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Comparative study of two chemical reactions with different behaviour in batch and semibatch reactors

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Abstract

Based on two reactions with different behaviour, a comparative study between batch and semibatch reactors performance has been carried out in a glass-jacketed reactor of 5 l provided with the measuring, data acquiring and controlling system. The reactions chosen were an acid–base reaction (ethyl acetate saponification), and an oxidation–reduction reaction with a high reaction heat (thiosulfate-peroxide reaction). A first difference was in the method used to establish the kinetic equation. For the acid–base reaction was used an isothermal method based on the conductivity profiles of the solution. For the oxidation reaction was used an adiabatic method based on the measurement of temperatures.

This work focuses in the interest to obtain the concentrations of the species in the reactor, by measuring experimentally with different sensors (pH, temperature, etc.) the needed values to get the concentration profiles. For the acid–base reaction it was possible to convert the pH measurements of the reaction solution to concentration values. In the case of the oxidation reaction, the concentration profiles were obtained by measuring only reactor temperature for the adiabatic batch mode of operation, and by simulation in the semibatch mode of operation. The mathematical model was previously validated with temperature profiles obtained experimentally.

Keywords: Batch and semibatch reactor; Modelling; Reaction kinetic

1. Introduction

The extraordinary flexibility of batch processes is well known. Batch processes are used in the domains of speciality chemicals, polymers and biotechnology. Batch processes are generally employed to obtain products with high added value. They are strongly governed by the chemistry of the reactions, which can be complex, and with kinetics poorly known.

The kinetic analysis of chemical reactions frequently takes place in a homogeneous liquid phase under isothermal conditions (Levenspiel [1]). This is the case of the saponification reaction, because it is possible to control the reactor temperature easily. There are also cases where it is more appropriate the application of non-isothermal methods for evaluating reaction rate models and kinetic parameters. That is the case of adiabatic experiments using batch systems to obtain temperature profiles from which the kinetic model and parameters for simple and complex systems can be extracted after application of a heat balance to relate temperature with conversion (Stoessel [2]). That is the case of the oxidation reaction, because it is impossible to maintain constant the reactor temperature. Studies with adiabatic reactors have been reported by several authors using the thiosulfate-peroxide reaction. For example Root and Schmitz [3] and Vetjasa and Schmitz [4] studied the reaction in a batch reactor and used the data obtained for the study of steady state multiplicity in a loop reactor and a stirred tank reactor (CSTR) respectively. Similar work was carried out by Chang and Schmitz [5]. Guha et al. [6] reported also an study of transient behaviour of an adiabatic CSTR.

In this work the kinetic equation can be derived from data obtained in a series of runs in which the initial reagent concentrations is held constant and the initial temperature is varied. The method used is similar to the one presented by Cohen and Spencer [7].

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Nomenclature

a	stoichiometric factor of reactant A
A_i	inside heat-transfer area (m^2)
A_0	outside heat-transfer area (m^2)
b	stoichiometric factor of reactant B
c_A	concentration of reactant A (NaOH or H_2O_2) ($kmol\,m^{-3}$)
c_{A0}	initial concentration of reactant A ($kmol\,m^{-3}$)
c_{A1}	initial concentration of reactant A in tank ($kmol\,m^{-3}$)
c_B	concentration of reactant B ($kmol\,m^{-3}$)
c_{B0}	initial concentration of reactant B ($kmol\,m^{-3}$)
c_{B1}	initial concentration of reactant B in tank ($kmol\,m^{-3}$)
c_P	concentration of products ($kmol\,m^{-3}$)
C_J	heat capacity of jacket fluid ($kJ\,kg^{-1}\,K^{-1}$)
C_P	heat capacity of reactants ($kJ\,kg^{-1}\,K^{-1}$)
C_M	heat capacity of wall ($kJ\,kg^{-1}\,K^{-1}$)
E_a	activation energy ($kJ\,kmol^{-1}$)
F_W	jacket fluid stream ($m^3\,s^{-1}$)
F_0	addition flow ($m^3\,s^{-1}$)
h_i	inside heat-transfer coefficient ($kJ\,s^{-1}\,m^{-2}\,K^{-1}$)
h_0	outside heat-transfer coefficient ($kJ\,s^{-1}\,m^{-2}\,K^{-1}$)
ΔH_r	heat of reaction ($kJ\,kmol^{-1}$)
k	rate constant ($m^3\,kmol^{-1}\,s^{-1}$)
k_0	specific rate constant ($m^3\,kmol^{-1}\,s^{-1}$)
Q_r	heat generated ($kJ\,s^{-1}$)
Q_J	outside heat-transfer rate ($kJ\,s^{-1}$)
Q_M	inside heat-transfer rate ($kJ\,s^{-1}$)
r	rate of reaction ($kmol\,m^{-3}\,s^{-1}$)
R	constant of gases ($kJ\,K^{-1}\,kmol^{-1}$)
t	time (s)
T	reactor temperature (K)
T_J	jacket temperature (K)
T_M	wall temperature (K)
T_{ad}	temperature of H_2O_2 added (K)
T_{J0}	inside jacket fluid temperature (K)
T_{set}	set-point temperature (K)
T_0	initial temperature in adiabatic experiments (K)
ΔT_{ad}	increment of adiabatic temperature (K)
V	volume of reaction mass (m^3)
V_J	jacket volume (m^3)
V_M	wall volume (m^3)
x	conversion

Greek letters

ρ	density of reacting mass ($kg\,m^{-3}$)
ρ_J	density of jacket fluid ($kg\,m^{-3}$)
ρ_M	density of wall ($kg\,m^{-3}$)

The thermal behaviour of batch and semibatch reactors has been investigated by Rafalimanana et al. [8], Kiparissides and Shah [9] and Rotstein and Lewin [10], but the evolution of the concentration of reactants and products was not investigated, which is very important to optimise the operation performance, as it has been pointed out by Hugo et al. [11].

In this work, for the acid–base reaction, the in situ concentration of the species present in the reactor was determined by measuring the pH of the solution. For the oxidation–reduction reaction the voltage profile of the reaction was obtained experimentally, but its conversion into a concentration profile was found to be very difficult. In this case, concentration profiles were obtained by simulation. A dynamic mathematical model was developed to predict both the thermal behaviour of batch reactors and the evolution of the concentration of reactants and products during the reaction. For this reaction, it has been possible to obtain the concentration profiles experimentally, only in the case of adiabatic operation. In this mode of operation it is possible to follow the concentration evolution by only measuring the reaction temperature.

For the acid–base reaction (with a low reaction heat), where the reactor temperature would be kept controlled, two modes of operation (batch or semibatch) are possible. In the case of the thiosulfate reaction (very exothermic reaction) temperature control is only feasible for the semibatch reactor. In this case, when a set-point is selected for the reaction mass temperature, it is possible to control the reaction by manipulating the feed rate of one of the reactants, maintaining the inlet jacket temperature at a prefixed value. Thus, this mode of operation can be used to control the reaction, and it is particularly useful for highly exothermic processes where safety is a major concern. In this sense, the works of Steensma and Westertep [12] and Stoessel [2] are very relevant. Hugo and Steinbach [13] make a safety comparison study between a fed-batch reactor and a continuous stirred tank reactor.

The paper is mainly scoped to the simulation of the concentration profiles from pH and temperature data, and then to predict the experimental behaviour of the control. Therefore, a key contribution of the present work focuses in a comparative study of the behaviour of two homogeneous reactions, carried out in batch and semibatch reactors. These reactions can be reproduced experimentally to get, using sensors of pH, temperature or potential, substantial amount of data that allow to obtain appropriate information to compare the behaviour of batch and semibatch reactor modes of operation. Usually, this comparison is made only using temperature measurements. This work gives special importance to obtain concentration profiles (through pH or temperature experimental measures), which show better the different behaviour between the two modes of operation. In this way, the study leads to an inferential way to control batch and semibatch reactors.

Moreover, the simple reactions used have been chosen in particular because, even in the development of the kinetic expression, the method used is different, making it possible to compare the behaviour of an isothermal reactor and an adiabatic reactor. The interest of the work consists also in comparing two reactions of very different reaction rate and thermal behaviour.

2. The mathematical model

The two reactions considered can be represented, in a general way, as:

$$aA + bB \rightarrow cC + dD$$

where a, b, c, and d are different for each reaction:

$$CH_3COOCH_2CH_3 + NaOH \rightarrow CH_3COONa + CH_3CH_2OH$$

$$Na_2S_2O_3 + 2H_2O_2 \rightarrow \tfrac{1}{2}Na_2S_3O_6 + \tfrac{1}{2}Na_2SO_4 + 2H_2O$$

The reaction rate is assumed to be proportional to the first order of the concentration of reactants A and B, and the solution density to be constant:

$$r = kc_A c_B \tag{1}$$

where k is a function of the temperature according to the Arrhenius expression:

$$k = k_0\, e^{-E_a/R(T+273)} \tag{2}$$

Kinetic parameters k_0 and E_a may be obtained by two methods.

2.1. Isothermal method

The conductivity profile of the solution at different temperatures is obtained. Thus, a set of values of k at different temperatures can be obtained, and then by plotting $\ln k$ versus $1/T$ in the logarithmic expression of Eq. (2), k_0 and E_a values can be readily obtained:

$$\ln k = \ln k_0 - \frac{E_a}{R}\frac{1}{T+273} \tag{3}$$

2.2. Adiabatic method

Taking into account that the energy balance equation is solely referred to the reaction mass, the following expression is obtained:

$$\frac{dT}{dt} = -\frac{\Delta H_r k c_A c_B}{\rho C_P} \tag{4}$$

Eq. (4) gives the rate constant at each time instant:

$$k = \frac{(dT/dt)\rho C_P}{(-\Delta H_r) c_A c_B} \tag{5}$$

The derivative dT/dt can be calculated from the recorded temperature–time curve. Then, $\ln k$ is calculated, using the values obtained from Eq. (5). The procedure that follows is similar to the isothermal method.

The dynamic behaviour of the batch and semibatch reactors could be described by a set of differential equations resulting from mass and energy balances of the reaction mixture, the energy balance of the jacket wall and the circulating fluid inside the jacket.

The overall mass balance of batch reactor:

$$\frac{d(\rho V)}{dt} = 0 \tag{6}$$

$$\frac{dV}{dt} = 0 \tag{7}$$

The overall mass balance of semibatch reactor:

$$\frac{d(\rho V)}{dt} = F_0 \rho \tag{8}$$

$$\frac{dV}{dt} = F_0 \tag{9}$$

The mass balance of components of batch reactor:

$$\frac{V\, dc_A}{dt} = -Vakc_A c_B \tag{10}$$

$$\frac{V\, dc_B}{dt} = -Vbkc_A c_B \tag{11}$$

The mass balance of components of semibatch reactor:

$$\frac{d(Vc_A)}{dt} = F_0 c_{A0} - Vakc_A c_B \tag{12}$$

$$\frac{d(Vc_B)}{dt} = -Vbkc_A c_B \tag{13}$$

For the acid–base reaction, conversion of pH values to concentration profiles requires different expressions for the different operation modes studied. If A represents NaOH and B ethyl acetate, the only contribution to pH is due to the presence of NaOH, because the contribution of sodium acetate may be disregarded. In these conditions:

$$\mathrm{pOH} = -\log c_A \tag{14}$$

or else

$$c_A = 10^{(\mathrm{pH}-14)} \tag{15}$$

Otherwise for a batch reactor, the concentration can be expressed as:

$$c_A = c_{A0}(1-x) \tag{16}$$

From Eqs. (15) and (16):

$$x = \frac{c_{A0} - 10^{(\mathrm{pH}-14)}}{c_{A0}} \tag{17}$$

when a semibatch reactor is considered, the addition effect of reagent A on the initial concentrations of the mixture must be contemplated during the addition time:

$$c_{A1} = \frac{c_{A0} F_0 t}{V + F_0 t} \tag{18}$$

and

$$c_{B1} = c_{B0}\left(\frac{V}{V + F_0 t}\right) \tag{19}$$

when the feeding of NaOH is stopped the reactor operates in batch mode and the modelling equations are those previously indicated.

For the oxidation reaction and the adiabatic batch reactor, from the Eqs. (4) and (10) it is obtained:

$$\mathrm{d}T = \frac{\Delta H_r}{a\rho C_P}\mathrm{d}c_A \tag{20}$$

By integrating this equation, the following expression is obtained:

$$T - T_0 = -\frac{\Delta H_r c_{A0}}{a\rho C_P}x \tag{21}$$

where the difference between initial and final temperatures, when conversion is $x = 1$, is defined as ΔT_{ad}:

$$\Delta T_{ad} = -\frac{\Delta H_r c_{A0}}{a\rho C_P} \tag{22}$$

The Eq. (21) can be rewritten as:

$$x = \frac{T - T_0}{\Delta T_{ad}} \tag{23}$$

The concentration of different reactants and products can be obtained using expression (23).

The energy balance for batch reactor:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\Delta H_r k c_A c_B}{\rho C_P} - \frac{Q_M}{V\rho C_P} \tag{24}$$

The energy balance for semibatch reactor:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{F_0(T_{ad} - T)}{V} - \frac{\Delta H_r k c_A c_B}{\rho C_P} - \frac{Q_M}{V\rho C_P} \tag{25}$$

The energy balance for jacket wall of batch and semibatch reactor:

$$\frac{\mathrm{d}T_M}{\mathrm{d}t} = \frac{Q_M - Q_J}{V_M \rho_M C_M} \tag{26}$$

where

$$Q_M = h_i A_i (T - T_M) \tag{27}$$

and

$$Q_J = h_0 A_0 (T_M - T_J) \tag{28}$$

The energy balance for jacket fluid of batch and semibatch reactor:

$$\frac{\mathrm{d}T_J}{\mathrm{d}t} = \frac{F_W(T_{J0} - T_J)}{V_J} + \frac{Q_J}{V_J \rho_J C_J} \tag{29}$$

The behaviour of the jacket fluid has been considered as a perfect mixing as it is indicated by Luyben [14].

3. Plant description

The experimental measures of pH, conductivity, voltage and temperature have been obtained in a pilot scale reactor (Fig. 1). It consists of a 5 l glass-jacketed reactor provided with a data acquisition system based on GPIB bus and PC software.

The flow rate of the circulating fluid in the jacket may be prefixed or controlled by differential on–off valves, providing an alternative heating–cooling fluid (hot water or cold water). Table 1 indicates the state of the valves for the different modes of operation.

All physically available analogue inputs and outputs as well as all virtual channels are automatically monitored and

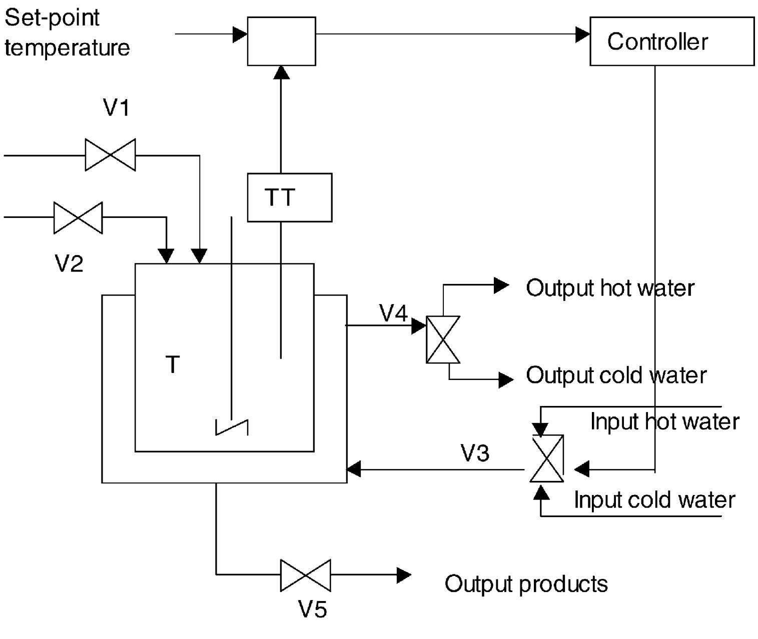

Fig. 1. Pilot plant.

Table 1
State of the valves

Valves	Action	I[a]	II[b]	III[c]
V1	Reactive A inlet	X	X (*)	
V2	Reactive B inlet	X		
V3	Jacket fluid inlet	X	X	
V4	Jacket fluid outlet	X	X	
V5	Products outlet			X

[a] Charge the reactor.
[b] Reaction development (*) only in semibatch mode.
[c] Empty the reactor (when the experiment is finished).

process values are stored. It is also possible to obtain on-line configured curves on the display screen.

4. Development of the experiments

Preliminary experiments to obtain the kinetic expression were carried out at different conditions for each reaction and in batch mode of operation.

Then, the two reactions indicated were carried out in the two modes of operation: batch and semibatch. For all the experiments, the jacket was filled with water circulating at a flow of $1.37 \times 10^{-5}\,\mathrm{m^3\,s^{-1}}$. The selected set-point temperature in the reactor was 308 K, and the volume of reactant A used was 1.3 l to mix with 2.7 l of reactant B, to obtain 4 l of reacting mass. Reactant A is NaOH in the saponification reaction and H_2O_2 in the oxidation reaction. Experiments 1 and 2 correspond to the saponification reaction in batch and semibatch mode of operation respectively, and Experiments 3 and 4 correspond to the oxidation reaction in batch and semibatch mode of operation respectively. Table 2 indicates the operation conditions. Experiments for the oxidation reaction were carried out in similar conditions for the reactant volumes to those used in the saponification experiments. In these conditions initial concentrations in the reactor are rather diluted. For the reaction of thiosulfate with hydrogen peroxide, several works (Szeifert et al. [15]) use more concentrated solutions with a ratio $c_{B0}/c_{A0} = 2/3$. Experiments 5 and 6 were examples of these conditions (Table 3). The initial concentrations of the reactants were half of those indicated in the table, because the volume of the two solutions was the same. These experiments were used to validate the mathematical model which was implemented in a software module written in FORTRAN 77 language. Experiments 7 and 8 were carried out with similar conditions to those of Experiment 5, but introducing the set-point temperature at 313 K.

Table 2
Operation conditions for Experiments 1–4

	Saponification reaction		Oxidation reaction	
	Experiment1	Experiment 2	Experiment 3	Experiment 4
T (K)	294.9	299.0	299.9	297.9
T_{J0} (K)	334.0	334.0	299.0	299.0
c_A (M)	1	1	1.2	1.2
c_B (M)	2	2	0.8	0.8
F_0 ($\mathrm{m^3\,s^{-1}}$)	–	7.4×10^{-7}	–	8.9×10^{-7}

Table 3
Operation conditions for Experiments 5–8

	T (K)	T_{set} (K)	T_{J0} (K)	c_A (M)	c_B (M)	F_0 ($\mathrm{m^3\,s^{-1}}$)
Experiment 5	293.2	–	293.5	1.2	0.8	3.1×10^{-6}
Experiment 6	293	–	293.9	1.2	0.8	4.7×10^{-6}
Experiment 7	293.5	313	294.1	1.2	0.8	3.1×10^{-6}
Experiment 8	293.2	313	294.2	1.2	0.8	3.1×10^{-6}

5. Results and discussion

The Arrhenius equation was obtained for the saponification and oxidation reactions. These results show a good agreement with those found by other investigators (Ortiz et al. [16]; Cohen and Spencer [7]). The two reactions show a very different reaction rate and thermal behaviour. Indeed, the oxidation reaction is faster than the saponification reaction because: $k_{0\,\mathrm{acid-base}} = 1.035 \times 10^6\,\mathrm{m^3\,kmol^{-1}\,s^{-1}}$, and $(E_a/R)_{\mathrm{acid-base}} = 4829.6\,\mathrm{K}$, in front of $8.13 \times 10^{11}\,\mathrm{m^3\,kmol^{-1}\,s^{-1}}$, and 9156 K for the oxidation reaction.

To compare the behaviour of the batch and semibatch mode of operation, the temperature profiles are shown in Fig. 2 for both reactions. For the saponification reaction, the initial slope and the over-shoot, in the batch mode, are much more pronounced than in semibatch mode. For the oxidation reaction, this difference is even more important. In the batch mode it is impossible to control the temperature evolution. For this reason this reaction will not be studied in this operation mode in this work. It is important to remark that for the saponification reaction the jacket fluid was initially hot

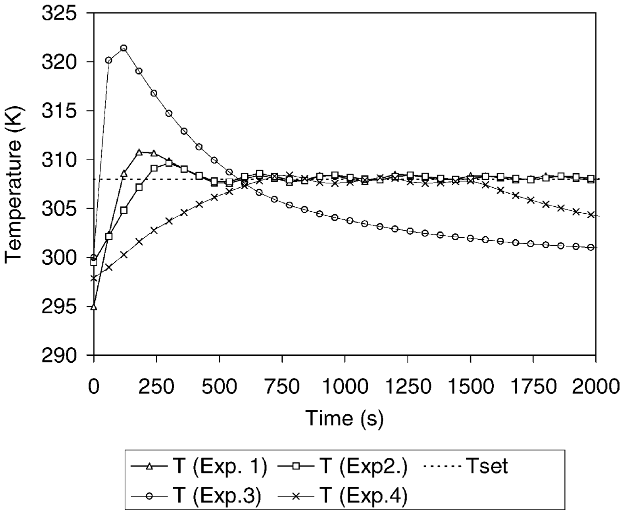

Fig. 2. Temperature profiles for Experiments 1–4.

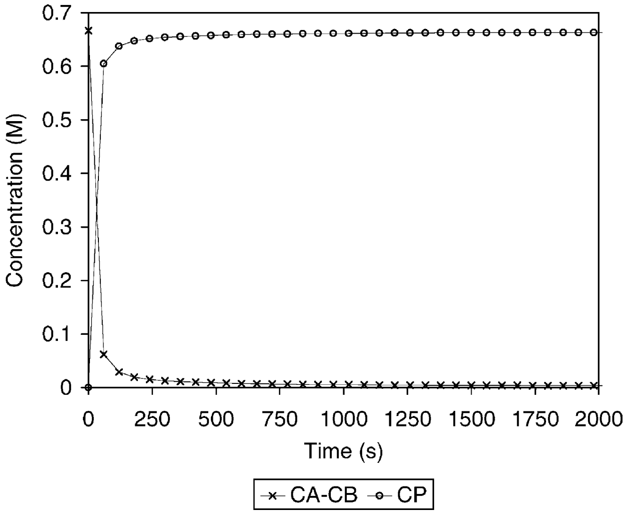

Fig. 3. Experimental concentration profiles for the batch reactor (saponification reaction, Experiment 1).

water (Table 2), because the reaction heat is very low and if jacket fluid would have been cold water, it would have not been possible to see the temperature rise.

To follow the concentration evolution of reactants, for the saponifaction reaction the pH was measured. Using Eqs. (14)–(19) it was possible to convert pH profiles into concentration profiles. The corresponding concentration evolution of reaction mixtures for batch and semibatch reactors is shown in Figs. 3 and 4, respectively. The feed of A is stopped after 1800 s when the stoichiometric input value is reached. It is possible to see the accumulation of NaOH added (C_A) in the reaction mixture. Once the maximum is reached, reaction evolution is similar to that of a batch reactor. With the same initial conditions, simulation was carried out based on mass balance equations (Eqs. (6)–(13)) as it is indicated in a previous work (Grau and Puigjaner [17]).

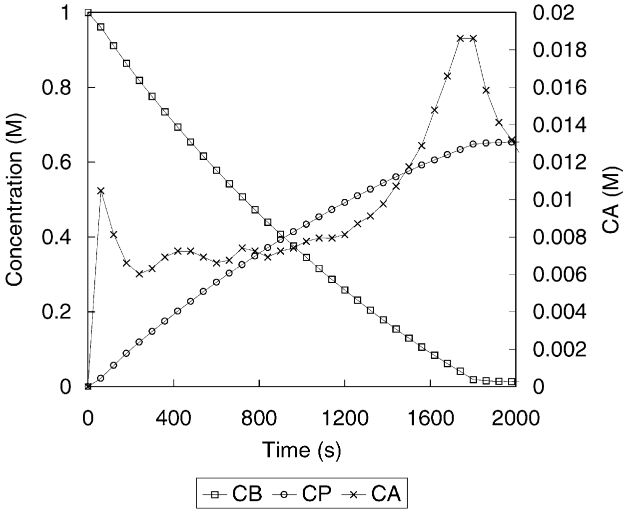

Fig. 4. Experimental concentration profiles for the semibatch reactor (saponification reaction, Experiment 2).

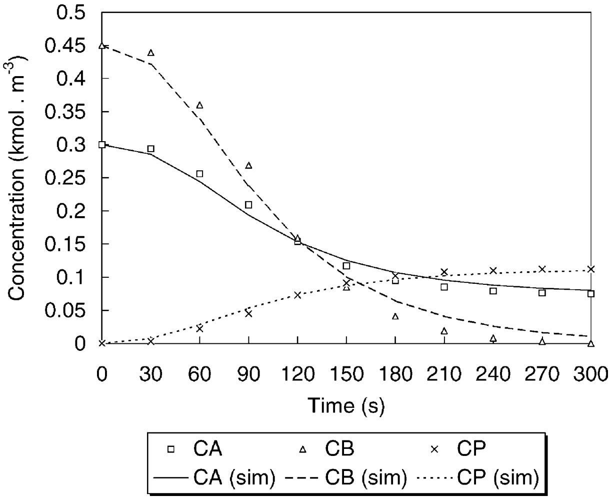

Fig. 5. Experimental and simulated concentration profiles for oxidation reaction (adiabatic mode).

Concentration profiles for the oxidation reaction using experimental data were obtained only for the adiabatic mode of operation. Using Eq. (23) the conversion was obtained at each time instant. The concentration profile of the reaction components is represented in Fig. 5. The mathematical model developed was validated with values of concentration obtained using experimental temperature profiles. The concentration profiles for the semibatch mode of operation were obtained by simulation. Previously, the mathematical model was validated using experimental temperature profiles. Fig. 6 shows a good agreement between experimental and simulated temperatures for Experiment 6 which operates with more concentrated reactants and maintaining the ratio $c_{B0}/c_{A0} = 2/3$. With the mathematical model already validated by simulation it was possible to obtain concentration profiles. It is very interesting to observe the accumulation of peroxide being added (Fig. 7). After 480 s all the

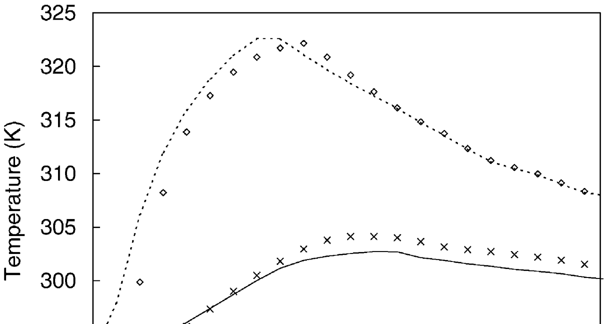

Fig. 6. Experimental and simulated temperature profiles for Experiment 6.

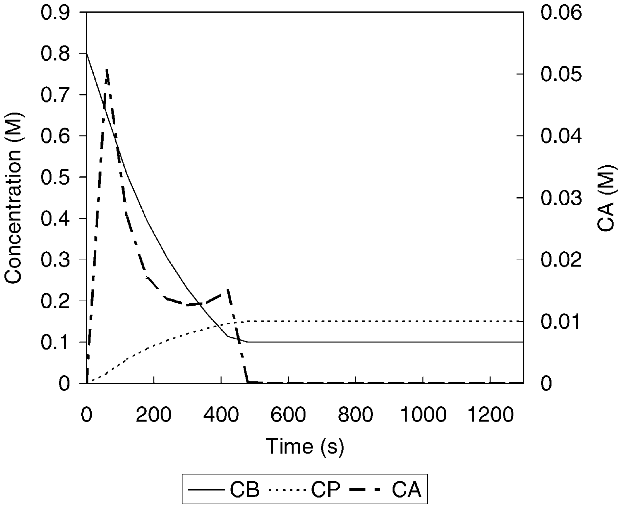

Fig. 7. Simulated concentration profiles for the oxidation reaction (semibatch reactor).

H_2O_2 is consumed and the concentration of $Na_2S_2O_3$ and products is 0.1 and 0.15 M, respectively.

Experiments 5 and 6 were carried out without changes in the jacket fluid, and without controlling the reactor temperature. When the set-point temperature was fixed (at 313 K) it was impossible to control the reaction temperature, in these operating conditions (Experiments 7 and 8), only by heat removal through the jacket fluid (Fig. 8), because the jacket is not able to remove the reaction heat.

For the same operating conditions (semibatch reactor) it was carried out an exhaustive study of the reaction between thiosulfate and hydrogen peroxide in a previous work (Grau et al. [18]). An optimization method was used to obtain the optimal temperature profile, using as variable the addition flow of peroxide.

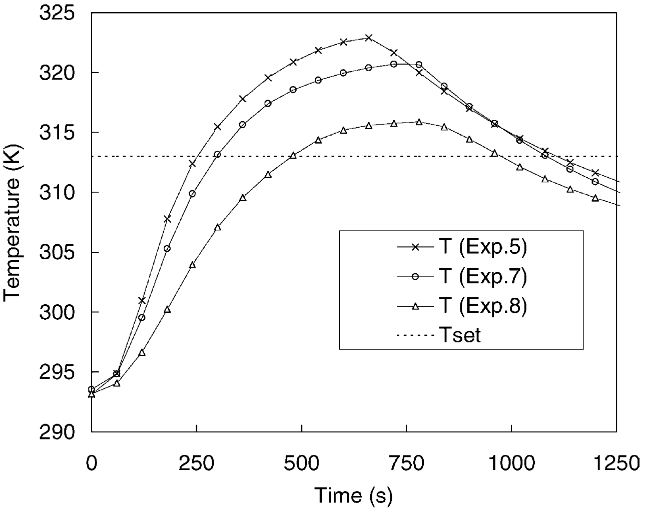

Fig. 8. Temperature profiles for oxidation reaction with set-point temperature.

6. Conclusions

Batch reactor operation has been compared with semibatch reactor operation for an acid–base low exothermic reaction, which was followed by pH measurement and for a very exothermic oxidation reaction. The results obtained show that for the saponification reaction it is possible to operate the reactor in both modes of operation (batch and semibatch). In the case of the oxidation reaction it is impossible to control the reaction temperature in batch mode, and only when the concentrations are very diluted it is possible to operate in semibatch mode by controlling the reaction temperature with the jacket fluid. In this case, when the reactants are more concentrated and the addition flow of peroxide is higher, it is necessary to use another parameter to control the reaction temperature: the addition flow of peroxide, because the heat-transfer is insufficient to remove the heat generated by the reaction. In all cases, the experimental results show a good agreement with the results obtained by simulation.

Concentration profiles are obtained for two reactions using different techniques. For the saponification reaction the concentration evolution with time of the different components has been obtained by means of experimental measures of the solution pH. In the case of oxidation reaction, only for the adiabatic mode of operation has been possible to obtain concentration profiles using experimental temperature profiles. A good agreement with the simulation results has been obtained, making it possible to validate the mathematical models developed. The knowledge of the concentration profiles is very interesting to understand the reaction behaviour. The methodology described provides an useful way for operation and control of batch and semibatch reactors, easy to implement in industrial practice.

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