

Adaptive Input-Output Linearization Control of pH Processes

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ABSTRACT: *pH control is a challenging problem due to its highly nonlinear nature. In this paper the performances of two different adaptive global linearizing controllers (GLC) are compared. Least squares technique has been used for identifying the titration curve. The first controller is a standard GLC based on material balances of each species. For implementation of this controller a nonlinear state estimator is used. Some modifications are proposed to avoid the singularity of the observer gain. The second controller is designed based on the reduced state equation. Through computer simulations, it has been shown that the performances of the second GLC is superior and it is more robust to process model mismatch. It should be also noted that the design of reduced state-based GLC is much easier and does not need observer for implementation.*

KEY WORDS: *pH control, Exact linearization, Nonlinear state estimator, Least-squares identification.*

INTRODUCTION

The main objective of pH processes is to control the effluent pH by manipulating the flow rate of titrating stream. The pH processes are difficult to control due to their nonlinear dynamics. So far, many authors have proposed nonlinear control strategies to overcome the difficulties involved in pH control. It must be noted that pH neutralization process is widely studied for two different reasons. First, because of its environmental effects and second, pH neutralization process is highly

nonlinear and is known as a challenging problem. Many papers on modeling and control of pH have been appeared in the literature. The first effort in this regard returns to *McAvoy et al.* [1]. *Gustafsson* and *Waller* [2] extended this method by introducing the concept of reaction invariant (RI) to general multi component pH processes. Strategies for controlling pH are usually based on some algorithms that are designed to account for the time varying characteristics and severe nonlinearity

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inherent in pH processes. One way to view this nonlinearity is to consider a linear model with time-varying gain and use adaptive techniques for control purposes. The works of *Mellichamp et al.* [3], *Gupta and Coughanowr* [4], *Buchholt and Kummel* [5], *Hurowitz and Bobkov* [6] are some examples of this type of controller. In case of nonlinear control, *Zhou et al.* [7] used H_∞ -controller with a linear function between pH and states which is obtained by linearization pH vs. states at each point. *Yoon et al.* [8] have proposed a nonlinear controller with an estimator for estimating the concentration of feed stream. *Lee et al.* [9] proposed an adaptive back stepping controller with state estimator for pH neutralization process. *Wright and Kravaris* [10], *Wright et al.* [11] reduced the pH process model to a first-order state equation and introduced the concept of strong acid equivalent (SAE). Their control strategy has a good performance and is robust to modeling error. If the nonlinear part of model (titration curve) is identified on-line, the controller performance will be improved (*Wright and Kravaris* [12], *Wright et al.* [13], *Lee and Choi* [14]). A different way to overcome the nonlinear characteristics of the pH is to consider multiple models for titration curve in which, the best model is selected based on an objective function and measured value of pH (*Pishvaie and Shahrokhi* [15], *Sun and Hoo* [16]). Intelligent approaches like artificial neural network and fuzzy set are also used for modeling and control of pH processes. Some examples of intelligent strategies are works of *Behera and Anand* [17], *Palancar et al.* [18], *Wang and Yoon* [19], *Akesson et al.* [20].

Among different nonlinear control techniques, feedback linearization attracts researchers' attention more than the others. Feedback linearization is used for canceling the nonlinearities of the system and applying the linear control strategies to the linearized system (*Slotine and Li* [21]). For implementation of GLC, the system states must be available. Since in most of practical application a few state are measured, a state estimator should be used for estimating the unmeasured states. *Baumann and Rugh* [22] developed a state estimator based on extended linearization. *Biagiola and Figueroa* [23] used the nonlinear state estimator proposed by *Ciccarella et al.* [24] for pH control. But it can be shown that the estimator can not be used for systems consisting of strong acid and base together.

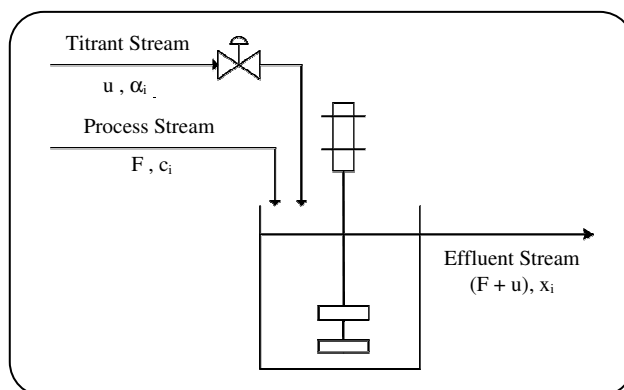


Fig. 1: pH neutralization process.

In this work the performances of two linearizing controllers have been compared. The first controller is designed based on reaction invariants. Since for implementation of this controller the system states should be available, a Luenberger-like nonlinear state estimator has been used to estimate the reaction invariants. For systems containing strong acid and base the observer gain becomes singular. To avoid this problem, it is proposed to use reduced order observer. By updating the titration curve, the adaptive version of this controller has been designed. The second controller is a GLC designed based on reduced state model proposed by *Wright and Kravaris* [10]. For implementation of this controller no observer is needed and design of controller is much simpler than the first one. Through the same procedure its adaptive version can be developed.

The paper is organized as follows. First, modeling of pH is presented. Second, feedback linearization is discussed followed by observer design. Next, the feedback recursive least-squares method has been used for developing the adaptive version of the controllers. Finally, the performances of two designed controllers have been compared through computer simulations.

pH PROCESS MODEL

Consider a pH neutralization process as shown in Fig. 1. V and F denote the volume of the reactor and process stream flow rate and are assumed to be constant. The output of the process is the pH value of the effluent stream, and the flow rate of titrating stream, u , is the control input. A dynamic model is derived using the conservation law. Assuming constant tank volume and perfect mixing, the standard ion balances and electro

neutrality condition along with chemical equilibrium relations yield the detailed nonlinear state space model of the process as given below:

$$\dot{x}_i = \frac{F}{V}(c_i - x_i) + \frac{(\alpha_i - x_i)}{V}u \quad i = 1 \dots n \quad (1)$$

$$\sum_{i=1}^n a_i(\text{pH})x_i + A(\text{pH}) = 0 \quad (2)$$

where $A(\text{pH}) = 10^{-\text{pH}} - 10^{\text{pH}-14}$ and x_i is the total concentration of the i th species in the effluent stream. α_i and c_i are the total ion concentrations of the i th species in the titrating and process streams, respectively and $a_i(\text{pH})$'s are functions of pH and dissociation constants as shown by Wright *et al.* [13].

In this study we have used the reduced model developed by Wright and Kravaris [10] which is discussed very briefly as follows. Under the assumption that α_i and c_i are not changing with time, from (1) we have:

$$V \frac{d}{dt} \left(\frac{c_i - x_i}{c_i - \alpha_i} \right) = u - (F + u) \frac{c_i - x_i}{c_i - \alpha_i} \quad (3)$$

This implies that if the system is initially at steady state, then

$$\frac{c_1 - x_1}{c_1 - \alpha_1} = \frac{c_2 - x_2}{c_2 - \alpha_2} = \dots = \frac{c_n - x_n}{c_n - \alpha_n} \quad (4)$$

Furthermore, defining:

$$X = \frac{c_i - x_i}{c_i - \alpha_i} \quad (5)$$

(3) can be written as:

$$V \frac{dX}{dt} = u - (F + u)X \quad (6)$$

The pH equation (2) becomes:

$$X \sum_{i=1}^n a_i(\text{pH})\alpha_i + (1-X) \sum_{i=1}^n a_i(\text{pH})c_i + A(\text{pH}) = 0 \quad (7)$$

Equations (6) and (7) form a first-order model for the process. In what follows we will use (1) for designing the first GLC and (6) for the second one.

INPUT-OUTPUT LINEARIZATION

Consider the nonlinear affine system described by:

$$\dot{x} = f(x) + g(x)u \quad (8)$$

$$y = h(x)$$

where f and g are vector fields and h is a scalar field. In input-output linearization the objective is generating a linear differential relation between the output y and a new input v . The system has a relative degree r if:

$$L_g L_f^i h(x) = 0 \quad 0 \leq i \leq r-2 \quad (9)$$

$$L_g L_f^{r-1} h(x) \neq 0$$

where the L_f is the Lie derivative in direction of f .

Assume that the system (8) is linearizable and has the relative degree of r . The input transformation:

$$u = \frac{v - L_f^r h - \sum_{k=0}^{r-1} \beta_{r-k} L_f^k h}{L_g L_f^{r-1} h} \quad (10)$$

results in a linear relation between y and v given by:

$$\frac{y(s)}{v(s)} = \frac{1}{s^r + \sum_{k=0}^{r-1} \beta_{r-k} s^k} \quad (11)$$

where β_i 's are arbitrary design parameters.

For pH processes, equation (8) becomes:

$$\dot{x} = f(x) + g(x)u \quad (12)$$

$$h(x, y) = 0, \quad y = \text{pH}$$

Depending on equations describing the system dynamics, two global linearizing controllers can be design. If (1) and (2) are considered as system model, we have:

$$f(x) = \frac{F}{V} \begin{bmatrix} c_1 - x_1 \\ \dots \\ c_n - x_n \end{bmatrix}, \quad g(x) = \frac{1}{V} \begin{bmatrix} \alpha_1 - x_1 \\ \dots \\ \alpha_n - x_n \end{bmatrix} \quad (13)$$

The controller obtained based on the above $f(x)$ and $g(x)$ is called GLC1.

If (6) and (7) are used as system model, we have:

$$f(X) = -\frac{F}{V}X, \quad g(X) = \frac{1-X}{V} \quad (14)$$

Controller designed based on (14) is called GLC2. For both controllers $L_g y$ can be written as given below:

$$L_g y = \frac{dy}{dx} \cdot g = -\frac{\partial h / \partial x}{\partial h / \partial y} \cdot g \quad (15)$$

It can be shown that:

$$L_g y = \frac{1}{v \frac{\partial h}{\partial y}} [-10^{-y} + 10^{y-14} - \alpha] \quad (16)$$

where, α is the titrating agent concentration.

It's clear that $L_g y \neq 0$ if $0 \leq y \leq 14$, therefore relative order is one and the linearization relation is as follows:

$$u = \frac{v - L_f y - \beta y}{L_g y} \quad (17)$$

Remark 1: For implementation of GLC1, according to equation (10) the system states are required while in case of GLC2, for calculating u (equation (17)) only reduced order state, X , is needed which can be obtained by solving equation (6).

Remark 2: In the linearization procedure, saturation of the actuator is not considered. Therefore, whenever the actuator is saturated, we don't expect fully linearized dynamic behavior.

NONLINEAR STATE ESTIMATOR

For implementation of many model based control algorithms the system states are required (like GLC1). For this reason, many researchers have focused their attention on the development of suitable algorithms for state estimation. In this regard, several techniques have been introduced to estimate state variables from the available measurements. For linear system the standard solution is the Luenberger observer for deterministic systems and the linear Kalman filter for stochastic systems. For nonlinear systems several algorithms have been proposed (Ciccarella et al. [24], Valluri and Soroush [25], Kazantzis and Kravaris [26], Lopez and Maya [27]).

One of the most common nonlinear state observers is the one proposed by Ciccarella et al. [24] and evaluated by Valluri and Soroush [25]. The basic structure of this estimator for the system described by (8) is as follow:

$$\dot{\hat{x}} = f(\hat{x}) + g(\hat{x})u + \left[\frac{\partial \Phi(\hat{x})}{\partial \hat{x}} \right]^{-1} K[y - h(\hat{x})] \quad (18)$$

where K is a constant vector and Φ defined as follows:

$$\Phi = \begin{bmatrix} h(x) \\ L_f h(x) \\ \dots \\ L_f^{n-1} h(x) \end{bmatrix} \quad (19)$$

In fact the matrix Φ performs a nonlinear change of coordinates, and is used to design the vector K such that the dynamics of (18) remains stable. Biagiola and Figueroa [23] used this estimator for a pH process for which the output can be written as an explicit function of states. Generally, when more than three components are present in the system, the output can not be expressed as an explicit function of states (12). In such this case Φ is defined by:

$$\Phi = \begin{bmatrix} y \\ L_f y \\ \dots \\ L_f^{n-1} y \end{bmatrix} \quad (20)$$

Therefore, (18) is revised into the following form:

$$\dot{\hat{x}} = f(\hat{x}) + g(\hat{x})u + \nabla \Phi^{-1} K[y - \hat{y}] \quad (21)$$

Remark 3: For the pH system consisting strong acid and base, it can be shown that all Lie derivatives appeared in the $\nabla \Phi$ matrix related to strong base ions are multiples of the term related to strong acid ions. In fact the two columns of matrix $\nabla \Phi$ (gradient of Φ) relating to strong acid and base are dependent, therefore $\nabla \Phi$ will be singular and uninvertible. In such cases we propose using reduced order observer or defining virtual state that will be discussed in what follows.

Case I: consider the neutralization of a feed stream containing a strong acid by a strong base as the titrating agent. In this case, to avoid the singularity of the matrix $\nabla \Phi$, we can use a reduced order observer to estimate the concentrations of all species in feed stream and calculate the concentration of the titrating base by solving its mass balance equation. Details of the reduced order observer design for a case containing four species (x_1 = strong acid concentration and x_2 = strong base concentration) are given in appendix A.

Case II: consider the neutralization of a feed stream containing a strong acid and strong base by a titrating stream which is also a strong base different from the one existing in the feed stream. Let x_1 and x_2 denote the

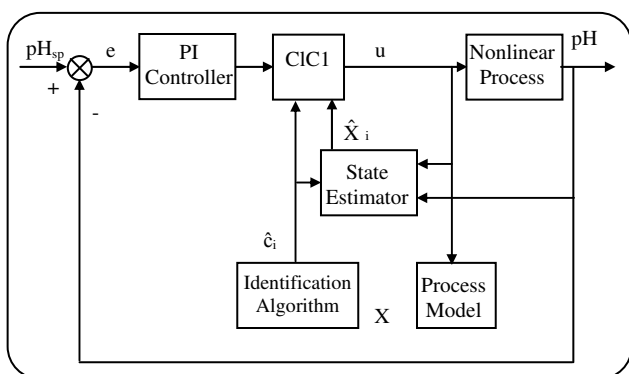


Fig. 2: Closed-loop block diagram of GLC1.

concentrations of strong acid and base in the feed stream respectively. We define a virtual state as $x' = -x_1 + x_2$ and use a reduced order observer to estimate x' and concentrations of the other species present in the feed stream. Using x' in calculating the $\nabla\Phi$ matrix results in a nonsingular matrix. The concentration of the titrating strong base is obtained as before i.e. by solving its mass balance equation.

Remark 4: The best performance is obtained when $y = 10^{\text{pH}}$ in the design of state estimator and $y = \text{pH}$ in the design of controller (GLC).

ON-LINE IDENTIFICATION OF TITRATION CURVE

As can be seen from the design equations of both controllers, the feed composition is needed for control implementation. If the feed composition changes, it can deteriorate the performances of controllers. To overcome this problem the adaptive version can be used. To update the titration curve, an on-line estimator can be designed. It's reasonable to assume that the titrant stream concentration is known and is fixed. By rearranging (7) we have:

$$\sum_{i=1}^n a_i(\text{pH})c_i = \frac{1}{1-X} \left[-X \sum_{i=1}^n a_i(\text{pH})\alpha_i - A(\text{pH}) \right] \quad (22)$$

All terms appearing on the right-hand side of (22) are known because pH is measured, α_i are known and X can be readily calculated from (6). This leaves only c_i parameters to be estimated which appeared linearly. In a more compact notation, (22) becomes:

$$\phi^T \theta = \frac{1}{1-X} \left[-X \sum_{i=1}^n a_i(\text{pH})\alpha_i - A(\text{pH}) \right] \quad (23)$$

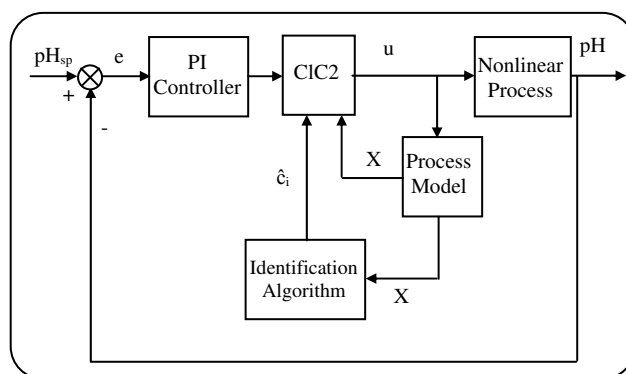


Fig. 3: Closed-loop block diagram of GLC2.

where ϕ is a vector of functions of $a_i(\text{pH})$ defined by Wright *et al.* (1998) and θ is a vector of c_i parameters. The vector of parameters can then be estimated on-line using a standard recursive least-squares algorithm:

$$\dot{\theta} = P\phi e \quad (24)$$

$$\dot{P} = \lambda P - P\phi\phi^T P$$

where e is the identification error and P is the covariance matrix. Combination of covariance resetting and forgetting factor has been used to avoid matrix P approaching zero.

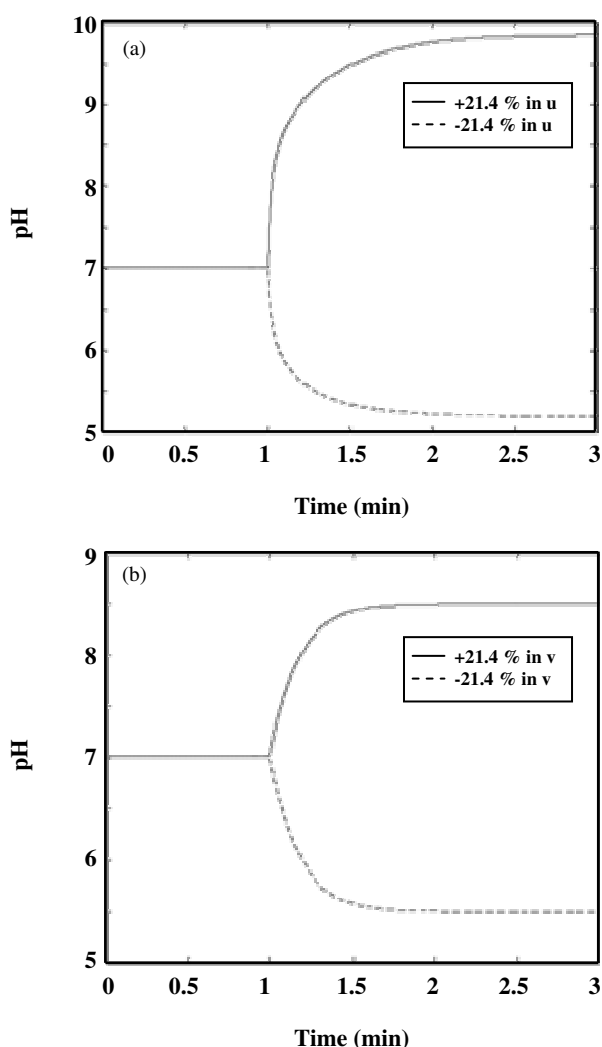
SIMULATION RESULTS

The closed-loop block diagrams of adaptive GLC1 and GLC2 are shown in Figs. 2 and 3 respectively. In both structures a PI controller is used for the linearized system. The IMC technique is used for tuning the PI controller. The integral time is set to $1/\beta$ and the controller gain is selected to be one for all simulations run. The observer gain is to $K^T = [10, 9, 8] \times 10^{-7}$ and all initial states were set to zero. To evaluate the performances of the designed controllers the following system has been considered. The simulated chemical system consists of HCl as a strong acid, HAc as a weak acid and $\text{NH}_3/\text{NH}_4^+$ as a weak base titrated with NaOH. The system parameters, initial steady-state values, nominal feed concentration (C_0) and two extremes of feed compositions (C_1, C_2) are given in Table 1. Fig. 4-a demonstrates the nonlinear nature of this process by applying $\pm 21.4\%$ step changes to the titrating flow rate. Fig. 4-b shows the behavior of the linearized system for the same changes in the virtual input (v) for $\beta=0.1$.

Load Rejection: To evaluate the performances of the closed-loop responses of the designed controllers, at

Table 1: Parameter values used in the simulation.

$F=200$ ml/sec	$V=5000$ ml	$u_{ss,C1}=19.94$ ml/sec		
$u_{min}=0$ ml/sec	$\alpha=0.04$ N	$u_{ss,C0}=39.87$ ml/sec		
$u_{max}=80$ ml/sec		$u_{ss,C2}=74.77$ ml/sec		
		Concentration $\times 10^3$ M		
		C_0	C_1	C_2
HCl		4	2	8
HAc ($pK_a = 4.8$)		6	2	8
NH_3 ($pK_b = 4.75$)		2	0	1

Fig. 4: Open-loop response for: (a) $\pm 21.4\%$ change in u and (b) $\pm 21.4\%$ change in v .

time 5 min. the process stream concentration is switched from C_0 to C_1 and next time from C_0 to C_2 . The results are shown in Figs. 5 and 6. As can be seen the GLC2 has a slightly better performance. In Fig. 7 the actual states and their estimates for GLC1 are illustrated. As can be seen all state estimates have converged to their actual values before the disturbance occurs. After disturbance is introduced the state estimates have converged to wrong values, although the output error has converged to zero. This can be explained as follows. Since the richness condition is not satisfied, the c_i estimates do not converge to their new values which in turn affect the performance of the state observer (wrong c_i values used in the observer equation results in the wrong state estimation). Fig. 8 shows the performance of titration curve identification algorithm when faced to disturbance in concentration. As can be seen for both cases (changing from C_0 to C_1 and from C_0 to C_2) the identified titration curve is close to the actual titration curve near the controlling pH valve. To evaluate the performances of controllers in presence of unknown component, 0.002 M of H_2CO_3 is added to feed stream at time 5 min. The results are shown in Fig. 9. As can be seen the GLC2 has a better performance.

Effect of Measurement Noise: To evaluate the performance of control system when the measurement is corrupted with noise, a noise with magnitude of ± 0.1 pH is added to pH measurement. The results of GLC2 are illustrated in Fig. 10. As can be seen the controller can handle this level of noise fairly well. The similar performance will be obtained if GLC1 is used.

Set-point Tracking: Fig. 11 depicts the performance of GLC2 for set-point tracking. As can be seen the controller can follow the desired trajectory outstandingly. The same result is obtained if GLC1 is used.

CONCLUSIONS

In this paper application of GLC for pH control has been considered. Two different adaptive linearizing controllers have been designed (GLC1 and GLC2). The first design needs observer for implementation and has more computational load. In designing the nonlinear observer for pH processes, it has been shown that if the system contains strong acid and strong base, the observer gain becomes singular. Two different methods for avoiding singularity have been proposed. The second proposed controller which is designed based on reduced

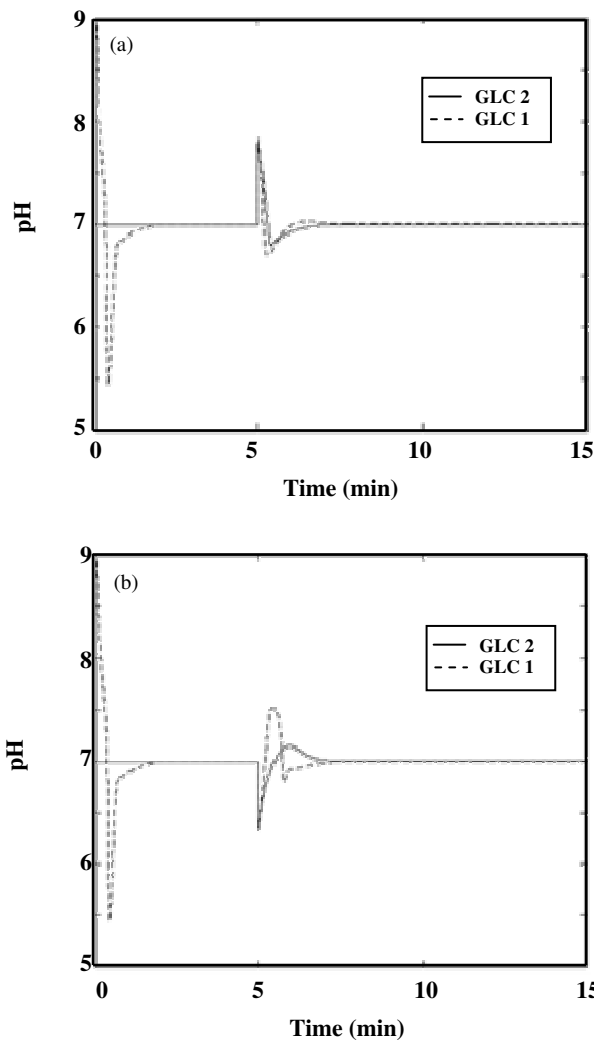


Fig. 5: Closed-loop responses of GLC1 and GLC2 for changing from (a) C_0 to C_1 and (b) C_0 to C_2 .

state representation does not require observer and needs less computational effort. Simulation results show that both controllers have satisfactory performances in load rejection and set-point tracking and they are robust to uncertainties in feed composition and measurement noise. Since design of the second controller is easier and its implementation requires less computational load, it is preferable. The difference between two designs becomes more evident as the number of components in the system increases.

APPENDIX A

Reduced order observer design

$$\dot{\hat{x}} = f(\hat{x}) + g(\hat{x})u + \nabla\Phi^{-1} \cdot K(y - \hat{y}) \quad (\text{A.1})$$

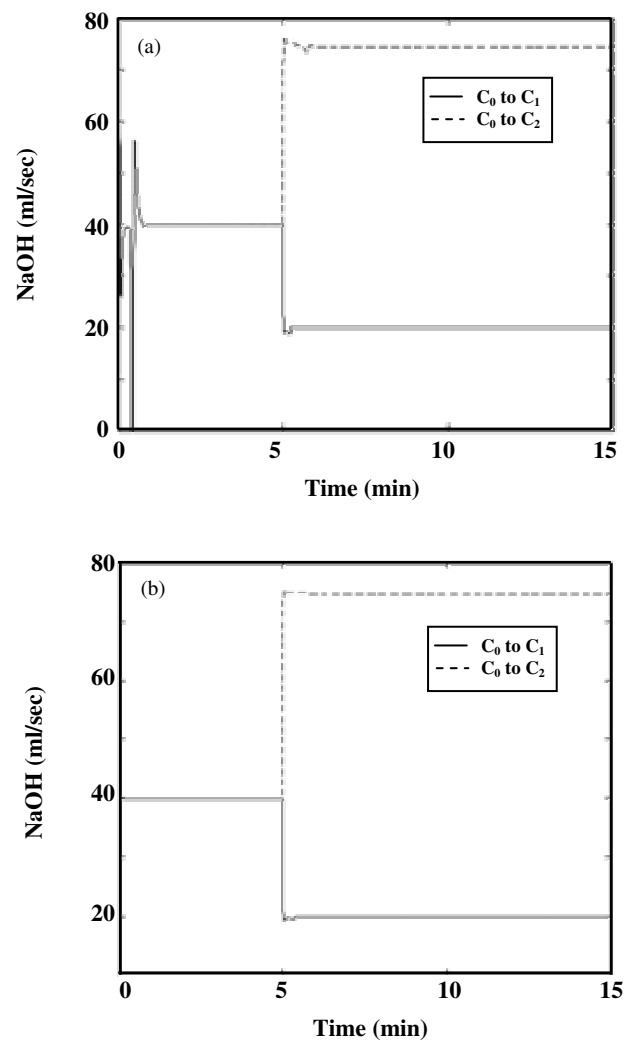


Fig. 6: Input variations for changing from C_0 to C_1 and C_2 : (a) GLC1 (b) GLC2.

$$f(\hat{x}) = \frac{F}{V} \begin{bmatrix} c_1 - \hat{x}_1 \\ c_3 - \hat{x}_3 \\ c_4 - \hat{x}_4 \end{bmatrix}, \quad g(\hat{x}) = \frac{1}{V} \begin{bmatrix} -\hat{x}_1 \\ -\hat{x}_3 \\ -\hat{x}_4 \end{bmatrix} \quad (\text{A.2})$$

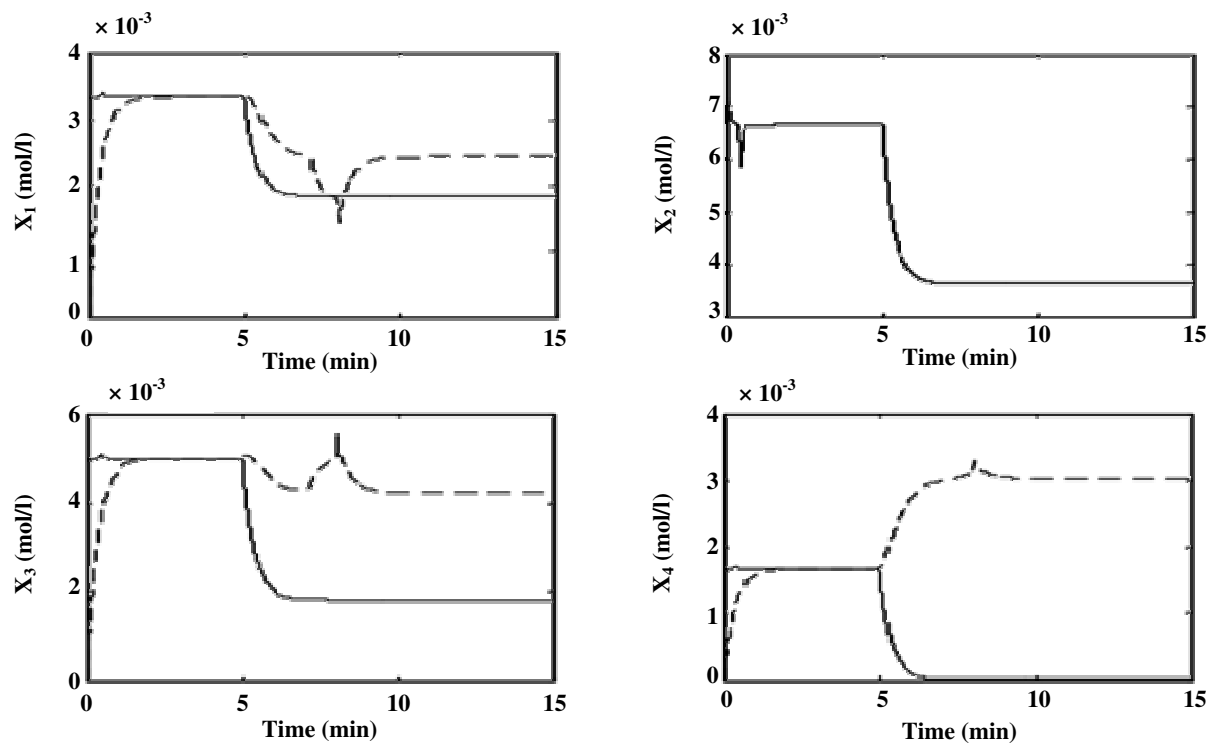
$$h(\hat{x}, \hat{y}) = -\hat{x}_1 + x_2 - \left(\frac{1}{1 + \hat{y}10^{\text{p}k_a}} \right) \hat{x}_3 + \quad (\text{A.3})$$

$$\frac{\hat{y}}{\hat{y} + 10^{(\text{p}k_b - \text{p}k_w)}} \hat{x}_4 + \hat{y} - \frac{10^{-\text{p}k_w}}{\hat{y}} = 0, \quad \hat{y} = 10^{-\text{pH}}$$

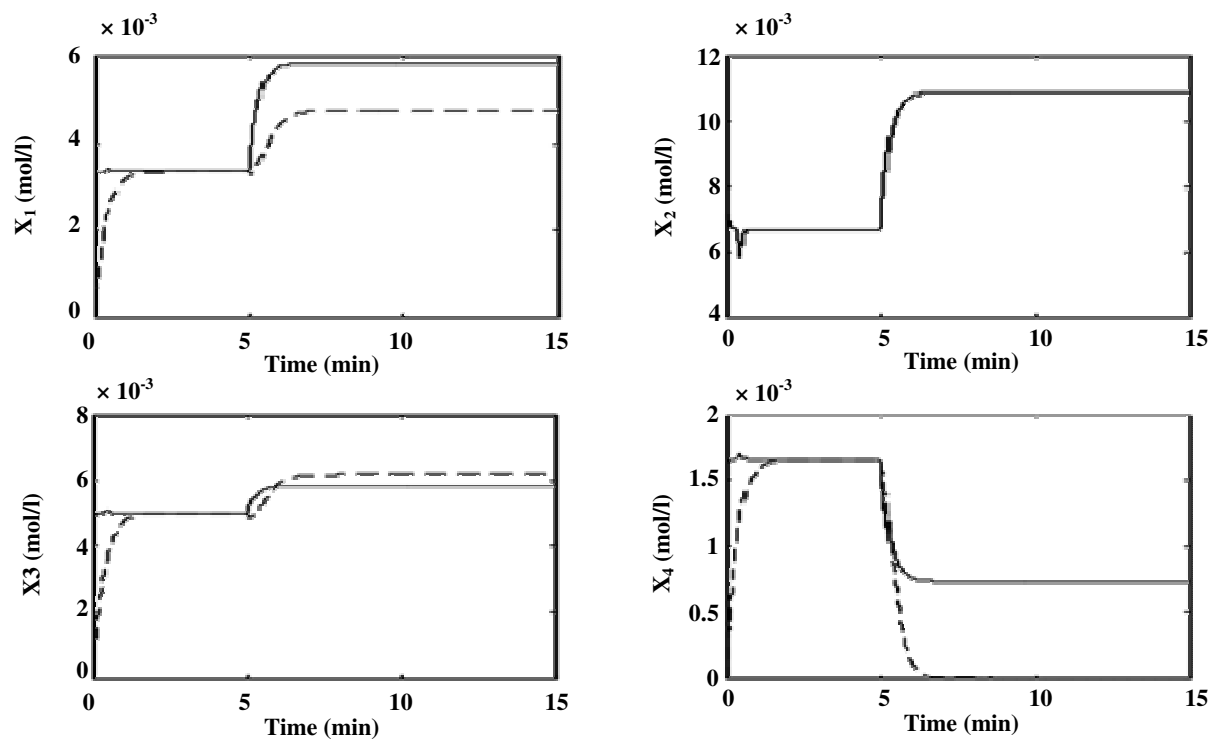
$$\frac{\partial h}{\partial \hat{x}} = \begin{bmatrix} -1 & -\frac{1}{1 + \hat{y}10^{\text{p}k_a}} & \frac{\hat{y}}{\hat{y} + 10^{(\text{p}k_b - \text{p}k_w)}} \end{bmatrix} \quad (\text{A.4})$$

$$\frac{\partial h}{\partial \hat{y}} = \frac{10^{\text{p}k_a}}{(1 + \hat{y}10^{\text{p}k_a})^2} \hat{x}_3 + \frac{10^{(\text{p}k_b - \text{p}k_w)}}{(\hat{y} + 10^{(\text{p}k_b - \text{p}k_w)})^2} \hat{x}_4 + \quad (\text{A.5})$$

$$1 + 10^{-\text{p}k_w} / \hat{y}^2$$



(a)



(b)

Fig. 7: State estimator performance for changing from : (a) C_0 to C_1 and (b) C_0 to C_2 (Solid line: Real, Dash line: Estimated).

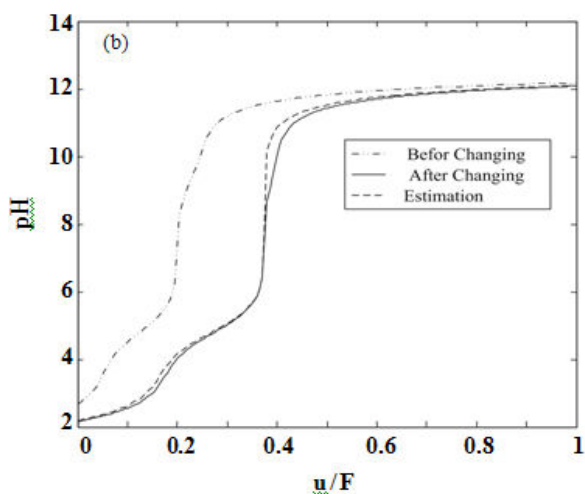
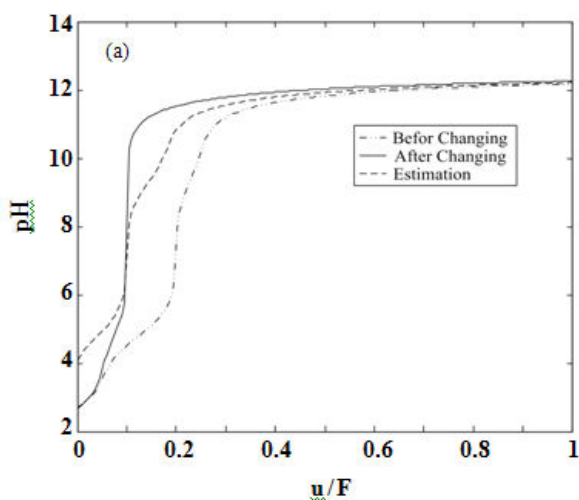


Fig. 8: Feed stream titration curve and its estimation for changing from: (a) C_0 to C_1 and (b) C_0 to C_2 .

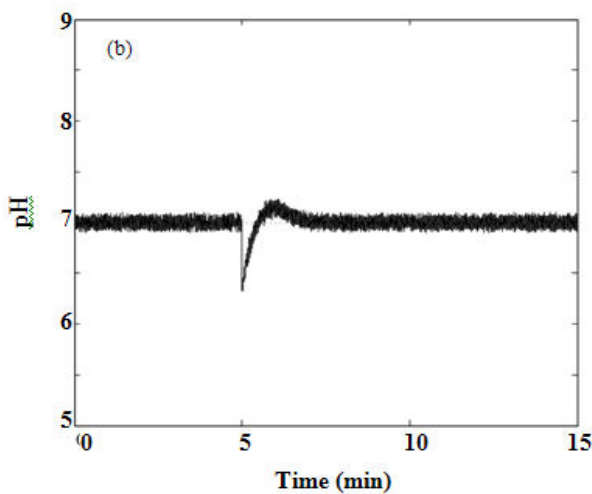
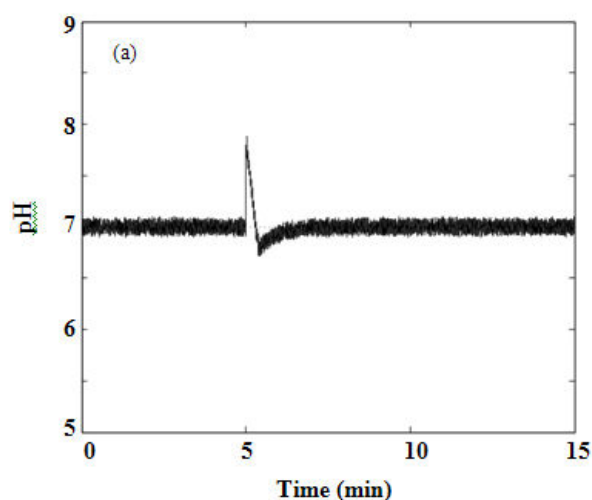


Fig. 10: Closed-loop performance of GLC2 in presence of measurement noise for changing from : (a) C_0 to C_1 and (b) C_0 to C_2 .

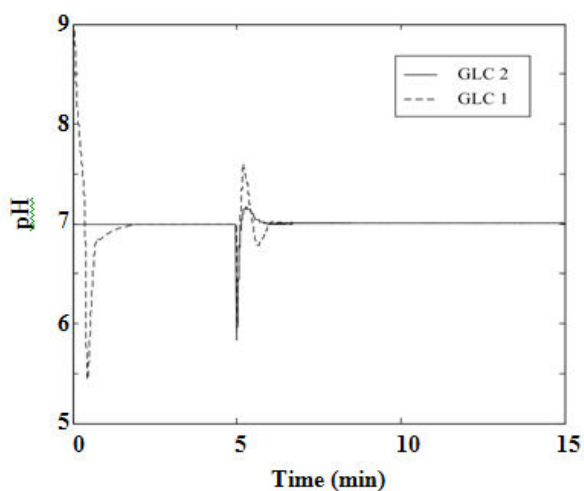


Fig. 9: Closed-loop responses of GLC1 and GLC2 for adding an unknown component at time 5 min.

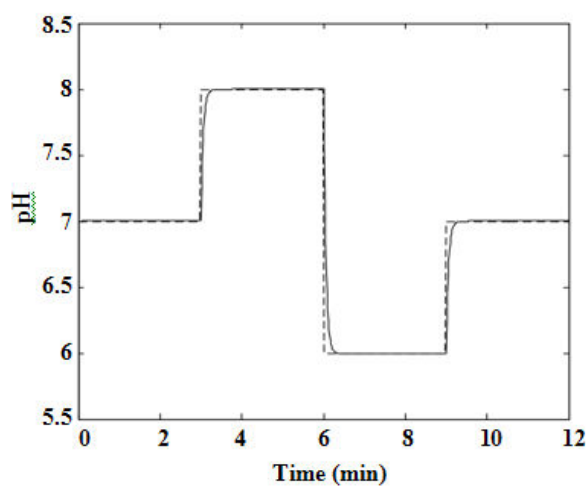


Fig. 11: Closed-loop performance of GLC2 for set point tracking.

$$L_f \hat{y} = -\frac{\partial h / \partial \hat{x}}{\partial h / \partial \hat{y}} \cdot f(\hat{x}) = \quad (\text{A.6})$$

$$\frac{F/V}{\partial h / \partial \hat{y}} \left[c_1 - \hat{x}_1 - \frac{c_3 - \hat{x}_3}{1 + \hat{y} 10^{\text{pk}_a}} - \frac{\hat{y}}{\hat{y} + 10^{(\text{pk}_b - \text{pk}_w)}} (c_4 - \hat{x}_4) \right]$$

$$\left\{ \begin{aligned} \frac{\partial L_f \hat{y}}{\partial \hat{x}_1} &= -\frac{F/V}{\partial h / \partial \hat{y}} \\ \frac{\partial L_f \hat{y}}{\partial \hat{x}_3} &= \frac{F/V}{\partial h / \partial \hat{y}} \left[-\frac{1}{1 + \hat{y} 10^{\text{pk}_a}} - \frac{\partial}{\partial \hat{x}_3} \left(\frac{\partial h}{\partial \hat{y}} \right) L_f \hat{y} \cdot \frac{V}{F} \right] \\ \frac{\partial L_f \hat{y}}{\partial \hat{x}_4} &= \frac{F/V}{\partial h / \partial \hat{y}} \left[\frac{\hat{y}}{\hat{y} + 10^{(\text{pk}_b - \text{pk}_w)}} - \frac{\partial}{\partial \hat{x}_4} \left(\frac{\partial h}{\partial \hat{y}} \right) L_f \hat{y} \cdot \frac{V}{F} \right] \end{aligned} \right. \quad (\text{A.7})$$

$$L_f^2 \hat{y} = \frac{\partial L_f \hat{y}}{\partial \hat{x}} \cdot f(\hat{x}) = \quad (\text{A.8})$$

$$\frac{(F/V)^2}{\partial h / \partial \hat{y}} \left[-c_1 + \hat{x}_1 - \frac{c_3 - \hat{x}_3}{1 + \hat{y} 10^{\text{pk}_a}} - \frac{\partial}{\partial \hat{x}_3} \left(\frac{\partial h}{\partial \hat{y}} \right) L_f \hat{y} \cdot \frac{V}{F} (c_3 - \hat{x}_3) + \frac{\hat{y}}{\hat{y} + 10^{(\text{pk}_b - \text{pk}_w)}} (c_4 - \hat{x}_4) - \frac{\partial}{\partial \hat{x}_4} \left(\frac{\partial h}{\partial \hat{y}} \right) L_f \hat{y} \cdot \frac{V}{F} (c_4 - \hat{x}_4) \right]$$

$$\left\{ \begin{aligned} \frac{\partial L_f^2 \hat{y}}{\partial \hat{x}_1} &= \frac{(F/V)^2}{\partial h / \partial \hat{y}} \\ \frac{\partial L_f^2 \hat{y}}{\partial \hat{x}_3} &= -\frac{1}{\partial h / \partial \hat{y}} \frac{\partial}{\partial \hat{x}_3} \left(\frac{\partial h}{\partial \hat{y}} \right) \left[L_f^2 \hat{y} + \frac{F}{V} \frac{\partial L_f \hat{y}}{\partial \hat{x}_3} (c_3 - \hat{x}_3) \right] \\ \frac{\partial L_f^2 \hat{y}}{\partial \hat{x}_4} &= -\frac{1}{\partial h / \partial \hat{y}} \frac{\partial}{\partial \hat{x}_4} \left(\frac{\partial h}{\partial \hat{y}} \right) \left[L_f^2 \hat{y} + \frac{F}{V} \frac{\partial L_f \hat{y}}{\partial \hat{x}_4} (c_4 - \hat{x}_4) \right] \end{aligned} \right. \quad (\text{A.9})$$

$$\nabla \Phi = \begin{bmatrix} \frac{\partial \hat{y}}{\partial \hat{x}_1} & \frac{\partial \hat{y}}{\partial \hat{x}_3} & \frac{\partial \hat{y}}{\partial \hat{x}_4} \\ \frac{\partial L_f \hat{y}}{\partial \hat{x}_1} & \frac{\partial L_f \hat{y}}{\partial \hat{x}_3} & \frac{\partial L_f \hat{y}}{\partial \hat{x}_4} \\ \frac{\partial L_f^2 \hat{y}}{\partial \hat{x}_1} & \frac{\partial L_f^2 \hat{y}}{\partial \hat{x}_3} & \frac{\partial L_f^2 \hat{y}}{\partial \hat{x}_4} \end{bmatrix} \quad (\text{A.10})$$

Nomenclatures

A	Term depending on pH in general titration curve equation
a_i	Function of pH which appears as a coefficient of the i th ionic total ion concentration
c_i	Concentration of the i th species in the process stream, (mol/l)
F	Flow rate of the process stream, (ml/sec)
K	Observer gain
K_{ai}	i th dissociation constant of acid
Kc	Controller gain
K_w	Dissociation constant of water, (10^{-14})
n	Number of ionic species in the pH process
pH	$-\log [H^+]$
r	Relative order
t	Time, (min)
u	Flow rate of the titrating stream, (ml/sec)
v	Linearizing input
V	Volume of the mixing tank, (ml)
x_i	Reaction invariant of i th species, (mol/l)
X	Reduced order state

Greek Symbols

α_i	Concentration of the i th species in the titrating stream, (mol/l)
β	Linearized system pole
θ	Titration curve parameters vector
ϕ	Vector of pH functions

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