Industrial SBR Process: Computer Simulation Study for Online Estimation of Steady-State Variables Using Neural Networks

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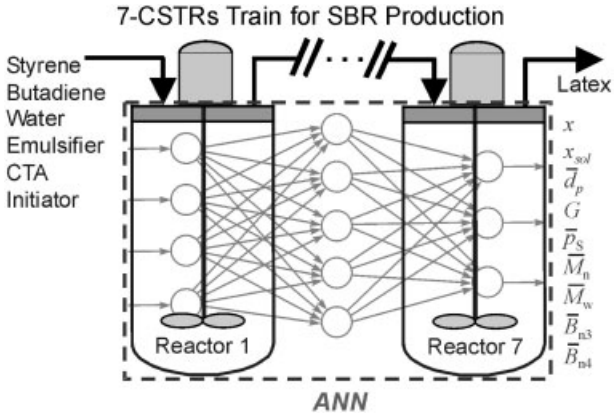
This work investigates the industrial production of styrene-butadiene rubber in a continuous reactor train, and proposes a soft sensor for online monitoring of several processes and polymer quality variables in each reactor. The soft sensor includes two independent artificial neural networks (ANN). The first ANN estimates monomer conversion, solid content, polymer production, average particle diameter, and average copolymer composition; the second ANN estimates average molecular weights and average branching degrees. The required ANN inputs are: (i) the reagent feed rates into the first reactor and (ii) the reaction heat rate in each reactor. The proposed ANN-based soft sensor proved robust to several measurement errors, and is suitable for online estimation and closed-loop control strategies.



Introduction

The production of polymers with controlled quality properties is a major challenge in research activities as well as in industrial applications. Unfortunately, online polymer reactor control strategies are usually difficult to be implemented due to the lack of instantaneous measurements of most of the polymer quality variables. Several state estimation and control techniques have been proposed, which are frequently based on some model representative of the polymerization process. A review on the measurement and control of polymerization reactors has been recently published.[1]

Mathematical models are useful for designing, controlling, and optimizing polymerization reactors. In emulsion polymerizations, the models based on first principles (FP)[2,3] generally consist of a large set of coupled differential and algebraic equations, which normally include several unknown parameters. Based on mathematical models, different online monitoring strategies have been proposed for rubber production through emulsion processes. For example, in the emulsion copolymerization of acrylonitrile and butadiene (nitrile rubber, NBR) through the batch process, Mutha et al.[4] developed a state estimator to monitor several polymerization variables

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on the basis of instantaneous measurements of density and on delayed measurements of copolymer composition, average particle size, and viscosity. Numerical simulations showed a good performance of the estimator, even better than that obtained through an extended Kalman filter with instantaneously available measurements.

Reaction calorimetry is probably the cheapest, easiest, and most robust monitoring technique used in emulsion polymerization processes. Unfortunately, some quality variables (e.g., copolymer composition and average molecular weights) are not directly observable from calorimetric measurements; however, they can be estimated by combining such measurements with a representative mathematical model of the polymerization. For example, Gugliotta and coworkers[5,6] employed calorimetric measurements in combination with a simplified FP model, for monitoring and control conversion, copolymer composition, average molecular weights, and branching degree in a semibatch industrial NBR process.

Styrene-butadiene rubber (SBR) is a general-purpose commodity that is mainly employed in the tire industry. It is produced by copolymerizing styrene (S) and butadiene (B) in "cold" emulsion processes carried out in up to 15 continuous stirred-tank reactors (CSTRs) in series. Compared with batch or semibatch processes, continuous systems offer improved efficiency, and better product consistency.[7–9] The most common industrial SBR grades are known as 1 712 and 1 502. Several average quality variables defined in the reaction system (e.g., the polymer particle diameters, the copolymer composition, the molecular weights, and the branching degree) determine the main SBR processability and end-use properties. In industry, the measured quality variables are the copolymer composition and the Mooney viscosity (that is indirectly related to molecular weights, copolymer composition, branching degree, and to possible incorporation of additives).[10] Unfortunately, these measurements are intolerably slow to be used for online control purposes. The SBR end-use properties are also directly influenced by the final monomer conversion, that in practice is limited to around 70% to avoid further deterioration of the rubber due to branching, crosslinking, and compositional drift. Also, a chain transfer agent (CTA) is usually added for directly controlling average molecular weights and branching degree, thus indirectly affecting the Mooney viscosity.

Based on a detailed mathematical model of an industrial SBR process,[11] and on measurements of the global polymerization heat rate, Minari et al.[12] developed an online estimation and control strategy for regulating the final monomer conversion during changes in the production level. Clearly, the large residence time in the reactor train and the lack of other instantaneous measurements make difficult to implement feedback control policies. Thus, the online estimation of some quality variables along the train is required for developing effective control strategies aimed at improving the end-product quality.

Main drawbacks of FP or detailed mathematical models are the rather difficult implementation of their computational codes (that require customized codes for different operating conditions), a normally low robustness, and high simulation times, that can restrict their application for implementing "online" estimation and control policies. As an alternative, artificial neural network (ANN) models make use of learning, parallel processing, and generalization capabilities, and can be used for modeling highly complex (or not well understood) processes, and for implementing advanced control strategies of nonlinear processes, pattern recognition engines, and robust classifiers, due to their ability to generalize while making decisions about imprecise input data.[13] In the last decade, ANNs have been widely applied to deal with modeling, estimation, control, and optimization of polymerization processes. A brief tutorial on the selection and use of neural networks in the field of polymerization has recently been published.[14] Some publications investigate the optimal operating conditions required to obtain polymers with prespecified end-use properties, either on the basis of ANN alone[15] or combined with genetic algorithms.[16]

Some polymerization systems have been extensively studied in applications that involved the use of ANNs. For example, in the batch solution homopolymerization of methyl methacrylate (MMA), stacked neural networks[14] were applied to infer quality polymer properties,[17] from measurements of the inlet and outlet jacket temperatures, the reactor temperature, the coolant flow rate, and the monomer conversion. This approach was extended to estimate the amount of reactive impurities during the first stage of the polymerization[18] and the reactor fouling.[19] For the same polymerization system, a recurrent neural network model[14,20] was used to design an optimal batch-to-batch control strategy aimed at reaching a desired end-product quality.[20] In the solution polymerization of butadiene carried out in a train of three CSTRs, ANNs were used to estimate the fluid and the Mooney viscosities from the main process variables.[21]

In the field of emulsion polymerizations, ANNs have been applied in the batch polymerization of vinyl acetate (VAc), to predict polymer quality variables,[22] and to determine the optimal reactor operating conditions for producing a polymer with specified quality and productivity values.[23] Hybrid FP/ANN models have also been used in some emulsion polymerizations.[22,24,25] Hybrid models exhibit the advantage of combining the theoretical tendency (or gradients) imposed by an FP model, with more accurate (absolute) data captured from experimental points.[22] For example, in the batch polymerization of VAc, hybrid models were applied for controlling average

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molecular weights and polydispersity from density measurements, by manipulating the initiator addition and the reaction temperature.[22] More recently, Arzamendi and coworkers developed a hybrid copolymerization model suitable for online optimization purposes.[24] To this effect, the polymerization rate and the instantaneous weight-average molecular weight ($\overline{M}_w$) were calculated through an ANN that was combined with the material balance of the FP model. Based on this reduced hybrid model, an optimal temperature trajectory was calculated to produce a polymer with a predefined evolution of the weight-average molecular weight.[25]

Although emulsion copolymerizations are complex processes, ANNs still proved efficient when applied to solve modeling, estimation, and control problems. For example, recurrent neural networks have been used to calculate the optimal temperature profile required to maximize the batch production of a copolymer with given values of average molecular weights and copolymer composition.[26] Strictly, copolymer composition cannot be calculated from calorimetric measurements; however, it can be estimated through a hybrid model that combines the reactor heat balance with an ANN that predicts the individual monomer conversions.[27] This estimation scheme was applied to the batch and semibatch polymerization of MMA, butyl acrylate (BuA), and methacrylic acid; and to the copolymerization of MMA and VAc.[27] The ANN inputs were the reaction temperature, the inlet and outlet jacket temperature, the time, the mass of the added pre-emulsified monomers, and the global conversion (in turn, calculated from the three acquired temperatures through the polymerization heat balance). In the continuous emulsion polymerization of VAc, BuA, and Veova 10 carried out in a loop reactor, stacked neural networks[14] were used to predict the global conversion and the average particle size, from the reaction and jacket temperatures, the initiator and emulsifier fractions, and the holdup.[28] The ANN was able to track the oscillations experimentally observed in the conversion and the particle size, during the reactor startup.

In this work, the industrial continuous production of SBR in a train of seven CSTRs is investigated, and an ANN-based soft sensor is developed for estimating the main steady-state (SS) process and quality variables in each reactor of the train, on the basis of the reagent mass flows fed into the first reactor, and the reaction heat rate measured in each reactor. A detailed monitoring of the process variable along the train is an intermediate step required for a future implementation of control strategies aimed at reducing the variability of the end-product quality. As far as the authors are aware, this is the first contribution on ANN-based monitoring of a continuous emulsion copolymerization process carried out in a train of reactors.

The Industrial Plant and the Proposed ANN-Based Soft Sensor

The investigated industrial plant involves the production of SBR grade 1502 in a train of seven identical CSTRs, property of Petrobras Energía S.A. (Pto. Gral. San Martín, Santa Fe, Argentina). Each reactor has a reaction volume of 17 473 L, and operates at 10 °C. All the reagents (monomers S and B, water, initiation system, emulsifier, and CTA) are continuously fed into the first reactor. Then, the unreacted monomers are recuperated, and the bulk rubber is separated from the latex, after its coagulation and filtering. Finally, the SBR is dried and baled.

To simulate the continuous production of the SBR latex, the FP polymerization model by Gugliotta et al.[11] was employed. This model is subdivided into two main modules: (1) a basic module, that predicts monomer conversion (x), solid content (x_{sol}), average particle diameter ($\overline{d}_p$), polymer production (G), and copolymer composition expressed as average mass fraction of S in the copolymer ($\overline{p}_S$) and (2) a molecular weights module, that predicts number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$, respectively), and average number of tri- and tetrafunctional branches per molecule ($\overline{B}_{n_3}$ and $\overline{B}_{n_4}$, respectively). The model parameters were adjusted to industrial measurements of both 1502 and 1712 grades, obtained under SS and transient operations. The SS experiments included measurements of x, x_{sol}, G, $\overline{p}_S$, $\overline{d}_p$, $\overline{M}_n$, and $\overline{M}_w$ along the reactor train. The transient experiments involved final product measurements of x_{sol}, $\overline{M}_n$, and $\overline{M}_w$ during a change of grade from 1712 to 1502.[11] Table 1 presents a base recipe of the SBR 1502 grade normally employed in the industrial plant, and some final process and quality variables of interest obtained in the last reactor of the train.

The complete soft sensor proposed for estimating the process and quality variables along the train has 15 input variables and 63 output variables. The input variables are the mass feed rates into the first reactor of all the reagents [styrene (F_S), butadiene (F_B), water (F_w), emulsifier (F_E), initiator (F_I), ferrous salt (F_{Fe}), reducing agent (F_{Ra}), and CTA (F_X)], and the measured reaction heat rates in each reactor, $Q_R^{(r)}$ [r (=1, ..., 7) is the reactor number]. The output variables are: $x^{(r)}$, $x_{sol}^{(r)}$, $\overline{d}_p^{(r)}$, $G^{(r)}$, $\overline{p}_S^{(r)}$, $\overline{M}_n^{(r)}$, $\overline{M}_w^{(r)}$, $\overline{B}_{n_3}^{(r)}$, and $\overline{B}_{n_4}^{(r)}$ (nine variables per reactor). Since the input variables have different sensitivities on each output variable, the problem has been divided and modeled by two independent ANNs. The ANN1 is used for estimating $x^{(r)}$, $x_{sol}^{(r)}$, $\overline{d}_p^{(r)}$, $G^{(r)}$, and $\overline{p}_S^{(r)}$; and therefore has 35 ($=5 \times 7$) output variables. The ANN2 is employed for estimating $\overline{M}_n^{(r)}$, $\overline{M}_w^{(r)}$, $\overline{B}_{n_3}^{(r)}$, and $\overline{B}_{n_4}^{(r)}$; and exhibits 28 ($=4 \times 7$) output variables. Feed-forward multilayer perceptrons (MLP)[29] with one hidden layer, sigmoid activation functions, and linear output neurons were adopted for both ANNs. The number of neurons in the

Table 1. SBR grade 1502. Base recipe and final process and quality variables.

Base recipe		Output variables[b)]	
q_T ($L \cdot min^{-1}$)	302.8	$G^{(7)}$ ($kg \cdot min^{-1}$)	57.9
S (pphm)[a)]	28.8	$x_{sol}^{(7)}$ (%)	22.6
B (pphm)	71.2	$x^{(7)}$ (%)	65.7
Water (pphm)	200.0	$\overline{d}_p^{(7)}$ (nm)	70.3
Emulsifier (pphm)	5.36	$\overline{P}_S^{(7)}$ (%)	23.1
Initiator (pphm)	0.040	$\overline{M}_n^{(7)}$ ($g \cdot mol^{-1}$)	105 000
Ferrous salt (pphm)	0.031	$\overline{M}_w^{(7)}$ ($g \cdot mol^{-1}$)	307 200
Reducing agent (pphm)	0.060	$\overline{B}_{n_3}^{(7)}$ (per molecule)	0.149
CTA (pphm)	0.182	$\overline{B}_{n_4}^{(7)}$ (per molecule)	0.056

[a)]Parts per hundred monomer; [b)]the super index indicates reactor number.

hidden layer was selected equal to the number of inputs of the ANN. Although a single hidden layer can be nonoptimal with respect to the learning time or generalization ability, the so-called universal approximation theorem guarantees that, given enough neurons in the hidden layer, there always exists a three-layer MLP neural network that can approximate any nonlinear continuous multidimensional function to any desired accuracy.[29]

Several SS operations of the train were simulated to obtain the data for training the ANN model. With respect to the base recipe, the reagent feeds into the first reactor were modified at regular intervals of 10%, with a maximum change of ±20%, that are compatible with the production variability typically observed in the industrial plant. The simulations were obtained by modifying either only one or simultaneously two of the reagent feeds, and the total volume feed rate (q_T), exploring all of the possible combinations. The reaction heat rate was calculated each 2 min, from the heat balance of each reactor.[12] This measurement frequency is in agreement with the data acquisition system implemented in the industrial plant, where all the calorimetric measurements (e.g., refrigerant flows, temperatures, and agitation power), are registered each 2 min. Since the characteristic time constant of the reactors is much higher than 2 min, the heat measurements can be considered as instantaneous for monitoring and all the practical purposes, and therefore some filtering action could be implemented to attenuate excessive measurement noises.

The available data have been divided into training (80%) and validation (20%). While the training set included extreme and intermediate points in the variation range of the input variables, the validation set only included intermediate points inside such a range. To improve the network accuracy and speed up the learning process, the input/output pairs were normalized to fall in the interval [0,1], and the network parameters were estimated using the Levenberg–Marquardt back-propagation algorithm,[30,31] together with an early stopping technique based on the cross-validation procedure, to avoid model over-fitting.[32] Both neural networks acceptably learned the training data, with a mean square error (calculated on the normalized output variables and over all the training samples) of $\approx 10^{-6}$. The ANNs successfully predicted the evolution of the output variables in all the validation cases.

Evaluation Examples

The performance of the proposed ANNs was evaluated under nontrained situations including (1) noisy heat rate measurements and (2) systematic measurement errors in some reagent feeds. Case (1) always occurs in practice, because $Q_R^{(r)}$ is derived from several sensor signals, and therefore it is unavoidably contaminated by noise. In contrast, case (2) constitutes a strong failure that in some cases can seriously affect the global process performance.

ANN Estimations under Noisy Measurements

To test the performance of the ANN model under noisy measurements, the reagent feed rates were considered as exactly known, while the "measured" reaction heat rates (sampled each for 2 min) were contaminated with an additive random noise, similar to that typically observed in the industrial plant.[5,6] Figure 1 shows the simulation

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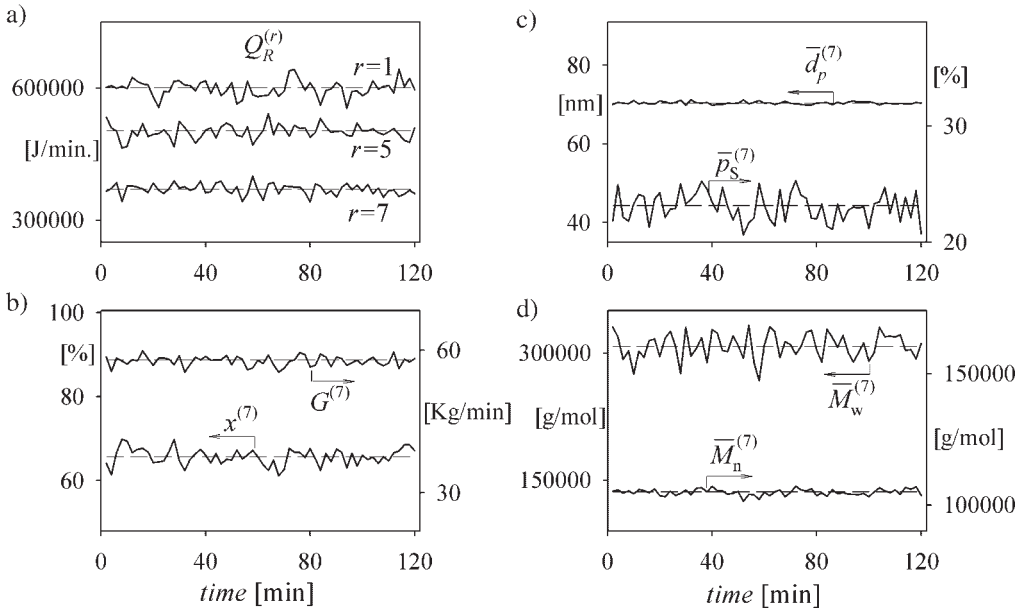

Figure 1. Soft sensor predictions under noisy measurements of the reaction heat rate. (a) Raw measurements in reactors 1, 5, and 7. (b–d) Estimated values of several output variables in the last reactor.

results corresponding to the base recipe of Table 1 (for comparison, the true output variables are indicated in dashed curves). In Figure 1(a), the noisy $Q_R^{(r)}$ values are shown for reactors $r = 1$, 5, and 7, along a period of 120 min. Figure 1(b)–1(d) present the ANN estimations for several output variables in the last reactor. Although not shown, predictions in the other train reactors exhibited similar tendencies.

Table 2 compares the true outputs with the mean (μ) of their estimated values along 120 min. The ratio between the standard deviation (σ) of the noisy signal and μ gives information about the quality of the estimation (the lower the σ/μ value the better the estimation). For example, a value of $\sigma/\mu = 0.01$ indicates that 68% of the estimates are within a band of ±1% around the mean value. In general, all the output variables are reasonably well-predicted, showing oscillations around the corresponding noise-free values. Unacceptable predictions are only observed for the mean copolymer composition, $\overline{p}_S$, where the specification bounds are relatively narrow, and therefore off-spec product is erroneously predicted. Highly oscillatory estimations are also observed in $\overline{M}_w$, but their estimated values can still be acceptable in standard industrial applications. Since ANNs are algebraic algorithms, they are incapable of smoothing the noisy measurements, but such oscillations could be filtered off through some digital pretreatment of the raw signals. For example, a simple averaging time-window of around 30 min proved effective to avoid erroneous off-spec predictions of the most restrictive variable, $\overline{p}_S$.

Table 2. Noise-free and noisy mean values of the estimated output variables in the last reactor of the train (after 120 min).

Property	True SS value	Monitored values	
		μ	σ/μ
$G^{(7)}$ ($kg \cdot min^{-1}$)	57.9	58.4	0.018
$x^{(7)}$ (%)	65.7	66.0	0.030
$\overline{d}_p^{(7)}$ (nm)	70.3	70.6	0.005
$\overline{p}_S^{(7)}$ (%)	23.1	23.3	0.056
$\overline{M}_n^{(7)}$ ($g \cdot mol^{-1}$)	105 000	106 600	0.011
$\overline{M}_w^{(7)}$ ($g \cdot mol^{-1}$)	307 200	311 900	0.054

ANN Estimations under Systematic Measurement Errors

Some sources of systematic errors are: undetected changes in a reagent feed concentration, failures in a flow sensor, drifts in the calibration of a sensor, etc. For example, a flow sensor measures a mass (or volume) flow, and therefore a change in a reagent feed concentration would remain undetected. Also, when a flow sensor fails (or its calibration becomes erroneous), then the devoted closed-loop control system will adjust a wrong feed rate value. Thus, changes in the "effective" reagent feed rate will

remain undetected for the process supervisor computer, and therefore the ANN model will receive an erroneous feed-rate value. To evaluate the performance of the soft sensor under this kind of errors, three testing cases were analyzed. In each case, the error in only one of the reagent flows was simulated, while the other reagent feed rates and the reaction heat rates were assumed as accurately measured. The simulation results are presented in Figure 2–4 (the symbols represent the true values, while the curves are the soft sensor predictions). The square symbols indicate the accurate performance of the proposed soft sensor under unbiased measurements. Note that the predictions that one would obtain with the FP model coincide with the continuous curves, either for the base case or for any of the simulated sensor failure cases.

Figure 2 shows the effect of an error of ±20% in the emulsifier flow, F_E. In all the cases, the ANN model adequately predicts the true evolutions (similar results were also observed under errors in the initiator flow, F_I). The simulation results suggest that the ANN predictions are practically unaffected by measurement errors in F_E and F_I. The reason is that the ANN model output is mainly determined by the reaction heat rates which remain accurately measured.

Figure 3 shows the effect of an error of ±20% in the B flow, F_B. The ANN model reasonably predicts the evolutions of x, but high errors are observed in $\overline{p}_S$, $\overline{M}_n$, $\overline{M}_w$, and $\overline{B}_{n_3}$ (similar results were observed under errors in the S flow, F_S). Particularly note that a positive error of +20% in F_B produces an increment of $\overline{M}_n$, $\overline{M}_w$, and $\overline{B}_{n_3}$ (triangles), with respect to the base case; while their corresponding ANN predictions are clearly underestimated (dash and dot curves). These results suggest that the ANN prediction of x becomes practically determined by the (accurately measured) reaction heat rate. In contrast, the $\overline{p}_S$ estimation is poor, because it results mainly determined by the (erroneous) feed flow of B, while it is only slightly affected by the reaction heat rate. Also, $\overline{M}_n$, $\overline{M}_w$, and $\overline{B}_{n_3}$ are underestimated as a consequence of an erroneously measured F_B, which in turn underestimates x. Notice that $\overline{p}_S$, $\overline{M}_n$, $\overline{M}_w$, and $\overline{B}_{n_3}$ could accurately be estimated from reaction heat measurements only when (i) a representative mathematical model is available and (ii) all the feed rates are perfectly known.

Figure 4 shows the effect of an error of ±20% in the CTA flow, F_X. The ANN model predictions of x and $\overline{p}_S$ are unaffected by errors in F_X, because the CTA has a negligible influence on the polymerization rate, and therefore on such variables. In contrast, the ANN is incapable of detecting the changes in $\overline{M}_n$, $\overline{M}_w$, and $\overline{B}_{n_3}$ originated by errors in F_X, because such errors do not modify the measured heat rates.

Conclusion

The SS operation of the continuous SBR process can be online monitored by means of an ANN-based soft sensor that combines information taken from an adjusted FP model with independent measurements of the

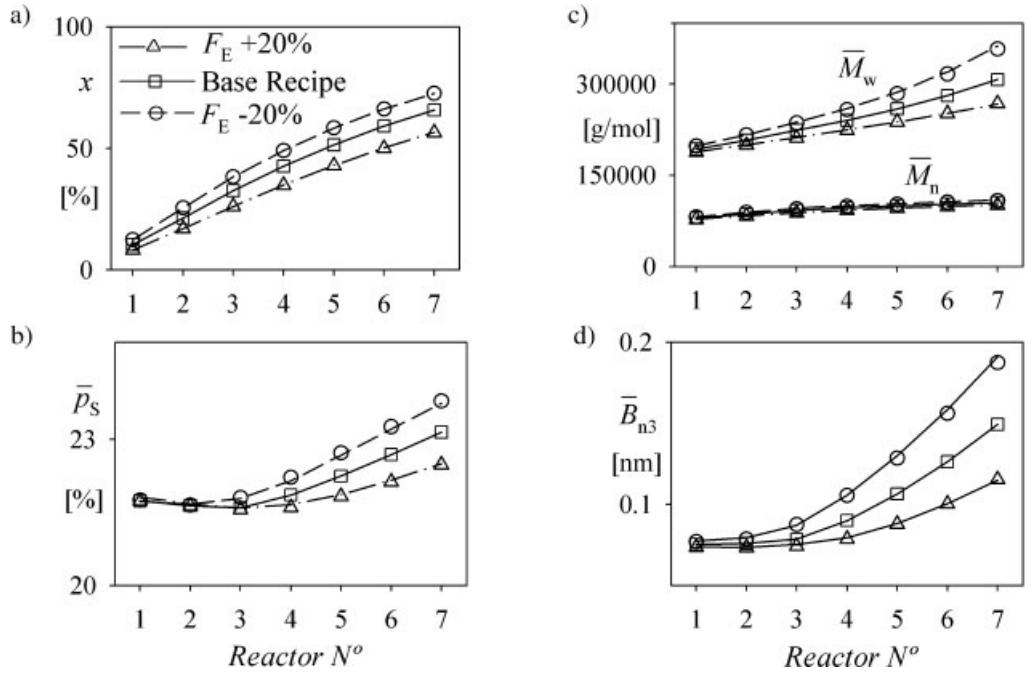

Figure 2. Simulation results for ±20% of error in F_E. Soft sensor estimates (curves) and true values (symbols). A positive error indicates that the true feed flow is higher than its measured value.

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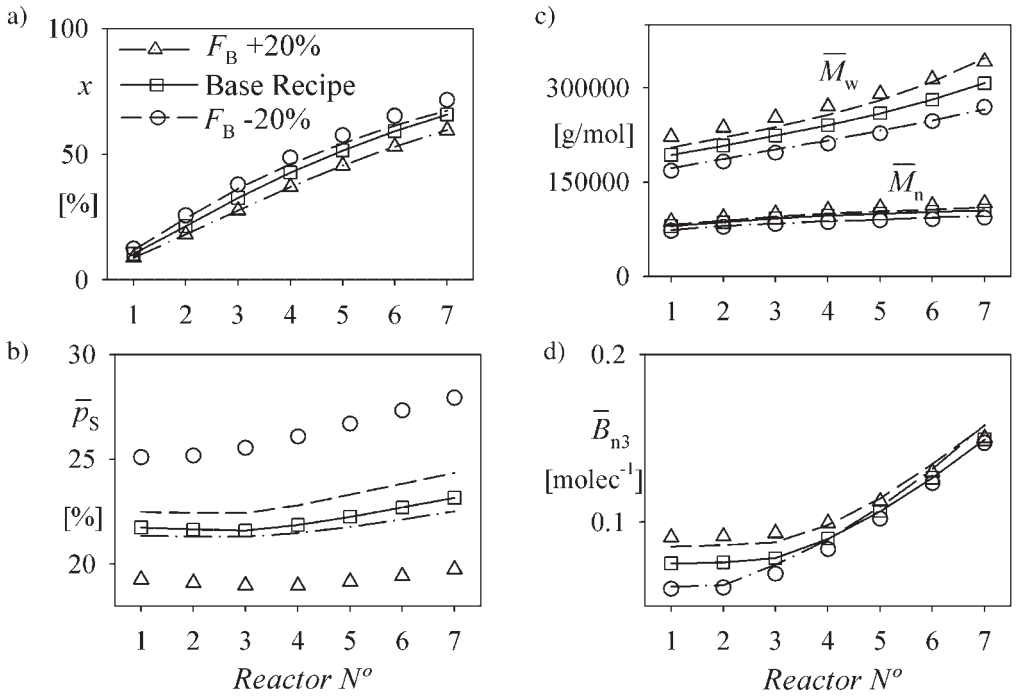

Figure 3. Simulation results for ±20% of error in F_B. Soft sensor estimates (curves) and true values (symbols). A positive error indicates that the true feed flow is higher than its measured value.

polymerization heat in each reactor. Two independent networks were proposed: ANN1, for predicting the basic production variables, and ANN2 for estimating the main macromolecular characteristics. Both ANNs were trained on the basis of simulations; however, additional experimental data can also be included in the training stage to improve their global estimation performance. Instead of using ANN1, some process variables [$x^{(r)}$, $x_{sol}^{(r)}$, $G^{(r)}$, and $\overline{p}_S^{(r)}$]

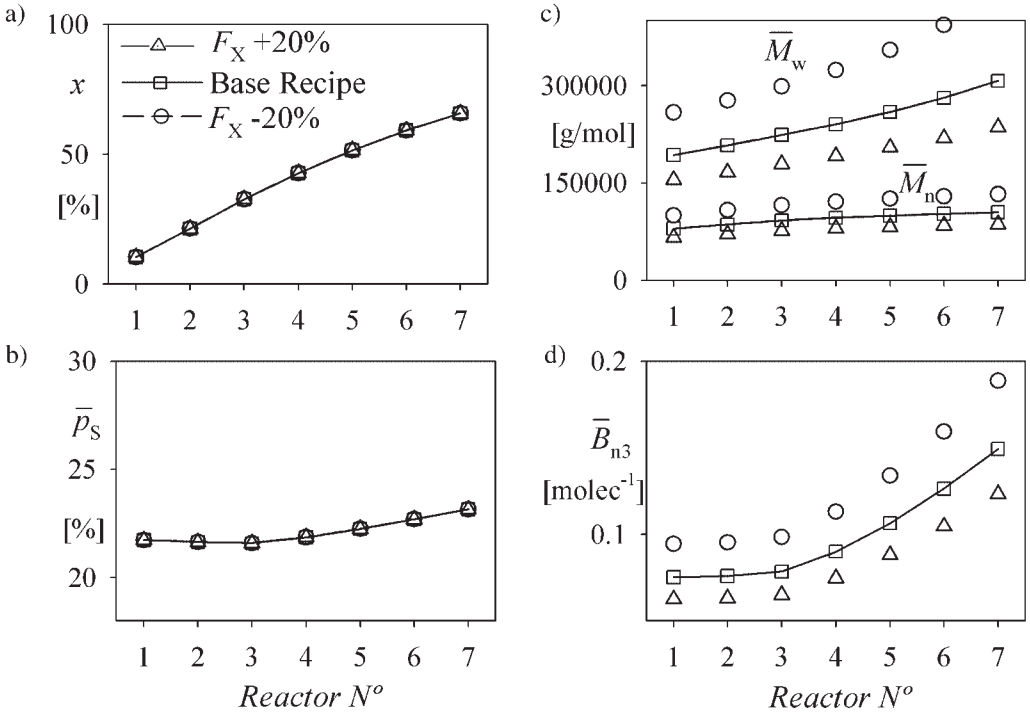

Figure 4. Simulation results for ±20% of error in F_X. Soft sensor estimates (curves) and true values (symbols). A positive error indicates that the true feed flow is higher than its measured value.

could directly be estimated from the measured polymerization heats; but this approach would require: (1) sequentially solving a set of algebraic equations for each reactor and (2) the exact knowledge of several model parameters (particularly, the reactivity ratios for adequately estimating the copolymer composition). Ideally, the FP model could be used by itself to predict all the process and quality variables, on the basis of the known feed flows and without requiring any measurement, but will probably produce biased estimates due to unavoidable model mismatches.

Most of the estimated variables proved relatively insensitive to noisy heat measurements. Particularly, the high oscillations observed in the copolymer composition can be smoothened by time-averaging the heat measurements. Under systematic errors in the initiator and/or the emulsifier feeds, the ANNs adequately estimated all the output variables. Except for conversion, errors in the monomer feeds originated high errors in all the other quality variables. In contrast, errors in the CTA feed only deteriorate the estimates of the macromolecular characteristics.

Regarding an industrial implementation, the main limitation is the required measurement of the polymerization heat in each reactor of the train. However, these reaction heats can easily be estimated from an energy balance and on the basis of typically available process measurements, such as temperatures, pressures, and refrigerant flows.[5] Since the ANNs accurately estimate the process and quality variables in each reactor, and exhibit low execution times and high robustness, they can be used for online reactor control and optimization purposes.

Finally, the proposed soft sensor was developed for the SS monitoring of the SBR process; and in a future work, the extension to track transient operations will be considered.

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