VIBRATIONAL CONTROL OF THE NEUTRALIZATION PROCESS

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ABSTRACT
Controlling of the pH system theoretically was achieved successfully using vibrational control method with very small offset. Modeling of pH system was derived using reaction invariants concept where the specific invariants combined and adapted in the mole balance equations with contribution the charge balance to give the final pH process model.

السيطرة الاهتزازية على عملية المعادلـة الحامضية

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الخلاصة
تمت السيطرة بنجاح على نظام حامض قوي وقاعدة قوية كمثال على عملية المعادلة الحامضية بشكل نظري وذلك بأستخدام طريقة السيطرة الاهتزازية والتي اعطت حيد قليل جدا عن القيمة المرغوبة. تم تكوين الانموذج الرياضي لعملية المعادلة الحامضية عن طريق اعتماد مبدأ ثوابت التفاعل ، ركبت هذه الثوابت المحددة في معادلات التوازن المولية لاعطاء النموذج الرياضي النهائي لعملية المعادلة الحامضية.

KEYWORDS: pH process, Neutralization Process, Vibrational Control, Nonlinear Adaptive Control, Reaction invariants.

NOMENCLATURE

$f(\omega t)$	Periodic zero mean function
α_k	Factor selected according to pH system
τ_I	Intrgral time
ω	frequency of the function
A	amplitude
a_{H^+}	activity of H^+ ions
C	Factor which convert nonlinear system state to linear state
CA	Acid invariant
CB	Base invariant
F_o	average flow rate
FA_c	Titration stream flowrate
Kc	Proportional gain
I	The identity matrix

p Vector whose components are the concentrations of chemical species involved in the system
s Vector of chemical symbols
t time.
v Volume of the tank
W^T Matrix of stoichiometric coefficients

1. INTRODUCTION

pH process is highly nonlinear process which put the pH control as a challenging problem especially in the strong acid strong base system (1) as shown in **Fig**.1. This complexity is due to the high sensitivity of the pH process at the neutral point or around it to a small change in the titration stream flow rate, which give very complex situation to control the pH of the effluent stream if the desired point pH equals to 7 or around it. This come essentially from the nature of the acidity function that can be represented by logarithmic term related to the hydrogen ion concentration as follow.

$$pH = -\log_{10}(a_{H^+}) \tag{1}$$

The basic idea to control the pH variations in some liquid flow is usually making the pH as close to 7 as possible.

pH control is very important in some industrial applications such as municipal waters treatment, pharmaceuticals, biotechnology. Some applications need to adjust pH value to approximately 7.5 to 8.0 which is found to prevent corrosion of water pipes and fixtures, particularly to prevent dissolution of lead into a potable water supply, and prevention of acid corrosion in boiler feed water typically requires pH adjustment in the range of 8.3 to 9.0.

The pH-control started back in 1975 at a process control laboratory with a 24-h record of the pH values of a wastewater tank of a chlorine plant. The records revealed an unstable control for one third of the day and a lazy control for the rest of day (25). However, the pH process dynamic model can be obtained from material balance and chemical equilibria (20), but controlling this model as a pH control is a difficult problem due to its inherent nonlinearity and time-varying characteristics especially if the desired point equal to 7.

Some researchers try to avoid this phenomena, first by using a different strategy to control the pH process (26) and second by using Mechanistic models. The Mechanistic models which is derived from specific observed behavior of the system are generally difficult to develop (19), However using empirical models was achieved by using different methods (22, 15, 7).

The control strategies side appears in the control of the pH process as advanced control techniques such as linear adaptive control (26), nonlinear adaptive control based on strong acid equivalent (31), ANN (8), model predictive control (32, 23), and adaptive backstepping control (28).
A control based on concentration difference ($[OH^-]$-$[H^+]$) has attracted several workers like Hewkin (14); Wright and Kravaris (30), Jayadeva et al. (16), and Kulkarni et al. (18). They calculated the concentration difference from the pH measurements only, but this is only possible for solutions containing strong acid strong base mixture.

Many control methods were applied for controlling pH value of the effluent stream depending on the modern ideas such as ANN method, PID controller using linearization through neural networks, Fuzzy logic principles (9), adaptive systems, system identification and control, Wiener model identification and Event-based predictive control of pH in tubular photobioreactors (1) ..etc.

These methods failed to control the pH value completely because of the high non-linear state and characteristics of the neutralization process.

The use of oscillatory actuation in a control setting was systematically studied by Bellman, Bentsman and Meerkov [2] in the framework of vibrational control and vibrational stabilization and they called then vibration control, that appear in form open loop control method, Where yet the use of oscillatory control is not used to control neutralization process.

It generally state that for modification of dynamic properties of linear and nonlinear systems by introducing fast, zero-average oscillations in the parameters of the system. In another word the process is forced to cycle by periodic variation of one or more of process variables.

However theoretical applications of vibrational control to chemical reactor engineering have been discussed early by Bellman [3]. Cinar et al [5, 6] applied his project with vibrational control as experimental application. Further investigation including experimental work appears in work of Rigopoulos et al [24], and Shu et al[27]. Brad Lehman [4] stated that "to apply vibrational control to a combustion system it may be possible to oscillate open and shut quickly) an intake valve".

All the researchers wrote in the parameter variation didn't discuss the pH problem in their research. Therefore there is no one thought to neglect the high sensitivity which arise from the titration curve by using oscillatory input in the titration stream to manipulate the process stream disturbances. Therefore, this paper is dedicated to study the vibrational method to control the pH value of strong acid strong base system.

2. THEORETICAL MODEL AND CONTROL

In this study, the task is to control the pH level of an aqueous solution of sodium hydroxide (*NaOH*) as process stream which is titrated with hydrochloric acid (*HCl*) in a continuous stirred tank. An overview of the process is shown in **Fig**.2, where the volume is considered constant, under constant temperature at 25^{o}C and no valve or pH probe dynamics with unity activity coefficients condition.

Mixing these two materials perfectly will lead to the following disassociation reaction:

$$NaOH + HCl + H_2O \rightarrow H_2O + Cl^- + Na^+ + H^+ + OH^- \qquad (2)$$

2.1. System Modeling

The acid-base reactions are ionic and can be considered to take place instantaneously, with the result that the rate of reaction can be ignored. Thus, the ionic concentrations of [Cl^-] and [Na^+] in the outflow from the tank would be related to the total flows FA, FB and to the feed concentrations of strong acid [HCl] and strong base [NaOH] entering the tank that appear in terms of CA and CB by using reaction invariants concept.

Eq. 2 can be described with the following equations:

$$H_2O \Leftrightarrow H^+ + OH^- \qquad (3)$$

$$NaOH \rightarrow Na^+ + OH^-$$

(5)

$$HCl \rightarrow H^+ + Cl^-$$

Mass balances can appear without employing reaction rates in the balance equations by using the concept of reaction invariant. The system can be adequately described by the following form:

$$W^T s = 0 \tag{6}$$

Where W^T is the matrix of stoichiometric coefficients and s is the vector of chemical variables that are given below:

$$W^T = \begin{bmatrix} 1 & 1 & 0 & 0 & -1 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & -1 \end{bmatrix} \tag{7}$$

$$s = \left[H^+ \quad Cl^- \quad OH^- \quad Na^+ \quad HCl \quad H_2O \quad NaOH\right]^T \tag{8}$$

The concentrations of chemical species involved in the system. It is given by

$$p = \left[[H^+] \quad [Cl^-] \quad [OH^-] \quad [Na^+] \quad [HCl] \quad [H_2O] \quad [NaOH]\right]^T \tag{9}$$

Therefore, the vector of reaction invariants represent as follow:

$$q = D \cdot p \tag{10}$$

Where, matrix D can be calculated by Eq. 10 as follows:

$$D = [(-W_2 W_1^{-1}) \quad I] \tag{11}$$

Where I is the identity matrix and W_1 and W_2 correspond to the partitioning of W:

$$W = \begin{bmatrix} W_1 \\ W_2 \end{bmatrix} \tag{12}$$

$$W_1 = \begin{bmatrix} 1 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{bmatrix} \cdot \quad W_2 = \begin{bmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{13}$$

Consequently, for this system, the vector of reaction invariants q is given by

$$q = \begin{bmatrix} [H^+]-[Cl^-]-[OH^-]+[Na^+] \\ [Cl^-]+[HCl] \\ [H^+]-[Cl^-]+[H2O] \\ [Cl^-]-[H^+]+[OH^-]+[NaOH] \end{bmatrix} \tag{14}$$

From vector q, the first component is suitable for the development of a dynamic model for the purpose of controlling the system and for carrying out the stability analysis. Since the combination of invariants is also an invariant, it can be shown that [Cl^-] and [Na^+] are also reaction invariants that can be designed as CA and CB with contribute [HCl] and [NaOH], respectively. Since, we know that q (1) for the pure neutral water equals to zero, it should remain equals to zero after the addition of strong acid and strong base. Hence, the titration curve can be written as follows:

$$[Na^+]-[Cl^-]=10^{pH-14}-10^{-pH} \tag{15}$$

Derivation of the following balance equations, depending on the reaction invariants of the system, is also straightforward;

$$V\frac{dCA}{dt}=FACA_o-(FA+FB)CA \tag{16}$$

$$V\frac{dCB}{dt}=FBCB_o-(FA+FB)CB \tag{17}$$

Combining Eq. 16 and Eq. 17 results in

$$V\frac{d(CA-CB)}{dt}=FACA_o-FA(CA-CB)-FB(CA-CB+CB_o) \tag{18}$$

Eq. 15 to Eq. 18 describe the structure of the model to be used for controlling of the hydrochloric acid-sodium hydroxide system.

2.2. pH Control

The purpose of pH-control is to keep the pH-value at a constant value, and against complex control problem as pH control the controller setting must be changed. This permission is to use a modification on PI controller, where the controlling near the neutral point has a specific condition and a different condition away from it, so it is an ideal environment to apply adaptive control method.

2.2.1. Nonlinear adaptive control

The modified PI control is form of nonlinear adaptive control which is designed to avoid the oscillatory problem according to the factor C which convert nonlinear system state to linear state. Eq. 16 and Eq. 17 represent system model are structurally similar, therefore according to Wrights and Kravaris non-linear equivalents (31), it can be reduce the above *HCl-NaOH* system model to:

$$V\frac{dC}{dt}=-FBC+(1-C)FA \tag{19}$$

Eq. 19 represents the system model with:

$$\begin{aligned} CA &= CA_oC \\ CB &= CB_o(1-C) \end{aligned} \tag{20}$$

The nonlinear control gives a manipulating variable according to the block diagram shown in **Fig**.3, which satisfies the following form [(31)]:

$$FAc = \frac{Kc}{1-C} . [\ e + \frac{1}{\tau 1} . \int_0^t e.dt\ ] \quad (21)$$

With the following parameters:

$$Kc = 1.414 .\omega \quad v - FB; \qquad \tau_I = \frac{Kc}{(\omega^2 V)}$$

2.2.2. Vibrational Control

Vibrational control technique doesn't require measurements of states or disturbances. It uses a specific tool to open loop modification of the system behavior. Theoretically, an effect to covert the parameter of the system to oscillation manner is needed. The acid flow rate is the input to the process and it affects whole the process. The right decision of the design is the input stream of the acid. Introducing vibrations into the input of the process will lead to identical oscillation of the input flow rate and the output flow rate.

Now, assuming that the feed rate is changing according to:

$$F(t) = F_o(1 + Af(\omega t)) \quad (22)$$

Where $f(\omega t)$ is in form :

$$\sum_{k=1}^{n} \alpha_k .Cos(k\omega.t) \quad (23)$$

3. RESULTS AND DISCUSSION

Through the non-linear control method, the factor C converts the system nearly into linear sate.

The Nonlinear strategy implements a successful tool in controlling pH at the critical region as shown in the **Fig**.4, and **Fig**.5, where only it oscillates in the beginning and then straight forward.

Vibration was introduced into input flow rate. Therefore, the output flow rate was oscillating identically with the input flow rate; this makes the tank volume constant at all time. Thus in case of a recycle stream no vibration is introduced to avoid the increasing in the volume of the solution in the tank that affect negatively the process, thus the constant volume condition will not occur and the model derived must be to agree with the new condition.

Through the implementation of the oscillatory control approach which is shown in the **Fig**. 6, and **Fig**. 7, where different values of the frequency was imposed where an increase in the frequency moves the pH -time curve toward the desired point for all forcing function.

4. CONCLUSIONS

The real examination region is neutral point of the system where the transition state between pH 2 and 11.78 may occur by drop of acid or base stream. The vibrational control method can be considered a preferable method for controlling pH system with small offset as a compare with another methods.

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FIGURES AND TABLES

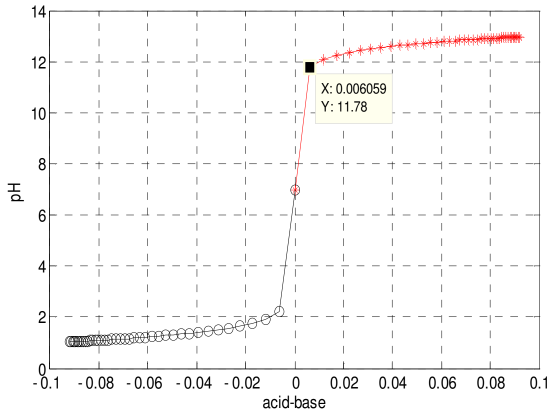

Fig.1 Titration Curve of strong acid/strong base system.

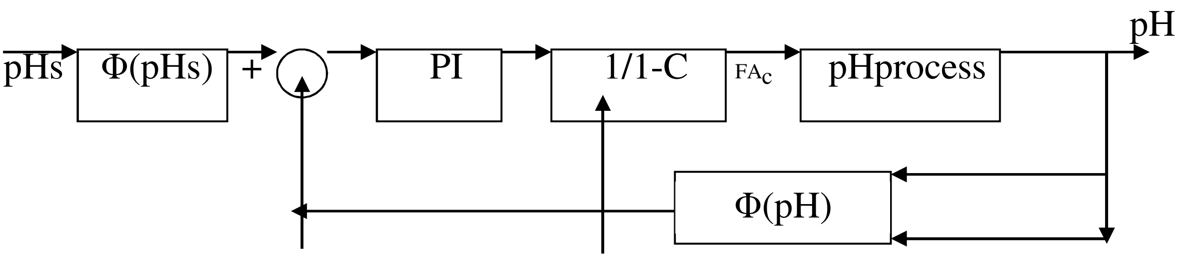

Fig. 2 Block diagram of linearizing control system.

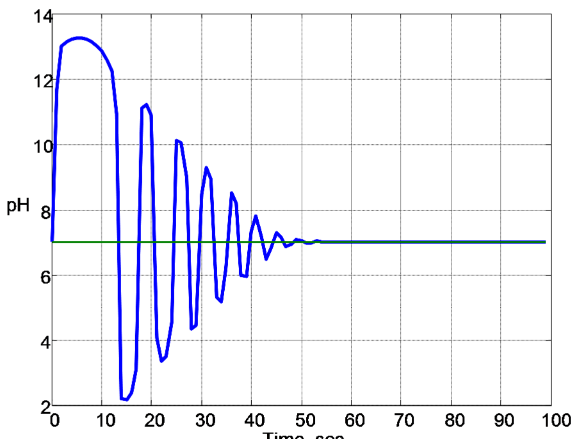

Fig. 4 pH response of hydrochloric acid- sodium hydroxide system set to pH 7 and step from 1 to 1.1 lit/sec. of Base flowrate using nonlinear adaptive PI control.

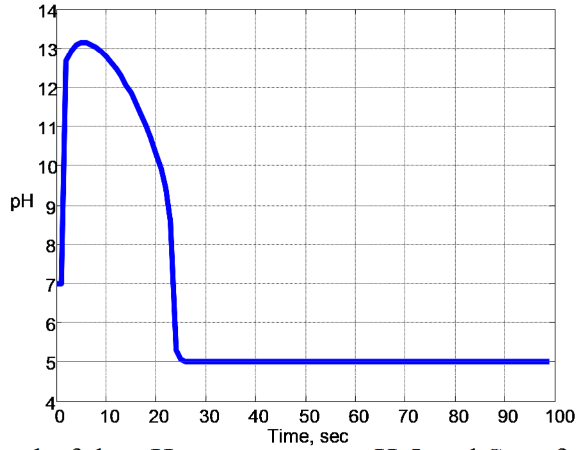

Fig. 5 Nonlinear Adaptive PI control of the pH system set to pH 5 and Step from 1 to 1.1 lit/sec. of Base flowrate.

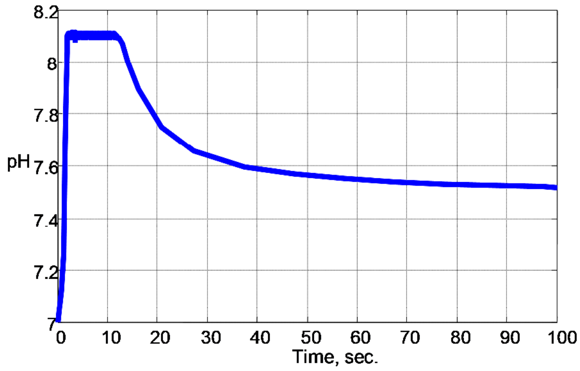

Fig. 6 Oscillatory control of the pH system using ω =2 according to a step in process stream equal to 0.1 lit/sec.

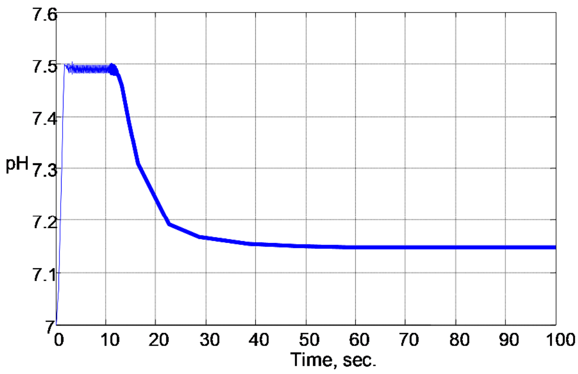

Fig. 7 pH system under the oscillatory control approach using ω =3 and a disturbance in the process stream equal to 0.1 lit/sec.