15th Triennial World Congress, Barcelona, Spain

POLYNOMIAL APPROXIMATION APPROACH TO MODELLING AND CONTROL OF PH PROCESS.

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Abstract: The aim of this paper is to present approximated model of pH process applicable for simulation and control. The highly nonlinear dynamical properties of the pH value to the addition of acid or base make the pH control very difficult. Changes in process sensitivity with pH makes difficult to design conventional controllers. Proposed pH model approximation allows formulating advanced control algorithm in relatively simple way. *Copyright © 2002 IFAC*

Key words: pH control; control algorithms; model based control; polynomial models; model approximation; computer simulation

1. INTRODUCTION

The control of pH is not merely a control problem but also a chemical equilibrium problem. The more difficult the control problem is, the more important is the appropriate modeling of the process. Especially advanced control of pH is largely dependent on the quality of the process model (Gustafsson et al., 1995). Several non-linear algorithms were proposed to solve this problem (Bucholt and Kumnel 1979; Graebe et al., 1996; Henson and Seborg, 1997). One of the first correct models was derived by McAvoy et al. (1972) In bibliography we can find much more complex models for multi species systems but they are not used directly in control algorithms (Musvoto et al. 2000). There were also several approaches of control based on different kinds of process model (Nihtila and Jutila, 1982, Jutila and Visala, 1984 Gustafsson et al., 1995). Although a lot of work was done there is still a lot work to do in field of pH processes, especially simple and enough accurate models for control purpose should be found. Presented in this work control algorithm is input-output linearization, process model based algorithm or GMC (Generic Model Control) (Lee and Sullivan, 1988; Henson and Seborg, 1990; Riggs and Rhinehart, 1990). It is worth to mention that efficient pH model for real-time simulation is needed (Stebel 2000) because testing a non-conventional controller at the real-world neutralization process is very expensive. That is why, the real time simulator of the neutralization process is interesting low-cost alternative to real-word process for testing and comparison of control algorithms (see e.g. Metzger, 2000). Polynomial approximation of strong nonlinear processes can be used for process model based control (see e.g. Metzger, 2001). The main contribution of this paper deals with the detailed discussion of possibility of polynomial pH process approximation taking into account technically real changes of the process variables such as flows and concentrations of the acids and the bases. The main advantage of such approach is that pH value is explicit function of process parameters, has relatively

simple form and only one ordinary differential equation independently on number of existing reagents.

2. PHENOMENOLOGICAL PH PROCESS MODELLING

Mathematical models of pH in well-stirred tanks are discussed in the literature. At first simple model proposed by McAvoy et al. (1972) is considered. This model consists of two bilinear ordinary differential equations, in accordance with the mixing characteristics of the reactor, coupled with two strongly nonlinear algebraic equations. Dynamic equations:

$$\frac{Vd\,x_1}{dt} = F_1 C_1 - (F_1 + F_2)\,x_1 \tag{1}$$

$$\frac{Vd\,x_2}{dt} = F_2 C_3 - (F_1 + F_2)\,x_2 \tag{2}$$

and pH equation

$$[H^+]^3 + [H^+]^2 \cdot (K_a + x_2) + \\ + [H^+] \cdot (K_a (x_2 - x_1) - K_w) - K_a K_w = 0 \tag{3}$$

$$pH = -\log_{10}(H^+) \tag{4}$$

Models for multi species systems are very complicated. To simulate such multi species systems one hypothetical weak acid and weak base are added to the previous system (1-4) to simulate unknown reagents. Two additional weak reagents cannot simulate accurately every multi species system. However it can be treated as a kind of approximation that allows us to observe main feature of such system. Following form will be considered (see e.g. Wright and Kravaris 1991)

$$\frac{Vd\,x_1}{dt} = F_1 C_1 - (F_1 + F_2)\,x_1 \tag{5}$$

$$\frac{Vd\,x_3}{dt} = F_1 C_{31} + F_2 C_{32} - (F_1 + F_2)\,x_3 \tag{6}$$

$$\frac{Vd\,x_2}{dt} = F_2 C_2 - (F_1 + F_2)\,x_2 \tag{7}$$

$$\frac{Vd\,x_4}{dt} = F_1 C_{41} + F_2 C_{42} - (F_1 + F_2)\,x_4 \tag{8}$$

and pH equation

$$[H^+]^5 + \ A \cdot [H^+]^4 + \ B \cdot [H^+]^3 + \ C \cdot [H^+]^2 + \\ + \ D \cdot [H^+] + E = 0 \tag{9}$$

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

Where:

$$A = x_2 + x_4 + K_a + K_b + K_c$$

$$B = K_a (x_2 - x_1) + K_c (x_2 - x_3) + K_b x_2 + (K_a + K_c) K_b + \\ + K_a K_c + (K_a + K_c) x_4 - K_w$$

$$C = K_a K_c (x_2 + x_4 - x_1 - x_3) + K_a K_b (x_2 - x_1) + \\ + K_b K_c (x_2 - x_3) + K_a K_b K_c - K_b K_w - (K_a + K_c) K_w$$

$$D = K_a K_b K_c (x_2 - x_1 - x_3) - (K_a + K_c) K_w K_b + \\ - K_a K_c K_w$$

$$E = -K_a K_b K_c K_w$$

x_1- acetic acid concentration in reactor
x_2- potassium base concentration in reactor
x_3- carbon acid concentration or other weak acid in reactor
x_4- calcium base concentration in reactor
V – volume of reactor (2 [liter])
$[H^+]$ – hydrogen ion concentration
K_a – acetic acid equilibrium constant ($1.8*10^{-5}$)
K_w – water equilibrium constant (10^{-14})
K_c – carbon acid equilibrium constant ($4.2*10^{-7}$)
K_b – calcium base equilibrium constant ($4.3*10^{-2}$)
C_{31}=0.0037[mole/l], C_{32}=0.003[mole/l] - carbon acid or other weak acid inlet concentration in F_1 and F_2 stream. C_{41}=0.0035[mole/l], C_{42}=0.0025[mole/l] – calcium base or other weak acid inlet concentration in F_1 and F_2 stream. Following coefficients ware taken from pilot plant installation (CSCE group, Institute of Automatic Control, Silesian Technical University, Poland): acetic acid inlet concentration C_1= 0.0085 [mole/l], potassium base inlet concentration C_2= 0.0089 [mole/l], acetic acid inlet flow F_{10}= 0.4 [l/min]= const., range of potassium base inlet flow F_2= 0÷0.8 [l/min].

Presence of any strong components does not change order of pH equation. The main problem in simulation is week acids and bases. Addition of any week component change order of pH equation and computation becomes more complex and difficult.

3. APPROXIMATION OF PH PROCESS

Idea of model approximation is shown on figure 1. Instead of two differential equations (1-2) in McAvoy model one differential equation can be proposed

$$\frac{Vd\,x_w}{dt} = F_2 C_2 - F_1 C_1 - (F_1 + F_2)\,x_w \tag{11}$$

Where new: $x_w = x_2 - x_1$ is a difference between reagent concentration in reactor. Analyze of equation (3) suggests that pH value depends mainly on reagent concentration difference x_w in reactor that is why this variable was chosen as a new state variable. Equation 3 cannot be effectively approximate using one polynomial function even if high order polynomial function is used. It is not easy problem to balance between high accuracy and simplicity of model. The idea was to find two or three simples functions with restriction that in case of switching

between them continuity of value and first derivative is assured. Finally third order polynomial functions were chosen. First function responsible for low part of titration curve

$$pH_1 = a_0 + a_1 \cdot x + a_2 \cdot x^2 + a_3 \cdot x^3 \qquad (12a)$$

Second function responsible for part in the middle of titration curve

$$pH_2 = b_0 + b_1 \cdot x + b_2 \cdot x^2 + b_3 \cdot x^3 \qquad (12b)$$

Third function responsible for upper part of titration curve

$$pH_3 = c_0 + c_1 \cdot x + c_2 \cdot x^2 + c_3 \cdot x^3 \qquad (12c)$$

Parameters for first and third function were identified using least-squares method but parameters of second function cannot be found in this way. To assure continuity of value and first derivation four following conditions have to be satisfied:

$$\mathrm{pH}_1(\mathrm{x}_{01}) = \mathrm{pH}_2(\mathrm{x}_{01}) \qquad (13a)$$

$$\mathrm{pH}_1'(\mathrm{x}_{01}) = \mathrm{pH}_2'(\mathrm{x}_{01}) \qquad (13b)$$

$$\mathrm{pH}_2(\mathrm{x}_{02}) = \mathrm{pH}_3(\mathrm{x}_{02}) \qquad (13c)$$

$$\mathrm{pH}_2'(\mathrm{x}_{02}) = \mathrm{pH}_3'(\mathrm{x}_{02}) \qquad (13d)$$

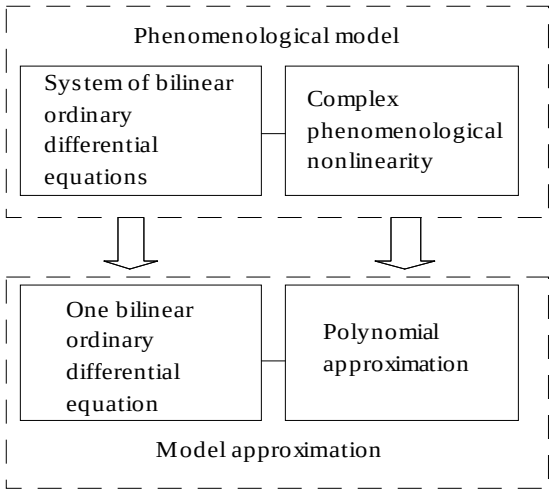

Fig. 1. Idea of model approximation

Value x_{01} and x_{02} are kind of threshold value, where functions have to be switched. Parameters for second function are fully defined by condition (13) if polynomial function is of third order. In this case second function connect first and third function but is not based on data coming from process.

Figure 2 shows that proposed approximation is almost ideal. It is not possible to distinguish between original titration curve and approximation of this curve. Only choosing narrow interval where the titration curve is steepest small differences are visible (figure 3). It was found that titration curve which is a function of reagents concentration difference does not depend on flow changes and inlet concentration deviations. Only changes in acid equilibrium constant have not negligible influence on boundary values (figure 4).

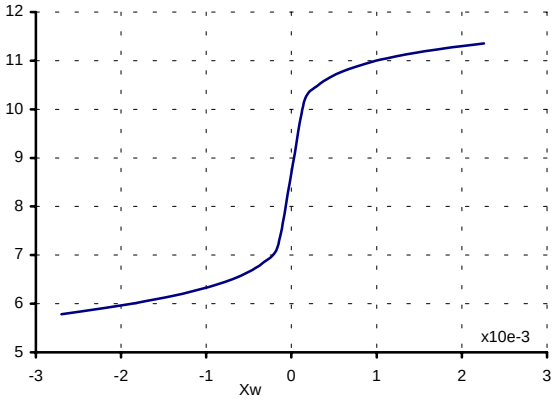

Fig. 2. Titration curve: (equation 3-4) and approximation of titration curve using polynomial functions (equation 12).

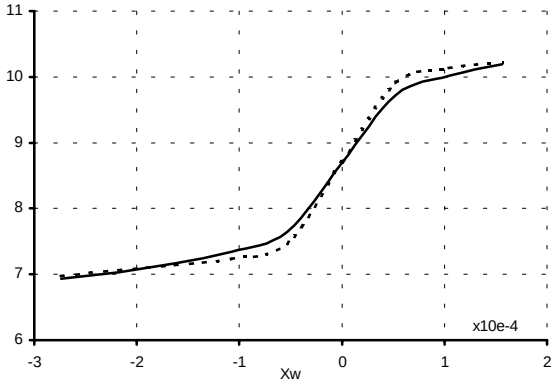

Fig. 3. Titration curve: (a) phenomenological model (solid line), (equation 3-4), b) approximation of titration curve using polynomial functions (dotted line), (equation 12) in neighborhood of equivalence point.

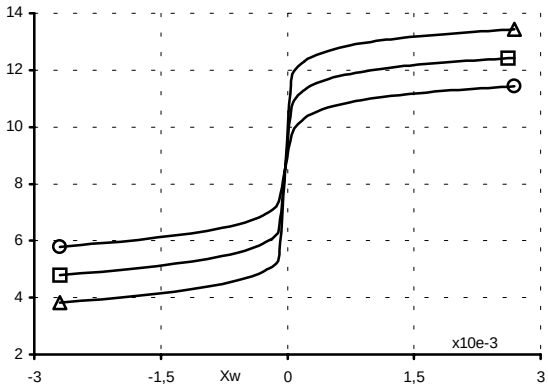

Fig. 4. Acid equilibrium constant influence on titration curve: circular marker K_a=1.8e-6, square marker K_a=1.8e-5, triangular marker K_a=1.8e-4.

Approximation of titration curve is satisfying for control algorithms, but dynamical response has to be

evaluated in case this model will be used for modeling purpose. Dynamical comparison is shown on figure 5.

Concerning weak acid and strong base system very good results were obtained. In further considerations multi species system is taken into account (equations 5-10) were $x_w = x_2 + x_4 - x_1 - x_3$ in this case model approximation has the same form (equations 11-12) It can be expected that this system will present more complex behavior than previous one. It was found that shape of titration curve is also independent on inlet flow F_1 but changes in inlet concentrations slightly change shape (figure 7) for boundary values of pH. Similar behavior is observed when any equilibrium constant changes but their influence on titration curve is much more complex. Although system is much more complicated then the previous system very good results are obtained (figure 8). Comparison of figure 2 and figure 8 shows that both systems are approximated with high accuracy.

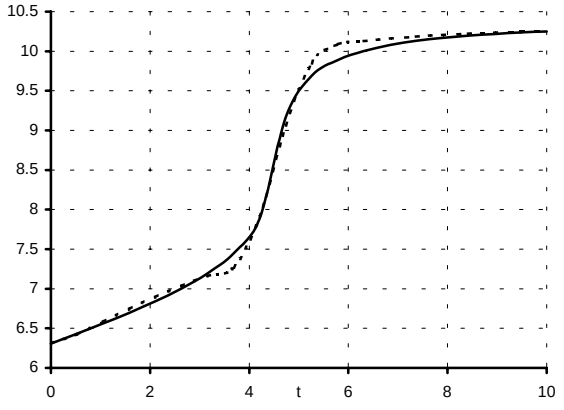

Fig. 5. Comparison of dynamical responses a) phenomenological model (solid line), b) model approximation (dotted line).

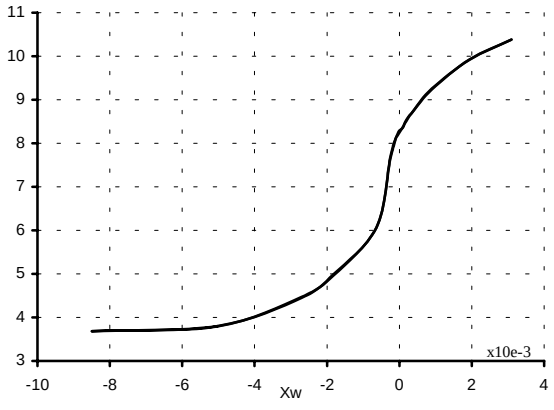

Fig. 6. Real-world titration curve and approximation of this curve.

Titration curve taken from pilot plant installation was also successfully approximated using this method. Results are shown on figure 6 original curve and their approximation is overlapped. Values x_w were calculate using approximately known values of concentrations and flows in pilot plant installation. It should be verified if in real world installation changes of F_1, C_1, and C_2 do not change shape of titration curve.

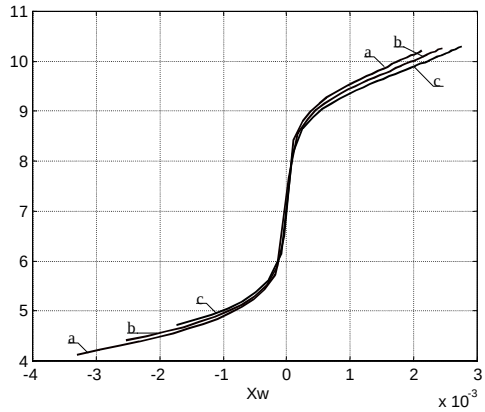

Fig. 7. Titration curves for multi species system a) C_{41}=0.0035 [mole/l] b) C_{41}=0.0045 [mole/l] c) C_{41}=0.0035 [mole/l];

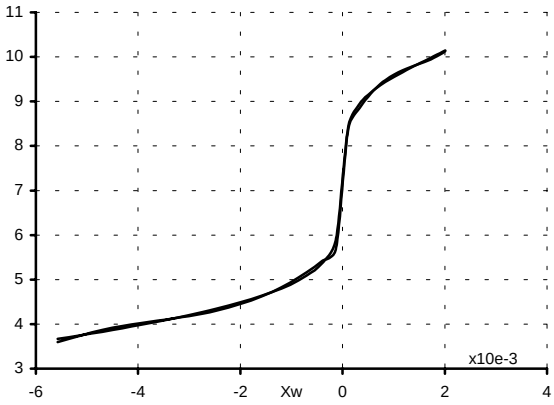

Fig. 8. Titration curve for multi species system (equation 9-10) and approximation of this curve using polynomial functions (equation 12).

4. APPROXIMATED MODEL APPLIED FOR CONTROL

GMC control algorithm was chosen to evaluate suitability of approximated model for control purpose. According to Lee and Sullivan (1988)

$$\dot{y} = \ddot{e}\left(y_{sp} - y\right) + \ddot{e}_0 \int_0^t \left(y_{sp} - y\right) \qquad (14)$$

$\ddot{e}$, $\ddot{e}_0$ - Tuning algorithm parameters

Using equation (11,12) and (14) control law (15) is obtained:

$$F_2 = \frac{\left(\ddot{e}\left(y_{sp} - y\right) + \ddot{e}_0 \int_0^t \left(y_{sp} - y\right)\right) \cdot V}{C_2 \cdot z(x) - w(x) - y} + \qquad (15)$$

$$+ F_1 \cdot \frac{C_1 \cdot z(x) + w(x) + y}{C_2 \cdot z(x) - w(x) - y}$$

Where

$$w(x) = -b_0 + b_2 \cdot x^2 + 2 \cdot b_3 \cdot x^3$$

$$z(x) = b_1 + 2 \cdot b_2 \cdot x \ + 3 \cdot b_3 \cdot x^2$$

Coefficients of polynomial functions

a_0 =7.419461;
a_1 =1.845777e+003;
a_2 =8.924798e+005;
a_3 =1.633864e+008;
b_0 =8.707082;
b_1 =2.733257e+004;
b_2 =-3.978208e+006;
b_3 =-1.543673e+012;
c_0 =9.948482;
c_1 =1.884192e+003;
c_2 =-1.009666e+006;
c_3 =2.005594e+008;

Threshold values, where functions have to be switched

g_d =-7.524071e-005;
g_g =7.348664e-005;

Control law used in this work for phenomenological model has following form (see e.g. Stebel 2001)

$$F_2 = \frac{\left(\ddot{e}\,(y_{sp} - y) + \ddot{e}_0 \int_0^t (y_{sp} - y)\right) \cdot V \cdot \dfrac{\partial c(x,y)}{\partial y} + 10^{-y} K_a x_1 + \left(10^{-2y} + 10^{-y} K_a\right) \cdot (C_2 - x_2)}{+ \dfrac{10^{-y} K_a F_1 \cdot (C_1 - x_1) + \left(10^{-2y} + 10^{-y} K_a\right) \cdot F_1 x_2}{10^{-y} K_a x_1 + \left(10^{-2y} + 10^{-y} K_a\right) \cdot (C_2 - x_2)}} \quad (16)$$

Where:

$$\frac{\partial c(x,y)}{\partial y} = -\ln 10 \cdot$$

$$\cdot \left(3 \cdot 10^{-3y} + 2 \cdot 10^{-2y} (K_a + x_2) + 10^{-y} (K_a (x_2 - x_1) - K_w)\right)$$

Comparing equations 15 and 16 it is obvious that equation 16 is much more complicated than equation 15 mainly because of necessity of rising to a fractional power. Tuning parameters $\lambda = 10$ and $\lambda_0 = 50$ are the same for both control algorithms. As a way of their evaluation absolute error sum (AES) was chosen. Process disturbances were modeled in following way:

$$F_1 = F_{10} + 0.05 \cdot F_{10} \cdot \sin(0.5 \cdot t) \quad (17)$$

Figures 9 and 10 show performance of controllers with assumption of full information accessibility it means that control algorithm uses accurate values of all parameters existing in this algorithm. In this case AES has following values: for algorithm based on phenomenological model AES=13.65 and for algorithm based on approximated model AES=14.28, hence control quality difference is negligible.

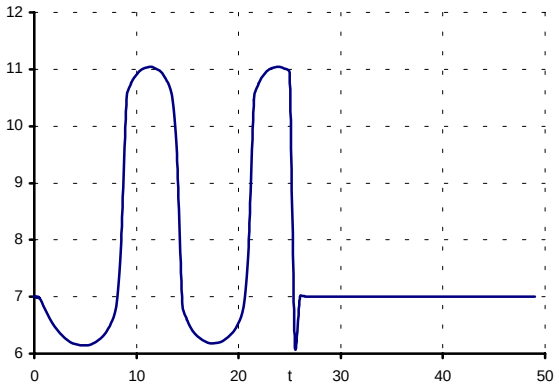

Fig. 9 pH value response for t= 0÷25min without any regulation, for t>25min control algorithm based on approximated model with assumption of full information accessibility – ideal case.

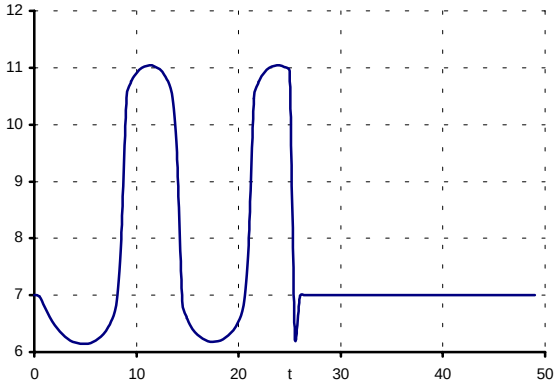

Fig. 10. pH value response for t= 0÷25min without any regulation, for t>25min control algorithm based on phenomenological model with assumption of full information accessibility – ideal case.

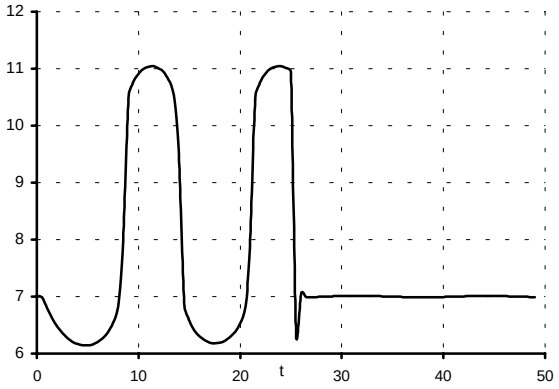

Fig. 11. pH value responses for t= 0÷25min without any regulation, for t>25min control algorithm based on approximated model with assumption of partial information accessibility – realistic case.

Comparison in case of partial knowledge about process shows sensitivity on parameters uncertainty. It was assumed that nominal value of flow F_1=F_{10} and nominal concentrations x_* are known. Results are shown on figure 11 and 12. AES has following

values: for algorithm based on phenomenological model AES=17.16 and for algorithm based on approximated model AES=17.86. In this case similar situation is obtained. Because of limited information about process AES parameters are a little worse in both cases but still comparable.

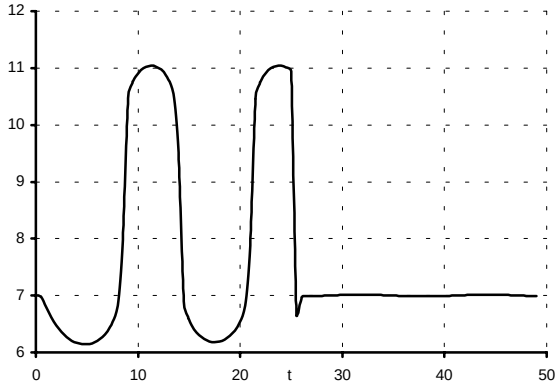

Fig. 12. pH value response for t= 0÷25min without any regulation, for t>25min control algorithm based on phenomenological model with assumption of partial information accessibility – realistic case.

5. CONCLUSIONS

This paper presents results of simulation study of approximated pH model for control and simulation. For simple two reagents system obtained approximation is not sensitive on changes in reagents flows and concentrations. Only acid equilibrium constant has influence on shape of titration curve but not in most critical range. In case of multi species system model is sensitive on parameter changes but quality of model is still very good. Such approach allows us to use only one ordinary differential equation independently how many reagents exists is system. Comparing same control algorithm based on full model and approximated model almost identical results are obtained in spite of simpler form approximated model. Obtained results are very promising but they need further verification on pilot plant installation.

ACKNOWLEDGEMENTS

This research was supported by the National Committee for Scientific Research (KBN)

REFERENCE

Bucholt F. and Kumnel M. (1979) Self-tuning Control of a pH – Neutralization Process, *Automatica* 15. 665.

Graebe S. F., Seron M. M., and Goodwin G. C., (1996) Nonlinear tracking and input disturbance rejection with application to pH control, *J. Proc. Cont.* Vol. 6, No2/3, pp. 195-202

Gustafsson T. K., Skrifvars B. O., Sandstrom K. V. and Waller K. V., (1995) Modeling of pH for Control, *Ind. Eng. Chem. Res.*, Vol. 34, pp. 820-827

Henson M. A. and Seborg D. E., (1997) Adaptive input-output linearization of a pH neutralization process, *Int. J. of Adaptive Control and Signal Proc*. vol. 11, pp. 171-200

Henson, M.A. and Seborg, D.A., 1990, Input-output linearization of general nonlinear process. *AICHE J*. 36, pp. 1753-1757.

Lee P.L. and G.R. Sullivan. 1988. "Generic model control (GMC)." *Comput. Chem. Engng.*, 12, 573-580.

McAvoy T. J., (1972) Time Optimal Ziegler-Nichols Control, *Ind. Eng. Chem. Process Des. Develop*, Vol. 11, No. 1 (1972)

Metzger M. (2000*) Modeling, simulation and control of continuous processes.* Edition of Jacek Skalmierski, Gliwice.

Metzger M. (2001). Easy programmable MAPI controller based on simplified process model. *Preprints of the IFAC Workshop on Programmable Devices and Systems*. Gliwice, Proceeding by the Elsevier in print, pp. 166-170.

Musvoto E. V., Wentzel M. C., Loewenthal R. E. and G. A. Ekama (2000) Integrated chemical-physical processes modeling – I. Development of a kinetic-based model for mixed weak acid/base systems. *Wat. Res.* Vol. 34. No.6, pp 1857-1867.

Nihtila M. and JutilaP., (1982) Dynamic models and state-linear filtering schema for pH processes, *Symposium on Application of Multivariable Systems Theory*, Plymouth, England, Oct. 25-28, , pp.185-194.

Jutila P. and Visala A., (1984) Pilot Plant Testing of an adaptive pH-control Algorithm based on physico-chemical modeling, *Mathematics and Comp. in Sim*. XXVI 523-533.

Riggs, J.B. and Rhinehart, (1990), Comparison between two nonlinear process-model based controllers. *Comput. Chem. Engng*. 14, 1075-1081.

Stebel K. (2000), Analysis of physical appropriateness of semi-analytical solution of pH-process mathematical model for real-time simulation, *16th IMACS World Congress*, Lausanne

Stebel K. (2001), Input-output linearization and PI control algorithms applied for pH process, *Proc. Of the 7th IEEE International Conference*, Vol 2 Poland Miedzyzdroje

Wright R. A. and C. Kravaris, (1991), Nonlinear control of pH processes using strong acid equivalent. *Ind. Eng. Chem. Res*., Vol. 30, No. 7 pp. 1561-1572