Nonlinear Self-tuning Regulator for Neutralization of Weak Acid Streams by a Strong Base

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Abstract : A nonlinear self-tuning regulator for a neutralization process of a weak acid and strong base system is proposed. Rearranging the state equation of the process model, we first obtain equations which are linear for a manipulated variable or unknown parameters. Then to these equations we apply the standard procedure used in designing linear self-tuning regulators. Simulation results show that the regulator provides very good performances for various realistic situations and traces variations of the unknown parameters. Since computations are simple and additional measurements except the effluent pH value are only flow rates of influent streams, it can be easily applied to real processes such as a waste water treatment process.

1. Introduction

The acidities measured with pH meters are required to be regulated in some recently important chemical processes such as a waste water treatment process. The regulation of pH is subject to several difficulties such as highly nonlinear dynamics and its dependence on temperature, and shift of the pH value due to slow neutralization reactions. For these reasons, controls by conventional PID controllers or advanced controllers based on linear system theories are ineffective.

Since a weak acid and strong base system reveals more complicated dynamic behavior due to varying buffering effects of the weak acid, its pH value is very difficult to control.

For severely nonlinear systems similar to the pH control system, the nonlinear adaptive control method which utilizes the structure of nonlinear dynamics of a specific process was reported to provide significant improvement over conventional controllers or linear adaptive methods.

Here we propose a new nonlinear adaptive control method for a weak acid and strong base system which applies the well-known linear self-tuning regulator technique to the rigorous dynamic model of the pH process systematically. For this, we select the concentration of the strong base ion and the effluent pH value as state variables for the dynamic model(McAvoy, 1972), so that the dynamic model becomes linear for a manipulated variable or unknown parameters; the concentration and the dissociation constant of the influent weak acid. To this dynamic model we apply the basic linear self-tuning regulation technique such as the recursive least squares method with a variable forgetting factor for parameter identification and the one-step ahead control law for manipulated variable calculation.

This regulator handles a stream of one-component weak acid solution. However, since it estimates the concentration of influent weak acid stream and the dissociation constant, it would be applicable to regulating the pH value of a multi-component weak acid stream with an effective hypothetical weak acid concentration and a dissociation constant as shown in Choi and Rhinehart(1987).

2. Description of the process

Consider a control system shown in Fig. 1. An acetic acid(CH_3COOH) stream with a flow rate F_1 and a concentration C_1 flows into the tank of the volume V and is neutralized with a stream of sodium hydroxide($NaOH$) with a flow rate F_2 and a concentration C_2.

From material balances we have

$$d\eta/dt = F_2C_2/V - (F_1+F_2)\eta/V \qquad (1)$$
$$d\xi/dt = F_1C_1/V - (F_1+F_2)\xi/V \qquad (2)$$

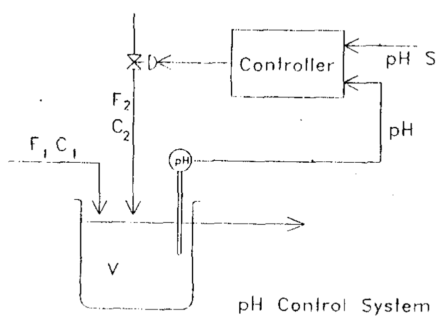

Fig. 1 A pH control system

where $\eta=[Na^+]$, $\zeta=[CH_3COOH]+[CH_3COO^-]$ and [ ] means concentration of a substance in the tank. And from electroneutrality and dissociation equilibrium of acetic acid and water, we have

$$[H^+]^3 + (K_a+\eta)[H^+]^2 + (K_a\eta-K_a\zeta-K_w)[H^+] - K_aK_w = 0 \quad (3)$$
$$pH=-\log_{10}[H^+]$$

where K_a is the dissociation constant of the weak acid and K_w is the ion product of water, that is, $K_a=[CH_3COO^-][H^+]/[CH_3COOH]$ and $K_w=[H^+][OH^-]$.

Here we design a nonlinear self-tuning regulator which estimates the unknown parameter K_a and the unmeasured influent weak acid concentration C_1 of the nonlinear rigorous dynamic model and calculates the strong base flow rate which compensates the variations of the effluent pH value with estimated unknowns. Since equations (1) to (3) are not adequate to apply the self-tuning regulator technique, we obtain a new state equation by differentiating equation (3) with respect to pH. That is,

$$dy/dt = \{F_1[z^3+K_az^2-(K_w+K_aC_1)z-K_aK_w] + F_2[z^3+(K_a+C_2)z^2-(K_w+K_aC_2)z -K_aK_w]\}/\{V\ln(10)[2z^3+(K_a+\eta)z^2 +K_aK_w]\} \quad (4)$$

where $z=[H^+]$ and $y=pH=-\log_{10}z$.

Then from equation (1) and (4) we get a discrete model,

$$\eta_{k+1} = \eta_k\exp[-(F_1+u_k)T/V] +\{1-\exp[-(F_1+u_k)T/V]\}u_kC_2 /(F_1+u_k) \quad (5)$$

$$(y_{k+1}-y_k)/T = \{F_1[z_k^3+K_az_k^2 -(K_w+K_aC_1)z_k-K_aK_w]+u_k[z_k^3 +(K_a+C_2)z_k^2-(K_w+K_aC_2)z_k-K_aK_w]\} /\{V\ln(10)[2z_k^3+(K_a+\eta_k)z_k^2+K_aK_w]\} +\varepsilon \quad (6)$$

where T is a sampling period, u_k is the F_2 at instance k and ε is the error due to discretization by the Euler integration rule.

3. Nonlinear self-tuning regulator

From equations (5) and (6), we obtain

$$[(2d_{k+1}-F_1-u_k)z_k^3+(d_{k+1}\hat{\eta}_k-u_kC_2)z_k^2 +(F_1+u_k)K_wz_k]+K_a[(d_{k+1}-F_1-u_k)z_k^2 -u_kC_2z_k+(d_{k+1}+F_1+u_k)K_w]+K_aC_1[F_1z_k] +\varepsilon[d_{k+1}z_k^2]+\delta\{V\ln(10)[2z_k^3 +(K_a+\hat{\eta}_k+\varepsilon)z_k^2+K_aK_w]\} = 0 \quad (7)$$

where

$$d_{k+1} = V\ln(10)(y_{k+1}-y_k)/T,$$
$$\hat{\eta}_{k+1} = \hat{\eta}_k\exp[-(F_1+u_k)T/V] +\{1-\exp[-(F_1+u_k)T/V]\} u_kC_2/(F_1+u_k), \qquad \hat{\eta}_0=0 \quad (8)$$

and δ is the error due to the difference between initial values of η and $\hat{\eta}$. Error δ goes to zero exponentially as time increases and error ε also becomes negligible with a small sampling period T.

We estimate the unknown parameters K_a and C_1 of equation (7) via the recursive least squares method with a variable forgetting factor. Let

$$r_{k+1} = [(2d_{k+1}-F_1-u_k)z_k^3+(d_{k+1}\hat{\eta}_k -u_kC_2)z_k^2+(F_1+u_k)K_wz_k]/z_k^2 \quad (9)$$
$$\hat{\underline{\theta}} = (\hat{K}_a,\hat{K}_a\hat{C}_1)^T \quad (10)$$
$$\underline{s}_{k+1} = (-[(d_{k+1}-F_1-u_k)z_k^2-F_2C_2z_k +(d_{k+1}+F_1+u_k)K_w]/z_k^2 ,-[F_1z_k]/z_k^2)^T \quad (11)$$

Then we have

$$\underline{K}_{k+1} = \underline{P}_k\underline{s}_{k+1}/(1+\underline{s}_{k+1}^T\underline{P}_k\underline{s}_{k+1})$$
$$\hat{\underline{\theta}}_{k+1} = \hat{\underline{\theta}}_k+\underline{K}_{k+1}(r_{k+1}-\underline{s}_{k+1}^T\hat{\underline{\theta}}_k)$$
$$\lambda_{k+1} = 1-(1-\underline{s}_{k+1}^T\underline{K}_{k+1})(r_{k+1}-\underline{s}_{k+1}^T\hat{\underline{\theta}}_{k+1}) /0.01$$
$$\text{if } \lambda_{k+1} < 0.1 \text{ then } \lambda_{k+1} = 0.1$$
$$\underline{P}_{k+1} = (\underline{P}_k-\underline{K}_{k+1}\underline{s}_{k+1}^T\underline{P}_k)/\lambda_{k+1}, \quad \underline{P}_0=10^5\underline{I}$$

With estimated K_a and C_1, we calculate the control input as

$$u_{nom} = \{V\ln(10)[2z_{k+1}^3(\hat{K}_a+\hat{\eta}_{k+1})z_{k+1}^2 +\hat{K}_aK_w](y_s-y_{k+1})/T-F_1[z_{k+1}^3 +\hat{K}_az_{k+1}^2-(K_w+\hat{K}_a\hat{C}_1)z_{k+1}-\hat{K}_aK_w]\} /[z_{k+1}^3+(\hat{K}_a+C_2)z_{k+1}^2 -(K_w+\hat{K}_aC_2)z_{k+1}-\hat{K}_aK_w]$$
$$u_{k+1} = \exp(-T/\tau)u_k +[1-\exp(-T/\tau)]u_{nom} \quad (12)$$

where τ is the time constant of the first order filter for smoothing control input fluctuations.

4. Simulation Results

The data used for simulation study are shown in Table 1. The static behaviors for K_a and C_1 changes are shown in Fig. 2. We can see that the steady-state gain changes drastically in magnitude as the operating condition varies.

To simulate the process, we integrated equations (1) and (2) analytically and obtained analytic solutions of the cubic equation (3). The analytic solutions of the cubic equation (3) were further refined with the Newton -Raphson iteration. Equation (4) is not adequate to simulate the process because it is stiff around the neutral point. For the closed-loop runs, a sequence of changes in the set point, y_s, the unknown parameter, K_a, and the unmeasured influent weak acid concentration, C_1, were made. That is, to investigate the effects of abrupt variations of the dissociation constant K_a and the concentration C_1 of the influent weak acid, K_a was set to 1.8×10^{-5} mol/l initially and was changed to 1.8×10^{-6} mol/l between 2400 and 3600 seconds. The concentraton C_1 of influent weak acid was 0.02 mol/l initially and was changed to 0.03 mol/l between 1000 and 1600 seconds. The set point of pH value was 7 initially and was changed to 6 between 2000 and 3000 seconds. The control input and the estimates of K_a and C_1 were bounded with upper and lower limits given in Table 1.

First, PID controllers with three different proportional gains were applied. But we failed to find a good control performance.

On the other hand, our self-tuning regulator gave good control performances. Simulated results are shown in Fig. 3. Fig.3 shows the case with random measurement noises between ±0.05 pH values. As a noise, a zero-mean uniform random signal was used. For first 30 samples the bang-bang control was used in order to accelerate convergence of the parameter estimates. The parameter estimates are shown in Fig.4 for low measurement noises. For higher measurement noises poor and biased estimates of parameters were obtained. It might be mainly because the identification scheme did not include the noise dynamics.

We also investigated the effects of mismatches of K_w and F_1 which were assumed to be a known constant and a measured variable, respectively. Fig.5 and 6 show the performances of the proposed controller with $K_w=10^{-12}$ mol^2/l^2 and $F_1=0.008$ l/sec, respectively, which are different from those used for the process simulations. We can see that the mismatches of K_w and F_1 between the controller and the process are not very sensitive.

Table 1. Data for the simulation study

Description	Value in Process Model	Value in Controller
V Volume of the tank	4.67 liters	4.67 liters
F_1 Flow rate of the influent weak acid stream	0.01 l/sec	0.01 l/sec
F_2 Flow rate of the base stream (control input)		initial: 0.002 l/sec limits: [0, 0.005 l/sec]
C_1 Concentration of the influent weak acid stream	0.02 mol/l 0.03 mol/l for 1000<t(sec)<1600	initial: 0.012 mol/l limits: [10^{-4}, 1mol/l]
C_2 Concentration of the strong base stream	0.1 mol/l	0.1 mol/l
K_w Ion product of	10^{-14} mol^2/l^2	10^{-14} mol^2/l^2
K_a Dissociation constant of the weak acid	1.8×10^{-5} mol/l 1.8×10^{-6} mol/l for 2400<t(sec)<3600	initial: 10^{-5} mol/l limits: [10^{-8}, 10^{-2} mol/l]
T Sampling period	2 sec	2 sec
τ Time constant of the first order filter		3.915 sec
y_s Set point of pH		7 6 for 2000<t(sec)<3000

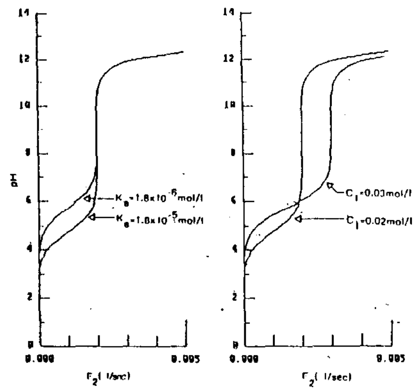

Fig. 2. Steady-state titration curves for the dissociation constant and concentration variations of the influent weak acid

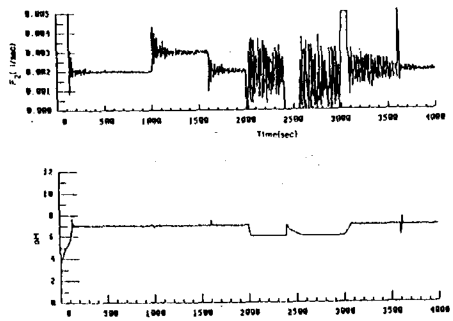

Fig. 3. Result of the proposed self-tuning regulator in the case with measurement noises of ±0.05 pH values

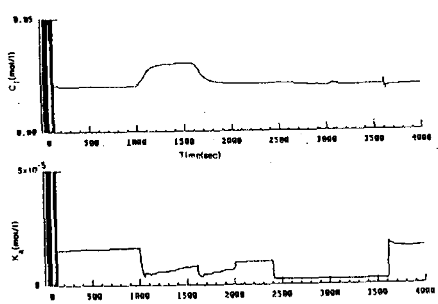

Fig. 4. Estimated parameters of the proposed nonlinear self-tuning regulator in the case with measurement noises of ±0.01 pH values

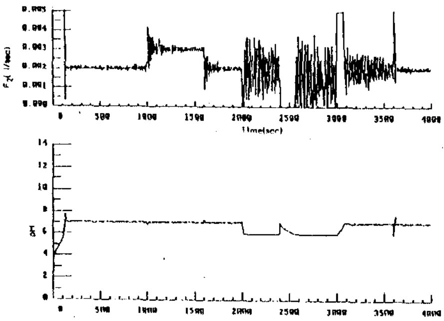

Fig. 5. Result of the proposed self-tuning regulator when $K_w=10^{-12}\ mol^2/l^2$ is used for controller design

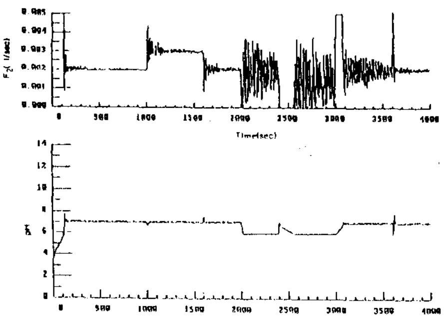

Fig. 6. Result of the proposed self-tuning regulator when $F_t=0.008$ l/sec is used for controller design

5. Conclusion

We proposed a nonlinear self-tuning regulator for controlling pH value of weak acid streams by a strong base. A standard recursive least squares identification method and one-step ahead control law were used. Since a rigorous model describing the real pH neutralization process of a weak acid and strong base system was used, unknown parameters were estimated with good estimates and could be bounded properly. Simulation results showed that the self-tuning regulator provided good control performances in spite of measurement noise, variations of influent weak acid concentration and dissociation constant of the weak acid.

For wide applications to real pH processes, further studies such as theoretical stability analysis, robustness and extension to neutralization process of multi-component influent weak acid streams would be required.

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