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Experimental Simultaneous State and Parameter Identification of a pH Neutralization Process Based on an Extended Kalman Filter

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Abstract−The pH neutralization process is a representative nonlinear process. If a change in feed or buffer streams is introduced, the characteristics of the titration curve are altered and the way of change in titration curve is highly nonlinear. Moreover, if the changes are introduced in the middle of operation, then the nature of the process becomes nonlinear and time-varying. This is the one of the reason why conventional PID controller may fail. Even though the use of buffer solution may alleviate the nonlinearity, the improvement may be limited. A better way to tackle this type of process is to use nonlinear model-based control techniques with online parameter estimation. However, in most cases, the measurements of the process are not adequate enough so that the full state feedback control techniques can be utilized. If the states and crucial parameters are estimated online simultaneously, the effectiveness of the nonlinear state feedback control can be greatly enhanced. Thus, in this study, the capability of simultaneous estimation of states and parameters using Extended Kalman Filter (EKF) are experimentally investigated for a pH neutralization process. The process is modelled using reaction invariants and the concentrations of reaction invariants of the effluent stream (states) and the feed concentrations (parameters) are estimated online. From the comparison of experiments and simulations, it is found that the states and parameters can efficiently be identified simultaneously with EKF so that the estimated information can be exploited by state-feedback control techniques.

Key words: pH Neutralization Process, Reaction Invariant Model, Extended Kalman Filter, Parameter Estimation

INTRODUCTION

It is widely known that the neutralization of a pH process exhibits its nonlinear and time-varying nature even for some nonimal operating conditions [Waller and Gustaffson, 1983]. Thus, it has long been taken as a representative benchmark problem of nonlinear chemical process control. It is not only due to its importance in various chemical and related industries but also due to the intricate and tricky intrinsic nonlinearities that may change sensitively to small changes in process conditions. Several different approaches for control have been proposed in order to deal with this nonlinear system. These include a simple PID for regulation, self tuning adaptive control, nonlinear linearization control and various model based control. Addressing such nonlinear characteristics, recent pH control studies are mostly directed to development and/or application of model-based nonlinear control techniques. However, as has been indicated in Waller [1985] and Gustafsson [1992] and Henson and Seborg [1992, 1994], performance enhancement from the employment of nonlinear control techniques may be only marginal compared to that of well-tuned linear controllers despite the computational complexity. One of the reasons for this is the limitation of the nonlinear pH models. Most models are tuned only over a narrow operating region or constructed under quite restricted assumptions such as constant buffer compositions and/or constant feed compositions, and so on. Because a small change in buffer may cause a large change in the titration curve [Jutila and Orava, 1981; Jutila, 1983], nonlinear model-based control techniques may not be successful in real situations unless some provisions are furnished to relax such restrictive assumptions.

Due to the importance of the model for the model-based control, many efforts have been exerted in the development of the model for pH neutralization system. They can be grouped into two basic categories. The first approaches are based on the black-box model including neural networks [Loh et al., 1995] or fuzzy logic [Cho et al., 1999; Nie et al., 1996]. The other groups explicitly use the chemical nature of pH processes. The latter approach based on physico-chemical laws and provides more insights on physical parameters. A general dynamic model of the pH neutralization process had been discussed earlier by the one of the second groups, McAvoy et al. [1972] They derived a mathematical model from the first principles, *i.e.*, ionic balances and chemical equilibria. Jutila [1981] and Jutila et al. [1981] developed their model for hypothetical species along the lines of McAvoy. Then they used a Kalman filter to estimate the concentrations and the parameters of titration curves are identified. Later, Waller and Mäkilä [1981] proposed to use the concept of reaction invariant in modeling and control of a pH neutralization process. If the reaction invariants were used, the total amount of the reaction invariant would not be influenced by the extent of reaction and component balance with respect to reaction invariants greatly could simplify the modeling procedure [Gustaffson and Waller, 1983, 1992; Gustaffson et al., 1995]. These reaction invariants were estimated by a least-squares method. Instead of considering a detailed component balance, Wright et al. [1991] proposed a simplified model using the concept of the strong acid equivalent. The strong acid equivalent is a formula to account for the total contribution of the acidic ions to pH. They developed an on-line identification technique for the parameters valid over an arbitrary pH range

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and evaluated the performance in an experimental pH neutralization apparatus [Wright and Kravaris, 1998, 2001].

Even though an accurate model is obtained, the time-varying nature of the process has to be accounted for. For example, the concentration of the buffer stream causes drastic changes in titration curve as mentioned above. Also, the inaccuracy of the estimate of the unmeasured states can affect the performance of the identification and control scheme. To overcome the problems caused by the inaccuracy of the model or changes of operating conditions, the process model has to be updated with appropriate parameter identification techniques [Lee et al., 1999, 2001; Yoon et al., 1999]. Thus, many different model-based control methods have been proposed under different problem settings. Generally, the control strategies using this modeling technique are classified into non-adaptive linear, adaptive linear, non-adaptive non-linear, and adaptive non-linear controls. Among them, the non-adaptive linear control methods are adequate for processes insensitive to operating condition changes and the linear adaptive controllers perform well only if titration curve shows that the process dynamic properties are fixed [Henson and Seborg, 1997]. Gustafsson and Waller [1992] designed an adaptive nonlinear controller for buffered pH neutralization processes. Their experiment demonstrated that the proposed adaptive nonlinear controller outperforms the conventional PID and linear adaptive controllers. Henson and Seborg [1997] proposed an indirect adaptive controller based on a filtered regressor identifier for linearly parameterized non-linear system. This indirect adaptive controller estimates the time-varying parameters of the model on the basis of observed data and error signals. They show that their model-based nonlinear controller has a good performance through simulations. In the study of Wright and Kravaris [2001], they identified crucial parameters to account for the nonlinearity and then designed a control algorithm in terms of the Strong Acid Equivalent, and they tested the proposed algorithm to an industrial pH neutralization.

As described above, in many control techniques, a good model is imperative for implementing an effective control. In the light of control view points, the dynamic models for various model-based controllers involve state variables. However, in most cases, the full states are not available on-line for the state feedback control. If the states for the state feedback control are not available, then they should resort to state estimators. This study is concerned with designing an on-line identification method for the system of which nonlinearity is unknown and time-varying. In buffered process, the titration curve can be changed significantly by the changes in buffer concentration, and this leads to the time-varying nonlinearity. Once these changes can be estimated, the reaction invariant model can effectively represent the pH process. The extended Kalman filter (EKF) is one of the well-known nonlinear identification methods [Kalman, 1960; Ljung, 1979]. The EKF can estimate the states and the unknown parameters in stochastic dynamic systems where the process noise characteristics are known in advance [Jazwinski, 1970]. However, one can hardly find the experimental results of simultaneous state and parameter estimation via EKF for the pH neutralization processes. Thus, in this study, the EKF has been experimentally applied to the simultaneous estimation of states and process parameters of pH neutralization process, which can provide the reliable state and parameter measurements for nonlinear model-based controls. Using the reaction invariant model, the reaction invariants of the influent and effluent streams are chosen as the parameters and states. The performance of the on-line EKF has been evaluated experimentally and compared to the simulation results.

EXPERIMENTAL APPARATUS FOR pH NEUTRALIZATION

An experimental apparatus is used to examine the performance of the EKF for simultaneous identification of states and parameters. The schematic diagram of pH neutralization experimental apparatus is given in Fig. 1 and the nominal operating conditions are shown in Table 1. The reactor type is a continuous stirred tank reactor (CSTR) and its volume is 2.5 *l* and baffles are installed to reduce swirling. The exit flow rate is decided by the amount of the overflow through a partition so that the perfect level control can be assumed. The inlet streams consist of a strong acid stream (q_1: feed solution), a weak acid stream (q_2: buffer solution) and a strong base stream (q_3: titrating solution). The acid feed stream is composed of HNO_3 and $NaHCO_3$, the buffer stream contains $NaHCO_3$, and the titrating stream is composed of NaOH and $NaHCO_3$. Each stream is supplied by a peristaltic pump and mixed in the reactor. Both the feed flow rate and the buffer flow rate are adjusted manually. Hence, their flow rate changes are considered to be measurable. The effluent pH is measured by pH electrode and the signal is sent to a computer through ADC. The computer controls the flow rate of the titrating (base)

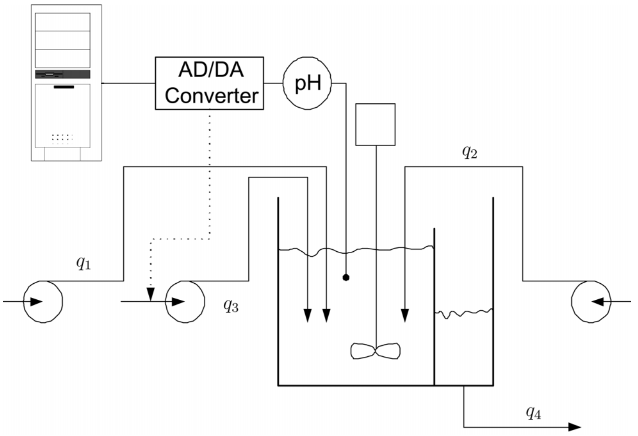

Fig. 1. The experimental apparatus for pH neutralization.

Table 1. Nominal operating conditions and parameters

Symbols	Values	Symbols	Values
V	2,500 [ml]	q_3	8.5 [ml/s]
K_{a1}	4.47×10^{-7}	pH_4	7.00
K_{a2}	5.62×10^{-11}	W_{a1}	2.95×10^{-3} [M]
$[q_1]$	0.003 [M] HNO_3	W_{b1}	5.00×10^{-5} [M]
	5.0×10^{-5} [M] H_2CO_3	W_{a2}	-0.01 [M]
$[q_2]$	0.01 [M] $NaHCO_3$	W_{b2}	0.01 [M]
$[q_3]$	0.003 [M] NaOH	W_{a3}	-3.05×10^{-3} [M]
	5.0×10^{-5} [M] $NaHCO_3$	W_{b3}	5.00×10^{-5} [M]
q_1	9.0 [ml/s]	W_{a4}	-4.50×10^{-4} [M]
q_2	0.6 [ml/s]	W_{b4}	5.50×10^{-4} [M]

stream through DAC. The experiments are assumed to be carried out under the assumptions of a perfect mixing, a constant temperature (at room temperature 25 °C) and complete solubility of the ions involved. The sampling period for pH measurement and control is 3 sec, and dynamics of pumps and sensor are assumed to be negligible.

MODEL OF pH NEUTRALIZATION PROCESS

The general mathematical model for pH neutralization process with reaction invariants is presented in this section. A schematic diagram of the experimental apparatus is shown in Fig. 1. The process flows consist of an acid stream (q_1), a buffer stream (q_2), a base stream (q_3) and an effluent stream (q_4). For this process, the chemical reactions in the reactor are assumed as equilibrium reactions with only weak acid solutions because the strong acid and base solutions are completely ionized. The chemical reactions occurred in the system are as follows.

$$\begin{aligned}&H_2CO_3 \leftrightarrow HCO_3^- + H^+\\ &HCO_3^- \leftrightarrow CO_3^{2-} + H^+\\ &H_2O \leftrightarrow OH^- + H^+\end{aligned} \tag{1}$$

The equilibrium constants for these reactions are

$$\begin{aligned}&K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}\\ &K_{a2} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}\\ &K_w = [H^+][OH^-]\end{aligned} \tag{2}$$

The chemical equilibria are modeled using the concept of reaction invariant [Gustafsson and Waller, 1983]. For this system, two reaction invariants are involved for each stream (i=1−4).

$$\begin{aligned}&W_{ai} = [H^+]_i - [OH^-]_i - [HCO_3^-]_i - 2[CO_3^{2-}]_i\\ &W_{bi} = [H_2CO_3]_i + [HCO_3^-]_i + [CO_3^{2-}]_i\end{aligned} \tag{3}$$

The invariant term W_a is a charge-related quantity and W_b is the concentration of the carbonate ion. These invariants are independent of the extent of the reaction. A relation between a hydrogen ion concentration and reaction invariants can be rewritten with Eqs. (2) and (3).

$$W_{bi}\frac{K_{a1}/[H^+] + 2K_{a1}K_{a2}/[H^+]^2}{1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2} + W_{ai} + \frac{K_w}{[H^+]} - [H^+] = 0, \quad (i=1-4) \tag{4}$$

Actually, the pH value is not defined as a hydrogen ion concentration but as ion activity. However, it can be assumed that the ion activity is same as the ion concentration for the infinitely diluted solution. Hence, the pH value can be determined using the above equations and the negative logarithm of the hydrogen ion concentration if W_{ai} and W_{bi} are known.

$$pH = -\log([H^+]) \tag{5}$$

A dynamic process model for the pH neutralization process can be derived from the component material balance for the reaction invariants.

$$V\frac{dW_{a4}}{dt} = q_1(W_{a1} - W_{a4}) + q_2(W_{a2} - W_{a4}) + q_3(W_{a3} - W_{a4})$$

$$V\frac{dW_{b4}}{dt} = q_1(W_{b1} - W_{b4}) + q_2(W_{b2} - W_{b4}) + q_3(W_{b3} - W_{b4}) \tag{6}$$

In the above model, it can be reasonably assumed that all the flow rates of the streams and the concentrations of the base stream are known because the flow rates of streams are controlled by pumps and the titrating stream is prepared as needed. The reaction invariants of the effluent stream are chosen as states and then the remaining unknowns are concentrations for the feed and buffer streams. For the sake of investigation, we chose two disturbance variables. They are the charge-related reaction invariant in feed stream (W_{a1}) and the carbonate ion-related reaction invariant (W_{b2}). Then, the concerned pH process model can be rewritten in the following nonlinear state space model.

$$\begin{aligned}&\dot{x} = f(x,t) + g(x,t)u + F_\theta\theta\\ &c(x,y) = 0\end{aligned} \tag{7}$$

where

$$f(x,t) = \frac{1}{V}\begin{bmatrix} q_2(W_{a2} - x_1) - q_1x_1 \\ q_1(W_{b1} - x_2) - q_2x_2 \end{bmatrix}, \quad g(x,t) = \frac{1}{V}\begin{bmatrix} W_{a3} - x_1 \\ W_{b3} - x_2 \end{bmatrix}$$

$$F_\theta = \frac{1}{V}\begin{bmatrix} q_1 & 0 \\ 0 & q_2 \end{bmatrix}, \quad \theta = \begin{bmatrix} W_{a1} \\ W_{b2} \end{bmatrix}, \quad x = \begin{bmatrix} W_{a4} \\ W_{b4} \end{bmatrix}$$

$$u = q_3, \quad y = pH_4, \quad pK_1 = -\log K_{a1}, \quad pK_2 = -\log K_{a2}$$

$$c(x,y) = x_1 + 10^{y-14} - 10^{-y} + x_2\frac{1 + 2\times10^{y-pK_2}}{1 + 10^{pK_1-y} + 10^{y-pK_2}}$$

In the above, θ contains the unknown parameters chosen. The reasoning behind this choice is as follows: W_{a1} represents a charge related quantity and gives the hydrogen ion related information of the feed stream. In practical situations, major ionic species contained in the feed stream are usually fixed but the composition of each species may vary significantly. In our case, the feed consists of a large amount of nitric acid and a very small amount of carbonic acid. Hence, the W_{b1} can be regarded as zero and the effect of carbonate ion on the resulting pH is lumped as W_{b2}. The W_{b2} is the key condition of the buffer stream. As is well known, the buffer stream plays a very important role in deciding the characteristics of a neutralization process. Unless a neutralization process involves only strong acid and base, a buffer stream must be added to avoid an erratic change in titration curve. Although the buffer stream is prepared as prescribed, the W_{b2} is treated as an unknown parameter because the inaccuracy of the information on W_{b2} can result in a significant consequence in the characteristics of neutralization process.

EXTENDED KALMAN FILTER

The extended Kalman filter is a predictor-corrector type linear estimator obtained by the linearization of a nonlinear model at each time step. It is used to estimate the states and parameters of a nonlinear system through the measurements using a function of the linearized model with additive Gaussian white noise [Grewal and Andrews, 1993; Brown and Hwang, 1997]. The EKF procedure consists of two steps: time update step and measurement update step. The time update step projects forward the current state and error covariance estimates to obtain the *a priori* estimates for the next time step. The measurement update step incorporates a new measurement into the *a priori* estimate to get an improved *a posteriori* estimate. In other words, the time update step is a model prediction and the measurement update step is a measurement correction.

The EKF can be used to find the unknown parameters θ by extending the state x to z that is augmented with the parameter vector θ. This augmented states are defined as following form,

$$\dot{z}(t)=\begin{bmatrix}\dot{x}\\ \dot{\theta}\end{bmatrix}=\begin{bmatrix}f(x,t)+F_{\theta}\theta\\ 0\end{bmatrix}+\begin{bmatrix}g(x,t)u\\ 0\end{bmatrix} \tag{8}$$

For discrete-time EKF design, a simple first-order Euler approximation is used over sampling period, Δt. Then the discrete-time process model can be obtained as follows:

$$z_{t+1}=\begin{bmatrix}A\ B\\ O\ I\end{bmatrix}z_t+D \tag{9}$$

where

$$A=\begin{bmatrix}1-(q_1+q_2+u_t)\dfrac{\Delta t}{V} & 0\\ 0 & 1-(q_1+q_2+u_t)\dfrac{\Delta t}{V}\end{bmatrix},\ B=\begin{bmatrix}q_1\dfrac{\Delta t}{V} & 0\\ 0 & q_2\dfrac{\Delta t}{V}\end{bmatrix}$$

$$I=\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix},\ O=\begin{bmatrix}0 & 0\\ 0 & 0\end{bmatrix},\ D=\begin{bmatrix}(q_2W_{a2}+uW_{a3})\dfrac{\Delta t}{V} & (q_1W_{b1}+uW_{b3})\dfrac{\Delta t}{V} & 0\ 0\end{bmatrix}^T$$

Since the output equation in Eq. (7) is an implicit nonlinear function of output variable, this problem does not yield an analytical solution in general. To solve the problem, the output equation is linearized at x_t and y_t:

$$y_{t+1}=y_t+c_y^{-1}c_x(x_{t+1}-x_t) \tag{10}$$

where

$$c_x=\left.\frac{\partial c(x,y)}{\partial x}\right|_{x=x_t}=\left[1\ \frac{1+2\times10^{y-pK_2}}{1+10^{pK_1-y}+10^{y-pK_2}}\right]$$

$$c_y=\left.\frac{\partial c(x,y)}{\partial y}\right|_{y=y_t}$$

$$=(\ln 10)\left\{10^{y-14}+10^{-y}+x_2\frac{10^{pK_1-y}+10^{y-pK_2}+4\times10^{pK_1-pK_2}}{(1+10^{pK_1-y}+10^{y-pK_2})^2}\right\}$$

The system models in Eqs. (9) and (10) are redefined as stochastic process model including gaussian white noise terms, w_t and v_t. Their covariances are Q and R, respectively. Because the integrated white noise model gives a better convergence of the parameter estimation, although the model parameters are actually constant, the parameter values can be considered to be driven by a fictitious noise [Lee and Ricker, 1994; Lee and Datta, 1994].

$$\theta_{t+1}=\theta_t+w_{t2} \tag{11}$$

With the integrated white noise, the augmented state-space model becomes

$$z_{t+1}=F_tz_t+D+\begin{bmatrix}w_{t1}\\ w_{t2}\end{bmatrix} \tag{12}$$

$$y_{t+1}=y_t+H_{t+1}(z_{t+1}-z_t)+v_t$$

The EKF method uses linearized model along the trajectory that is continually updated with the state estimates resulting from the measurements. Thus, the nonlinear discrete process model should be linearized with respect to the estimates $z_t=z_{t|t}$.

$$F_t=\left.\frac{\partial f(z,u)}{\partial z}\right|_{z_{t|t},u_t}=\begin{bmatrix}A & B\\ O & I\end{bmatrix},\ H_{t+1}=\begin{bmatrix}-c_y^{-1}c_x\ 0\ 0\end{bmatrix}$$

The extended Kalman filter algorithm can be summarized the following formulas.

$$\begin{aligned}&\hat{z}_{t+1}^{-}=F_t\hat{z}_t^{+}+D\\ &P_{t+1}^{-}=F_tP_tF_t^T+Q\\ &K_{t+1}=P_{t+1}^{-}H_{t+1}^T[H_{t+1}P_{t+1}^{-}H_{t+1}^T+R]^{-1}\\ &\hat{z}_{t+1}^{+}=\hat{z}_{t+1}^{-}+K_{t+1}(y_{t+1}-\hat{y}_{t+1}(\hat{z}_{t+1}^{-}))\\ &P_{t+1}^{+}=\{I-K_{t+1}H_{t+1}\}P_{t+1}^{-}\end{aligned} \tag{13}$$

where the superscript $^-$ represents the value without measurement correction and the superscript $^+$ represents the corrected value with measurement. In the above equations, the state error covariance update P_{t+1}^{+} should be checked for the symmetry and positive definiteness. In order to satisfy these conditions, another equivalent expression for P_{t+1}^{+} called the Joseph form is used [Grewal and Andrews, 1993].

$$P_{t+1}^{+}=\{I-K_{t+1}H_{t+1}\}P_{t+1}^{-}\{I-K_{t+1}H_{t+1}\}^T+K_{t+1}RK_{t+1}^T \tag{14}$$

EXPERIMENTAL AND SIMULATION RESULTS WITH DISCUSSIONS

The laboratory scale plant of a nonlinear time-varying pH neutralization process was built to test the performance of the simultaneous state and parameter estimation and the details of this system was described previous section. The states to be estimated were the reaction invariants of the effluent stream, which were W_{a4} and W_{b4}. If these states were determined, the output pH could be calculated from the nonlinear output equation, Eq. (4). The unmeasured disturbances, W_{a1} which represented the acidity of the feed stream and W_{b2} which implied the concentration of carbonate ion in the buffer stream, would be estimated as parameters. To describe the behavior of the pH neutralization process, these values should be known as exactly as possible. However, it was difficult to directly measure these values with sensors. Therefore, the extended Kalman filter was used to estimate these values.

In order to capture the characteristics of the pH neutralization process, the titration curves were obtained experimentally and they were shown in Fig. 2 together with the simulated titration curves. Fig. 2 showed two pairs of titration curves at different buffer concentrations. Note that the process gain at a particular operating point was the slope of the titration curve at that condition. For the nominal buffer concentration ($[NaHCO_3]_{q_2}$=0.01 M), the process gain varied severely over the region shown. Moreover, the titration curves for $[NaHCO_3]_{q_2}$=0 M was dramatically different from the curve obtained under nominal conditions. As shown in Fig. 2 the simulation and experimental titration curves matched reasonably well and it was evident that the model can describe the process correctly.

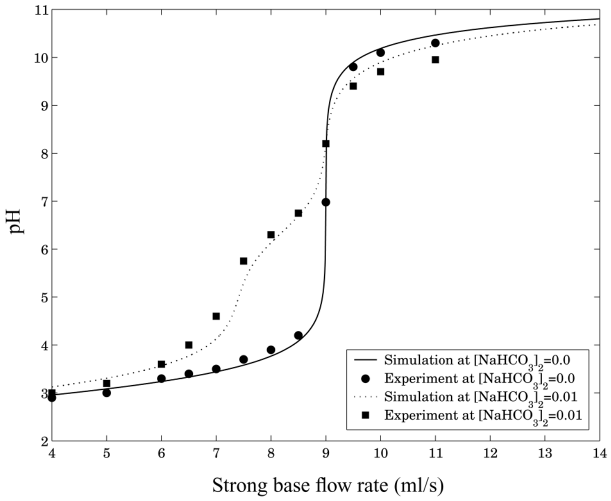

Fig. 2. Comparison of titration curves for two different buffer concentrations.

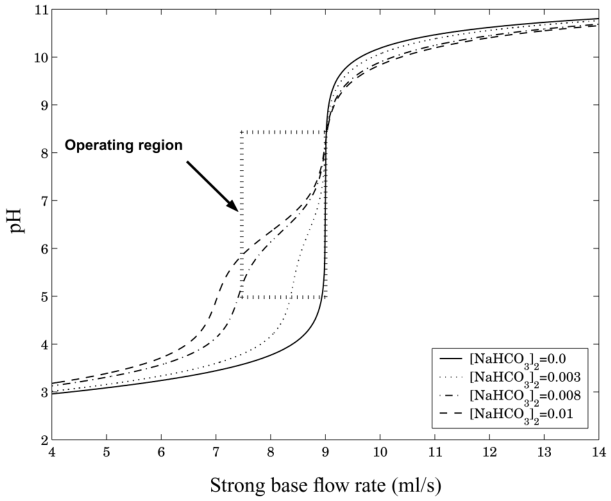

Fig. 3. Comparison of titration curves for four different buffer concentrations in simulation.

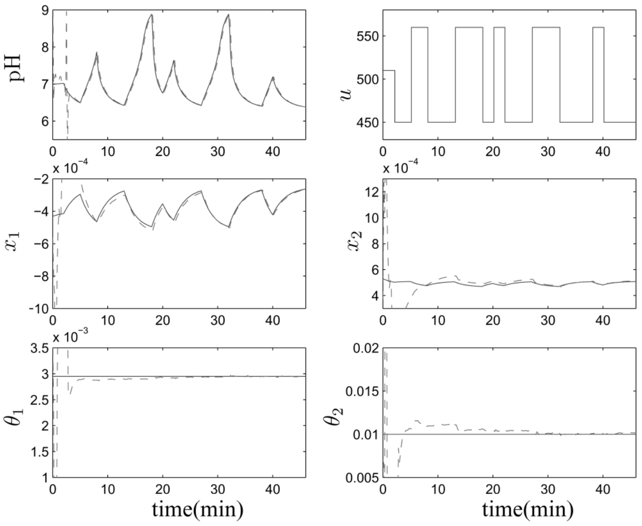

Fig. 4. Performance of estimator in simulation: the true values (solid) and the estimates (dashed).

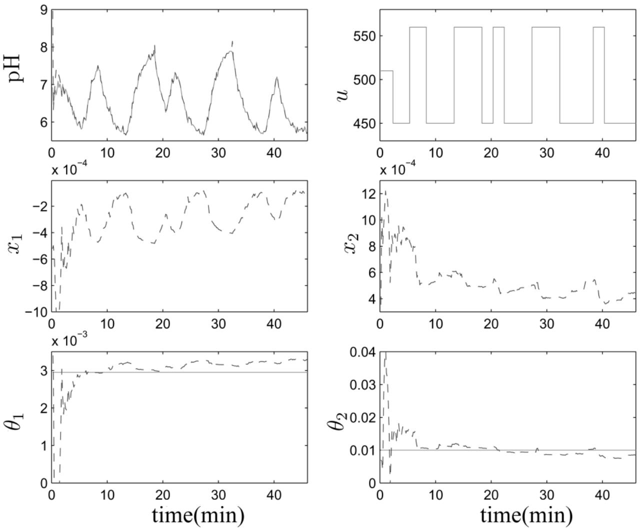

Fig. 5. Performance of estimator in experiment: the true values (solid) and the estimates (dashed).

The first experiment was conducted to test the performance of the estimator under nominal operating condition. For this experiment the flow rate of the base stream (q_B) was manipulated to excite the process via a pseudo random binary sequence (PRBS) input sequence. The size of PRBS was ±60 ml/min. Due to the process nonlinearity, the pH changes showed highly asymmetric behavior. Figs. 4 and 5 showed the performances of the on-line EKF in both simulation and experiment. The initial guesses of the state and parameter were deviated from their true values by ±30%. Since the concentration of feed and buffer streams were prepared in the laboratory very carefully, the true values of parameters could be calculated from the prepared concentrations by Eq. (3); θ_1 was 0.00295 and θ_2 was 0.01. The estimates of states and parameters closely followed their true values after some initial transients. Also, the estimated pH values of the effluent stream were almost exact to the true values over the whole simulation and experiment time as expected. The estimated parameter values, $\hat{\theta}_1$ converged to the true values faster than $\hat{\theta}_2$. This result implied that pH values were less sensitive to the changes in the carbonate ion of the streams as one could guess. It indicated that the parameter estimation of W_b from the pH values of the effluent stream might be slow and difficult.

The next two experiments were performed to test the tracking ability of the EKF for the time-varying parameter. The experiments were conducted for the concentration changes of the feed and buffer stream. These disturbance caused to shift the titration curve or change its shape, which represented the process nature. In Figs. 6 and 7, the performance of the EKF for an abrupt change in θ_1 of feed had been shown in simulation and experiment. The value of θ_1 was decreased by 30% (0.003 M $HNO_3 \rightarrow$0.0021 M HNO_3) at 15 min, which meant that the hydrogen ion in the feed stream was abruptly decreased. The both simulation and experimental results illustrated the sudden increase of pH in response to decrease in feed concentration. They showed that the change of θ_1 was well traced by the estimator but the experimental estimation of θ_2 resulted in a little

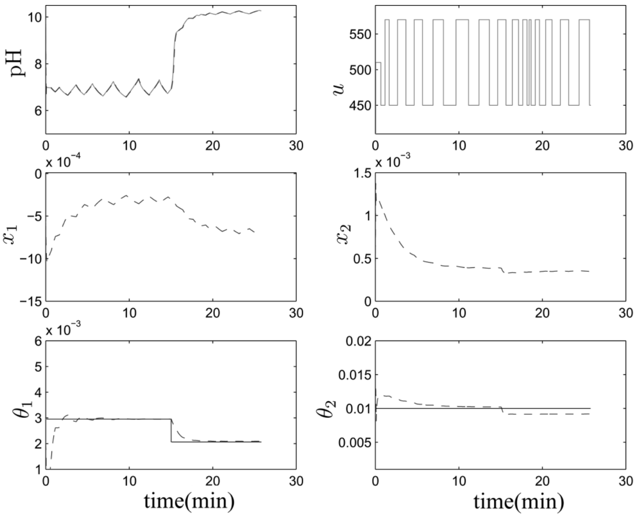

Fig. 6. Performance of estimator in simulation corresponding to a change in feed composition: the true values (solid) and the estimates (dashed).

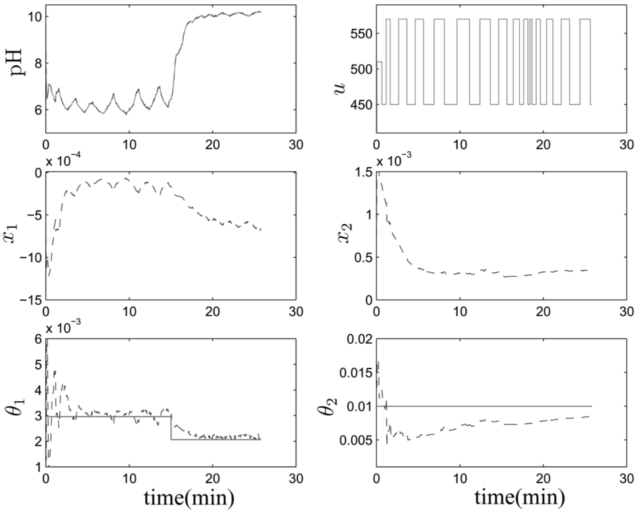

Fig. 7. Performance of estimator in experiment corresponding to a change in feed composition: the true values (solid) and the estimates (dashed).

biased value. Even though there were some error in θ_2, still the estimated pH values coincided with the measured values. Because there was no significant difference in the titration curves for [NaHCO$_3$]$_{q_2}$= 0.01 M and 0.008 M over the operating range above pH 6 as shown in Fig. 3, the 20% difference in concentration of buffer solution did not significantly affect the characteristics of process at those conditions.

Figs. 8 and 9 showed the results for a sudden change in θ_2 which caused a change in the concentration of carbonate ion in the reactor (Fig. 3). To impalement the decrease in θ_2 of the buffer stream, the concentration of NaHCO$_3$ was reduced to 0.003 M (70% decrease) at 12 min. In this case, there were three notable differences in estimation compared to the previous experiment. The first one was that, from the composition of buffer stream and the definitions of reaction invariants, the W$_{a2}$ should vary in the same manner as $-$W$_{b2}$

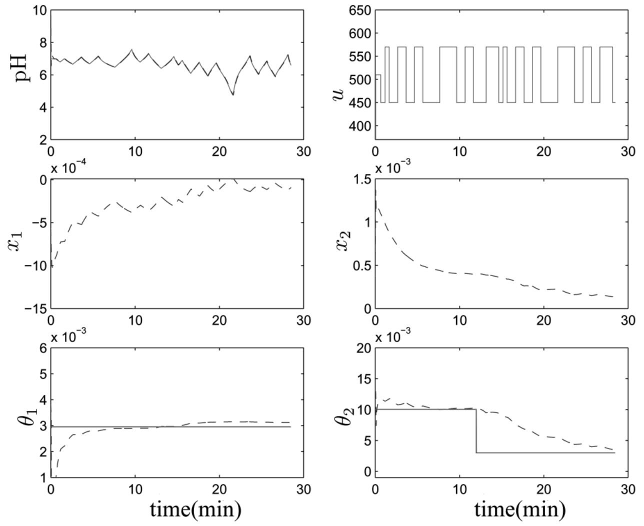

Fig. 8. Performance of estimator in simulation corresponding to a change in buffer composition: the true values (solid) and the estimates (dashed).

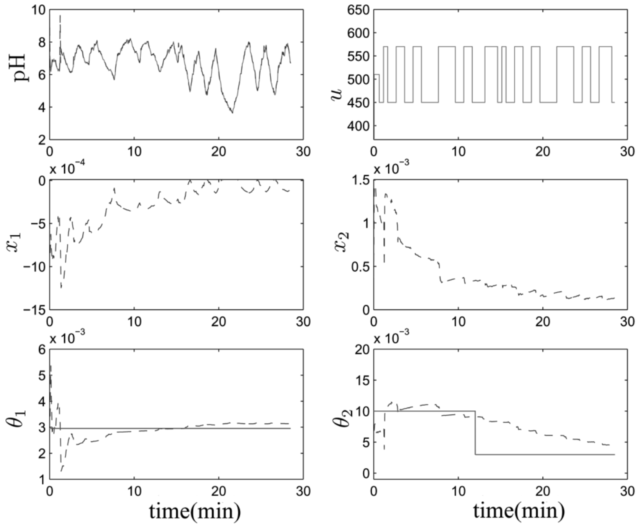

Fig. 9. Performance of estimator in experiment corresponding to a change in buffer composition: the true values (solid) and the estimates (dashed).

because NaHCO$_3$ was dissociated into Na$^+$ and HCO$_3^-$ and HCO$_3^-$ affected both reaction invariants as shown in Eq. (3). This fact had to be incorporated in the design of estimator. The second one was that the pH response of the effluent stream for the decreased buffer concentration was very slow because the flow rate of the buffer stream was very small (36 ml/min). Finally, a change of the buffer concentration significantly altered the characteristics of pH neutralization process because the shape of titration curve depended on the buffer concentration. From Fig. 3, when the buffer stream concentration decreased from the nominal operating condition to 70%, process gain increased significantly. The second and third phenomena were observed in the Figs. 8 and 9. At the moment when disturbance was imposed, the pH appeared not to change, however, the output response increased as time past. This gain increase in process characteristics could also be noticed from the increased range of the changes in the output pH value for the same size of PRBS inputs. Though the tracking rate of the parameter was slow, the changes of nonlinear properties were effectively estimated. Both the experimental and simulation results showed that the estimation of the changes in the buffer stream concentration exhibited the similar behaviors as predicted.

From the above experimental and simulation results, it could be seen that the EKF could efficiently estimate the states and parameters simultaneously so that the model identification for the nonlinear model-based control and state estimation for state feedback were feasible. The experimental application to control using this result could be the next research topic.

CONCLUSIONS

The nature of the pH neutralization process is nonlinear and time-varying. For the better control of this type of processes, the model-based nonlinear state feedback control technique is often recommended. However, the lack of state measurements and parameter estimates for more accurate process model make this approach difficult. The time-varying nature of the pH neutralization process is often caused by the change in buffering capacity which either comes from the feed changes or buffer changes. It is known that the changes in the process can be identified via the parameter estimation of crucial process parameters. In this study, the simultaneous state and parameter estimation by the EKF has been investigated both experimentally and in simulation. From the comparison of experiments and simulations, it is found that the states and parameters can be identified efficiently with EKF in cases of changes in feed composition and buffering change, and the possibility of state-feedback model-based control using the obtained information has been verified.

NOMENCLATURE

K_{a1} : equilibrium constant
K_{a2} : equilibrium constant
K_w : equilibrium constant
pH : pH value for stream
q : flow rate [ml/s]
[q] : concentration of stream [mole]
V : reactor volume [ml]
W : reaction invariant

Subscripts

1 : feed stream
2 : buffer stream
3 : base stream
4 : effluent stream
a : hydrogen ion related reaction invariant
b : carbonic ion related reaction invariant

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