DESIGN OF AN ON-LINE TITRATOR FOR NONLINEAR pH CONTROL

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Abstract: A new on-line titrator for pH control has been developed. The on-line identification method generates an estimate of the inverse titration curve as a continuous smooth function eliminating the need for selection of the important break points of the titration curve. The time required to obtain the titration curve in the spanned pH range is approximately twice the settling time of the titrator and thus no significant identification lag is introduced. The results of the titrator are used directly to linearize the pH process output enabling the application of a simple and yet effective linearizing feedforward-feedback control strategy.

Keywords: pH control; nonlinear control; recursive estimation; feedforward control

1. INTRODUCTION

The time-varying characteristics of pH processes make them difficult to control with fixed-gain controllers and motivate the use of adaptive control. The standard adaptive control approach to the pH problem is shown schematically in Figure 1. Linear adaptive pH control can provide satisfactory results for well-buffered processes, as long as the static gain (titration curve) does not change rapidly. Nonlinear adaptive control provides a better alternative, since some knowledge of the origin of the underlying nonlinearity is incorporated into the control strategy (Gustafsson and Waller, 1992; Henson and Seborg, 1994). However, many of these earlier approaches assume that the chemical composition of the process feed stream (i.e. all the species present and the dissociation constants of the weak species) is known. In reality, this is often not the case and, as a result, the application of such approaches is limited. When

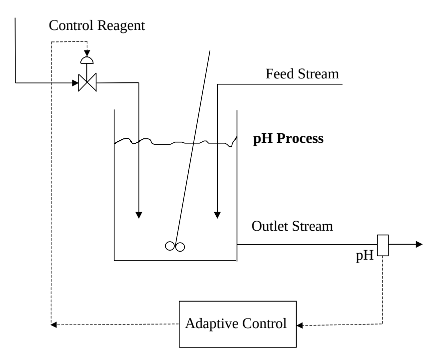

Fig. 1. Adaptive pH control approach.

the location of the buffer region of the titration curve does not change with time, the composition of the process feed stream can be approximated by

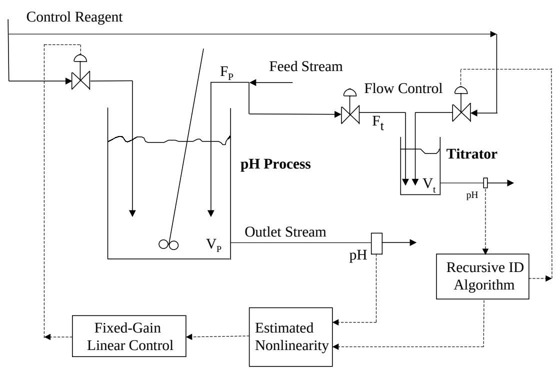

Fig. 2. On-line-titrator based pH control approach.

hypothetical species with dissociation constants that closely represent the nonlinear characteristics of the process. These dissociation constants could be measured off-line or estimated on-line to extend the applicability of these adaptive strategies. However, in the general case, when changes in the titration curve result from changes in the concentrations and composition (dissociation constants) of the feed stream, the increased number of parameters that need to be estimated may lead to deterioration of the controller performance.

In more recent years, attempts have been made to reduce the number of parameters required to represent the nonlinear behaviour of the pH process. The adaptive control strategy used by Sung *et al.* (1998) estimates on-line the total ion concentration and the dissociation constant of a fictitious weak acid. This idea, which has its roots in earlier work by Lee *et al.* (1994), works well as long as no new chemical species enter the feed stream that would drastically change the shape of the titration curve. In Wright *et al.* (1998), a system representation consisting of a combination of basis functions is proposed that relies on on-line identification of a small number of adjustable parameters. With this latter approach, the user must make a suitable choice of basis functions to ensure a reasonable fit to the titration curve as it changes over time.

In parallel with this work in adaptive control, there is continued interest in the development of on-line titration devices for identifying the process titration curve. This alternative approach to the pH control problem is schematically shown in Figure 2. Here, the device consists of a small neutralization tank that accepts a small side-stream of the process feed and performs separate identification of the titration curve using a small portion of the control reagent. The main advantage of these titrators is that they can be used to characterize titration curves with complex shapes over a wide pH region without relying on data generated by the pH process itself. This notion of physically separating the identification and control functions by introducing a titrator can be traced back to Mellichamp *et al.* (1966), Gupta and Coughanowr (1978) and, more recently, Sung *et al.* (1995).

Most commercial titrators mimic the traditional off-line approach of obtaining the titration curve. As a result, a substantial amount of time is required to obtain the titration curve, since for each steady-state point, a time equal to the settling time of the titrator vessel is needed. This introduces a lag in the identification, unless the dynamics of the titrator are very fast compared to the actual process and/or only a few points on the titration curve are identified. Limiting the number of identified points may deteriorate the quality of the nonlinear fit, especially for steep titration curves. Furthermore, selecting the location of these points, i.e. the break points of the titration curve, may be very crucial for the quality of the identification. Also, since the information obtained consists of only a set of discrete points, some kind of interpolation must still take place in order to represent the entire titration curve.

A new on-line titrator is proposed here for the control of pH processes that builds on earlier work described by the authors in Kalafatis *et al.* (2003*a*) and Kalafatis *et al.* (2003*b*). Both the identification in the titrator and the control in the main pH process are based on the idea of using a Wiener model structure to represent the pH process. Section 2 of this paper describes the design of the on-line titrator and Section 3 presents simulated pH control results that test the performance of the on-line titrator and associated control strategies under both increasing and decreasing buffering conditions.

2. DESIGN OF THE ON-LINE TITRATOR

As shown in Figure 2, the titrator consists of a small, well-mixed neutralization tank that has as its feed a small portion of the process feed stream and an adjustable flow rate of control reagent, and a pH sensor in its outlet stream. As a general rule, the portion of the feed that enters the titrator should be small enough to avoid the need for a large recycle stream of the off-specification titrator effluent but large enough to provide fast titrator dynamics.

A simple method has been developed in order to estimate in an on-line fashion the time-varying changes in the titration curve associated with the feed stream (Kalafatis *et al.*, 2003*b*). The method is based on the use of continuous sinusoidal adjustments to the flow rate of control reagent to the titrator and a recursive least squares algorithm. The method also incorporates automatic adjustment of the mean level of the control reagent flow rate in order to ensure that the titration curve is identified in the pH operating region of interest. The estimated inverse of the titration curve (or what is referred to as the estimated nonlinearity in Figure 2) is updated on a user-specified estimation cycle for use by the control strategy. Linearization by output transformation of the pH signal from the process outlet stream is then used to make the relationship between the control reagent process flow rate and the process pH reading appear linear, enabling the use of a linear, fixed-gain feedback controller. In addition to linearizing feedback control, a simple linearizing feedforward control scheme, based on the same estimate of the inverse titration curve in the vicinity of the target pH and a measurement of the process feed flow rate, is included to further enhance the pH control performance (Kalafatis *et al.*, 2003*a*).

The flow rate of the titrator feed (F_t) is controlled by a valve or a variable-speed pump and is maintained at a constant value. As a result, the titrator does not respond to variations in the process feed flow rate (F_p), which do not on their own alter the shape of the titration curve.

If concentration and/or composition changes occur in the process feed stream, the output pH of the titrator will move away from the desired operating point and the estimation method will provide the inverse of the titration curve over the spanned pH region. Automatic adjustments of the mean level of the titrator input signal eventually move this region around the pH setpoint of the process (usually after one or two estimation cycles).

In order to obtain fast titrator dynamics, and thus achieve fast identification cycles, the volume of the titrator vessel (V_t) should be small. The smaller the volume of the titrator, the faster the dynamic response, and hence, a faster data sampling rate must be used in order to acquire enough input-output data.

3. SIMULATED CLOSED-LOOP RESULTS USING THE ON-LINE TITRATOR

The model used for simulating the pH process is outlined in Kalafatis *et al.* (2003*a*) and consists of a continuous stirred tank reactor (CSTR) where a strong base ($NaOH$) reacts with two separate feed streams, a strong acid (HCl) and a buffering solution ($NaHCO_3$), while an overflow exit line maintains a constant liquid volume in the reactor. An identical model is used for the titrator, except with different parameter values. The pH process being controlled in Figure 2 has a mixing tank volume of $V_p = 158\ l$ and a nominal feed flow rate (acid plus buffer) of $F_p = 17.22\ l$/min. The titrator volume is $V_t = 2.1\ l$ and the flow rate of the titrator feed stream is $F_t = 1.722\ l$/min. The nominal conditions for both the process and the titrator are summarized in Table 1 along with all other key model parameters. As indicated by the mixing tank time constants, the dynamics of the titrator are 7.5 times faster than those of the pH process considered. For all the simulations that follow, the estimation cycle in the titrator for updating the inverse nonlinearity is 10 min (approximately twice its settling time). The sampling interval used in the identification algorithm is 1 sec and the value of the fixed forgetting factor used in the recursive least squares algorithm is $\lambda = 0.97$. The sampling interval for the pH control algorithm is 15 sec.

Table 1. Nominal operating conditions of the simulated pH process and titrator.

Variable	Process	Titrator
Base stream flow rate (l/min)	11.64	1.164
Acid stream flow rate (l/min)	13.62	1.362
Buffer stream flow rate (l/min)	3.60	0.360
Base concentration (M)	0.00286	0.00286
Acid concentration (M)	0.00250	0.00250
Buffer concentration (M)	0.004	0.004
pH inside the tank	7.00	7.00
Volume of the tank (l)	158	2.1
Mixing tank time constant (min)	5.5	0.75
pH measurement time delay (sec)	30	10
pH probe time constant (sec)	25	10
Flow loop time constants (sec)	15	6
Sampling interval (sec)	15	1

3.1 *Decreased buffering conditions*

With both the process and the titrator initially at steady-state under the nominal conditions outlined in Table 1, at $t = 0$ min, a -83% change in the buffer stream flow rate is introduced. Although the change in the feed flow rate is small (-17.4%) the resulting new values of the reaction invariants ($c_1,\ c_2$) are significantly different as shown in Table 2. While the process remains under the decreased buffering conditions, additional changes of -25% and $+50\%$ are introduced into the feed flow rate at $t = 40$ min and at $t = 60$ min, respectively, while maintaining the ratio of acid to buffer stream flow rate constant (see Table 2). As expected, these latter flow rate changes do not affect the reaction invariant values and do not alter the titration curve. However, they still represent severe disturbances that force the output pH away from the setpoint, and thus form a good benchmark for evaluating the controller performance.

The titrator feed stream flow rate remains constant at its nominal value ($F_t = 1.722\ l$/min)

Table 2. Simulated process conditions under decreased buffering.

t (min)	acid flow (l/min)	buffer flow (l/min)	c_1 (mol/ml)	c_2 (mol/ml)
0-	13.620	3.60	-1.141	0.836
0	13.620	0.60	-2.226	0.169
40	10.215	0.45	-2.226	0.169
60	20.430	0.90	-2.226	0.169

and the composition/concentration of the titrator feed stream is always the same as the process feed stream. The base flow rate (control reagent) into the titrator is a single sinusoid with a frequency of $\bar{\omega} = 1.2566$ rad/min (corresponding to a period of 5 min, i.e. slightly greater than the titrator settling time) and an amplitude of 0.36 l/min around its mean value (which is adjusted at the end of each estimation cycle). As shown in Figure 3, at $t = 0$ min the titrator reacts to the severe

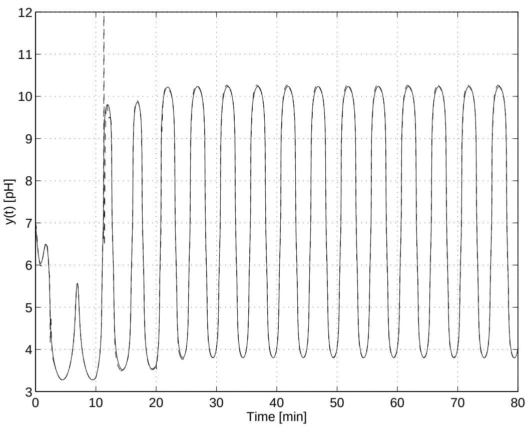

Fig. 3. Comparison of the simulated (solid line) and predicted (dashed line) titrator outputs. At $t = 0$, the process buffer stream flow rate is decreased by 83%.

buffer decrease and its spanned pH range is shifted into the region of pH $3.2 - 5.6$, below the desired operating point of pH$= 7$. At the end of the first estimation cycle ($t = 10$ min), the inverse titration curve is identified across this pH region, and the mean level of the input signal is adjusted. As a result of this adjustment, the spanned pH range is shifted around the desired operating point during the second estimation cycle. The inverse titration curve is again obtained at the end of this cycle ($t = 20$ min) and is shown in Figure 4. Even better identification results are obtained in the third cycle where the mean input signal level converges to its final value. Since the titrator operates on a constant feed flow rate, it does not react to the process flow rate changes introduced at $t = 40$ min and $t = 60$ min.

Using the pH process parameters listed in Table 1 and a desired closed-loop time constant $\tau_c = 1.4$ min, the parameters of the linearizing feedback (PI) controller are calculated to be $K_C = 83.4$ l/min and $\tau_I = 5.5$ min. Figure 5 demon-

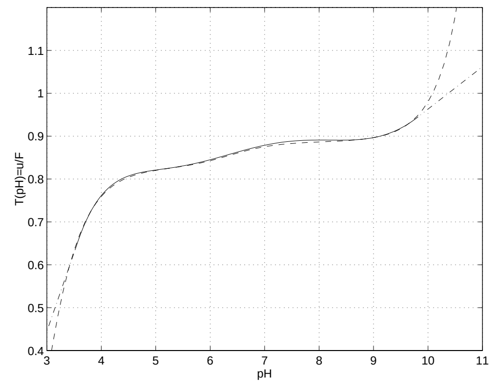

Fig. 4. Comparison of the identified (solid line) and theoretical (dashed line) inverse titration curves for an 83% decrease in the process buffer stream flow rate. The identified inverse nonlinearity is extrapolated with straight lines (dash-dotted) outside the excited input-output range.

strates the controller performance in response to

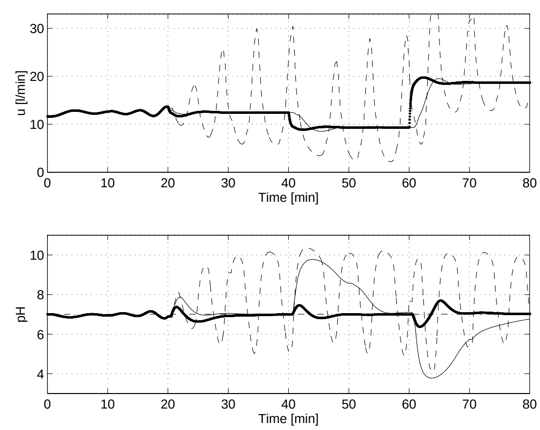

Fig. 5. Controller performance (top: manipulated control reagent flow rate; bottom: pH in process outlet stream) in the case of decreased buffering and in response to the disturbances listed in Table 2. (Dashed line: linearizing feedback control based on the initial titration curve; solid line: linearizing feedback control based on the identified inverse titration curve starting at $t = 20$ min; bold line: linearizing feedforward-feedback control based on the identified inverse titration curve starting at $t = 20$ min; dash-dotted line in the lower graph: pH setpoint.)

the decrease in buffering and the flow rate disturbances listed in Table 2, if the titrator identification results are not utilized and linearization by output transformation continues to be based on the initial titration curve. The increased process gain due to low buffering conditions makes the closed-loop system unstable, and the pH output experiences large oscillations at $t > 25$ min. The addition of linearizing feedforward control would not help the situation and would even worsen the closed-loop response, since the control action would be based on an incorrect titration curve.

By utilizing the new inverse titration curve identified at $t = 20$ min (shown in Figure 4) and basing the linearizing feedback controller on this new curve starting at $t = 20$ min and updating it every 10 min, the closed-loop system is stabilized. However, large deviations from the setpoint occur after the introduction of the disturbances in the feed stream flow rate at $t = 40$ min and $t = 60$ min. Due to the steep titration curve, resulting from the low buffering conditions, the feedback linearizing controller is not able to respond quickly enough to these disturbances. Even if the linearizing feedback controller is based on the exact theoretical titration curve, in which case the ideal feedback control performance would be obtained, the closed-loop results are very similar.

The addition of linearizing feedforward control starting at $t = 20$ min, based on the newly identified inverse titration curve, dramatically improves the control performance, as shown in Figure 5. The advantage of this combined feedforward-feedback controller scheme is that the feedforward control action does not rely on the output pH measurement. As a result, its response is very fast, while the feedback control action compensates for inaccuracies in estimating the inverse titration curve and in measuring the feed flow rate.

3.2 *Increased buffering conditions*

The previous set of simulations showed the effectiveness of the on-line titrator in maintaining the stability and performance of the control system under decreased buffering conditions. In the case where the amount of buffering increases (if the concentration of the weak species increases or new weak species enter the process feed) the stability of the system is not affected. However, the closed-loop response may be very sluggish and the controller performance unacceptable if the linearization by output transformation is based on the low buffering conditions. This occurs in practice if the tuning of the pH controller is based on the worst-case scenario, i.e. the lowest expected buffering conditions.

In the following simulations, the process is assumed to be initially under the decreased buffering conditions encountered in the previous simulations. At $t = 0$ min, the buffer stream flow rate is increased to its original nominal value. Then, at $t = 20$ min and at $t = 50$ min, a decrease of 50% and an increase of 100% in the feed flow rate are introduced, respectively, while maintaining the ratio of the acid to the buffer stream flow rate constant (see Table 3). The input signal to

Table 3. Simulated process conditions under increased buffering.

t (min)	acid flow (l/min)	buffer flow (l/min)	c_1 (mol/ml)	c_2 (mol/ml)
0-	13.62	0.60	-2.226	0.169
0	13.62	3.60	-1.141	0.836
20	6.81	1.80	-1.141	0.836
50	27.24	7.20	-1.141	0.836

the titrator is, as before, a single sinusoid with an amplitude of 0.36 l/min around its mean value (which is adjusted at the end of each estimation cycle). As shown in Figure 6, at $t = 0$ min the titrator responds to the buffer increase and its spanned pH range is now shifted in the region of pH 7.4−10.3, which is above the desired operating point of pH= 7. At the end of the first estimation cycle ($t = 10$ min), the inverse titration curve is identified across this pH region, and the mean level of the input signal is adjusted. At the end of the second estimation cycle ($t = 20$ min), the titration curve, shown in Figure 7, is obtained across the new spanned range that includes the

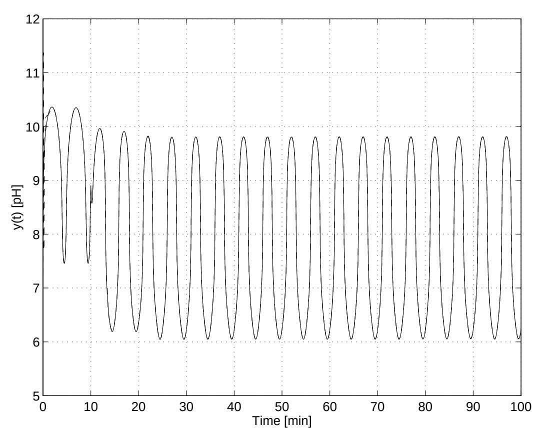

Fig. 6. Comparison of the simulated (solid line) and predicted (dashed line) titrator outputs. At $t = 0$, the process buffer stream flow rate is increased to its original nominal value.

desired operating point. The mean input level converges to its final value in the third identification cycle.

As shown in Figure 8, without utilizing the online titrator identification results, the closed-loop response to the flow rate disturbances is very sluggish. Linearization by output transformation based on the initial titration curve, which corresponds to low buffering conditions, produces a small loop gain when the amount of buffering increases. Thus control system performance is severely affected. Specifically in rejecting the second flow rate disturbance at $t = 50$ min, it takes more than one hour for the process output to return to its setpoint ($pH_{sp} = 7$). By basing the linearization on the identified inverse nonlinearity shown in Figure 7, starting at $t = 20$ min, the disturbance rejection is significantly improved as seen Figure 8. The addition of linearizing feedforward control to the feedback loop, substantially reduces the output deviations from setpoint even further (see Figure 8).

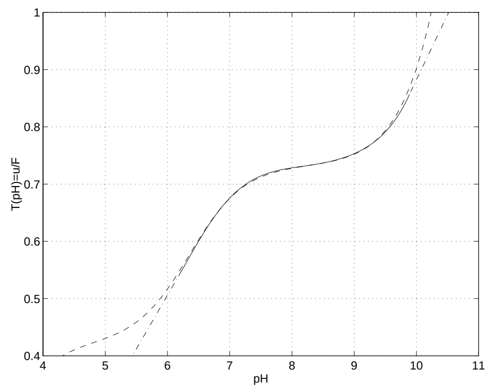

Fig. 7. Comparison of the identified (solid line) and theoretical (dashed line) inverse titration curves for an increase in the process buffer stream flow rate to its original nominal value. The identified inverse nonlinearity is extrapolated with straight lines (dash-dotted) outside the excited input-output range.

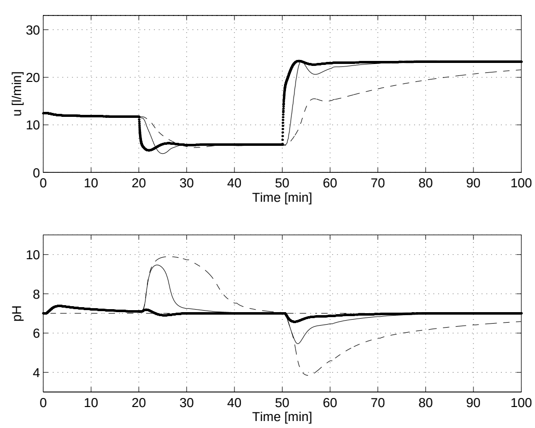

Fig. 8. Controller performance (top: manipulated control reagent flow rate; bottom: pH in process outlet stream) in the case of increased buffering and in response to the disturbances listed in Table 3. (Dashed line: linearizing feedback control based on the initial titration curve; solid line: linearizing feedback control based on the identified inverse titration curve starting at $t = 20$ min; bold line: linearizing feedforward-feedback control based on the identified inverse titration curve starting at $t = 20$ min; dash-dotted line in the lower graph: pH setpoint.)

4. CONCLUSIONS

An on-line titration device for pH control has been designed and tested using simulations. The titrator is placed in parallel with the pH process and accepts a portion of the process feed stream. Since the identification of the inverse titration curve takes place in the titrator, the actual pH process is not disrupted. The on-line identified titration curve is used directly to linearize the pH process output and thus allows for the use of a simple fixed-gain, linear controller (e.g. a PI-type). The effectiveness of a titrator-based linearizing feedforward-feedback control scheme has been evaluated under a variety of conditions and has demonstrated excellent performance.

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