

Online monitoring of an industrial semi-batch vinyl acetate polymerization reaction by programmable logic controllers

Fernando Aller*, L. Felipe Blázquez*, Luis J. Miguel**

*Department of Electrical and Automatic Control and Systems Engineering, University of León, E.I.I.I., Campus de Vegazana s/n, 24071 León, Spain. (Tel: 34 987293471; e-mail: {etcfma00,diefbq}@unileon.es).

**Department of Automatic Control and Systems Engineering, University of Valladolid, E.I.I., Paseo del Cauce s/n, 47011 Valladolid, Spain. (Tel: 34 983423545; e-mail: ljmiguel@eii.uva.es).

Abstract: This paper describes a virtual online monitoring of the non-measurable conditions inside a real-life industrial reactor for the production of polyvinyl acetate. These non-measurable conditions are the conversion, the polymerization rate, the viscosity and the solids content. The goal of this paper is to use them for control strategies, which can be implemented and solved in real time on common industrial programmable logic controllers (PLCs). Currently, these non-measurable conditions can be estimated from the measured variables by a detailed dynamic model, which is composed of a set of differential and algebraic equations, which can only be solved by means of iterative numerical methods. In this work, this model has been simplified and discretized to allow its implementation in industrial PLCs, which is the common practice in the industry. As a result, the PLC available at the factory can estimate the internal status of the reactor in real time with a high accuracy.

Keywords: Polyvinyl acetate; model reduction; inverse dynamic problem; real-time systems

1. INTRODUCTION

Semi-batch emulsion polymerization is one of the main processes employed for the production of polyvinyl acetate. Although it has been addressed in several studies, its control, optimization and repeatability, especially under industrial-scale conditions, remain as challenges. The control of the semi-batch emulsion polymerization of polyvinyl acetate has proved to be a difficult task due to the unknown conditions in the interior of the reactor. Laboratory scale reactors usually allow the sampling of the latex during the reaction. In industrial reactors, sampling is usually not allowed, both for safety and quality reasons. The exact measurement of the main variables of the process is not possible. To overcome this issue, calorimetric models and sensors have been proposed.

There are several studies at laboratory level which served as a basis for the development of the current work. Fevotte *et al.*, (1996a) developed an inferential measurement strategy for monitoring the conversion. It combined calorimetric data with gravimetric measurements. The measuring strategy was tested on a laboratory reactor. Later on, Fevotte *et al.*, (1996b) tested the use of two computers working in parallel to monitor, control and modify the polymer properties. In Fevotte *et al.*, (1998) the use of a non-linear observer which used an adaptive inferential calorimetric measurement scheme to obtain estimates of the evolution of the polymerization reaction was suggested. In all cases, computers connected to the process were needed to solve the

differential and algebraic equations. Saenz de Buruaga *et al.*, (1996) used reaction calorimetry to control emulsion polymerization reactors. That work was performed by connecting a commercial reactor calorimeter to an external computer which solved the equations. Zeaiter *et al.*, (2001) developed a first principles model to estimate the conversion during the reaction. The model was again solved by an external computer and tested on a laboratory scale reactor. Esposito *et al.*, (2010) showed that it was possible to obtain good in-line estimations of conversion without the use of experimental conversion data to re-estimate the heat transfer coefficient during the reaction. Rincón *et al.*, (2013) tested the performance of unscented and extended Kalman filters for the online monitoring of batch vinyl acetate polymerization reactions. The laboratory scale monitoring was solved by an external computer.

A lot of work has been done in estimating the conversion and other relevant variables in laboratory scale reactors. However, the developed models demand a high processing capacity and cannot be implemented in the programmable logic controllers (PLCs) usually available at real industrial facilities. This work aims to develop a simpler calorimetric estimator which can be solved in real time in industrial PLCs so that the calculated variables are available to the control strategies in real time. It takes previous works of the authors as a starting point, where the first principles model applied to an industrial scale reactor was presented (Aller *et al.*, 2007; Aller *et al.*, 2009); and where this model was completed and refined (Hvala *et al.*, 2011). The model proved reliable in the prediction of the final quality variables of the product and it

was shown to be useful for the control reactants feed rate. A calorimetric model was used to estimate the temperature profile, which allowed the offline validation of different control strategies and the selection of the most efficient one.

This paper is organized as follows. Section 2 describes the industrial polymerization process. Section 3 presents the complete calorimetric model corresponding to this process, based on a set of differential and algebraic equations. Section 4 explains the process followed to simplify and discretize the previous model. In Section 5, the results of the simplified model are presented and compared to results of the complete one. Section 6 gathers the conclusions, potential applications and future lines of research and finally some references are provided.

2. PROCESS DESCRIPTION

The process considered is the emulsion polymerization of vinyl acetate at the factory of Mitol in Sežana, Slovenia. Potassium persulfate is used as the initiator and polyvinyl alcohol as the protective colloid. The process is performed in a semi-batch, industrial reactor. A picture of the factory can be seen in Fig. 1.



Fig. 1: Industrial polymerization facilities.

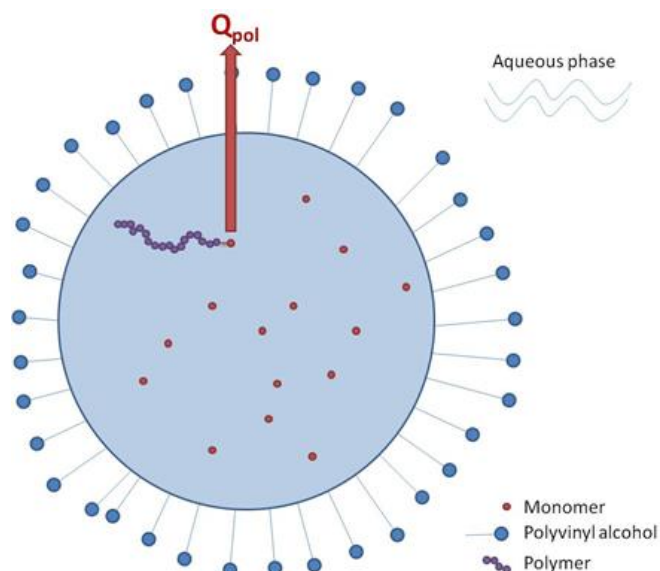


Fig. 2: Exothermic polymerization reaction.

Initial amounts of monomer, initiator, polyvinyl alcohol and water are added at the beginning of the process. The reactor is heated by pumping hot water into the heating jacket. Heating is stopped when the reactor reaches 338-343 K. The exothermic reaction, depicted in Fig. 2, and where Q_{pol} is the heat produced, keeps increasing the reactor temperature from this point. The temperature is used as an indicator, based upon the experience of the factory, to estimate that the conversion is high enough to start the addition of the remaining monomer. The monomer is pumped into the reactor with a continuous flow. The temperature of the added monomer is the external temperature.

The temperature inside the reactor is controlled by the addition of initiator when it starts to decrease. When all the monomer has been added to the reactor, a larger amount of initiator is added in order to terminate the reaction. The temperature is then allowed to reach 90°C, and the reaction is considered to be finished when the temperature starts to decrease again. The measured process-output variables are the conversion, the solids content and the viscosity. As can be seen, the temperature is used as an indirect estimation of the status of the reaction.

3. DIFFERENTIAL CALORIMETRIC MODEL

In this real life industrial polymerization process, only some external variables are measured. These variables are the temperature of the water going into and out of the heating jacket, the temperature of the water flowing through the condenser, both at the entrance and exit, the temperature inside the reactor, and the feed flows of monomer and initiator. Figure 3 shows a screenshot of the supervisory control and data acquisition (SCADA) system of the industrial polymerization reactor, where the measured variables can be observed.

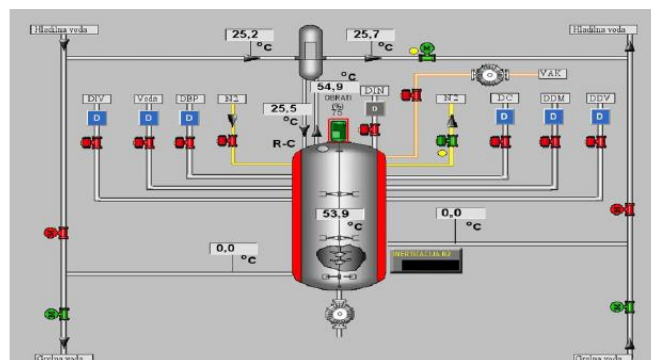


Fig. 3: SCADA screenshot of the industrial polymerization reactor.

None of these variables can be directly used to control the process, but we can calculate more relevant variables from them by means of the calorimetric model (Aller *et al.*, 2007; Aller *et al.*, 2009; Hvala *et al.*, 2011). This model consists of a set of differential and algebraic equations, which was initially used for the estimation of the temperature inside the reactor. The calculation of the temperature was needed to correctly assess the realism of the model and to test different

control strategies. It has proved useful to test different control strategies offline.

The work presented in this paper goes one step further and makes these variables available to the controller in real time. A calorimetric model based on a set of differential and algebraic equations can only be solved by numerical calculation programs and usually demands a high processing load. Industrial processes are mostly controlled by PLCs, with a limited calculation capacity. Since the reaction is not very fast, the approach presented in this paper is to try and replicate the estimations of the model by means of an exclusively algebraic model, which can be implemented and solved by industrial PLCs. In order to make this data available for the control strategies in real time, it has been necessary to reduce the model to a sequence of algebraic operations which can be solved directly in the PLC.

The reaction heat capacity K_R is represented at any time by (1), where M_i is the mass of reactant i , MW_i is its molecular mass and $C_{p,i}$ is the specific heat. The subindex i stands for the monomer (*mono*), polymer (*pol*), water and polyvinyl alcohol (*PVOH*).

$$K_R = M_m MW_m C_{p,mono} + M_{pol} MW_{pol} C_{p,pol} + M_w MW_w C_{p,water} + M_{PVOH} MW_{PVOH} C_{p,PVOH} \quad (1)$$

The derivative of the enthalpy provided by the heating jacket H_{jacket} during the initial phase is given by (2), where T_{jacket} is the temperature of the hot water through the reactor jacket, U is the heat transfer coefficient, A is the heat transfer area, and T_r is the temperature inside the reactor.

$$\frac{dH_{jacket}}{dt} = U \cdot A \cdot (T_{jacket} - T_r) \quad (2)$$

The monomer added to the reactor also adds energy to the reactor system. This variation of enthalpy H_{mono} is represented by (3), where q_{mono} is the feed flow rate of monomer and T_{mono} is its temperature.

$$\frac{dH_{mono}}{dt} = q_{mono} \cdot MW_m C_{p,mono} T_{mono} \quad (3)$$

The main addition of heat to the reactor is produced by the exothermic polymerization reaction. The heat of the polymerization H_{pol} is the product of the polymerization rate r_{pol} by the enthalpy of the polymerization h_r , as shown in (4). In the calorimetric model presented in the cooling of the reactor by the reflux through the condenser, Q_{cond} could not be calculated. There is no measurement available of the reflux flow rate or its temperature. The heat removed by the condenser was experimentally estimated and assigned a fixed value.

$$\frac{dH_{pol}}{dt} = h_r \cdot r_{pol} \quad (4)$$

The heat losses to the surroundings, H_{losses} , were modelled as shown in (5), where C_{losses} has been experimentally

determined and T_{ext} is the temperature outside the reactor. The enthalpy balance can be expressed as shown by (6).

$$\frac{dH_{losses}}{dt} = C_{losses} \cdot (T_r - T_{ext}) \quad (5)$$

$$K_R \frac{dT}{dt} + T \frac{dK_R}{dt} = \frac{dH_{mono}}{dt} + \frac{dH_{pol}}{dt} + \frac{dH_{cond}}{dt} + \frac{dH_{losses}}{dt} + \frac{dH_{jacket}}{dt} \quad (6)$$

4. CALORIMETRIC MODEL REDUCTION TO A SET OF ALGEBRAIC EQUATIONS

The model presented in the previous Section is inverted to use the real measures from the process sensors to calculate parameters representative of the status of the reaction and the batch. The resulting model is simplified and discretized to allow its solution in an industrial controller in real time. The variables presented in table 1 are measured at any moment i .

Table 1. Measured variables. Inputs

Variable	Description	Units
$T_{cond,in}^i$	Temperature of the cooling water at the entrance to the condenser	K
$T_{cond,out}^i$	Temperature of the cooling water at the entrance to the condenser	K
T_r^i	Temperature inside the reactor	K
q_{mono}^i	Monomer feed flow rate	Mol/s

Table 2. Variables used in the simplified model

Variable	Description	Units
k_r^i	Rate of increment of K_r	$J K^{-1} s^{-1}$
K_r^i	Reactor heat capacity	$J K^{-1}$
M_{conv}^i	Mass of monomer which has been converted into polymer	Mol
M_{tot}^i	Mass of monomer added in the reactor from the beginning	Mol
Q_{cond}^i	Heat removed by the reflux through the condenser	$J s^{-1}$
Q_{losses}^i	Heat losses to the surroundings of the reactor	$J s^{-1}$
q_{mono}^i	Monomer feed flow rate	$mol s^{-1}$
Q_{mono}^i	Heat added by the monomer feed	$J s^{-1}$
Q_{pol}^i	Heat produced by the polymerization exothermic reaction	$J s^{-1}$
Q_r^i	Total heat transfer in the reactor	$J s^{-1}$
r_{pol}^i	Polymerization rate	$mol s^{-1}$
sc	Solids content	dimensionless
T_{ext}^i	Temperature outside the reactor	K
T_{mono}^i	Temperature of the monomer fed into the reactor	K
T_r	Temperature inside the reactor	K
ν	Viscosity of the latex	Poise
X^i	Conversion	dimensionless

The inverse model calculates the change in the variables from one time interval to the next. In order to determine the absolute value of any of the variables, initial conditions must be provided. The mass of all components added in the initial stage is known from the recipe. The initial heat capacity of the reactor is calculated from the initial mass of the components from (7), where $C_{p,n}$ is the specific heat of material n , M_n is the initial mass of reactant n , and T_r is the temperature inside the reactor.

$$K_r^0 = \sum C_{p,n} \cdot M_n \cdot T_r \quad (7)$$

The initial temperature is 333 K. Since the estimation of the status of the reaction is meant for control purposes, the estimation will begin from the point when the polymerization starts. Polymerization begins with the decomposition of potassium persulfate at around 333 K. Finally, the initial value of the conversion is 0. The variables used in the discretized algebraic model are described in table 2.

4.1 Model reduction and discretization

The derivatives of enthalpy with respect to time are substituted by a heat variable Q_j , which is the rate of energy exchange due to the physical effect j , and is expressed in J/s. The heat added by the heating jacket Q_{jacket} has been neglected. Hot water is pumped through the heating jacket until the temperature reaches 338-343 K. The heat added to the reactor from the time when the estimation starts (333K) is negligible compared to that produced by the reaction itself. The heat removed by the reflux condenser Q_{cond}^i can be calculated through the heat absorbed by the cooling water flowing through it as expressed by (8), where Eff_{cond} is the efficiency of the condenser. This parameter has been experimentally set.

$$Q_{cond}^i = C_{p,water} q_w \frac{T_{cond,out}^i - T_{cond,in}^i}{Eff_{cond}} \quad (8)$$

The heat added to the reactor by the feed flow of monomer Q_{mono} is proportional to the temperature of the incoming monomer T_{mono} as shown in (9). Since the monomer is stored in tanks in a location close to the reactor, the temperature in the factory T_{ext} has been considered equal to the temperature of the raw monomer.

$$Q_{mono}^i = q_{mono}^i MW_m C_{p,mono} T_{mono}^i \quad (9)$$

In (10) the constant of losses C_{losses} to the environment has been experimentally set by the observation of the cooling of the reactor in the absence of other reactions or reflux through the condenser.

$$Q_{losses}^i = C_{losses} \cdot (T_r^i - T_{ext}^i) \quad (10)$$

The heat in the reactor Q_r , given by (11), changes due to two variables, the temperature in the reactor T_r and the heat capacity of the reactor K_r . In order to calculate Q_r we need to

calculate the heat capacity of the reactor K_r . It is calculated by adding the change in its value to the previous value as expressed by (12).

$$Q_r^i = K_r^i \cdot \frac{(T_r^i - T_r^{i-1})}{\Delta t} + k_r^i \cdot T_r^i \quad (11)$$

$$K_r^i = K_r^{i-1} + \Delta t \cdot k_r^i \quad (12)$$

The initial heat capacity of the reactor K_r^0 has been previously calculated according to (7). K_r changes at a rate k_r due to the addition of a feed flow of monomer q_{mono} and the conversion of monomer into polymer. Monomer and polymer have different specific heats, so the polymerization reaction changes the total specific heat of the reactor proportionally to the polymerization rate r_{pol} as (13) shows.

$$k_r^i = MW_m (q_{mono}^i + r_{pol}^i (C_{p,mono} - C_{p,pol})) \quad (13)$$

The heat balance expressed in (14) allows the calculation of the heat produced by the polymerization reaction.

$$Q_{pol}^i = Q_r^{i-1} + Q_{cond}^{i-1} + Q_{losses}^{i-1} + Q_{mono}^{i-1} \quad (14)$$

Since the heat produced by the exothermic polymerization reaction is a known parameter, the rate of polymerization r_{pol} can be calculated in turn by (15).

$$r_{pol}^i = \frac{Q_{pol}^i}{h_r} \quad (15)$$

The monomer converted into polymer is calculated by adding the product of the rate of polymerization by the time interval considered to its previous value, as (16) shows.

$$M_{conv}^i = M_{conv}^{i-1} + \Delta t \cdot r_{pol}^i \quad (16)$$

The total amount of monomer M_{tot} is calculated in (17) from its previous value and the feed flow rate of monomer q_{mono} during the time interval between samples.

$$M_{tot}^i = M_{tot}^{i-1} + \Delta t \cdot q_{mono}^i \quad (17)$$

From these variables, we can easily calculate the main variables which provide insight into the reactor status in real time. The conversion is the current fraction of monomer converted into polymer. It is expressed by (18).

$$X^i = \frac{M_{conv}^i}{M_{tot}^i} \quad (18)$$

The quality of the final product is mainly expressed by the solids content and the viscosity. These variables can also be monitored in real time. The solids content is expressed as the sum of the weights of the polymer and the polyvinyl alcohol divided by the total weight of the latex, as (19) shows. The viscosity is estimated by (20), given by Immanuel *et al.*, (2003). Table 3 describes the values of the parameters used in the previous formulas.

$$SC = \frac{M_{conv} \cdot MW_{mono} + M_{PVOH} \cdot MW_{PVOH}}{M_{tot} \cdot MW_{mono} + M_{PVOH} \cdot MW_{PVOH} + M_{water} \cdot MW_{water}} \quad (19)$$

$$\vartheta = \frac{\vartheta_0}{\left(1 - \frac{sc}{sc_{ref}}\right)^2} \quad (20)$$

Table 3. Parameters

Parameter	Description	Value
$C_{p,water}$	Specific heat of the water	$4.18 \text{ J g}^{-1} \text{ K}^{-1}$
Eff_{cond}	Condenser efficiency	0.88
M_n	Mass of raw material n	-
MW_m	Vinyl acetate molecular weight	86.09 g mol^{-1}
$C_{p,mono}$	Vinyl acetate specific heat	$1.17 \text{ J g}^{-1} \text{ K}^{-1}$
C_{losses}	Reactor heat losses constant	175.2 J K^{-1}
$C_{p,pol}$	Polyvinyl acetate specific heat	$1.77 \text{ J g}^{-1} \text{ K}^{-1}$
h_r	Heat of polymerization	87.5 KJ mol^{-1}
sc_{ref}	Adjustable parameter	1.09
Δt	Time interval	5 s
ν_0	Viscosity of the water at 80°C	0.355 poise

5. RESULTS AND DISCUSSION

The model calculates the variables at discrete intervals Δt . The polymerization reaction takes several hours and changes are not very abrupt. For this reason, a Δt of 5 seconds has been considered to be sufficient. The conversion calculated by the simplified model has been compared to the results of the complete calorimetric model presented in Section 3. The results are fairly equal, as can be seen in Fig. 4.

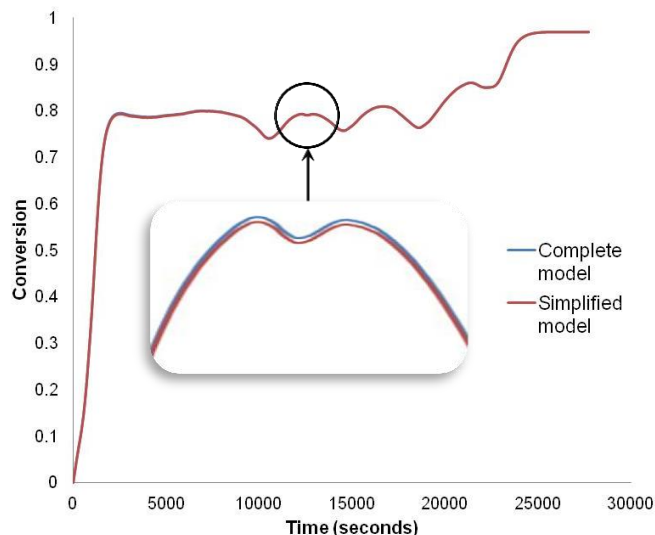


Fig. 4. Conversion profile estimated by the complete model and by the simplified algebraic model.

The results are so close that it is not possible to appreciate the difference. For the sake of clarity, Fig. 5 depicts the percentage of difference in the estimation of the conversion given by (21). The error is higher in the beginning, mainly due to the removal of the heat provided by the heating jacket.

However, the error is still so low (below 0.5%) that it confirms that this variable has been correctly neglected.

$$Error = \frac{X_{complete} - X_{simplified}}{X_{complete}} \cdot 100 \quad (21)$$

The online monitoring of the conversion provides a powerful tool for the development of control algorithms, but it is not the only parameter that we can make available to the PLC to implement control strategies. Figure 6 shows the polymerization rate during the reaction. The impulsive slopes show the moments of addition of initiator. A smoother addition of the initiator should achieve a more controllable temperature inside the reactor.

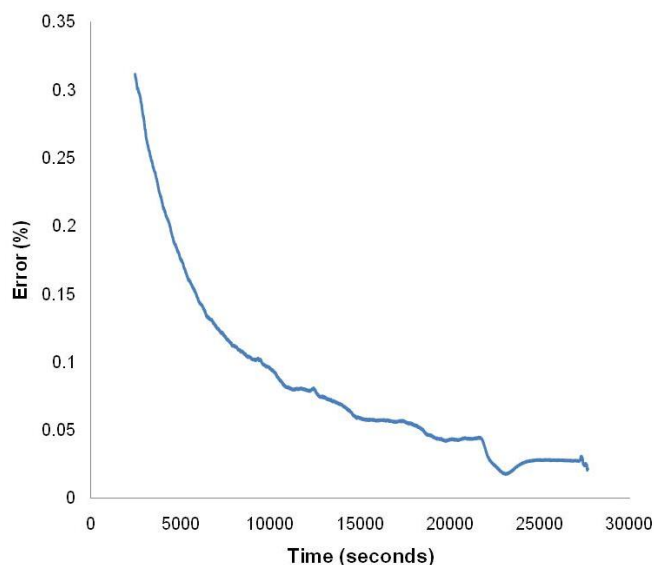


Fig. 5: Percentage of difference between the complete model and the simplified model.

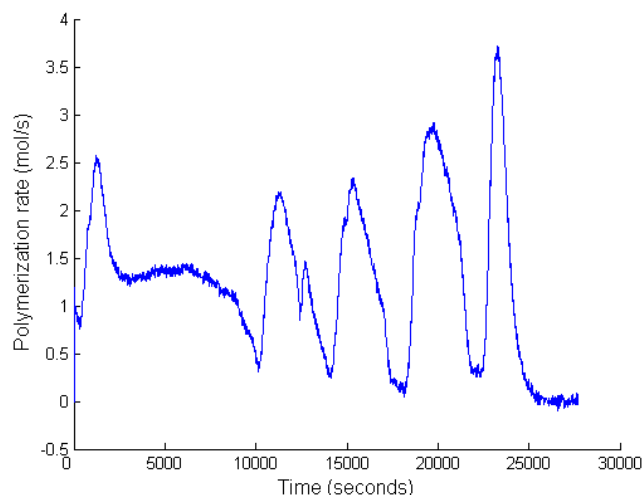


Fig. 6: Polymerization rate profile estimated by the simplified algebraic model.

The quality parameters can also be monitored in real time. This would allow to test that they are inside acceptable margins based upon experience with batches with good results. Figure 7 shows the solids content profile, and Fig. 8 depicts the evolution of the viscosity.

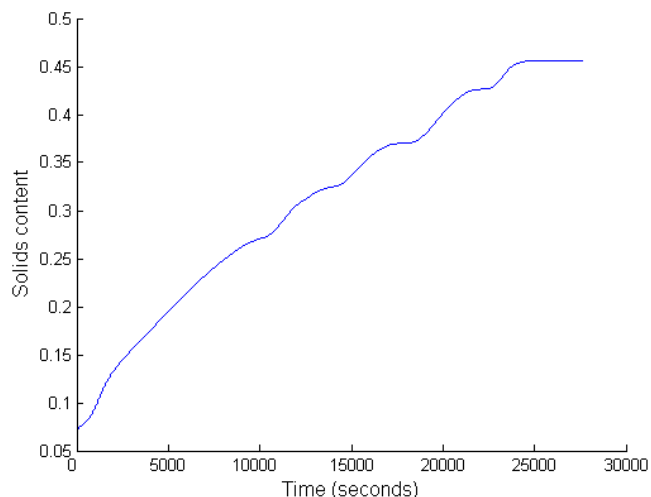


Fig. 7. Solids content profile estimated by the simplified algebraic model.

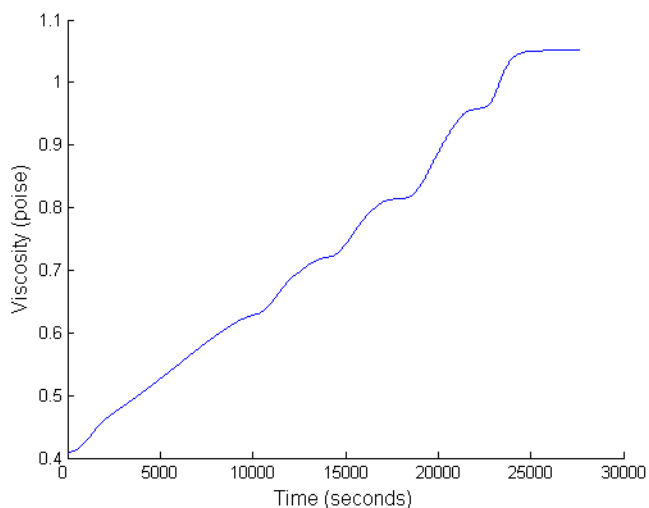


Fig. 8. Viscosity profile estimated by the simplified algebraic model.

6. CONCLUSIONS

The calorimetric model of an industrial polymerization reaction has been inverted to allow the calculation of the internal variables of the reaction. It allowed the calculation of the profiles of such variables as the conversion, polymerization rate, solids content or viscosity from the measured variables. However, it was made on a set of differential and algebraic equations, so it could be used for offline testing of control strategies, but not for the control of the reaction.

Thus, the inverse calorimetric model has been simplified and discretized to allow its solution by conventional PLCs which are the common practice in the industry. The results have been compared to those obtained by the complete set of differential and algebraic equations and found acceptable. It opens the door to the development and implementation of real time control strategies based upon the internal variables of the reactor in industrial scale reactors.

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