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Mathematical model for neutralization system

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ABSTRACT

A modified model for the neutralization process of Stirred Tank Reactors (CSTR) reactor is presented in this study. The model accounts for the effect of strong acid [HCL] flowrate and strong base [NaOH] flowrate with the ionic concentrations of [Cl-] and [Na+] on the Ph of the system. In this work, the effect of important reactor parameters such as ionic concentrations and acid and base flowrates on the dynamic behavior of the CSTR is investigated.

Keywords: *Stirred Tank Reactors, Neutralization, Mathematical model, Dynamic studies.*

INTRODUCTION

A rigorous and generally applicable method of deriving dynamic equations for pH neutralization in Continuous Stirred Tank Reactors (CSTRs) was presented by McAvoy in the year 1972 (McAvoy, Hsu, & Lowenthals 1972). The research work done by McAvoy was essential to the development of the fundamental modelling approach of the pH neutralization process in CSTRs. As cited and described in other literature, the use of the CSTR in developing the pH neutralization model was started over 50 years ago by Kramer (1956) and by Geerlings (1957). However those early studies concentrated largely on the dynamic behaviour of the pH electrode system. Subsequently, two crucial points in developing a pH neutralization process model which describes the nonlinearity of the neutralization process have emerged from published research. The two points are as follows:-

i. Material balances in terms of hydrogen ion or hydroxyl ion concentrations would be extremely difficult to write down. This is due to the fact that the dissociation of water and resultant slight change in water concentration would have to be accounted.
ii. Instead, material balances are performed on all other atomic species and all additional equilibrium relationships are used. The electroneutrality principle is used to simplify the equations.
Jutila, P. & Orava, J. P. 1981, control and estimation Algorithms for Physico-Chemical model of pH-pocesses in Stirred Tank Reactors (CSTR).In 1983

Gustafsson and Waller (Gustafsson 1982;Gustafsson & Waller 1983a) reinforced McAvoy's modelling principles for pH neutralization processes and emphasised the fact that mass balances on the invariant species are inherently independent of reaction rates. As described in this paper, the "invariant species" is actually the species that remain chemically unchanged by the governing of reactions in the neutralization process whereas the "variant species" are the species that change in the neutralization process, such as the hydrogen ions.Another interesting and widely used account of work involving the modelling of a pH neutralization process is by Wright and Kravaris 1991. Their work provided a new approach to the design of nonlinear controllers for pH processes by defining an alternative equivalent control objective. That new approach results in a control problem that is linear. A minimal order model was produced by assuming that the flowrate of the titrant required to operate the reactor was negligible in comparison with the flow rate of the process streams.Abdul Aziz Ishak et al. 2001 study of the dynamics and control of a semibatch wastewater neutralization process in modeling and simulation is presented.Zainal Ahmad and Fairuoze Roslin 2007 provide modeling of real pH neutralization process using multiple neural networks (MNN) combination technique.

Rosdiazli Ibrahim 2008 provide an adequate dynamic nonlinear pH neutralization model, based on physical and chemical principles that can represent the real pH neutralization plant.

Mathematical models of chemical systems were developed for many reasons. Thus, they may be constructed to assist in the interpretation of experimental data, to predict the consequence of changes of system input or operating conditions, to deduce optimal system or operating conditions and for control purposes. Usually there is an interest for dynamic model made to design and/or test the proposed control system. The dynamic and steady state simulation model for pH neutralization process consists of a system of equations based on mass and charge balances on the continuous stirred tank reactor (CSTR).

DESCRIPTION OF THE IMPROVED MATHEMATICAL MODEL

The process can be considered as a continuous stirred tank reactor (CSTR) to neutralize a strong acid with a strong base manipulated by a control valve. The process consists of an influent stream (HCl), reagent stream (NaOH) to regulate the pH of the effluent stream, and an effluent stream. A schematic diagram is shown in Figure (1). The data of this reaction was taken from a previous experimental work by [Ai-Poh Loh., 2006].

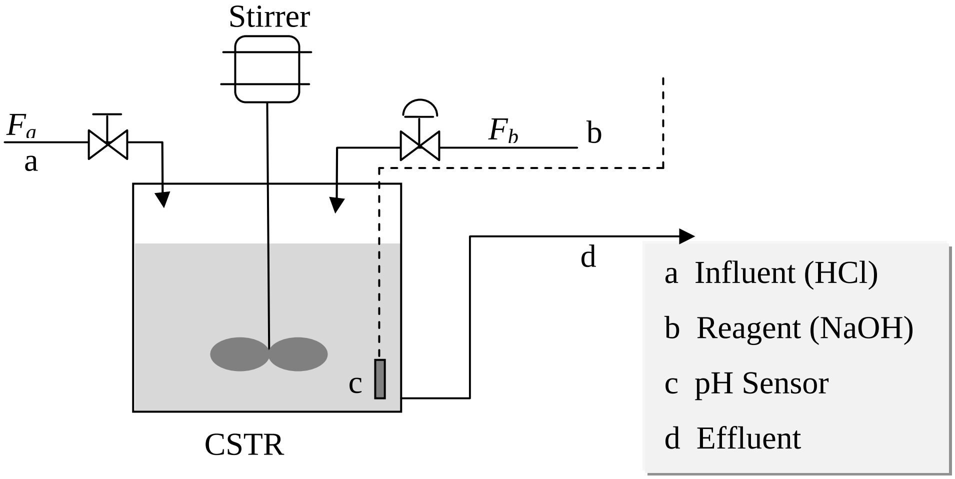

Figure 1: Schematic of a pH neutralization process.

Assumption for the Present Model:

A dynamic model of the process is obtained from the component material balance and the equilibrium relationship under the following assumptions:

The acid-base reactions are ionic and can be considered to take place, with the result that the rate of reaction can be considered. The stirred tank process dynamics in this case would thus be not similar to the case of mixing or blending non reacting streams.

The system is in an ideal condition without any pollutant influence. Constant temperature of 25 0C. pH electrode potential is temperature dependent and this should be accounted for with high temperature applications.

Perfect mixing.
No valve dynamics. Usually, the valve dynamics are much faster than the process dynamics and, thus, can be ignored.
pH probe dynamics can be significant and are often represented by a first order lag.

The volume of the reacting mixture in the tank is constant and equal to V.

The basic model is considered adequate for this case study since it represents the dominant nonlinear characteristics of this single acid-single base continuous stirred tank reactor (CSTR) process.

MODEL FOR STRONG ACID-STRONG BASE SYSTEM

Consider a stirred tank into which hydrochloric acid of concentration [HCl] flows into the tank at a rate Fa (influent stream) and is neutralized by sodium hydroxide of concentration [NaOH] flows at a rate Fb (reagent).

The chemical reaction of these two solutions occurring in the stirred tank reactor is

$$NaOH + HCl + H_2O \rightarrow H_2O + Cl^- + Na^+ + H^+ + OH^-$$

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. Rate constant of*** reaction (k1) (Perry's book, 1997).Hence, the mass balances on NaOH and Sodium ion

Cb = [NaOH]

$$\frac{d[C_b]}{dt} = \frac{1}{V}\{C_bF_b - (F_a + F_b)C_b\} - k_1C_bC_a \qquad (1)$$

$$\frac{d[Na^+]}{dt} = \frac{1}{V}\{-Na^+(F_a + F_b)\} + k_1C_aC_b \qquad (2)$$

Mass balance on HCl and Chloride ion

Ca = [HCl]

$$\frac{d[C_a]}{dt} = \frac{1}{V}\{C_aF_a - (F_a + F_b)C_a\} - k_1C_bC_a \qquad (3)$$

$$\frac{d[Cl^-]}{dt} = \frac{1}{V}\{-Cl^-(F_a + F_b)\} + k_1C_aC_b \qquad (4)$$

Acids and bases have free hydrogen and hydroxyl ions, respectively.

Since the relationship between hydrogen ions and hydroxide ions in a given solution is constant for a given set of conditions, either one can be determined by knowing the other

$$[H^+]\,[OH^-] = K_w = 10^{-14}$$

$$[OH^-] = \frac{K_w}{[H^+]} \qquad (6)$$

Taking the derivative of equation (6)

$$\frac{d[OH^-]}{dt} = \frac{d}{dt}\left(\frac{K_w}{[H^+]}\right) = -\frac{K_w}{[H^+]^2}\frac{d[H^+]}{dt} \qquad (7)$$

Electroneutrality balance

$$[H^+] + [Na^+] = [Cl^-] + [OH^-] \tag{8}$$

Rearranging equation (8) as;

$$[H^+] - [OH^-] = [Cl^-] - [Na^+] \tag{9}$$

Taking the derivative of equation (9)

$$\frac{d[H^+]}{dt} - \frac{d[OH^-]}{dt} = \frac{\mathrm{d}[Cl^-]}{\mathrm{dt}} - \frac{d[Na^+]}{dt} \tag{10}$$

Substituting [OH-] from the equation (7) into (10) yields

$$\frac{d[H^+]}{dt} + \frac{K_w}{[H^+]^2}\frac{d[H^+]}{dt} = \frac{\mathrm{d}[Cl^-]}{\mathrm{dt}} - \frac{d[Na^+]}{dt} \tag{11}$$

$$\frac{d[H^+]}{dt}\left(\frac{[H^+]^2 + K_w}{[H^+]^2}\right) = \frac{\mathrm{d}[Cl^-]}{\mathrm{dt}} - \frac{d[Na^+]}{dt} \tag{12}$$

Substituting of equations (2) and (4) into equation (12) gives;

$$\frac{\mathrm{dH}}{\mathrm{dt}} = \left(\frac{(\mathrm{H}^+)^2}{(\mathrm{H}^+)^2 + \mathrm{K_W}}\right)\left[\frac{1}{\mathrm{V}}\{-\mathrm{Cl}^-(\mathrm{F_a} + \mathrm{F_b})\} + \mathrm{k_1 C_a C_b} - \frac{1}{\mathrm{V}}\{-\mathrm{Na}^+(\mathrm{F_a} + \mathrm{F_b})\} + \mathrm{k_1 C_a C_b}\right] \tag{13}$$

We can rearrange last equation as follows;

$$\frac{\mathrm{dH}}{\mathrm{dt}} = \frac{1}{\mathrm{V}}\left(\frac{(\mathrm{H}^+)^2}{(\mathrm{H}^+)^2 + \mathrm{K_W}}\right)(\mathrm{F_a} + \mathrm{F_b})[\mathrm{Na}^+ - \mathrm{Cl}^-] \tag{14}$$

After rearranging;

Substituting [OH-] from the equation (8) into (14) yields

$$\frac{\mathrm{dH}}{\mathrm{dt}} = \frac{1}{\mathrm{V}}\left(\frac{(\mathrm{H}^+)^2}{(\mathrm{H}^+)^2 + \mathrm{K_W}}\right)(\mathrm{F_a} + \mathrm{F_b})[\mathrm{OH}^- - \mathrm{H}^+] \tag{15}$$

Equation (15) can be solved numerically for [H+], while the pH is a logarithmic function; a change of one pH unit represents a ten-fold change in hydrogen ion concentration

pH = - log [H+] (16)

MODEL SOLUTION AND ANALYSIS

The previously described process model equations (1-16) incorporating the parameter values of Table (1) were solved in Matlab using the Differential Algebraic Equation solver (DAE) with the fourth order Runge kutta method. Physical constants and operating parameters for the mathematical model system were used in Table (1).The process was simulated for the effects of [NaOH], [HCl],[Na+] and [Cl-] on pH with variable time. In the following sections the simulation results are described for the different concentrations of the system.

Figure (2) shows the effect of [HCL] flow rate on the pH of the system. The pH profile has an inverse relationship with the increase in flow rate of [HCL]. Figure

(3) shows the effect of [NaOH] flow rate on the pH of the system. The pH profile has an proporational relationship with the increase in flow rate of [NaOH].

Figures (4) and (5) show the effect of concentrations [Cl-] and [Na+] on the pH with respect to time.It can be seen that the pH depends on the concentrations [Cl-] and [Na+]. The pH has an inverse relationship with the increase in concentrations [Cl-] as shown in Figure (4). The pH has proporational relationship with the increase in concentrations [Na+] as shown in Figure (5). All these behavior are mention above can be represented in Figures (4) and (5) respectively.

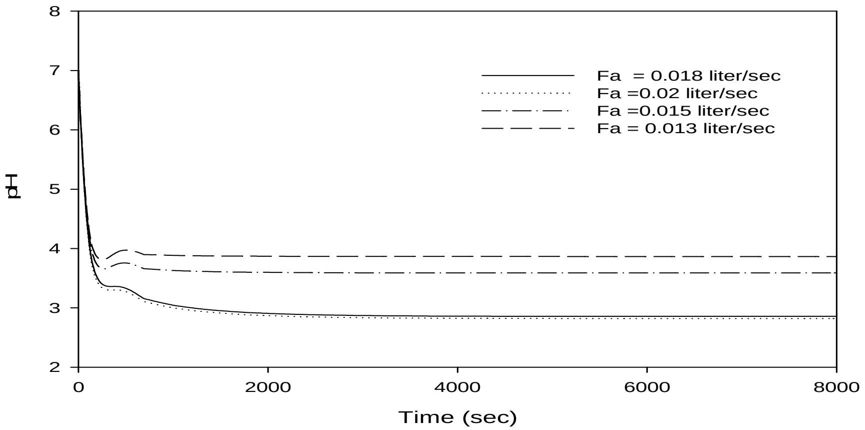

Figure 2: Effects of acid flowrate in the pH with variable time.

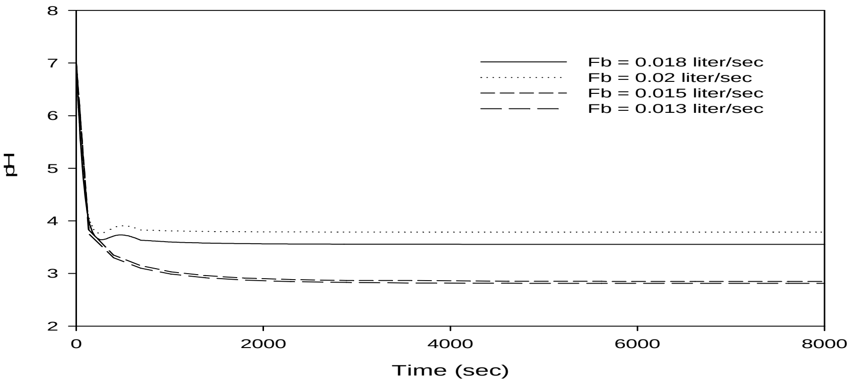

Figure 3: Effects of base flowrate in the pH with variable time.

CONCLUSION

A modified dynamic structure model was developed in this work. This model takes into account the presence of acid and bases in the reaction with ions which depend on chemical reactions of acid and bases concentrations feeds. In addition, the concentrations effect of acid and bases on the system were included. Model simulations indicate that it is capable of predicating reactor performance indicators as well as calculating the changes of ions through chemical of the reaction. we can conveniently use this model as a predictive tool to study the effects of operating, kinetic and hydrodynamics parameters on the reactor performance. The model developed here will also be used in model-based prediction control to control the reactor which is part of our future work.

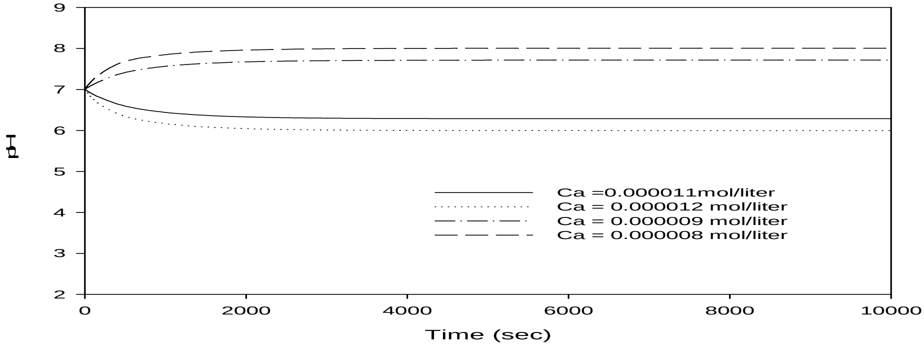

Figure 4: Effects of concentation of [Cl-] in the pH with variable time.

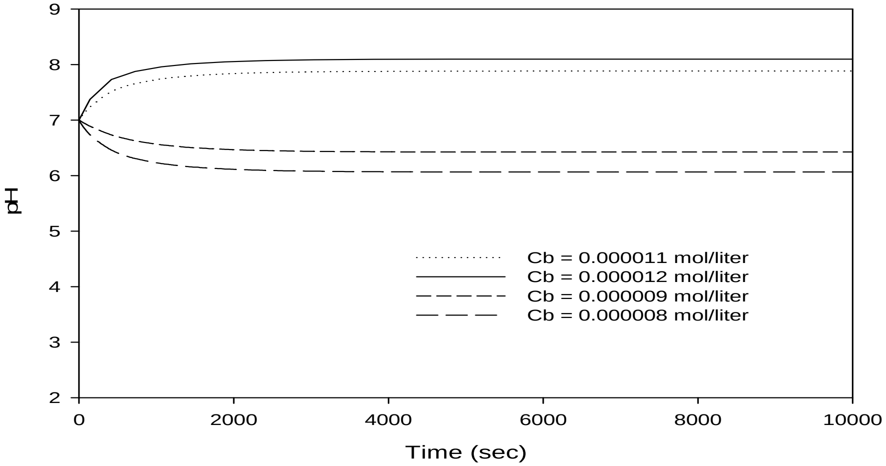

Figure 5: Effects of concentration of [Na+] in the pH with variable time.

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