



Model based control of a fed batch process used for catalyst support production

Bilal Youssef^{a,*}, Yann Creff^a, Nicolas Petit^b

^a IFP Energies nouvelles, Rond-point de l'échangeur de Solaize BP3, 69360 Solaize, France

^b MINES ParisTech, 60, boulevard Saint-Michel, 75272 Paris, France

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ABSTRACT

In this paper, a model based control of a fed batch process used for catalyst support synthesis is proposed. The considered model is derived from mass balances and an algebraic equilibrium equation identified using titration experiments. The catalyst quality requires that three variables are controlled during the production process: pH, volume and concentration. A global control structure enabling to simultaneously control the three considered variables is given. The pH controller adjusts a reactive base flow rate while the volume and concentration controllers act on water and reactive acid flow rates, respectively. The process model is used to derive control laws that impose asymptotically stable dynamics. Representative experimental results are presented to prove the relevance of the proposed approach.

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1. Introduction

Alumina is a low cost material, used as catalyst or catalyst support in many industrial applications (Gélin & Primet, 2002; Pineda & Palacios, 1997; Zhao, Guo, Hu, & Zhao, 2006). It is widely used in different chemical processes such as hydrodesulfurization, dehydration, and cracking. Catalytic performance is strongly affected by the alumina support characteristics as the pore structure and the specific surface (Chen, Zhang, Hu, Contescu, & Schwarz, 1991; He, Sun, Bai, Dai, & Wang, 2009). Several methods exist to synthesize alumina, such as the precipitation, sol–gel, and thermal decomposition (Parida, Pradhan, Das, & Sahu, 2009; Yilmaz, Kutmen-Kalpakli, & Yilmaz, 2009; Zhu, Liu, Sun, & Yang, 2009). The system considered here is part of a process based on the precipitation method which allows to control the pore size and the surface area by adjusting some synthesis variables, for instance pH and concentration. This paper deals with the control design for a laboratory fed batch reactor operated at IFP Energies nouvelles Lyon. During the production process, it is desired that the pH remains as close as possible to a prescribed setpoint and the concentration at the end of the synthesis reaches a desired setpoint. Furthermore, a given volume must be prepared, which leads, as for the concentration, to a setpoint to be reached by the volume at the end of the synthesis. These setpoints are kept constant for a given batch. The pH and concentration setpoints can take several values according to the target

product. In this context, the considered control problem is challenging for two reasons. On the one hand, the considered ranges of operating points are wide. This induces significant variations of the dynamics. On the other hand, the reactor is operated in batch mode. To address these specificities, a dedicated strategy is proposed. It relies on the following assumptions: the reagents are well known and their dissociations can be identified off line. pH control is a constant requirement in chemical processes, and many researches have been investigated in the literature. A pH neutralization process based on a generalized predictive controller is proposed in Altinten (2007). In Kalafatis, Wang, and Cluett (2005) and Barraud, Creff, and Petit (2009), a feedforward control law derived from the process model, coupled with a feedback controller, is used. Many nonlinear controllers have been also reported (Gustafsson & Waller, 1992; Shahin, Mohammad, & Ali, 2009; Wright & Kravaris, 1991). In general, the inlet concentrations are poorly known (Gustafsson & Waller, 1992; Henson & Seborg, 1994; Kalafatis, Arifin, Wang, & Cluett, 1995; Wright & Kravaris, 2001). On-line adaptation that has sometimes been used in pH control to deal with unmeasured disturbances (Gustafsson & Waller, 1992; Henson & Seborg, 1994), is not required here. In the presented case, the inlet products are well known, and the various coefficients in the equilibria static equation relating the pH to the precursor concentrations can be efficiently estimated off-line through a collection of titration experiments.

This paper proposes a global control structure including pH, volume and concentration controllers. According to the model obtained for this process, the setpoints tracking can be achieved by imposing linear asymptotically stable dynamics. Proof of asymptotic convergence is derived. The paper is organized as follows. The process under consideration is described in Section 2. In Section

* Corresponding author. Tel.: +33 4 37 70 22 20; fax: +33 4 37 70 23 09.

E-mail addresses: Bilal.Youssef@ifpen.fr (B. Youssef), Yann.Creff@ifpen.fr (Y. Creff), Nicolas.Petit@mines-paristech.fr (N. Petit).

Nomenclature

V	volume of the solution
F_{tot}	total feed volume flow rate
F_w	water volume flow rate
q_A	Al^{3+} molar flow rate provided by the reactive acid
q_B	Al^{3+} molar flow rate provided by the reactive base
C_{A0}	concentration of alumina in the storage tank of the reactive acid A_0
C_{B0}	concentration of alumina in the storage tank of the reactive base B_0
N_A	total number of moles of Al^{3+} provided by the reactive acid
N_B	total number of moles of Al^{3+} provided by the reactive base
c_A	Al^{3+} concentration provided by the reactive acid
c_B	Al^{3+} concentration provided by the reactive base
$h_0(\text{pH})$	function accounting for $[H_3O^+]$ and $[OH^-]$ in the main algebraic equation
$h_A(\text{pH})$	function summarizing the dissociations of the reactive acid
$h_B(\text{pH})$	function summarizing the dissociations of the reactive base
pH^r	pH set point
N_B^r	set point for the number of moles of reactive base
χ	tuning parameter of the feedforward part for the final implementation
τ	time constant of the first order dynamics imposed on $N_B - N_B^r$
T_i	integral time for the final implementation
T	synthesis duration
V^0	initial volume
V^f	desired volume at the end of the synthesis (time T)
V^r	desired volume trajectory
τ_v	time constant of the first order dynamics imposed on $V - V^r$
C	alumina concentration
C^f	desired concentration at the end of the synthesis (time T)
$M_{Al_2O_3}^{RA}$	partial alumina mass provided by the reactive acid
$M_{Al_2O_3}^{RB}$	partial alumina mass provided by the reactive base
$M_{Al_2O_3}^{mol}$	alumina molar mass
$N_{Al_2O_3}$	instantaneous alumina molar number existed in the solution.
N	total number of moles of Al^{3+}
q	total Al^{3+} molar flow rate
N^f	desired total number of moles at the end of the synthesis (time T)
N^r	desired trajectory of the total number of moles
τ_n	time constant of the first order dynamics imposed on $N - N^r$

3, the process is modelled, from global and partial mass balances and the equilibria static equation. Off line identification results are presented. In Section 4 the global control design is exposed. The stability analysis is detailed in Section 5. Representative experimental results which clearly show the performance of the proposed control structure are given in Section 6.

2. Process description

The process considered in this work is used to produce catalyst supports from an acid aluminum salt, such as aluminum nitrate,

aluminum chloride or aluminum sulfate, and an alkali-metal aluminate such as sodium or potassium aluminate. The first compound is called the reactive acid and the second one the reactive base (see Fig. 1). The product quality depends on the pH value during the synthesis as well as the concentration at the end. The product quantity is the total volume at the end of the synthesis. In order to control these variables, the reactive base flow is adjusted to keep the pH of the mixture around its desired value while the concentration control is done by adjusting the reactive acid flow, in conjunction with the water flow that is dedicated to volume control. It is desired to keep the pH as long as possible within ± 0.2 around the prescribed set point. The concentration at the end of the synthesis should reach its desired value with 5% maximum error. The paper proposes a model based control design which can be used, in batch production mode, over a wide range of operating conditions. The process is of fed-batch type. Production is scheduled as follows. At the beginning, the reactor contains a volume of water V_0 . Then, a reactive acid A_0 and a reactive base B_0 feed the reactor at predetermined constant mass flow rates. In regulation mode, the reactive base flow is manipulated in order to control the pH of the reactional mixture and the reactive acid flow is manipulated in order to reach the desired concentration. Water is also added and its flow rate is regulated so that the total volume flow rate set point is kept constant during the batch. By means of pumps, the products are fed into the reactor from separate storage tanks placed on balances. In closed loop, the masses measured by the balances are used to control the flow rates through variations of the pumps amperages. These low-level regulators are not described in this paper (see Barraud (2006) for details).

3. Process modelling

This section briefly describes the process model used hereafter in the design of the control strategy. This model is detailed in reference Barraud et al. (2009). The process under consideration involves complex dissociations, for which no accurate picture of the reaction scheme is available. Moreover, the relative importance of the various ions involved is poorly known. Several reactions have been identified for such mixtures. However, as detailed in reference Barraud et al. (2009), it is possible to derive a general form for equilibrium equations, from mass balance equations, the mass action law, the ionic product of water, and the electric neutrality of the solution. The resulting model is nonlinear and can be derived based on mass balances and equilibrium relation.

Global mass balance and partial mass balances can be written under the form

$$\frac{dV}{dt} = F_{tot} = F_w + \alpha_A \frac{q_A}{C_{A0}} + \alpha_B \frac{q_B}{C_{B0}}, \quad \frac{dN_A}{dt} = q_A, \quad \frac{dN_B}{dt} = q_B \quad (1)$$

where

- c_{A0} (resp. c_{B0}) is the concentration in the storage tank of the reactive acid A_0 (resp. of the reactive base B_0);
- q_A (resp. q_B) is the Al^{3+} molar flow rate provided by the reactive acid (resp. the reactive base).
- α_A (resp. α_B) depends on the molecular weight of alumina $M_{Al_2O_3}^{mol}$ and its mass percentage in the reactive acid $P_{Al_2O_3}^{A_0}$ (resp. in the reactive base $P_{Al_2O_3}^{B_0}$).

$$\alpha_I = \frac{M_{Al_2O_3}^{mol}}{2} \cdot \frac{100}{P_{Al_2O_3}^I} \quad I \in \{A, B\}$$

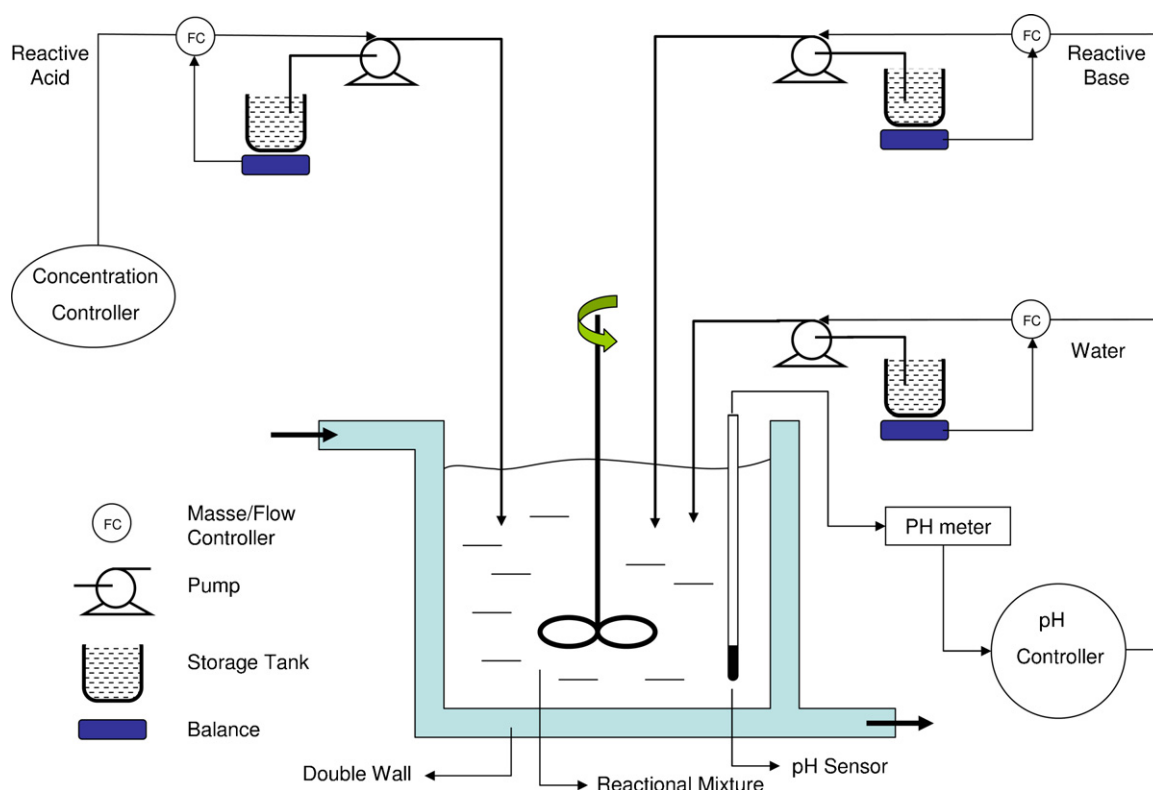


Fig. 1. Process schematic diagram. Reactive acid and reactive base are fed to a batch reactor. Product quality critically depends on the pH during the synthesis and the concentration at the end.

- F_w is the water volume flow rate.
- N_A is the total number of moles Al^{3+} provided by the reactive acid and corresponds to a concentration c_A ;
- N_B is the total number of moles Al^{3+} provided by the reactive base and corresponds to a concentration c_B .

The successive decompositions of the reactive acid (resp. the reactive base) are considered at equilibrium and can be summarized as a function of N_A and pH (resp. N_B and pH). Moreover, these decompositions are such that this function is linear in N_A (resp. N_B) and can then be written $h_A(pH)N_A$ (resp. $h_B(pH)N_B$). In the batch mode of this example, such relations are interesting because the control variables q_A and q_B directly appear by derivation with respect to time. This is very helpful both for the control design and for the analysis of closed-loop stability. It is not required to invoke reaction invariants (Gustafsson and Waller (1983); Rios-Patron and Braatz (1999)).

In the general case, assuming reactions reach their equilibrium instantaneously, the implicit equation linking pH to c_A and c_B nonlinearly depends on c_A and c_B . However, under the assumption that the reactions that occur consist in gaining or losing a single proton, after some computations reported in Barraud et al. (2009), the following equilibrium relation is obtained

$$h_0(pH)V + h_A(pH)N_A + h_B(pH)N_B = 0 \quad (2)$$

with

$$h_0(pH) = \left(10^{-pH} - \frac{K_e}{10^{-pH}} \right)$$

and $K_e = 10^{-14}$, h_A and h_B being nonlinear functions obtained by experimental identification as shown in the following.

An interesting property of Eq. (2) is that the functions h_A and h_B can be easily identified off-line through distinct titration experi-

ments. To identify $h_A(pH)$, titrations by soda (NaOH) of the reactive acid are carried out for various concentrations c_A . In these titrations, Eq. (2) is replaced by

$$h_0(pH) + h_A(pH)c_A + C_{NaOH} = 0$$

This last equality is used to express $h_A(pH)$ from the total reactive acid concentration, the soda concentration, and the measured pH. Experiments are carried out with different initial concentrations of reactive acid. Experimental values can be averaged and interpolated to obtain an analytical expression for $h_A(pH)$ (see top curve in Fig. 2).

A similar method has been used to identify h_B . Titrations by sulphuric acid (H_2SO_4) of the reactive base are carried out for various concentrations c_B . In this case Eq. (2) is replaced by

$$h_0(pH) + h_B(pH)c_B - 2C_{H_2SO_4} = 0$$

and the identified function is shown in the bottom curve of Fig. 2.

4. Control laws

The process model described in the previous section is used to derive control laws by imposing linear asymptotically stable dynamics. In this section, the control design related to the following controllers is developed:

- pH controller.
- Volume controller.
- Concentration controller.

The pH controller adjusts the reactive base flow while the volume and concentration controllers act on the water and reactive acid flows, respectively.

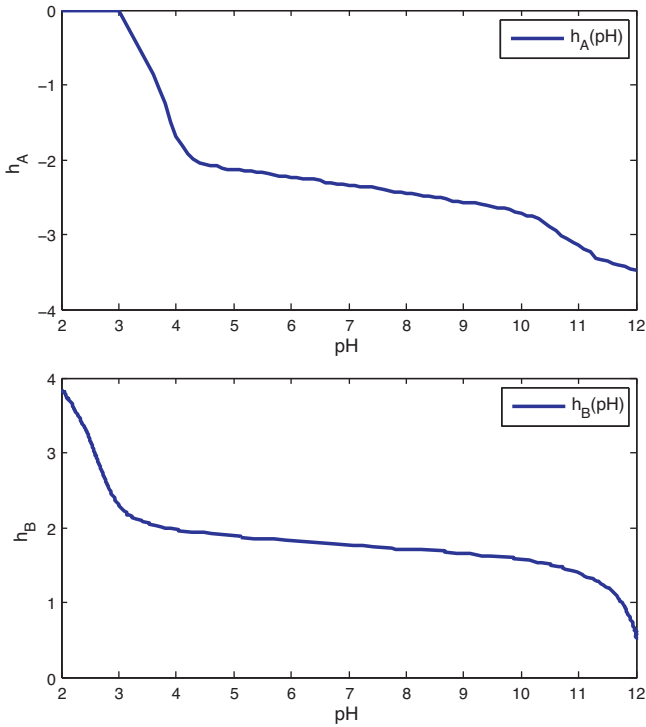


Fig. 2. Experimental identification of functions h_A and h_B .

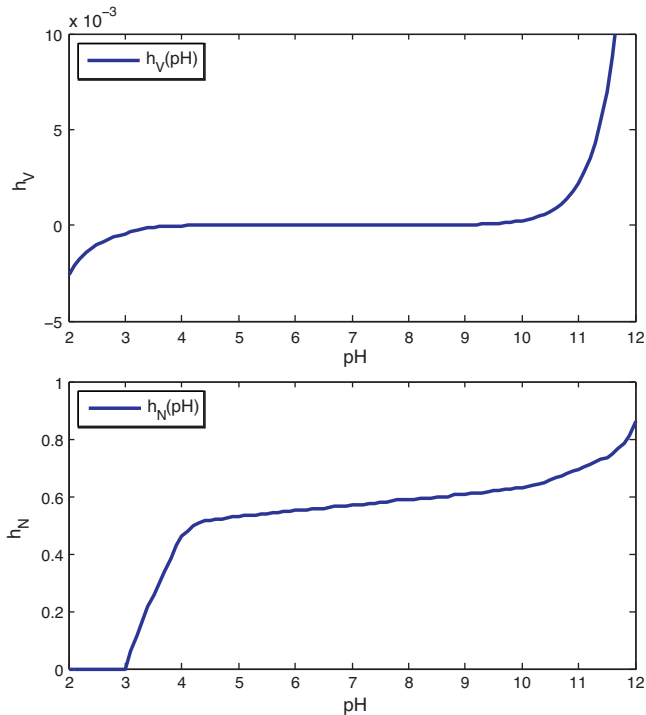


Fig. 3. Functions h_V and h_N are continuous and monotonic.

4.1. pH controller

In Barraud et al. (2009) the pH control is achieved by means of additional acid or base flowrates. Here, pH is controlled by manipulating the reactive base, without using any additional actuator. The process model in this case can be written as follows:

$$\begin{aligned} \frac{dV}{dt} &= F_{tot} = F_w + \alpha_A \frac{q_A}{C_{A0}} + \alpha_B \frac{q_B}{C_{B0}}, & \frac{dN_A}{dt} &= q_A, \\ \frac{dN_B}{dt} &= q_B, & h_0(\text{pH})V + h_A(\text{pH})N_A + h_B(\text{pH})N_B &= 0 \end{aligned} \quad (3)$$

The pH regulation problem consists in deriving a control law which allows to calculate the reactive base flow rate q_B at each time so that the pH follows its reference pH^r . Let

$$h(\text{pH}, t) = h_0(\text{pH})V + h_A(\text{pH})N_A$$

The equilibrium equation (2) writes

$$h(\text{pH}, t) + h_B(\text{pH})N_B = 0$$

Based on the previous equation, it is easy to compute the desired number of moles of reactive base N_B^r which corresponds to the setpoint pH^r :

$$h(\text{pH}^r, t) + h_B(\text{pH}^r)N_B^r = 0$$

Conversely, if $N_B = N_B^r$ then $\text{pH} = \text{pH}^r$, as the involved relations are one-to-one. Consequently, the pH regulation problem consists in controlling the flow $q_B = (dN_B/dt)$ such that the number of moles N_B follows its reference N_B^r . In this work, it is proposed to compute the control q_B by imposing an exponentially decaying control error:

$$\frac{d(N_B - N_B^r)}{dt} = -\frac{1}{\tau}(N_B - N_B^r)$$

The reactive base flow rate can be deduced instantaneously as follows:

$$q_B = \frac{dN_B}{dt} = \frac{dN_B^r}{dt} - \frac{1}{\tau}(N_B - N_B^r) \quad (4)$$

with, as pH^r is constant,

$$\frac{dN_B^r}{dt} = -\frac{1}{h_B(\text{pH}^r)} \frac{dh(\text{pH}^r, t)}{dt}$$

In order to take into account the different approximations and the modelling errors (especially those related to the identified functions h_A and h_B), an integral term can be added as well as a coefficient χ before the feedforward term $q_B^r = (dN_B^r/dt)$, which allows to adjust the compensation if necessary.

The applied control is given by:

$$\begin{aligned} q_B &= -\frac{\chi}{h_B(\text{pH}^r)}(h_0(\text{pH}^r)F_{tot} + h_A(\text{pH}^r)q_A) - \frac{1}{\tau} \left(\frac{h(\text{pH}^r, t)}{h_B(\text{pH}^r)} - \frac{h(\text{pH}, t)}{h_B(\text{pH})} \right) \\ &\quad - \frac{1}{T_i} \int_0^t \left(\frac{h(\text{pH}^r, \tau)}{h_B(\text{pH}^r)} - \frac{h(\text{pH}, \tau)}{h_B(\text{pH})} \right) d\tau \end{aligned}$$

with

$$h(\text{pH}, t) = h_0(\text{pH})V(t) + h_A(\text{pH})N_A(t),$$

$$h(\text{pH}^r, t) = h_0(\text{pH}^r)V(t) + h_A(\text{pH}^r)N_A(t)$$

where T_i is the integral time and the coefficient χ is determined experimentally after some control tests for different pH setpoints. It should be calibrated to minimize the integral term contribution

$$-\frac{1}{T_i} \int_0^t \left(\frac{h(\text{pH}^r, \tau)}{h_B(\text{pH}^r)} - \frac{h(\text{pH}, \tau)}{h_B(\text{pH})} \right) d\tau$$

with respect to the feedforward term

$$-\frac{\chi}{h_B(\text{pH}^r)}(h_0(\text{pH}^r)F_{tot} + h_A(\text{pH}^r)q_A)$$

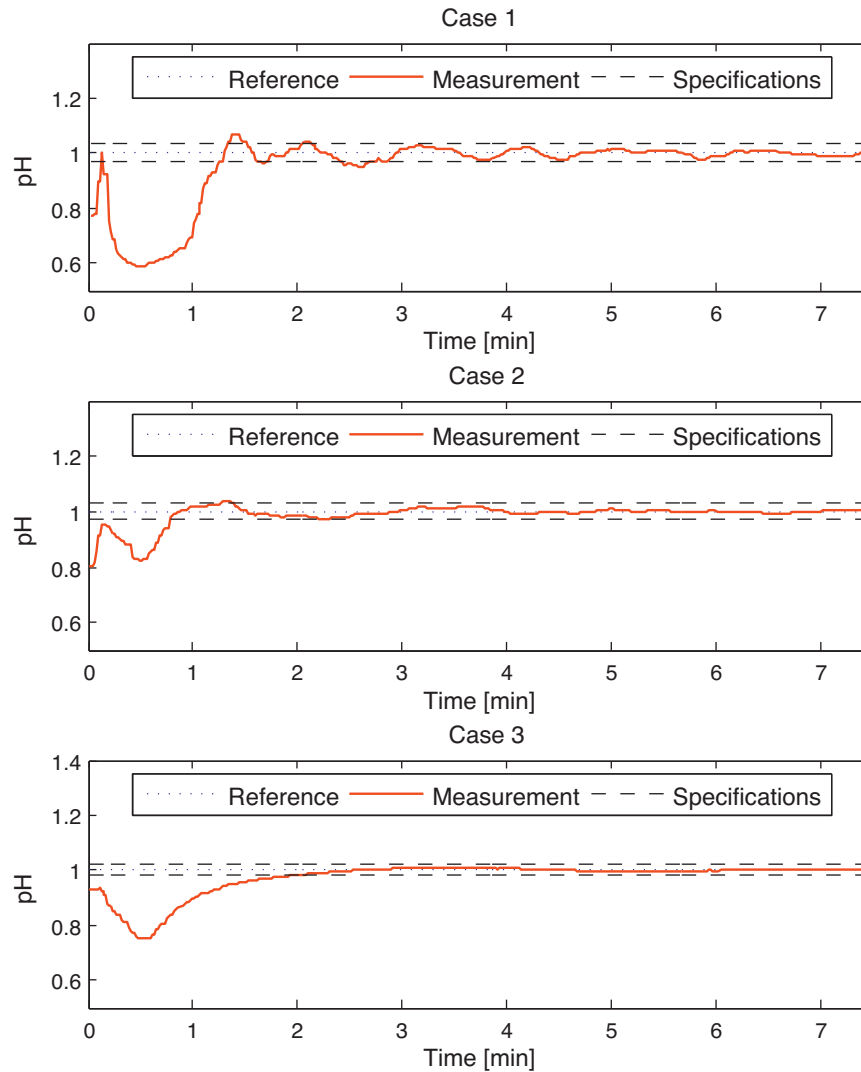


Fig. 4. Typical pH control results obtained for different operating conditions.

The gain $1/\tau$ related to the proportional term is calibrated with respect to the desired regulation dynamics.

4.2. Volume controller

The final volume V^f is specified for time T , $V(T)=V^f$. To satisfy the above volume constraint, one controls the water flow rate such that the volume follows a desired affine reference trajectory

$$V^r(t) = \frac{V^f - V^0}{T}t + V^0$$

In order to define the water control flow rate, an exponential decay on the volume error is imposed:

$$\frac{d(V - V^r)}{dt} = -\frac{1}{\tau_v}(V - V^r) \tag{5}$$

The volume variation results from the addition of reactive acid, reactive base and water:

$$\frac{dV}{dt} = F_w + \alpha_A \frac{q_A}{C_{A0}} + \alpha_B \frac{q_B}{C_{B0}}$$

Consequently the water flow F_w which allows to follow the desired volume reference is given by:

$$F_w = \frac{V^f - V^0}{T} - \alpha_A \frac{q_A(t)}{C_{A0}} - \alpha_B \frac{q_B(t)}{C_{B0}} - \frac{1}{\tau_v}(V(t) - V^r(t)) - \frac{1}{T_{iv}} \int_0^t (V(\tau) - V^r(\tau))d\tau$$

For the sake of robustness, an integral term has been added in the above expression, T_{iv} being the integral time.

Note that the volume regulation is independent of the pH regulation defined in the previous section. It only takes into account the reactive base flow rate provided by the pH controller as well as the reactive acid flow rate provided by the concentration controller which is described in the next section.

4.3. Concentration controller

The value C^f of the final concentration is specified. It is desired that the concentration at the end of synthesis (time T) reaches its desired value, $C(T)=C^f$. In the case of pH regulation by additional acid or base flow rates described in Barraud et al. (2009),

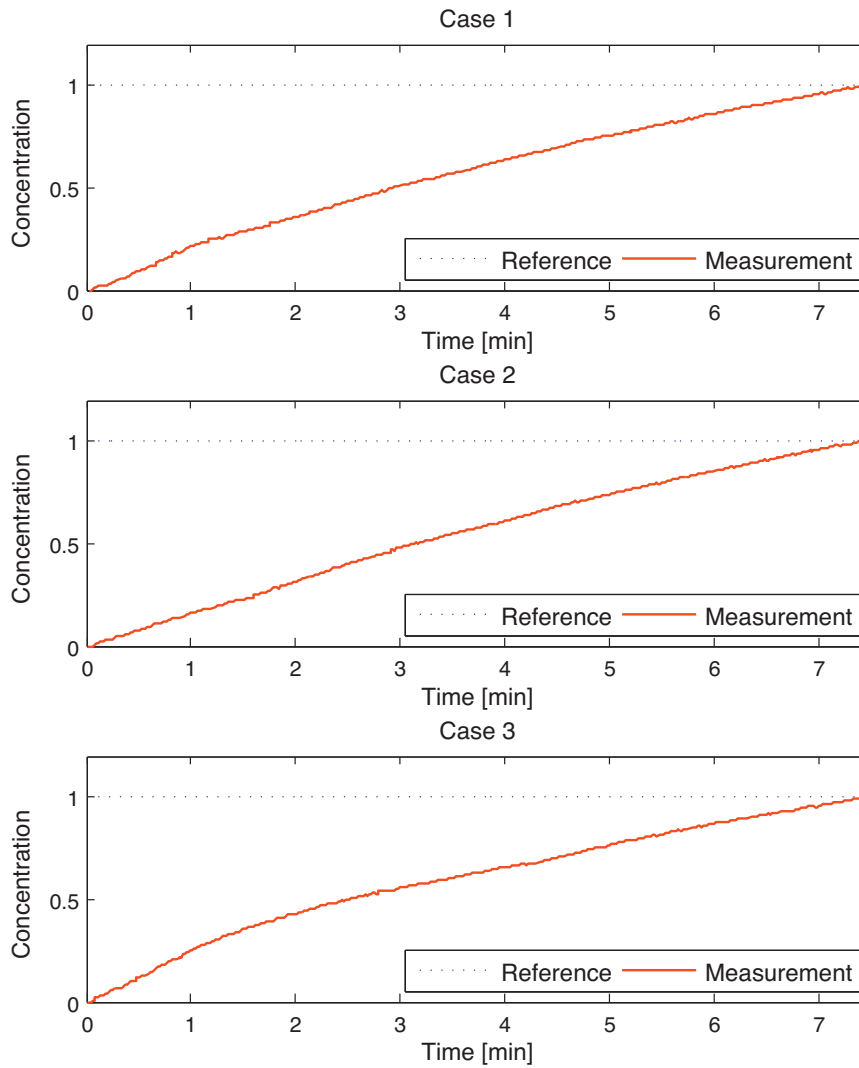


Fig. 5. Alumina concentration reaches its desired value at the end of the synthesis thanks to the volume and molar number controllers.

the enforcement of the final volume constraint ensures to reach the desired final concentration (reactive acid and base flow rates remain constant during the whole synthesis). Here, the pH regulation is done using the reactive base flow, thus satisfying the final volume constraint does not guarantee that the desired final concentration is reached.

To satisfy the final concentration constraint, the alumina amount injected in the solution is controlled by manipulating the reactive acid flow rate q_A . The concentration is given by the following expression:

$$C_{\text{Al}_2\text{O}_3}(t) = \frac{M_{\text{Al}_2\text{O}_3}^{\text{RA}} + M_{\text{Al}_2\text{O}_3}^{\text{RB}}}{V(t)} = M_{\text{Al}_2\text{O}_3}^{\text{mol}} \frac{N_{\text{Al}_2\text{O}_3}(t)}{V(t)}$$

with

- $M_{\text{Al}_2\text{O}_3}^{\text{RA}}$ is the partial alumina mass provided by the reactive acid,
- $M_{\text{Al}_2\text{O}_3}^{\text{RB}}$ is the partial alumina mass provided by the reactive base,
- $V(t)$ is the instantaneous total volume,
- $M_{\text{Al}_2\text{O}_3}^{\text{mol}}$ is the alumina molar mass,
- $N_{\text{Al}_2\text{O}_3}(t)$ is the instantaneous alumina molar number existed in the solution.

The number of moles in the solution results from the number of moles of Al^{3+} provided by the reactive acid and base. As each mole of Al_2O_3 provides two moles of Al^{3+} ,

$$N_{\text{Al}_2\text{O}_3}(t) = \frac{N_A(t) + N_B(t)}{2}$$

This yields to

$$C_{\text{Al}_2\text{O}_3}(t) = \frac{M_{\text{Al}_2\text{O}_3}^{\text{mol}}}{2} \frac{N_A(t) + N_B(t)}{V(t)}$$

The volume trajectory $V(t)$ is given by the water flow controller, thus the regulation of concentration can be achieved by controlling the total number of moles:

$$N(t) = N_A(t) + N_B(t) \quad (6)$$

Consequently, the final concentration constraint is transformed into a constraint $N^f = N(t)$ on the total number of moles at the end of the synthesis:

$$N^f = \frac{2}{M_{\text{Al}_2\text{O}_3}^{\text{mol}}} C^f V^f$$

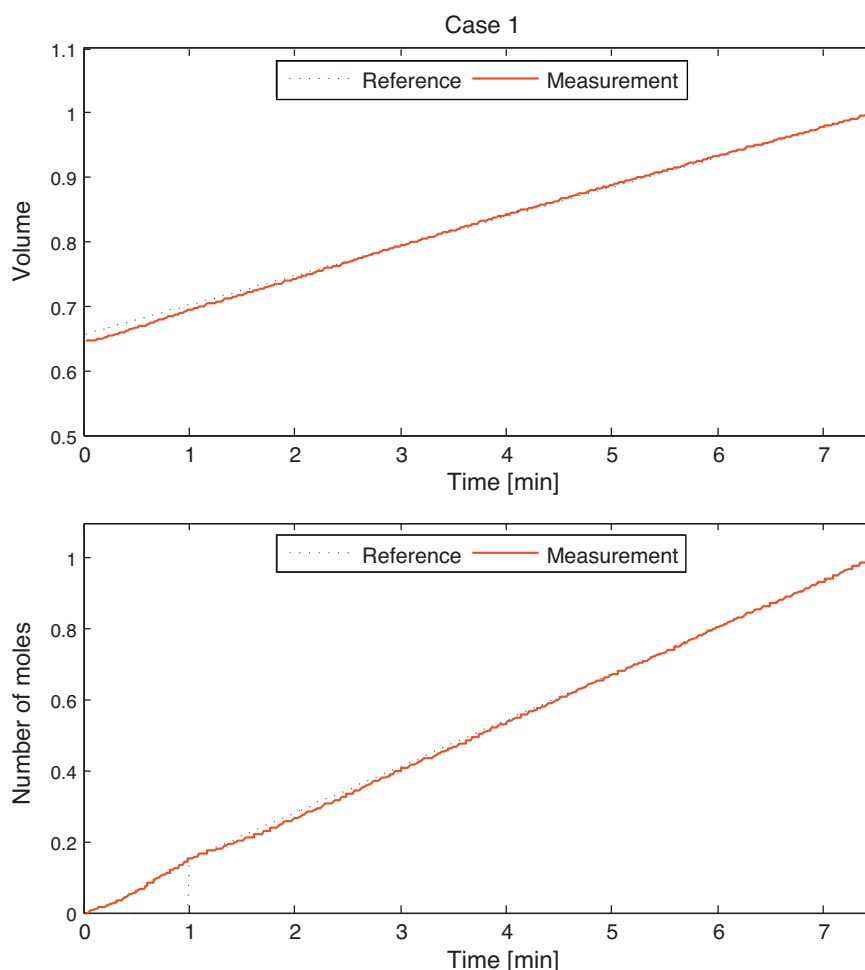


Fig. 6. The total volume and the number of moles follow the desired trajectories.

To satisfy the above constraint on the number of moles, the reactive acid flow rate q_A is controlled such that the total number of moles $N(t)$ follows its setpoint $N^r(t)$ defined as follows:

$$N^r(t) = \frac{N^f - N^C}{T - T^C}(t - T^C) + N^C, \quad \text{for } T \geq T^C$$

where N^C is the estimated value (from balances) of $N(t)$ at time T^C , $0 \leq T^C < T$, which corresponds to the beginning of the activation of the concentration regulation. The latter should be correctly chosen with respect to the pH regulation and in such a way that the final concentration can be reached at time T .

To define the control law on the reactive acid flow rate, an exponential decay is imposed on the error of the total number of moles as follows:

$$\frac{d(N(t) - N^r(t))}{dt} = -\frac{1}{\tau_n}(N(t) - N^r(t)) \quad (7)$$

The variation of the total number of moles is given by

$$\frac{dN(t)}{dt} = \frac{dN_A(t)}{dt} + \frac{dN_B(t)}{dt}$$

In the above equation, $(dN_B(t)/dt)$ is imposed by the pH controller. To satisfy the exponential decay, the reactive acid flow rate q_A is manipulated as follows:

$$q_A = \frac{dN_A(t)}{dt} = \frac{N^f - N^C}{T - T^C} - \frac{1}{\tau_n}(N(t) - N^r(t)) - \frac{dN_B(t)}{dt}$$

An integral term can be added in order to eliminate possible static error due to different uncertainties.

Remark 1. To calculate the acid flow rate, the base flow rate is used, which in turn requires the use of the acid flow rate. In order to avoid any oscillation, and as pH control must react faster than concentration control, the base flow rate used in the calculation of the acid flow rate is filtered.

Remark 2. The concentration controller should be tuned in such a way to minimize the disturbance effect on the pH regulation due to the acid flow rate variations.

Remark 3. Note that the above concentration control is independent of the pH regulation. It just takes into account the base flow given by the pH controller. However, the concentration regulation depends on the volume control. In fact, if the final volume constraint is not satisfied, following the setpoint of the total number of moles does not guarantee that the desired final concentration is reached, as the molar number setpoint is defined under the assumption that the final volume is reached.

5. Stability analysis

This section investigates the stability analysis of the whole control structure. The Lyapunov's first method inspires the proof of exponential convergence of the controlled variables toward their desired references. The proof is derived from the one found in Barraud et al. (2009), that must be modified, first because $N_A + N_B$

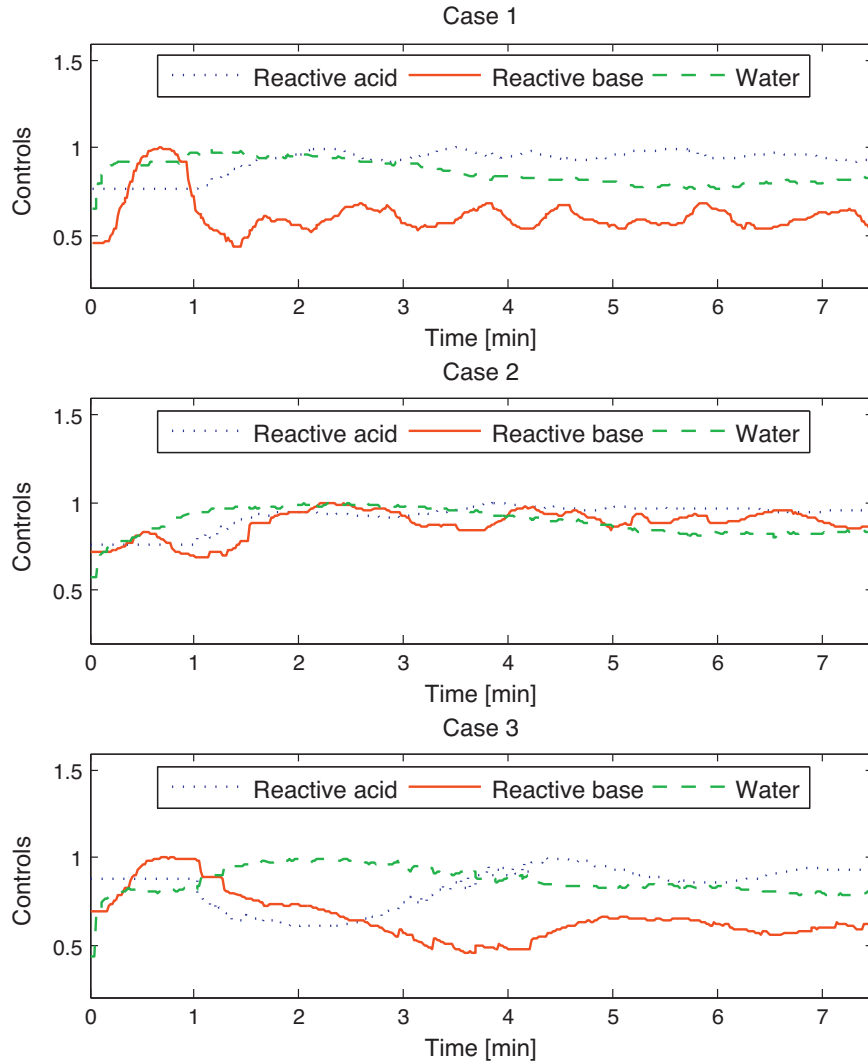


Fig. 7. Process controls: reactive base flow for pH control, water flow for volume control and reactive acid flow for concentration control.

is under control, which must be accounted for in the analysis of pH control stability, then to cope with the concentration and volume controls.

The last equation of (1) writes

$$h_0(\text{pH})V + h_A(\text{pH})N_A + h_B(\text{pH})N_B = 0$$

Replacing the reactive acid molar number by its expression deduced from (6) leads to

$$N_B = \frac{h_0(\text{pH})}{(h_A(\text{pH}) - h_B(\text{pH}))}V + \frac{h_A(\text{pH})}{(h_A(\text{pH}) - h_B(\text{pH}))}N$$

or

$$N_B = h_V(\text{pH})V + h_N(\text{pH})N = H(\text{pH}, t) \quad (8)$$

with

$$h_V(\text{pH}) = \frac{h_0(\text{pH})}{(h_A(\text{pH}) - h_B(\text{pH}))}, \quad h_N(\text{pH}) = \frac{h_A(\text{pH})}{(h_A(\text{pH}) - h_B(\text{pH}))}$$

Let us denote $q(t) = q_A(t) + q_B(t)$ and

$$\phi(\text{pH}, t) = \frac{dh_V}{d\text{pH}}(\text{pH})V(t) + \frac{dh_N}{d\text{pH}}(\text{pH})N(t) = \frac{\partial H}{\partial \text{pH}}(\text{pH}, t),$$

$$\psi(\text{pH}, t) = h_V(\text{pH})F_{\text{tot}} + h_N(\text{pH})q(t) = \frac{\partial H}{\partial t}(\text{pH}, t)$$

Differentiating Eq. (8) leads to

$$\frac{d\text{pH}}{dt} = -\frac{\psi(\text{pH}, t)}{\phi(\text{pH}, t)} + \frac{q_B}{\phi(\text{pH}, t)} \quad (9)$$

The functions h_V and h_N are continuous and strictly monotonic in the pH range [3, 12] of interest (see Fig. 3), thus

$$N_B^r = H(\text{pH}^r, t)$$

From Eq. (4),

$$q_B = \frac{dN_B}{dt} = \frac{dN_B^r}{dt} - \frac{1}{\tau}(N_B - N_B^r)$$

Thus

$$q_B = \psi(\text{pH}^r, t) - \frac{1}{\tau}(H(\text{pH}, t) - H(\text{pH}^r, t)) \quad (10)$$

Since the pH reference is considered constant, using Eqs. (9) and (10) leads to

$$\frac{d(\text{pH} - \text{pH}^r)}{dt} = -\frac{1}{\phi(\text{pH}, t)} \times \left((\psi(\text{pH}, t) - \psi(\text{pH}^r, t) + \frac{1}{\tau}(H(\text{pH}, t) - H(\text{pH}^r, t))) \right)$$

Consider now the following positive pH error function

$$\nu(\text{pH}) = \frac{1}{2}(\text{pH} - \text{pH}^r)^2 \quad (11)$$

Its derivative is given by

$$\frac{d\nu}{dt} = -\frac{1}{\phi(\text{pH}, t)} \times \left((\psi(\text{pH}, t) - \psi(\text{pH}^r, t) + \frac{1}{\tau}(H(\text{pH}, t) - H(\text{pH}^r, t))) (\text{pH} - \text{pH}^r) \right)$$

From the intermediate value theorem applied on the scalar function

$$\text{pH} \mapsto \kappa_t(\text{pH}) = \psi(\text{pH}, t) + \frac{1}{\tau}H(\text{pH}, t)$$

there exists a $\text{pH}^0(t)$, with $\text{pH}^0(t) \in [\text{pH}, \text{pH}^r]$ or $\text{pH}^0(t) \in [\text{pH}^r, \text{pH}]$ such that

$$\frac{d\nu}{dt} = -\frac{1}{\phi(\text{pH}, t)} \left(\frac{\partial\psi}{\partial\text{pH}}(\text{pH}^0(t), t) + \frac{1}{\tau} \frac{\partial H}{\partial\text{pH}}(\text{pH}^0(t), t) \right) (\text{pH} - \text{pH}^r)^2$$

Yet, from the definitions of h_V and h_N (see Fig. 3), there exists $\phi_{\min} > 0$ such that, $\phi(\text{pH}^0, t) \geq \phi_{\min} > 0$ for all t . Moreover, the function ϕ can be uniformly bounded in time

$$0 < \phi_{\min} \leq \phi \leq \phi_{\max}$$

and

$$\frac{\partial\psi}{\partial\text{pH}} \geq 0$$

Then

$$\frac{d\nu}{dt} \leq -2 \frac{\phi_{\min}}{\tau\phi_{\max}} \nu$$

Consider now the global positive error function

$$\varpi(\text{pH}) = \frac{1}{2}(\text{pH} - \text{pH}^r)^2 + \frac{1}{2}(V - V^r)^2 + \frac{1}{2}(N - N^r)^2$$

Using Eqs. (5), (7) and (11) the derivative of ϖ writes

$$\frac{d\varpi}{dt} = \frac{d\nu}{dt} - \frac{1}{\tau_V}(V - V^r)^2 - \frac{1}{\tau_N}(N - N^r)^2$$

Consequently

$$\frac{d\varpi}{dt} \leq -2 \frac{\phi_{\min}}{\tau\phi_{\max}} \nu$$

So, ϖ exponentially converges towards 0, and

$$\lim_{t \rightarrow \infty} \text{pH} = \text{pH}^r, \quad \lim_{t \rightarrow \infty} V = V^r, \quad \lim_{t \rightarrow \infty} N = N^r$$

6. Experimental results

The control structure developed in Section 5 is implemented and tested on the real process described in Section 2. The proposed control strategy has been validated for several operating conditions covering the whole pH range. Some typical experimental results are presented in this section. The results presented here correspond to three different cases. Activation time for the concentration control is $T_C = 1$ min. For the sake of confidentiality, all displayed curves are normalized.

Fig. 4 shows the regulation results of the pH control. The measured pH follows its reference in a short time and range within the prescribed zone (± 0.2 around the set point). Note that it is difficult to shorten the transient time because it depends on the initial conditions and the operating mode. In fact, the pumps dealing with the reactive acid and base operate in open loop. The feedforward part

of q_B starts when mass measurements become significant while the feedback part is added few seconds later.

Fig. 5 displays the concentration curves which reach the desired values at the end of the synthesis. The constraint of 5% maximum error is respected for all cases. The concentration reaches its desired value thanks to the volume and number of moles controllers.

Fig. 6 shows an example of the regulation results corresponding to the first case. The three controls are shown in Fig. 7. The reactive base flow rate is used to regulate the pH. The water flow rate and the reactive acid flow rate are used for the volume and concentration regulations, respectively.

7. Conclusion

In this paper, a model based approach to control the pH, the volume and the concentration in a fed-batch reactor has been presented. The control design is simple and can be easily implemented. Since the proposed approach is based on models, it can be easily adapted for other configurations. Asymptotic convergence has been proven. The global control structure has been validated experimentally in a laboratory reactor. The results were obtained quickly thanks to a light amount of the calibration efforts.

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