. **2008**, 271, 26–37
DOI: 10.1002/masy.200851104

In-Line Monitoring of Bulk Polypropylene Reactors Based on Data Reconciliation Procedures

*Diego Martinez Prata, Enrique Luis Lima, José Carlos Pinto**

Summary: The main objective of this work is the implementation of a nonlinear dynamic data reconciliation (NDDR) procedure for the in-line monitoring of the bulk propylene polymerization, as performed in a real industrial site. Special attention is given to monitoring of the melt flow index (MI) of the polymer product obtained in an industrial extruder at different operating conditions. In order to do that, a model is developed to describe the polymerization process and the controlled degradation of polypropylene in a reactive extruder. The model is implemented in real time, allowing for in-line and real-time monitoring of the plant operation.

Keywords: in-line industrial process monitoring; melt index; nonlinear dynamic data reconciliation; parameter estimation; real polymerization plant data

Introduction

Modern industrial plants may provide very detailed and rich data sets for development of fundamental modeling studies. However, as information concerning plant variables comes from real in-line measurements and/or laboratory analyses, data values are normally corrupted by errors (random noise, spurious values and systematic biases). For this reason, real data generally do not satisfy process constraints (such as mass and energy balances). Thus, data reconciliation and process parameter estimation (DRPE) are essential for obtainment of reliable information.

The data reconciliation (DR) procedure may be defined as the adjustment of process measurements and model parameters in order to satisfy a certain set of conservation laws and process constraints, while minimizing some sort of objective function that weighs the deviations between corrected and observed plant values. The estimation of model parameters from available plant data can certainly be included in this context. First, a mathematical model has to be built to provide the process constraints that must be satisfied by the measured data. Second, model parameters (and process measurements) have to be adjusted to minimize the deviations observed between process measurements and process constraints. As model predictions are compared to plant measurements during the DRPE analysis, plant data have to be filtered to allow for removal of inconsistent values from the process data sets used for model building. The literature regarding DR strategies is very huge and good reviews can be found elsewhere (Crowe, 1996;[1] Mah, 1990;[2] Narasimhan and Jordache, 2000;[3] Romagnoli and Sanchez, 2000[4]). Although DRPE procedures are intended to be used at plant site, very little is described in the open literature about the use of DRPE procedures in actual industrial applications. This is particularly true for industrial polymerization processes (Arora e Biegler 2004).[5]

Mathematical models play a very important role in the field of polymerization engineering. Polymerization models may be used at plant site for a number of different applications. As final polymer properties and process responses depend in a very complex and nonlinear manner

---

Programa de Engenharia Química/COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP: 68502, Rio de Janeiro, 21945-970 RJ, Brazil
E-mail: pinto@peq.coppe.ufrj.br

upon the process operation conditions (Eliçabe and Meira, 1988),[6] it is actually very difficult to design and improve process operation conditions without the help of process models. Therefore, there are huge incentives for the in-line implementation of detailed dynamic process models that may be used to perform the rigorous control of the polymerization process and the optimization of the process operation.

The availability of in-line information regarding some of the final polymer properties (such as xylene solubles (*XS*) and melt flow index (*MI*) of polyolefins) may allow for more efficient operation and may significantly improve the performance of control procedures, especially when it is considered that laboratory analyses are normally delivered with long delays. The joint implementation of nonlinear dynamic data reconciliation (NDDR) and process parameter estimation schemes may be used to provide reliable in-line information about process operation variables and product properties, and may therefore constitute an important tool for implementation of advanced control procedures in the plant. In order to make this possible, an acquisition framework must be developed to handle in-line measurements and simultaneously solve the joint NDDR procedure in real time, respecting the hard time constraints of sampling intervals.

There are essentially three classes of numerical algorithms that can be used to solve NDDR problems (Kong *et al.*, 2000):[7] Extended Kalman Filters (EKF); Artificial Neural Networks (ANN) and Constrained Nonlinear Programming (CNLP). Although the use of EKF procedures has become very popular in the control field, EKF algorithms suffer from some deficiencies that have been pointed out in the scientific literature. For instance, EKF cannot handle inequality or equality constraints efficiently and can therefore give rise to infeasible estimates. Besides, EKF needs a linear or locally linearized model, which may lead to accumulation of modeling errors and bias (Vachhani *et al.*, 2005)[8]. Finally, EKF algorithms are difficult to tune and can give poor estimates of unmeasured parameters and disturbance variables. ANNs have also been used for data reconciliation successfully (Karjala and Himmelblau 1996).[9] However, as they require large data sets for efficient training, the practical implementation in a changing production environment can be very difficult, especially when frequent grade transitions are performed. On the other hand, CNLP techniques are commonly criticized by those who are interested in developing in-line applications because of its larger computer demands; however, the fast development of computer resources is making this argument less important.

In seems that the works of Vieira *et al.* (2003)[10] and Prata *et al.* (2006)[11] were the only ones that provided real industrial data to perform the DRPE procedure. Bindlish *et al.* (2003)[12] estimated two kinetic parameters using industrial data obtained from a polymerization process. They calculated the confidence intervals of the parameter estimates, but model parameters were not allowed to vary along the process operation. Other works (see Prata *et al.*, 2006)[11] used simulated data to analyze the operation of polymerization processes.

Prata *et al.* (2006)[11] used CNLP algorithms to solve NDDR problems for an industrial bulk polypropylene polymerization site and showed that in-line and real time implementation of the technique was indeed possible. As a result, *MI* and *XS* estimates might be delivered in real time for control purposes. In the present work, the technique is implemented in real time in an industrial data acquisition system. Besides, the model is extended to include the process extruder, where the *MI* of the final product can be monitored by a process rheometer and can be modified through addition of peroxides.

Formulation of the Data Reconciliation Procedure

Assuming that measurement errors are small, uncorrelated and follow the normal distribution with zero mean and known variance, the nonlinear dynamic data reconciliation problem with simultaneous parameter estimation can be formulated as the minimization of the following objective function:

$$S(\hat{\boldsymbol{\theta}}, \hat{\mathbf{z}}_j) = \sum_{j=0}^{C} \left[\hat{\mathbf{z}}_j - \mathbf{z}_j\right]^T \mathbf{V}^{-1} \left[\hat{\mathbf{z}}_j - \mathbf{z}_j\right] \qquad (1)$$

subject to

$$\begin{aligned} &\mathbf{f}\left[\tfrac{d\hat{\mathbf{z}}(\hat{\boldsymbol{\theta}},t_j)}{dt}, \hat{\mathbf{z}}\left(\hat{\boldsymbol{\theta}}, t_j\right)\right] = \mathbf{0} \\ &\mathbf{h}\left[\hat{\mathbf{z}}\left(\hat{\boldsymbol{\theta}}, t_j\right)\right] = \mathbf{0} \\ &\mathbf{g}\left[\hat{\mathbf{z}}\left(\hat{\boldsymbol{\theta}}, t_j\right)\right] > \mathbf{0} \end{aligned} \qquad (2)$$

where $\mathbf{z}_j$ and $\hat{\mathbf{z}}_j$are vectors of the discrete measured and reconciled variables at time j, $\mathbf{V}$ is a diagonal matrix of measurement error variances, $\hat{\boldsymbol{\theta}}$ is the vector of parameter estimates and $S\left(\hat{\boldsymbol{\theta}}, \hat{\mathbf{z}}_j\right)$ is the minimum value of the objective function at the optimized values of $\hat{\mathbf{z}}_j$ and $\hat{\boldsymbol{\theta}}$. The generic algebraic-dynamic model constraints are represented by the functions **f** and **h**, while **g** represent the inequality algebraic constraints. The subscript j indicates the sampling times (variables t_0 and t_c represent the initial and the current times, respectively).

Several strategies have been proposed to solve such constrained nonlinear dynamic programming problems (Biegler and Grossman, 2004).[13] In this work, a sequential strategy is applied to a time moving window where the differential equation system and the optimization problem are solved sequentially using the data measured over the current window, until convergence is reached.

For practical implementation on real dynamic systems, it is common to use a time moving window (moving horizon) to reduce the size of the optimization problem to manageable dimensions (Romagnoli and Sanchez, 2000).[4] The window size is a tuned parameter and is also utilized to capture the latest process behavior (Chen and Romagnoli, 1998),[14] being useful when process parameters can change with the operation conditions.

The optimization problem is solved here with the solver ESTIMA (Noronha *et al.*, 1993),[15] a standard software for the simultaneous data reconciliation and estimation of model parameters, based on a Gauss-Newton method (Anderson *et al.* 1978)[16]. Convergence control is performed as suggested by Bailey (1963)[17]. Objective function gradients are calculated by central finite differences. The system of differential equations is solved numerically with DASSL (Petzold, 1989).[18]

The Analyzed Process

Process Description

The analyzed process consists of the bulk polymerization of propylene in a single CSTR (LIPP-SHAC Shell Technology), with bleed and recycle streams, using high-activity fourth generation Ziegler-Natta catalyst ($TiCl_4/MgCl_2 + PEEB + TEA$) to produce polypropylene in liquid propylene (liquid pool or bulk reactor). The process is described in detail by Mattos Neto and Pinto (2001) [19] and is represented in Figure 1.

Polymerization heat is removed by condensation of boiling propylene. Monomer feed rates are usually limited by maximum solid hold-up in order to keep the suspension stable. The molecular weight distribution, estimated from the melting index (*MI*), is controlled by the hydrogen feed stream and can be modified through addition of peroxides. The operation pressures are high - around 30 atm. Important issues for this technology are the control of solids hold-up, liquid propane concentration, and the *MI* and *XS* of the final polymer material. The *XS* represents the fraction of polymer material that can be extracted by boiling xylene and the increase of *XS* indicates poor control of the degree of isotacticity. As variations of liquid propane concentration (C_a) may prejudice polymer productivity and modify the quality of the final resin, liquid bleed flow rates (m_{bleed}) must be manipulated to control the propane concentration in the liquid pool

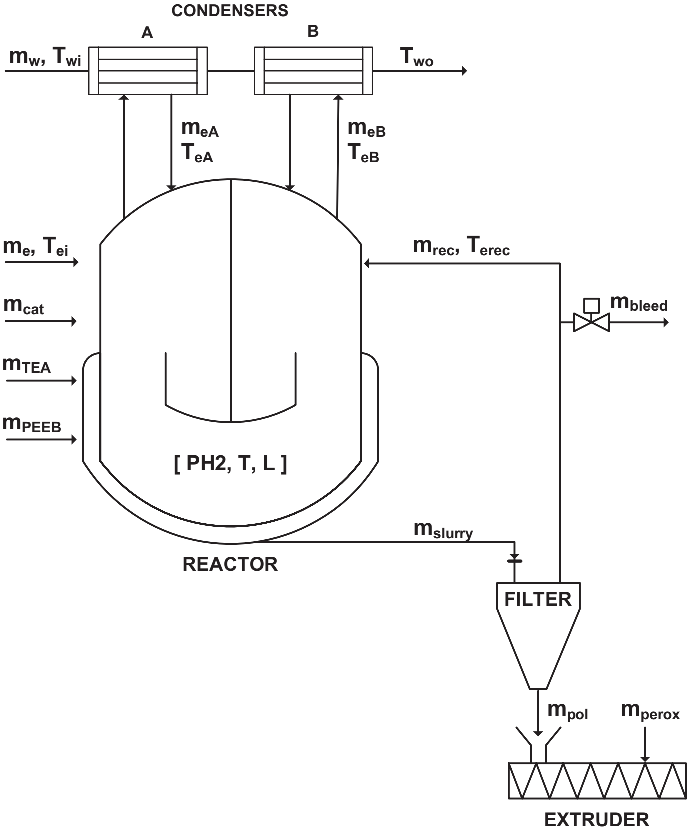

Figure 1.
Industrial polymerization process and extruder.

around 10%. In this process there are two important kinetic parameters C (kinetic constant for transfer to hydrogen) and K_p (kinetic constant for homo-propagation). Both constants are allowed to vary along the process operation because of modification of the levels of contaminants in feed and because of the modifications of the hydrogen partial pressure, which is used to control the MI and affects the catalyst performance. The characteristic time of this process is around 1h.

Phenomenological Model

A rigorous dynamic model of this process involves a system of algebraic and differential equations of considerable dimension, which renders the on-line data reconciliation problem unfeasible with current computer and numerical technology. A simplified dynamic model of this process can then be given by:

Mass Balances:

$$\frac{dPa}{dt} = m_e \cdot w_a - \left(\frac{Pa}{Pa + Pe}\right) \cdot m_{bleed} \tag{3}$$

$$\frac{dPe}{dt} = m_e \cdot (1 - w_a) - R_{pol} - \left(\frac{Pe}{Pa + Pe}\right) \cdot m_{bleed} \tag{4}$$

$$\frac{dPol}{dt} = R_{pol} - m_{pol} \tag{5}$$

$$\frac{dCat}{dt} = m_{Cat} - \left(\frac{Cat}{Pol}\right) \cdot m_{pol} - K_d \cdot Cat \tag{6}$$

$$\frac{dTEA}{dt} = m_{TEA} - \alpha \cdot \left(\frac{TEA}{Pe + Pa}\right) \cdot m_{bleed} - (1 - \alpha) \cdot \left(\frac{TEA}{Pol}\right) \cdot m_{pol} \qquad (7)$$

$$\frac{dPEEB}{dt} = m_{PEEB} - \left(\frac{PEEB}{Pol}\right) \cdot m_{pol} \qquad (8)$$

$$\frac{dN}{dt} = \frac{R_{pol}}{M_n^I} - \frac{m_{pol}}{M_n^{ac}} \qquad (9)$$

$$m_{pol} = m_{slurry} \cdot w_{pol} \qquad (10)$$

$$m_{slurry} = \frac{m_{rec} + m_{bleed}}{1 - w_{pol}} \qquad (11)$$

$$w_{pol} = \frac{Pol}{M} \qquad (12)$$

$$M = Pe + Pa + Pol + Cat + TEA + PEEB \qquad (13)$$

$$C_a = \frac{Pa}{Pa + Pe} \qquad (14)$$

$$R_{pol} = \frac{K_p \cdot Cat \cdot Pe}{M} \qquad (15)$$

$$MI = K_0 \cdot (M_w^{ac})^{\lambda} + \beta \cdot \frac{m_{perox}}{m_{pol}} \qquad (16)$$

$$M_n^I = \frac{PMPe}{\gamma + C \cdot \frac{(PH_2)}{\left(\frac{Pe}{Pa+Pe}\right)}} \qquad (17)$$

$$M_n^{ac} = \frac{Pol}{N} \qquad (18)$$

$$M_w^{ac} = PD \cdot M_n^{ac} \qquad (19)$$

$$V = \left(\frac{Pa}{\rho_a(T)} + \frac{Pe}{\rho_e(T)} + \frac{Pol}{\rho_{pol}(T)}\right) \qquad (20)$$

$$V(L) = 2.8708 \cdot L^2 + 1187.8540 \cdot L + 2771.8010 \qquad (21)$$

Energy Balance (EB):

$$\frac{dT}{dt} = \frac{m_e \cdot Cp_e(T) \cdot (T_{ei} - T) + m_{rec} \cdot Cp_e(T) \cdot (T_{erec} - T) + (-\Delta H) \cdot R_{pol} - Q_e}{\left(Pa \cdot Cp_a(T) + Pe \cdot Cp_e(T) + Pol \cdot Cp_{pol}(T)\right)} \qquad (22)$$

$$Q_e = m_{eA} \cdot \lambda_e(T) + m_{eA} \cdot Cp_e(T) \cdot (T - T_{eA}) + m_{eB} \cdot \lambda_e(T) + m_{eB} \cdot Cp_e(T) \cdot (T - T_{eB}) \qquad (23)$$

$$T_{wo} = \frac{Q_e + m_w \cdot Cp_w(T) \cdot T_{wi}}{m_w \cdot Cp_w(T)} \qquad (24)$$

All variables are defined in the Nomenclature. The studied problem involves 16 independent (in-puts) variables (m_e, m_{cat}, m_{TEA}, m_{PEEB}, m_{bleed}, m_{rec}, m_{eA}, m_{eB}, m_w, m_{perox}, T_{ei}, T_{erec}, T_{eA}, T_{eB}, T_{wi}, PH_2), 6 dependent (output or state) variables (C_a, m_{pol}, MI, L, T, T_{wo}), 7 initial conditions for each time varying moving window (Pe_0, Pa_0, Cat_0, TEA_0, N_0, L_0, T_0) and 2 process time-variant parameters (K_p and C). All unmeasured variables (m_{slurry}, M, M_n^I, M_n^{ac},M_w^{ac}, Q_e, R_{pol}, V, w_{pol}) can be observed with the proposed process model. Physical properties, such as densities (ρ_a, ρ_e, ρ_{pol}), heat capacities (C_{pa}, C_{pe}, C_{ppol}, C_{pw}) and the heat of vaporization (λ_e) are assumed to be known functions of reactor temperature. The others model parameters (α, β, ΔH, γ, λ, K_0, K_d, K_{xs}, PD, w_a, XS^R) are assumed to be known and their values can be found in Prata (2005),[20] except β. After variable classification procedure (Oliveira Júnior, 2006),[21] it has been observed that the initial conditions of $PEEB_0$ and Pol_0 have to be known. In order to guarantee the observation of the co-catalyst concentrations, an additional algebraic equation is used as

$$PEEB_0 = \frac{(Pa_0 + Pe_0 + Pol_0) \cdot m_{PEEB}}{m_{slurry}} \qquad (25)$$

The initial condition for Pol_0 is calculated with the help of Eq. (22), where it is assumed that V_0 (L_0) is known. The XS equation (Prata *et al.*, 2006)[11] has been neglected in the preset study because XS cannot be measured in-line at plant site yet.

Model Update – MI Equation

The model was extended to include the process extruder, where the *MI* of the final

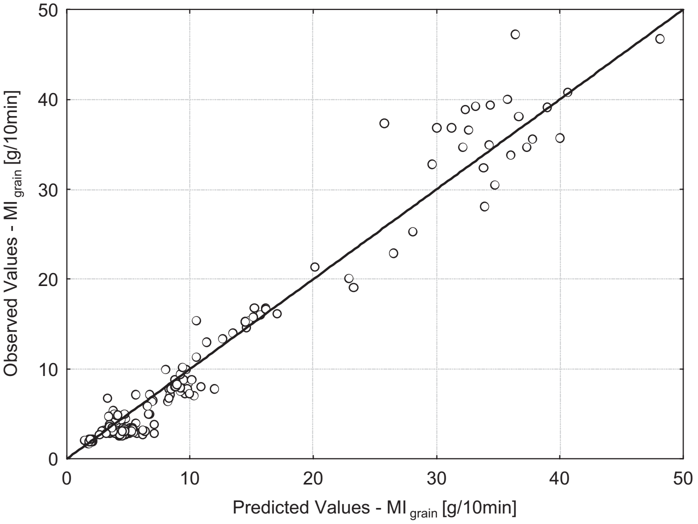

Figure 2.
MI values, as obtained experimentally and predicted by Equation (18).

product can be monitored in-line by a process rheometer and can be modified through addition of peroxides. The additional model equations are provided by Latado *et al.* (2001) [22] and Oliveira *et al.* (2006) [23], as described in Equation (18). Based on available experimental data, model parameters were estimated as $\mu = 0.96652 \pm 0.03207$ and $\beta = 65069.10 \pm 934.38$. Figure 2 illustrates the quality of the obtained model fitting.

In-Line Acquisition Framework

Measured data are sent from the DCS-PI to an EXCEL® spreadsheet, both running in Windows®. The framework was written in VBA for EXCEL®, with the exception of ESTIMA (FORTRAN executable), used for data reconciliation and estimation of model parameters. The EXCEL® "Main Plain" controlled the sampling times and the data flow among the distinct modules.

First, the subroutine "Window preparation" organizes the data in the actual moving window from DCS-PI. Afterwards, the subroutine "Pre-filter" looks for inconsistent data in the sample window. The inconsistent data are replaced by valid previous values (a zeroth-order filter). The valid window is exported as *.*txt* data file format that can be read by the ESTIMA code. During execution of ESTIMA, the module "Shell and Wait" is used to interrupt the VBA code until the NDDR problem has been completed solved. The results are written in *.*txt* data file, which is imported from another spreadsheet called "Results Plain". Reconciled data are then sent back to the DCS.

Results

The industrial data were obtained with the data acquisition framework described above. The magnitudes of the measurement errors (associated with the instrument) and of the process noise (associated with the operation) were evaluated for all process signals with available steady-state conditions. Figures 4 to 17 present results obtained with a sampling time of 5 min and a moving time window of 1h (13 sampling points of 5 min). Figures 4 and 5 show measured and reconciled data values for the propane concentration in the recycle stream (Ca) and for the input propylene flow rate (m_e). It can be observed that reconciled values

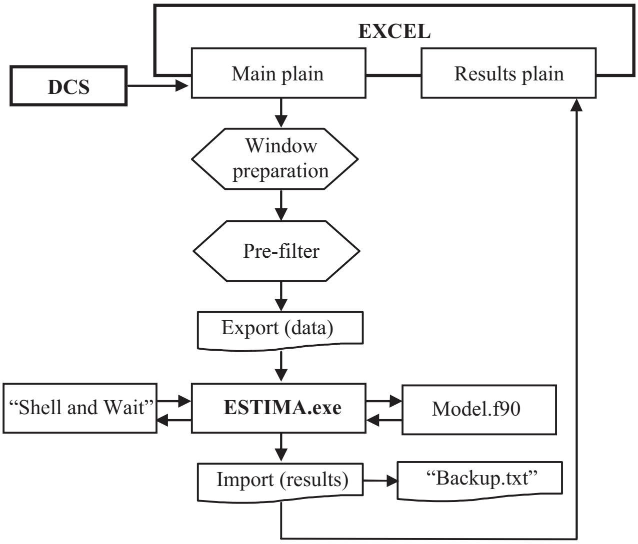

Figure 3.
In-Line Acquisition Framework.

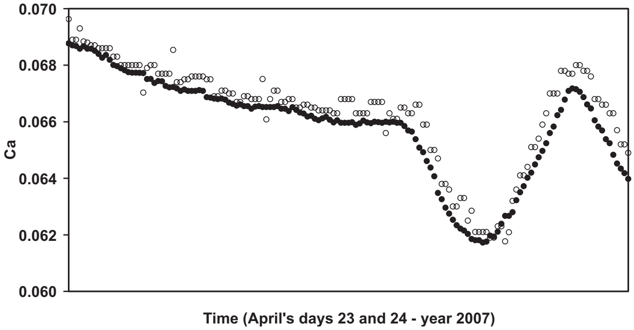

Figure 4.
Measured (○) and reconciled (●) propane concentration.

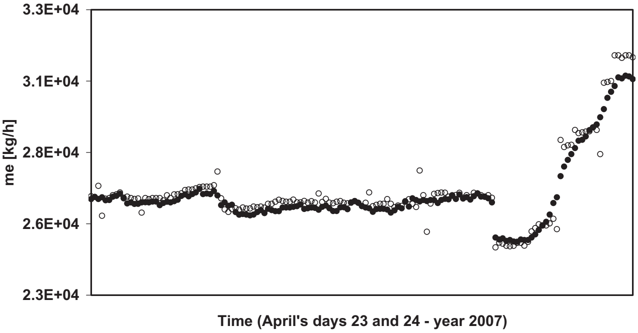

Figure 5.
Measured (○) and reconciled (●) propylene feed rates.

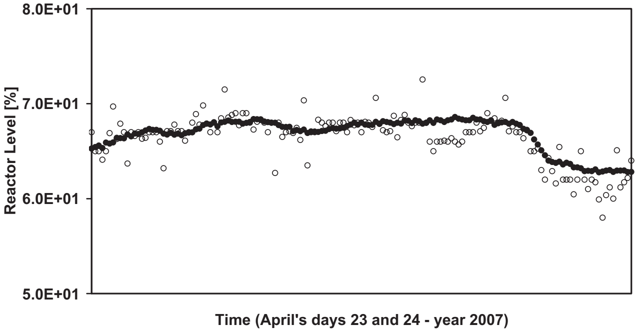

Figure 6.
Measured (○) and reconciled (●) reactor level.

are much more stable than measured values, which leads to improved controller performance. Figures 4 and 5 also show that mass balance constraints are satisfied with good precision at plant site.

Figures 6 and 7 show measured and reconciled values for reactor level and temperature, respectively. In both cases very good filtering of measured data can be observed. The reconciled values seem to represent the actual process operation conditions much more accurately than the available measured data, given the much lower noise levels. It is important to emphasize that temperature deviations from set point values cannot be larger than 0.3 values during operation; otherwise, control actions are taken in order to avoid potentially dangerous runaway conditions. Figure 7 shows that this maximum allowed deviation is violated frequently during the analyzed operation period, due to unknown process perturbations. However, reconciled data show that control actions were not necessary; therefore, the introduction of unnecessary control actions would only lead to additional perturbation of the normal process operation.

Figures 8 shows measured and reconciled values for the polymer production flowrate (m_{pol}). In this particular case, the mass flowrates of polymer production are subject to significant levels of noise, because the rates of polymer production are evaluated at the storage tanks, and not at the outlet reactor stream.[11] Therefore, the reconciled values probably represent the actual process operation conditions much more accurately than the available measured data, which incorporate production lags and other types of process fluctuations. Figure 9 shows the estimates

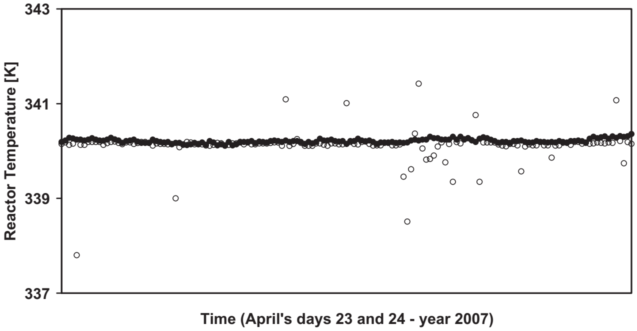

Figure 7.
Measured (○) and reconciled (●) reactor temperature.

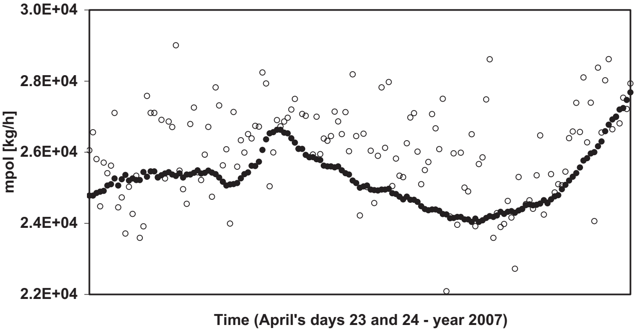

Figure 8.
Measured (○) and reconciled (●) polymer output flow rates.

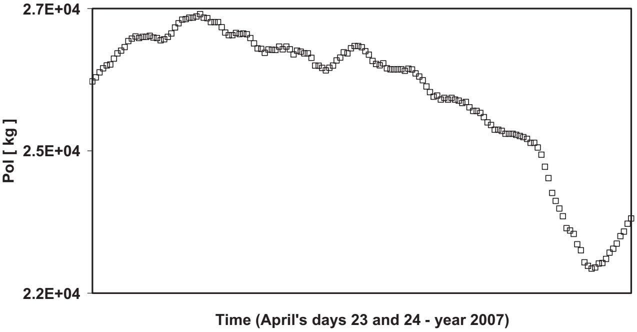

Figure 9.
Estimated polymer mass (□).

for the polymer mass inside the reactor vessel (an unmeasured process variable). It must be noted that the results presented in Figure 9 agree well with the results shown in Figures 5 and 8, as the decrease and subsequent increase of the polymer mass inside the reactor vessel are consequences of the observed variations of the input and output flow rates.

Figure 10 shows estimates of the kinetic constant for homo-propagation (K_p) (catalyst activity) along the process operation

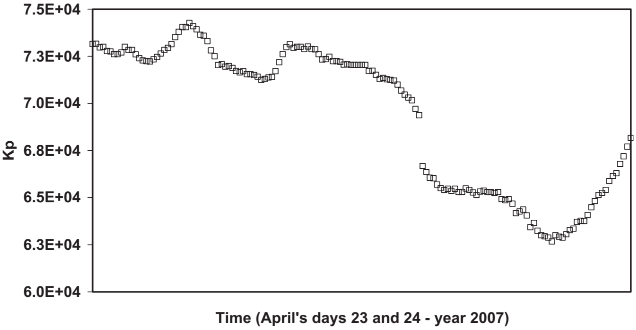

Figure 10.
Estimated propagation rate constant (□).

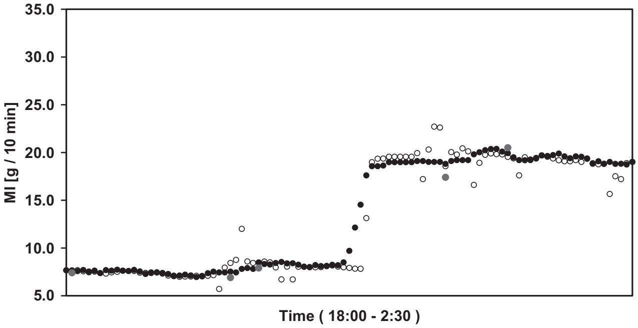

Figure 11.
Measured (○), reconciled (●) and laboratory (●) MI values.

after a grade change. One must observe that the increase of the hydrogen partial pressure (and of the *MI* values, as shown in Figure 11) leads to decrease of the catalyst activity. This is certainly against the usual knowledge, which assumes that the increase of hydrogen pressure leads to increase of the catalyst activity. Therefore, it may be assumed that some sort of reaction inhibition is taking place. In this very particular case, decrease of catalyst feed rates (in order to compensate for the expected increase of catalyst activity when hydrogen concentration is increased) would lead to serious operation problems. This shows very clearly how important the in-line identification of process parameters may be for proper operation of the polymerization reactor.

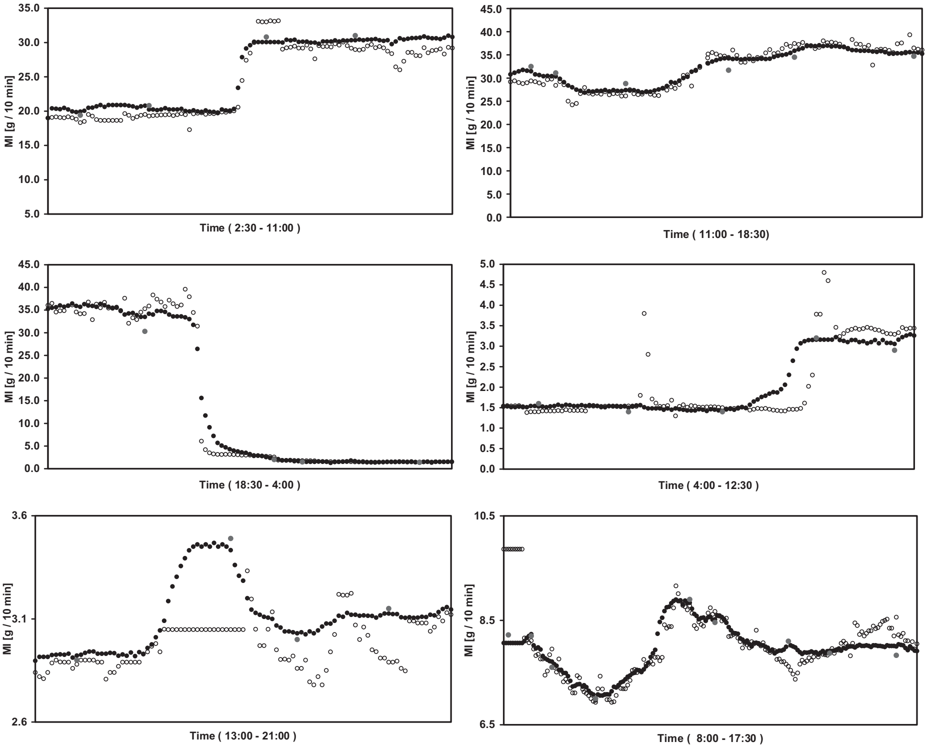

Figure 12.
Measured (○), reconciled (●) and laboratory (●) *MI* values.

Figures 12 shows measured and reconciled values for the melt flow index (*MI*) during grade transitions. Additional off-line laboratory analyses are also presented for comparison. It becomes very clear that in-line *MI* values provided by the process rheometer are subject to significant fluctuations, which are filtered very effectively by the data reconciliation procedure. Besides, it is also clear that the process rheometer fails quite often, while reconciled data are always in very good agreement with the available laboratory data, indicating that the data reconciliation scheme is able to provide more reliable *MI* values than the process rheometer.

It is important to notice that the computational time required to accomplish all the calculations for each moving window was around 90s (30s for solving the NDDR problem and 60s for handling data) in a standard Pentium 4 (2.4 GHz) with 512 MB memory. This leaves room for more frequent sampling, for implementation of advanced data preprocessing (for instance, for gross error detection) and /or implementation of advanced control schemes (for instance, model-based predictive controllers). This also means that the simultaneous NDDR and parameter estimation can be performed properly in a real industrial polypropylene polymerization system, using phenomenological models and standard desktop computers.

Conclusions

In this work, the simultaneous nonlinear data reconciliation and parameter estimation procedure was implemented in-line and in real time in an actual industrial polymerization plant. A moving time window approach was used to sample the process and the resulting nonlinear dynamic optimization problem was solved by a sequential strategy. The methodology was successfully applied to reconcile several sets of industrial data, including final polymer properties obtained after the process extruder. Obtained results indicate the successful application of the proposed monitoring scheme. Off-line laboratory analyses confirmed the effectiveness of the proposed procedure, as reconciled data could indicate frequent failures of the process rheometer, improving the robustness of the process operation. It must be noticed that the numerical procedures provide results in very short times in standard desktop computers, allowing for implementation of data preprocessing and advanced control routines.

Nomenclature

C:	kinetic constant for transfer to hydrogen
C_a	propane concentration in the recycle streams
Cat:	mass of catalyst in the reactor
C_{pa}, C_{pe}, C_{ppol}, C_{pw}:	heat capacities of propane, propylene, polymer and water
K_p:	kinetic constant for homo-propagation
K_d:	catalyst deactivation constant
K_0:	parameter
L:	reactor volume
M:	total mass in the reactor
m_{bleed}, m_{rec}, m_{preox}:	liquid bleed, recycle and peroxides flowrates
m_{cat}, m_e, m_{PEEB}, m_{TEA}:	input flowrates of catalyst, propylene(with propane traces), *TEA* and *PEEB*
m_{eA}, m_{eB}:	reflux flowrates of propylene from top condensers
m_{pol}, m_{slurry}:	output polymer and slurry flowrates
m_w:	water flowrate of top heat exchanger
M_n^I, M_n^{ac}:	instantaneous and cumulative number average molecular weights
M_w^a:	cumulative mass average molecular weight
MI:	melting index of the final resin
N:	number of polymer mols
Pa, Pe, $PEEB$, Pol:	masses of propane, propylene, *PEEB* and polymer in the reactor
PD:	polydispersity

PH_2:	hydrogen pressure in the reactor
$PMPe$:	propylene molecular weight
Q_e:	heat exchanged in the condenser
R_{pol}:	rate of polymerization
T:	reactor temperature
TEA:	mass of TEA in the reactor
T_{eA}, T_{eB}:	temperatures in reflux flowrates of propylene from top condensers
T_{ei}, T_{erec}:	temperatures in input and recycle streams of propylene
T_{wi}, T_{wo}:	temperatures of input and output water streams from top heat exchanger
V:	reactor volume
w_a:	propane concentration in the recycle stream
w_{pol}:	polymer concentration in the slurry stream
XS:	xylene extractable material of the final resin
α:	TEA recycle factor
B:	parameter
ΔH:	heat of reaction
γ:	parameter
λ:	parameter
λ_e:	latent heat of vaporization of propylene
ρ_a, ρ_e, ρ_{pol}:	densities of propane, propylene and polymer

Acknowledgements: The authors would like to thank CNPQ, CAPES and FAPERJ for financial support. The authors also thank Suzano Petroquímica. S. A. for providing technical information and extensive plant data.

[1] C. M. Crowe, *J. Proc. Cont.* **1996**, *6*, 89.

[2] R. S. H. Mah, "*Chemical Process Structures and Information Flows*", Butterworth Publishers, Stoneham, MA **1990**.

[3] S. Narashimhan, C. Jordache, "*Data Reconciliation and Gross Error Detection: An Intelligent Use of Process Data*", Gulf Professional Publishing, Houston, TX **2000**.

[4] J. A. Romagnoli, M. C. Sanchez, "*Data Processing and Reconciliation for Chemical Process Operations*", Volume 2 of Process System Engineering, Academic Press, San Diego **2000**.

[5] N. Arora, L. T. Biegler, *Ind. Eng. Chem. Res.* **2004**, *43*, 3616.

[6] G. E. Eliçabe, G. R. Meira, *Polym. Eng. Sci.* **1988**, *28*, 121.

[7] M. Kong, B. Chen, B. Li, *Comput. Chem. Eng.* **2000**, *24*, 749.

[8] P. Vacchani, R. Rengaswamy, V. Gangwal, S. Narasimhan, *AIChE Journal.* **2005**, *51*, 946.

[9] T. E. Karjala, D. M. Himmelblau, *AIChE Journal*, **1996**, *42*, 2225.

[10] R. A. M. Vieira, M. Embiruçu, C. Sayer, *et al.*, *Comput. Chem. Eng.* **2003**, *27*, 1307.

[11] D. M. Prata, E. L. Lima, J. C. Pinto, *Macromol. Symp.* **2006**, *243*, 91.

[12] R. Bindlish, B. J. Rawlings, R. E. Young, *AIChE J.* **2003**, *49*, 2071.

[13] L. T. Biegler, I. E. Grossmann, *Comput. Chem. Eng.* **2004**, *28*, 1169.

[14] J. Chen, J. A. Romagnoli, *Comput. Chem. Eng.* **1998**, *22*, 559.

[15] F. B. Noronha, J. C. Pinto, J. L. Monteiro, *et al.*, Technical Report, PEQ/COPPE/UFRJ, Rio de Janeiro, **1993**.

[16] T. F. Anderson, D. S. Abrams, E. A. Grens,II *AIChE J.* **1978**, *24*, 20.

[17] V. J. Law, R. V. Bailey, *Chem. Eng. Sci.* **1963**, *18*, 189.

[18] L. R. Petzold, DASSL code, Computing and Mathematics Research Division, Lawrence Livermore National Laboratory, L316, Po Box 808, Livermore, CA 94559, 1989.

[19] A. G. Mattos Neto, J. C. Pinto, *Chem. Eng. Sci.* **2001**, *56*, 4043.

[20] D. M. Prata, M. Sc. Thesis, PEQ/COPPE/ UFRJ, Rio de Janeiro, RJ, Brasil, **2005**.

[21] A. M. Oliveira Júnior, D. Sc. Thesis, PEQ/COPPE/ UFRJ, Rio de Janeiro, RJ, Brasil, **2006**.

[22] A. Latado, M. Embiruçu, A. G. M. Neto, J. C. Pinto, *Polymer Testing*, **2001**, *20*, 419.

[23] J. A. Oliveira, E. C. Biscaia Jr., J. C. S. Fadigas, J. C. Pinto, *Macromol. Mater. Eng.* **2006**, *291*, 552.