

FEEDBACK CONTROL OF INDUSTRIAL SOLUTION POLYMERIZATION OF ACRYLIC ACID USING NIR MEASUREMENTS

Othman¹, N., Egraz², J.B., Sau², J.M., Févotte¹, G.

¹LAGEP, UMR CNRS Q5007, Université Lyon 1, 43 bld. Du 11 novembre 1918, 69100 Villeurbanne. FRANCE. ²COATEX, ZI Lyon Nord. 69727 Genay. FRANCE

Abstract: In situ Near Infrared spectroscopy is used to monitor and control the concentration of monomer in solution polymerization processes. The Partial Least Square optimization technique is used to correlate the NIR spectrum with the concentrations of monomer and polymer in the reactor. Non linear input-output linearizing geometric control is then designed to control the concentration of monomer in the reactor. Controlling the concentration of monomer has a direct influence on the product quality and is very important to ensure the process safety. The control strategy is validated on-line during the solution polymerization of acrylic acid in an industrial pilot-scale reactor.
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1. INTRODUCTION

Recently, NIR (Near InfraRed) spectroscopy has found a wide spread use in the monitoring of polymerization processes since it presents several significant advantages. First of all, the fibre optic probe inserted in an existing reactor is directly in contact with the reaction medium, which ensures rapid measurements, without requiring any sample preparation. In aggressive industrial environments, fibre optics allow the spectrometer to be placed far away from the reactor and ensure rapid and accurate data transmission. Furthermore, a set of characteristics of the reacting medium can be evaluated in-line from the NIR spectrum by developing calibration models that can be transferred easily to other instruments.

The quality of the results of the NIR analysis depends on a number of arguments. In order to ensure good results, the impact of the required properties in the selected NIR region must be important. Moreover, the off-line measurements used for the calibration must be accurate and reliable. Finally, the performance of the instrument and the

mathematical treatment of the spectrum have to be adapted to the process.

Many applications of NIR spectroscopy in polymerization processes deal with the on-line monitoring of the concentration of monomer in reactors. Long et al. (1993) employed the NIR spectroscopy to estimate the conversion of styrene in solution polymerizations. On-line monitoring of the conversion of methyl methacrylate was studied by Chabot et al. (2000) and Aldridge et al. (1993) in emulsion polymerization systems.

NIR spectroscopy can also be used to estimate physical properties in real time. Gossen et al. (1993), applied the NIR spectroscopy to estimate the concentration of styrene and the particle size in an emulsion polymerization. Santos et al. (1998) used the NIR to estimate the particle size distribution in suspension polymerizations of styrene. They used the PLS (Partial Least Square) and Neural networks to correlate the absorbance with the particle size. These results allowed the authors to develop a technique for controlling the particle size distribution in a batch process (Santos et al., 2000).

In this work we are interested in controlling the concentration of acrylic acid in an industrial solution

polymerization reactor. In this case, the polymerization reaction is very fast and exothermic. Controlling the concentration of monomer is therefore essential to ensure the process safety through the mastery of the heat release of the reaction. Moreover, the concentration profile of the monomer in the reactor strongly influences the product quality – mainly the polymer molecular weight – during homopolymerization reactions, and the polymer composition during copolymerization processes so that suitable and reproducible concentration trajectories are required to ensure satisfactory and reproducible polymer properties. In order to ensure such control, a calibration model based on the NIR spectra was developed and validated to estimate the concentrations of monomer and polymer in the reactor. The measurement strategy is presented in the first part of the paper. In a second part, an estimator of the reaction rate is designed which is necessary to apply closed loop control strategies. Finally, a non linear geometric approach is developed to control the concentration of monomer during the reaction.

2. NIR MEASUREMENT STRATEGY

2.1 Experimental setup

The polymerization process is carried out in a 30 L jacketed well mixed reactor equipped with internal reflux condenser. The stirrer is equipped with a Rushton turbine, the stirring rate being 150 rpm. The reactor is operated under semi batch conditions: four volumetric pumps are used to feed the reactor with solvent, homogeneous catalyst, radical initiator and monomer. The four corresponding flow rates can be controlled on-line through the measurement of the mass of reactants and the manipulation of the set point flow rates of the pumps. The reactants initially fed in the load of the reactor are first heated using the jacket. After the starting of the reaction, the fluid in the jacket is used as a coolant since the process is very exothermal. The main temperatures of the plant are measured using Pt100 Ω probes. The acquisition and storage of the measurements (Temperatures and flow rates) is performed using a first computer equipped with Labview®. The state observer and the control law described below, which use the NIR measurements of the concentration of acrylic acid, are computed and applied using the same computer. The NIR transmission probe is immersed in the reactor, it is connected through fibre optics to a FOSS NIRSystems® industrial spectrometer; and the spectral data are acquired and processes by a second computer. Both computers are connected in order to exchange data.

With the process in question, the production of polyacrylic acid is performed following a rather complex operating policy including various heating, feeding and curing periods. The overall processing time is of the order of 2 hours. For the sake of confidentiality, no more details will be given about the operating procedure.

2.2 In-line NIR measurements of the conversion of acrylic acid

The NIR spectrum reflects the energy absorbed or reflected by the molecules present in any chemical medium crossed by a NIR light beam. For any wavelength, the energy absorbed by the molecules depends on the chemical and physical nature of the constituents, on their concentrations and on the volume of transmission. Some energy is also partly reflected without absorbance.

The near infrared spectral region, which covers the range from 700 to 2500 nm, expresses much of the chemical and structural information on the reaction medium, but the information tends to be in broad and overlapped bands. The processing of NIR spectral data was shown to allow the real-time evaluation of key parameters such as monomer concentration(s) or potential fluctuations of the quality of raw materials or to evaluate more specific variables such as the acid value during polyester production, density and melt index of polyethylene, the average particle diameter during emulsion or suspension polymerization processes; or the polymer composition during extrusion processes. Due to the variety and the complexity of the NIR spectral data, it is necessary to use "black-box" and multivariate data-processing models in order to extract the criterion of interest among the whole of the information contained in the recorded spectra. The "parameters" of such models are computed from a calibration data set and should be validated thereafter. The success of further on-line predictions depends on various criteria: the sampling technique, the off-line measurement method which was used and finally, the processing algorithm applied to the spectrum in order to draw the appropriate criterion.

It appeared that the main time variations in the spectrum during the polymerization under investigation can be observed between 1600 and 1900 nm. Fig.1 shows the difference between the spectrum obtained at the beginning of a semi-continuous polymerization of acrylic acid and that obtained 2 hours later. A PLS model was developed to correlate the spectrum with off-line measurements of the concentrations of acrylic acid, obtained through HPLC (High Pressure Liquid Chromatography) and of polyacrylic acid, obtained after heating the polymer solution at 140°C.

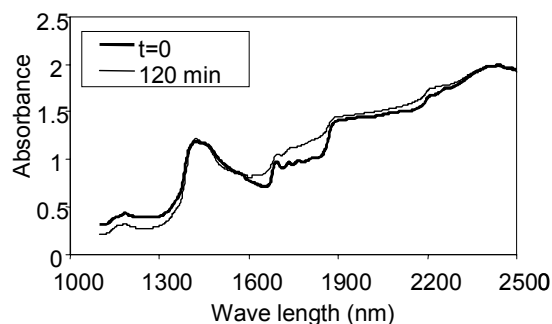


Fig. 1. NIR spectrum obtained at the beginning of a semi-continuous polymerization of acrylic acid and spectrum 2 hours later.

The “calibration model” was validated through the measurement of additional samples which were not taken into account during the calibration procedure. Fig. 2 displays the concentration values predicted using the calibration model against the calibration data set. Despite significant differences in the operating conditions involved during the acquisition of these data, the “measurements” appear to be rather reliable.

For validation purposes, NIR measurements were then performed during semi-batch and continuous polymerization reactions. Fig. 3 shows the in-line measurements obtained during the validation experiments.

The same calibration strategy was also applied to estimate the concentration of polymer in the reactor. In this case, the off-line calibration measurements were obtained through the gravimetric evaluation of the dry content. Figs. 3 and 4 display the validation results which were obtained, using the PLS model, during two polymerization operations. Samples were withdrawn from the reactor to assess the accuracy of the NIR estimates. As one can see, the in-line measurements of both acrylic acid concentration and polymer content were found to be really satisfactory.

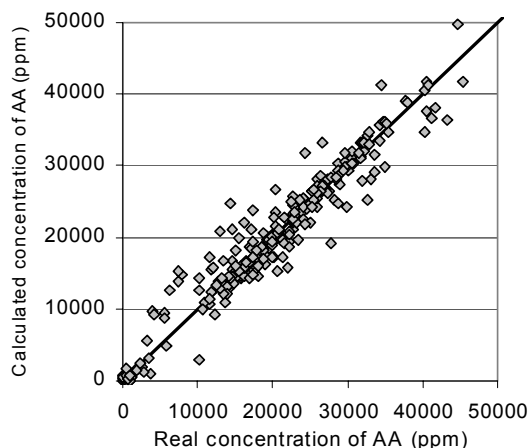


Fig. 2. Validation of the NIR calibration model. Estimation of the concentration of monomer during both semi-continuous and continuous reactions.

3. IN-LINE ESTIMATION OF THE POLYMERIZATION RATE

3.1 Simplified kinetic modeling of the polymerization reaction

The radical polymerization of acrylic acid is performed in aqueous solution. For the sake of confidentiality, the reactants which are used as co-solvents, catalyst and chain transfer agents will not be revealed in the present paper. The consumption of acrylic acid (AA) during the process can be described as follows:

$$\begin{aligned} \frac{dN_{AA}}{dt} &= Q_{AA}^{in} - R_p \\ &= Q_{AA}^{in} - \underbrace{k_p [R^*] N_{AA}}_{\text{propagation rate}} \end{aligned} \quad (1)$$

where N_{AA} is the number of moles of AA, Q_{AA}^{in} is the inlet molar flow rates of AA (mol/s), R_p is the reaction rate (mol/cm³), k_p is the propagation rate constant (cm³/mol/s), and $[R^*]$ is the concentration of radicals (mol/cm³).

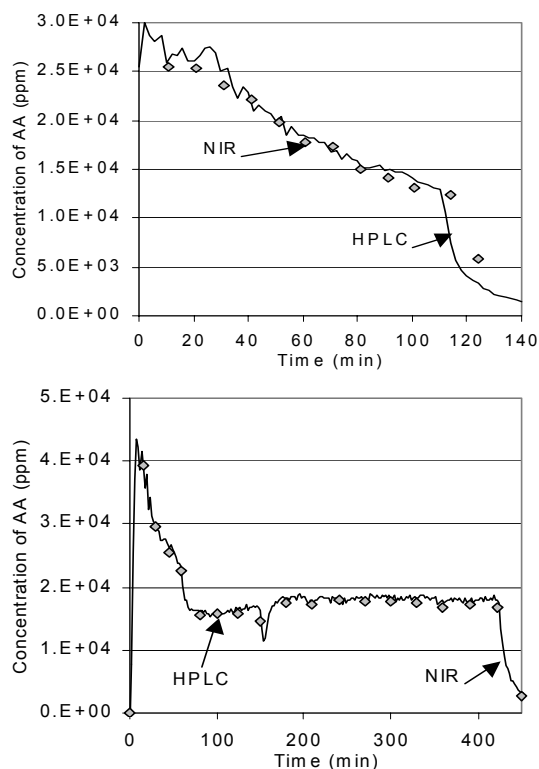


Fig. 3. Validation of the NIR calibration model: measurement of the concentration of monomer during both semi-continuous and continuous reactions.

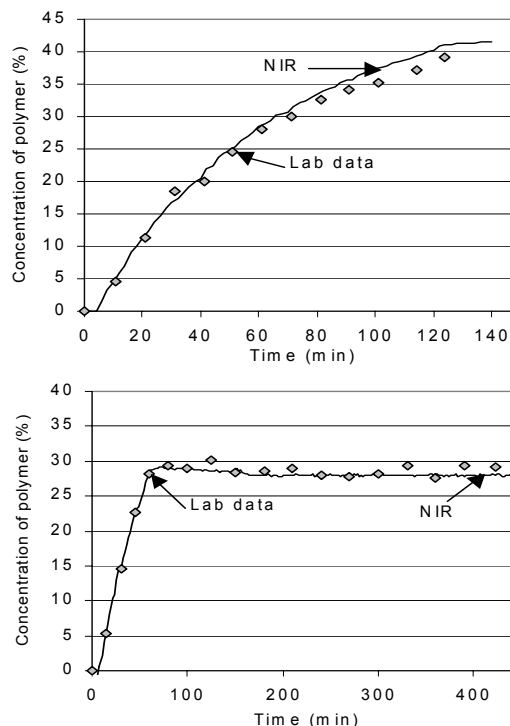


Fig. 4. Validation of the NIR calibration model: measurement of the polymer content during both semi-continuous and continuous reactions.

Expression (1) appears as a very simple, first order (with respect to AA), kinetic equation. However, whatever the reaction medium, it is well known that the polymerization in question is far from being simple as both the propagation rate constant and the concentration of radicals are likely to be significantly time varying, according to the concentration of reactants and products, complex pH variations and temperature.

For control purposes, and from an industrial point of view, it is not necessarily relevant to try a complex knowledge-based chemical modelling of the reacting system. Indeed, in the industrial context, efficient control can be designed without time-consuming and expensive theoretical studies. This is the reason why the reaction rate was estimated on-line, rather than predicted using any advanced model of the reaction.

3.2 A non linear high gain observer of the reaction rate of acrylic acid

The measurement of the concentration of monomer obtained by the NIR analysis allows us to estimate the reaction rate and, if the reaction rate constant is known, to estimate the concentration of radicals in the reactor $[R^*]$. In order to estimate the reaction rate of monomer, we set the following system where R_p is considered as a state variable with unknown dynamics:

$$\begin{bmatrix} \dot{N}_{AA} \\ \dot{R}_p \end{bmatrix} = \begin{bmatrix} Q_{AA}^{in} \\ 0 \end{bmatrix} + \underbrace{\begin{bmatrix} 1 & -1 \\ 0 & 0 \end{bmatrix}}_A \begin{bmatrix} N_{AA} \\ R_p \end{bmatrix} + \begin{bmatrix} 0 \\ \varepsilon \end{bmatrix} \quad (2)$$

ε represents the unknown dynamic of R_p .

A change of coordinates is required to put the system under a canonical form of observability. As the number of moles of acrylic acid is measured, we can use a high gain observer (see e.g., Farza et al., 1997, McKenna et al., 2000) to estimate the reaction rate as follows:

$$\begin{bmatrix} \dot{\hat{N}}_{AA} \\ \dot{\hat{R}}_p \end{bmatrix} = \begin{bmatrix} Q_{AA}^{in} \\ 0 \end{bmatrix} + \underbrace{\begin{bmatrix} 1 & -1 \\ 0 & 0 \end{bmatrix}}_A \begin{bmatrix} N_{AA} \\ \hat{R}_p \end{bmatrix} - \begin{bmatrix} 2\theta \\ \theta^2 \end{bmatrix} (\hat{N}_{AA} - N_{AA}) \quad (3)$$

The rate of convergence of the observer is very easy to tune using the single positive parameter θ .

The estimation results are shown on Fig. 5 for a semi-continuous reaction. Due to the operating conditions involved, it appears that the reaction rate is equal to the flow rate of monomer. This means that the monomer inlet feed rate in the reactor can be increased to allow improved productivity: the reaction is so fast that there is no monomer accumulation during the reaction. Moreover, the propagation rate coefficient is constant since pH does not change during the reaction. Consequently, the concentration of radicals is found to be constant during all the reaction time.

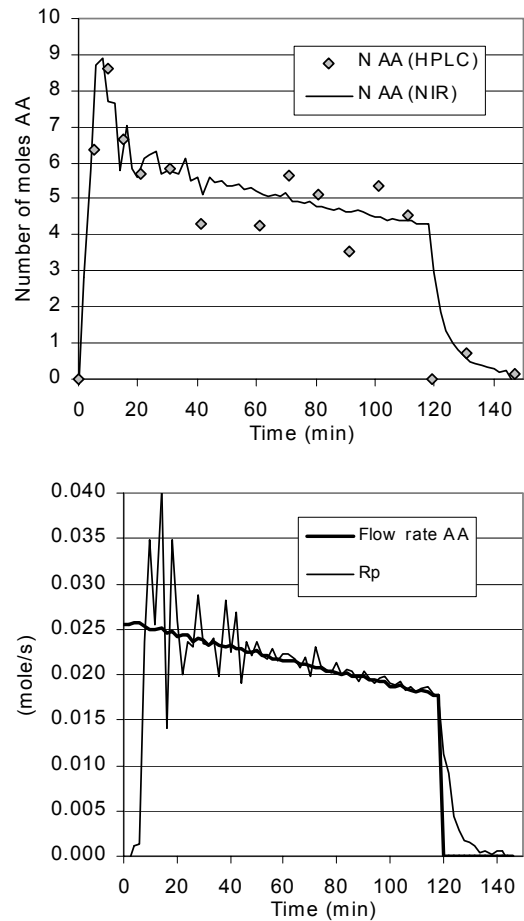


Fig. 5. State estimation of R_p in a semi-continuous reaction based on the on-line NIR measurement of the number of moles of acrylic acid, N_{AA} .

4. FEEDBACK CONTROL OF THE CONCENTRATION OF ACRYLIC ACID

Controlling the concentration of acrylic acid in the reactor allows us to maximize the process productivity by decreasing the reaction time while ensuring the process thermal safety. Actually, the polymerization of AA is very exothermic and fast. The amount of monomer in the reactor must therefore be calculated in a way that the cooling system remains able to evacuate the heat produced by the polymerization and allows to maintain the desired reaction temperature. Again, the amount of monomer in the reactor can be obtained using on-line NIR analysis and can be controlled by manipulating the inlet flow rate of monomer. The whole control system is schematically presented in Fig. 6.

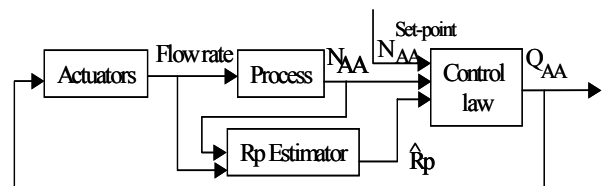


Fig. 6. Closed-loop system for the control of the monomer concentration during the semi-batch polymerization of acrylic acid, with state estimation of the polymerization rate R_p .

In order to design the controller, the following system is considered:

$$\begin{aligned} \dot{N}_{AA} &= Q_{AA}^{in} - R_P(N_{AA}) \\ y &= N_{AA} \end{aligned} \quad (4)$$

Since system (4) is nonlinear, a differential geometric nonlinear controller was designed in order to control N_{AA} . The adaptation of differential geometry for the analysis and design of nonlinear control systems was proposed by Herman and Krener (1977), Hunt et al. (1983) and Isidori (1989). The results generalize concepts and tools from linear control theory for a class of nonlinear systems, such as the state feedback.

The GLC framework is the calculation of a static-state feedback, under which the closed-loop I/O system is exactly linear. The state of the model need not to be transformed into linear one. Once the inner loop is closed, the controller design reduces to the design of an external linear controller with integral action.

The relative order, or the linearizability index r , of nonlinear systems can be calculated, as for linear systems, by calculating the derivative of the output. The relative order is the smallest order of derivative that depends explicitly on the input (Q_{AA}). For system (4), the relative order is equal to one. A geometric nonlinear input/output linearizing control can therefore be constructed as given by the following system :

$$Q_{AA}^{in} = R_P + \underbrace{\kappa_p}_{\varepsilon=error} (N_{AA}^{set-point} - N_{AA}) \quad (5)$$

We notice that controlling N_{AA} requires the estimation of R_P that we obtain from the high gain observer.

A set of experiments with different set-points was performed in order to validate the controller robustness. During experiment 170 the set point varies smoothly. Fig. 7 shows that N_{AA} takes some time to converge to the desired value. This dynamic behaviour is mainly due to the fact that there is no monomer in the initial charge. The delay in the convergence can therefore be improved by introducing an amount of monomer in the initial charge. However, this can be critical during the heating phase, especially in an industrial reactor. On the other hand, the delay in convergence is amplified by the inhibition during the few first minutes of the reaction and the rapid change in the reaction rate when the reaction starts. Moreover, the convergence time is influenced by some inaccuracies of the NIR measurements, especially when the amount of monomer is small at the beginning of the reaction.

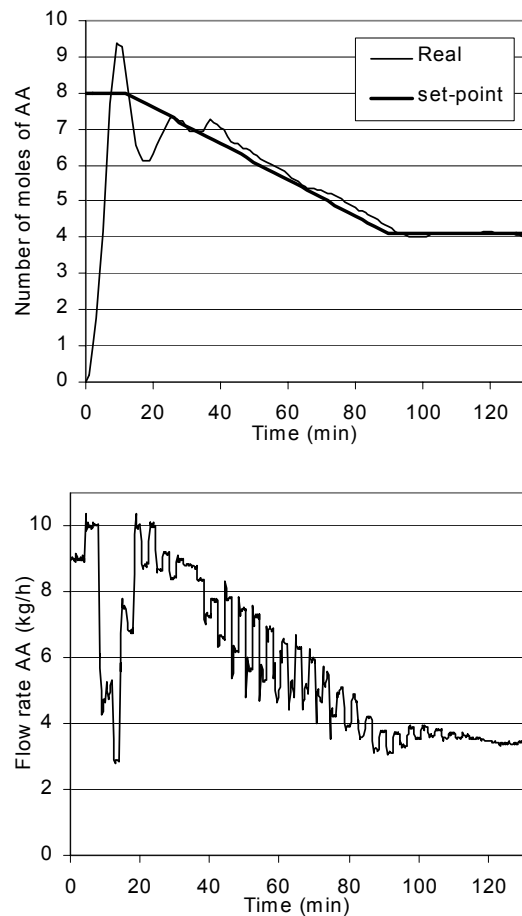


Fig. 7. Control of N_{AA} during experiment n°170. Tracking of trajectory for N_{AA} . The manipulated input is the inlet flow rate of AA.

In order to demonstrate that the convergence time is mainly due to physical limitations, and not to the controller itself, two experiments (referred to as run 173 and run 174 below) were performed with stiff changes in the set-point during the reaction. A step change of 1 and 1.5 moles are imposed during experiments 173 and 174, respectively. These experiments allowed us to assess the robustness of the controller under hard conditions even though such conditions are not supposed to occur during real industrial processing.

The obtained results are shown in Figs. 8 and 9.

From these figures, it can be observed that performances and closed-loop response of the controller are not the same at the beginning of the reaction compared with the rest of the polymerization process. The number of moles of acrylic acid N_{AA} converges more satisfactorily (i.e. fast convergence without oscillations) to the set-point during the reaction even with an important change in the set-point. This is due to the fact that once the reaction started, the reaction rate varies smoothly and allows the NIR measurements to be more precise.

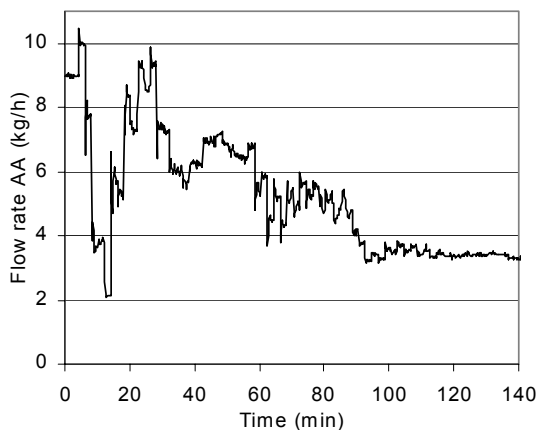
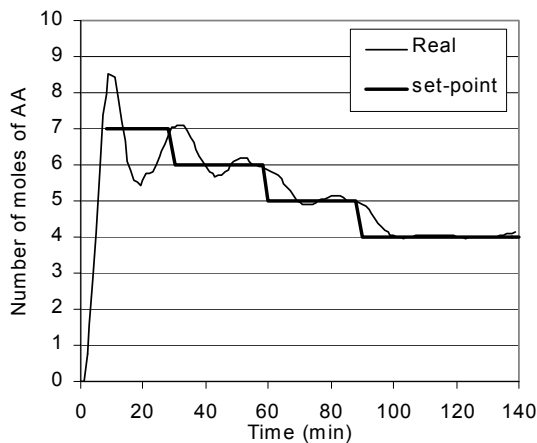


Fig. 8 Control of N_{AA} during Run 173: number of moles of AA and controlled flow rate of AA.

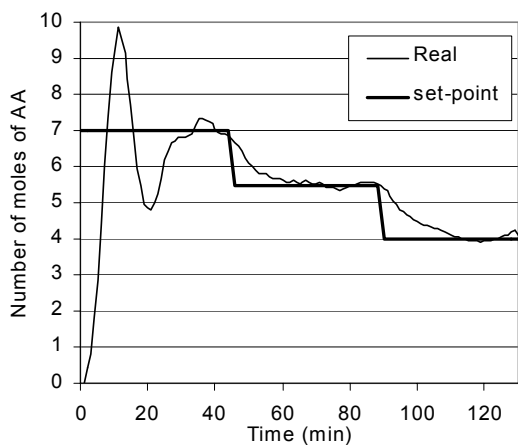


Fig. 8 Control of N_{AA} during Run 174: number of moles of AA and controlled flow rate of AA.

CONCLUSION

The control strategy developed in this work has been validated on an industrial pilot-scale reactor, taking into account real industrial constraints, in terms of aggressive environment and complex operating strategies). The control strategy gave good results even under hard conditions. In particular, it allowed to maintain the concentration of monomer in the reactor at a predefined value, which was calculated in such a way such the heat produced by the polymerization reaction did not affect the reaction temperature. Controlling the concentration of monomer in the reactor also allowed improving the

mastery over the obtained polymer molecular weights, which is a key product property in this process. Such mastery, notably in terms of improved reproducibility, represents a major economical issue. It is worth noting that such application was made possible thanks to the availability of new in situ NIR sensors, which are certainly destined for numerous future industrial applications in the field of chemical processes.

REFERENCES

- Aldridge, P., K.; J. J., Kelly; B. Callis. (1993) Noninvasive monitoring of bulk polymerization using short-wavelength near-infrared spectroscopy, *Analytical Chem.*, **65**, 381-3585.
- Chabot, P., L., Hedli; Ch. Olmstead. (1993) On-line monitoring of emulsion polymerization, AT-Process, *J. Proc. Analytical Chem.*, **2000**, 1-6.
- Farza, M., H., Hammouri, S., Othman, K., Busawon (1997) Nonlinear Observers for Parameter Estimation in Bioprocesses. *Chem. Eng. Sci.*, **23**, 52, 4251-4267.
- Gossen, P.D., J.F., MacGregor; R.H., Pelton (1993) Composition and particle diameter for styrene/methyl methacrylate copolymer latex using UV and NIR spectroscopy, *Applied spectroscopy*, **47**, 11.
- Herman, R. and A., Krener. (1977) Nonlinear controllability and observability, *IEEE Trans. Aut. Cont.*, **AC-22**, 5.
- Hunt, R., Su, G., Meyer. (1983) Global transformations of nonlinear systems, *IEEE Trans. Aut. Cont.*, 1983, **AC-28**, 24-31.
- Isidori, A., (1989) Nonlinear control systems. An introduction (2nd Edition), Springer-Verlag, Berlin.
- Long T.E., H.Y., B., Liu, A., Schell, D.M., Teegarden, D. S. Uerz. (1993) Determining of solution kinetics by NIR infrared spectroscopy. 1. Living anionic polymerization processes, *Macromolecules*, **26**, 6237-6242.
- McKenna, T.F., S., Othman, G., Fevotte, A.M. Santos, H. Hammouri (2000) An integrated approach to polymer reaction engineering: a Review of Calorimetry and State Estimation. *Polym. React. Engng*, **8**, 1-38.
- Santos, A.F., E.L., Lima, J.C., Pinto (1998) In-line evaluation of average particle size in styrene suspension polymerizations using near-infrared spectroscopy, *J. Appl. Polym. Sci.*, **70**, 1737.
- Santos, A.S., E.L., Lima, J.C., Pinto (2000) Control and Design of average particle size in styrene suspension polymerizations using NIRS, *J. Appl. Polym. Sci.*, **77**, 453-462.