CALORIMETRIC ESTIMATION OF VISCOSITY AND ACID NUMBER IN ALKYD REACTORS

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Abstract: In the industrial operation of batch alkyd polymerization reactors, the process evolution is monitored by measuring the acidity and the viscosity of samples withdrawn from the reactor. The synthesis is stopped at the maximum yield allowed by the gelation point of the cold product. In this work, a software sensor that estimates the C(cold)-viscosity and the conversion of acid groups on the basis of the continuous measurement of the heat exchange rate between a continuous stirred vessel appended to the reactor and a cooling coil is designed and experimentally tested. The identification of the underlying time-varying observability property yields the designs of the heat exchange devise and of the corresponding robust nonlinear geometric observer. The resulting software sensor is experimentally tested in a pilot plant reactor. *Copyright© 2003 IFAC.*

Keywords: polymer reactor, cold-viscosity, acid number, alkyd reactor, calorimetric estimator, nonlinear observer, software sensor.

1. INTRODUCTION

Oil-modified polyesters, commonly known as alkyd resins, have a high demand as coating resins due to their low production cost and variety of properties (durability, color retention, brightness, etc.). Commonly, an industrial batch alkyd cook is monitored, controlled and stopped on the basis of discrete-delayed measurements of acidity and C(cold)-viscosity. The acidity measures the conversion of monomers into polymer, and the C-viscosity reflects the complex branched molecular architecture of the polymer. The batch must be stopped at a certain conversion below the gelation point of the cold product. A drift from the prescribed C-viscosity trajectory signifies that the polymer structure is drifting from its nominal value, and an abrupt change means that the cook is running away from its nominal motion. Recently, on-line continuous measurements of C-viscosity have been considered (Händel, 1996) to improve the monitoring and control schemes via a continuous sampling-cooling loop with a viscosimeter. However, this scheme has the drawback of the investment and maintenance costs associated to the *in situ* operation of a viscosimeter instrument.

Due to the lack of reliable kinetic models and the uncertainty of the monomers structure (Patton, 1962), the standard nonlinear extended Kalman filter and Luenberguer model-based observer techniques (Eliçabe and Meira, 1988; Mutha *et al.*, 1997; Alvarez and López, 1999, Ellis *et al.* 1994) cannot be directly applied to alkyd reactors. To overcome this problem, López *et al.* (2000) designed a geometric estimator on the basis of an uncertain kinetic model augmented with an observable (i.e., adjustable) parameter and discrete-delayed measurements of C-viscosity, according to the robust geometric estimator design presented in Hernández and Alvarez (2003). This study with experimental testing established the feasibility of using a model-based observer to yield present estimates and time-ahead predictions of C-viscosity and acid conversion, and recommended the development of software sensors based on indirect C-viscosity measurements to improve the estimation-prediction scheme. On the other hand, the calorimetric estimation technique has been extensively and successfully used to estimate and control variables in solution and emulsion polymer reactors (Sáenz de Buruaga *et al*., 2000; Othman *et al*., 2001; Zaldo *et al*. 2002 and references there in). In particular, Zaldo *et al*. (2002) estimated the heat generation rate and the heat exchange coefficient on the basis of temperature and flow measurements.

In this paper the problem of designing and experimentally testing a heat exchange devise to infer the C-viscosity and the acid conversion in an alkyd reactor is addressed. The underlying time-varying nonlinear observability property is identified, yielding the design of the heat exchange devise and the construction of the corresponding nonlinear observer with a robust convergence criterion coupled to a simple tuning scheme.

2. SOFTWARE SENSOR DESIGN PROBLEM

Consider the alkyd reactor presented in Figure 1, where fatty acids, polybasic acids, and polyols are terpolymerized via an endothermic polyesterification reaction. Since the polymerization reaction is endothermic, heat must be added to maintain a constant temperature (typically 240 °C), and water product must be removed to favor the reaction advance. In an industrial reactor, the monitoring of viscosity and acidity is periodically executed with a 30 to 60 minutes delay period between the sample acquisition and its analysis in the laboratory. These results in conjunction with a calibrated C-viscosity (referred to 25°C) versus acid group conversion chart are employed in an advisory type control scheme to decide on corrective additions of acid groups, to predict the gelation point of the cold product, and to decide the end of the batch. In principle, the overall reactor performance should benefit from the passage from this advisory control scheme towards one more systematic with continuous measurements or suitable estimates and with feedback control actions, and this is the motivation for the consideration of an on-line C-viscosimeter (Händel, 1996).

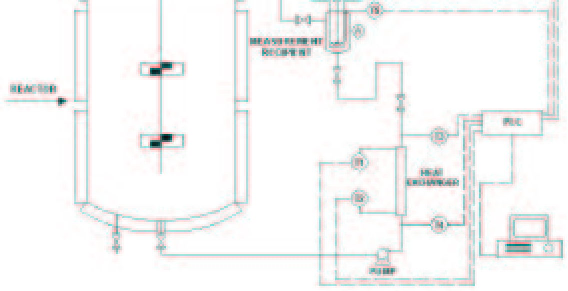

Figure. 1. Software sensor system

In this work, the main idea is the replacement of the aforementioned on-line viscosimeter by the heat exchange device (A) shown in Figure 1. The proposed hardware consists of a continuous sampling recirculation loop equipped with a heat exchanger to cool the resin down to a suitable temperature T_v and a stirred vessel with a cooling coil, so that the measured heat exchange rate

$$y = w_j\, c_{pj}\, (T_{ji} - T_{jo}) \qquad (1)$$

reflects the C-viscosity of the resin in the vessel. w_j is the mass flow rate of cooling water, c_{pj} is its specific heat capacity, and T_{ji} (or T_{jo}) is its inlet (or outlet) temperature. From a steady-sate heat balance follows that the total heat exchange rate between the resin in the test vessel and its cooling coil is given by

$$\begin{aligned} Q &= U(\mu, \mu_w)\, (\pi D_o\, L_c)\, \tau\, (T_v, T_{ji}, T_{jo}) \qquad (2a)\\ &:= \theta\, (c, T_v, T_{ji}, T_{jo}, p_\theta) \end{aligned}$$

where D_o (or L_c) is the coil outside diameter (or length), τ is the log-mean temperature difference, and U is the global heat transfer coefficient (Oldshue, 1983):

$$U(\mu, \mu_w) = [1/h_r(\mu, \mu_w) + (r_2/r_1)\,(1/h_j)]^{-1} \qquad (2b)$$

$$h_r(\mu, \mu_w) = a_h\, (k_r/D)\, [R_e(\mu)]^{b_h} [P_r(\mu)]^{c_h} [\mu/\mu_w]^{d_h} \qquad (2c)$$

$$P_r(\mu) = (\mu c_{pr}/k_r), \qquad R_e(\mu) = (D^2 N\rho/\mu) \qquad (2d)$$

$$\tau\, (T_v, T_{ji}, T_{jo}) = (T_{ji} - T_{jo})/\ln[(T_v - T_{ji})/(T_v - T_{jo})] \qquad (2e)$$

$$T_j = T_v - \tau\, (T_v, T_{ji}, T_{jo}) : = ?\ (T_v, T_{ji}, T_{jo}) \qquad (2f)$$

$$T_w = T_j - Q/[h_j\, (\pi D_i\, L_c)] := \iota\, (T_v, T_{ji}, T_{jo}) \qquad (2g)$$

$$p_\theta = [c_{pr}, c_{pj}, D_i, D_o, D, h_j, k_r, L_c, N, \rho, \rho_j\,]'$$

h_r is the resin heat transfer coefficient, h_j is the coil-fluid heat transfer coefficient, r_1 (or r_2) is the coil outside and inside radius, D is the vessel diameter, D_i is the coil inside diameter, k_r is the resin conductivity, T_j is the coil-fluid mean temperature, μ is the resin viscosity at the vessel temperature T_v, μ_w is the resin viscosity at the temperature T_w of coil wall, P_r is the Prandtl number, and R_e is the Reynolds number.

The resin viscosity depends on the temperature (T) and the acid conversion (c) via the free volume-type expression:

$$\begin{aligned} \mu = \exp\{&a_\eta(T) + b_\eta(T)\ln[A_0(1-c)] \qquad (3)\\ &+ c_\eta(T)\,[\ln (A_0\,(1-c))]^2\} := \alpha(c, A_0, T, p_\eta), \end{aligned}$$

$$c = 1 - A/A_0, \qquad p_\eta = [a_\eta, b_\eta, c_\eta]'$$

A is the acid number (i.e., mg of KOH required to neutralize one g of resin), A_0 is its initial value, and c is the related conversion. p_η is the parameter vector of the relationship viscosity-conversion.

Our hardware sensor problem consists in choosing the dimension, geometry, mixing pattern, stirring, and mass flow (w_r) of the stirred vessel as well as the material, diameter, length, and cooling fluid inlet temperature of the coil. Our software problem consists in designing a robust nonlinear observer that yields estimates of the C-viscosity (η) and of the conversion (c):

$$\eta = \alpha(c, A_0, T_v, p_\eta) \qquad (4)$$

Methodologically speaking, we are interested in identifying a physically interpreting the nonlinear time-varying observability property that underlies the hardware and software designs of the finite-time batch alkyd polymer reactor.

3. ESTIMATION MODEL

Phenomenological second and third apparent-order models have been employed in alkyd kinetic studies (Flory, 1953; Lin and Hsieh, 1977; Aigbodion and Okieimen, 1996), and none of the existing models apply to the entire course of the reaction. Any of these models with an adjustable (i.e. observable) constant leads to a third order nonlinear estimator (López et. al. 2000). To reduce the model order by one, let us recall a well-known fact in alkyd kinetic studies and industrial reactor operation: at constant temperature, the C-viscosity increases exponentially with time. It means that, in C-viscosity coordinate Eq. (4), the third-order conversion model can be replaced by the following second-order model:

$$\dot{\eta} = k\,\eta, \qquad \eta(0) = \eta_0 \qquad (5a)$$

$$\dot{k} = u_k(t) = v_k\,[\eta, A_0, T_v, \dot{T}_v, w, \dot{w}, p_\kappa] \approx 0, \qquad (5b)$$

$$y = h(\eta, d, p), \qquad c = \beta(\eta, A_0, T_v, p_\eta) \qquad (5c,d)$$

where w is a set of unmodeled variables related to the polymer molecular architecture, p_κ is a parameter vector associated to reaction rate, and β is the inverse map of the map α (Eq. 4) with respect to c. It is,

$$\beta[\alpha(c,A_0,T_v,p_\eta),T_v,p_\eta] = c \qquad (6)$$

Finally, h is the heat rate exchange measurement map θ Eq. (2a) expressed in C-viscosity coordinate (η):

$$h(\eta, d, p) = \theta[\beta(\eta, A_0, T_v, p_\eta), T_{ji}, T_{jo}, p_\theta] \qquad (7)$$

In vector notation, the estimation model (5) is given by

$$\dot{x} = f(x), \qquad x(0) = x_0,\ 0 \le t \le t_f \qquad (8a)$$

$$y = H[x, d(t), p], \qquad c = B(x, p_\eta) \qquad (8b)$$

where

$$x = (\eta, k)', \qquad d = [T_v, T_{ji}, T_{jo}]', \qquad p = [p_\theta, p_\eta]'$$

$$f(x) = (k\eta, 0)', \quad H[x, d(t), p] = h(\eta, d, p)$$

$$B(x, p_\eta) = \beta(\eta, A_0, T_v, p_\eta)$$

Since the maps f, H and B are continuously differentiable, a given data triplet $[x_0, d(t), p]$ uniquely determines a state motion x(t) and an output trajectory y(t):

$$x(t) = \tau_x[t, 0, x_0, d(t), p], \quad 0 \le t \le t_f \qquad (9a)$$

$$y(t) = H[x(t), d(t), p] \qquad (9b)$$

4. OBSERVABILITY PROPERTY

In this section is characterized the time-varying nonlinear observability property that underlies the solvability of the hardware and software design problems.

From the definition of nonlinear motion observability given in Alvarez and López, (1999) and Hernandez and Alvarez (2003), the observability property is defined for one particular finite-time motion x(t), or equivalently, for one particular input-output realization [y(t)-d(t)] of the batch reactor. The reactor motion x(t) is observable if at each time t, the state x(t) is uniquely determined by the measurement y(t) and its time derivative, or equivalently, if the state x(t) is the unique solution of the algebraic equation pair at time t:

$$y = h(\eta, d, p) := \phi_1(\eta, d, p), \quad \delta = (d, \dot{d}) \qquad (10a)$$

$$\dot{y} = [\partial_\eta h(\eta, d, p)]k\eta + [\partial_d h(\eta, d, p)]\dot{d} := \phi_2(\eta, k, \delta, p) \qquad (10b)$$

or

$$\psi = \phi(x, \delta, p), \quad \psi = (y, \dot{y}), \quad \phi = (\phi_1, \phi_2) \qquad (10c)$$

From the local inverse theorem (Isidori, 1995), follows that this equation has a unique solution for x if the *nonlinear observability matrix*

$$O(x, \delta, p) = \partial_x \phi(x, \delta, p) = \begin{bmatrix} \partial_\eta h(\eta,d,p) & 0 \\ \sigma(x,d,p) & \eta\,\partial_\eta h(\eta,d,p) \end{bmatrix} \qquad (11)$$

$$\sigma(x, d, p) = \partial_\eta \phi_2(\eta, k, \delta, p) = k[\eta\,\partial_{\eta\eta} h(\eta, d, p) +$$

$$\partial_\eta h(\eta, d, p)] + [\partial_{d\eta} h(\eta, d, p)]\, \dot{d}$$

is nonsingular along the reactor motion x(t). The determinant (det) of O and its ∞-norm) minimum singular value (*msv*) s are given by

$$\det[O(\eta, d, p)] = \eta[\partial_\eta h(\eta, d, p)]^2$$
$$\text{msv}[O(\eta, d, p)] := s(\eta, d, p) = \partial_\eta h(\eta, d, p)$$

Thus, the motion x(t) is locally (nominally) observable if

$$\partial_\eta h[\eta(t), d(t), p] \neq 0 \;\; \forall\, t \in [0, t_f]$$

Let X_0 and D are sets of perturbed initial and exogenous inputs about x(t) and d(t), respectively:

$$X_0 = \{\hat{x}_0 \mid |\hat{x}_0 - x_0| \leq \delta_0\}, \quad D = \{\hat{d}(t) \mid \|\hat{d}(t) - d(t)\| \leq \delta_d\}$$
$$\|\hat{d}(t) - d(t)\| = \max_{[t,\, t_f]} |\hat{d}(t) - d(t)|$$

where |x| is the norm of x, and δ_0 (or δ_d) is the radius of X_0 (or D). Let X be the corresponding bundle set o perturbed motions $[\hat{x}(t)]$ about x(t)

$$X = \{\hat{x}(t) = \tau_x[t, 0, \hat{x}_0, \hat{d}(\cdot), p], 0 \leq t \leq t_f \mid [\hat{x}_0, \hat{d}(t)]$$
$$\in X_0 \times D, \; \|\hat{x}(t) - x(t)\| \leq \varepsilon_x(\delta_0, \delta_d)\}, \; \varepsilon_x(0, 0) = 0$$

with $\varepsilon_x(\delta_o, \delta_d)$ being the radius of X. According to the definition of practical (i.e., no local) observability given in Alvarez *et al.* (2000), the (unperturbed) motion x(t), or equivalently, its uniquely associated input-output realization [d(t)-y(t)], is robustly observable for X (determined by X_0 xD) and a given lower bound s_* for the msv of the observability matrix if the following inequality is met

$$\partial_\eta h[\hat{\eta}(t), \hat{d}(t), p] > s_*, \;\; \forall\, [\hat{x}(t), d(t)] \,\varepsilon\, X \times D \qquad (12)$$

The fulfillment of this robust detectability property signifies that the reactor state motion x(t) can be robustly reconstructed via a nonlinear observer (Alvarez and López, 1999), with a measurement error (in y and h) propagation proportional to $1/s_*$.

Once the robust observability condition is met, the design of the corresponding geometric (i.e., Luenberguer-type) nonlinear observer follows from a straightforward construction-tuning scheme. This subject will be further discussed in subsection 5.3.

On physical grounds, the resin viscosity $\mu(c, T)$ decreases with temperature; the heat exchange rate h increases with temperature. The dependency ($\partial_\eta h$) of h on the C-viscosity (at T_v) η diminishes with the increase of the vessel temperature T_v, meaning that this temperature T_v must be set sufficiently low to yield an admissible sensitivity of the heat exchange rate with respect to acid conversion changes along the course of the reaction, or equivalently, to adequately meet the robust motion observability condition Eq. (12). On the other hand, the considerations of mixing and flow through pipe impose restrictions on the lowest resin temperature that can be reached in the sample vessel. Thus, the hardware design problem amounts to finding a vessel temperature T_v that represents a suitable compromise between the fulfillment of the robust observability condition Eq. (12) and the handling of a cold (i.e., viscous) resin fluid in the vessel and pipes of the sampling circulation loop. This subject on the hardware design will be discussed in subsection 5.1.

5. SOFTWARE SENSOR DESIGN

5.1. Experimental setting (Hardware design)

In order to calibrate the estimation model, an initial alkyd polymerization was carried out at 210 °C in an 80 L reactor with the system shown in Figure 1. The reactor was loaded with a mixture of fatty acids, phthalic anhydride, glycerine, and pentaerytritol. For industrial confidentiality reasons, the composition of initial load cannot be revealed. Following previous reports (Händel, 1996), the sample vessel temperature was set at T = 125 °C. At the reactor high temperature (210 °C), the term $\partial_\eta h$ in the observability condition Eq. (12) is very small, meaning that the model observability is very poor. Consequently, the resin temperature had to be decreased to increase the value of $\partial_\eta h$ and have adequate sensitivity. It was verified that the vessel temperature T_v = 125 °C was an adequate value to meet the robust observability condition with a manageable flowrate in the recirculation loop.

The kind of vessel stirrer and its revolutions per minute N, as well as the baffles were chosen according to standard design mixing equipment considerations (Oldshue, 1983), enhancing the macromixing for heat exchange purposes. The inlet coil water temperature was fixed at T_{ji} = 20 °C. The coil diameter was fixed at D_o, and an initial value for the jacket fluid flow-coil length pair $(w_j\text{-}L_c)_0$ was chosen according to the aforementioned heat transfer correlations, in the understanding that this pair will be adjusted in order to adequately meet the robust observability condition Eq. (12). The temperature of the vessel and the input and output temperatures of the coil were on line measured and the heat exchange rate was measured. Samples of the resin were taken from the reactor and off-line analyzed: the C-viscosity is measured with an ICI cone-plate viscosimeter over the temperature range of [100, 150°C, i.e., bracketing the one of 125 °C reported by Händel (1996)], and the acid number was determined by KOH titration.

5.2. Model calibration

The C-viscosity at different temperatures and acid number measurements obtained from the samples were fed to a nonlinear regressor, yielding the coefficients of the free-volume type (Eq. 3) nonlinear map α (Eq. 4):

$$a_\eta(T) = 3477.99/(T + 273) - 3.1815$$
$$b_\eta(T) = -456.961/(T + 273) - 1.9603$$
$$c_\eta(T) = -185.203/(T + 273) + 1.1656$$

From the measured heat exchange values, the parameters of the heat exchange coefficient expression (Eq. 2c) were adjusted, obtaining the following results for this equation,

$$a_h = 1.178\ ,\ b_h = 2/3,\ c_h = 1/3\ ,\ d_h = 0.14$$

Finally, it was found that the agitation due to the recirculation loop amounted to an effective stirred speed (N) of 200 rpm (i.e. 30 rpm more than in the case without recirculation.)

5.3. Software design

Given the nonlinear nonsingular observability matrix (Eq. 11), and having designed the hardware so that the robust observability condition Eq. (12) is adequately met in the light of equipment specifications and restrictions, the construction of the corresponding geometric nonlinear observer follows from a straightforward application of the procedure given in Alvarez and López (1999):

$$\dot{\hat{x}} = f[\hat{x}, d(t), p_e] + G[\hat{x}, d(t), p_e]\{y - h[\hat{x}, d(t), p_e]\}$$
$$G(\hat{x}, d, p_e) = [O^{-1}(\hat{x}, \delta, p)]\ k_e\ (\zeta, \omega)'$$
$$k_e\ (\zeta, \omega) = (2\zeta\omega, \omega^2)$$

where G is a nonlinear gain matrix, ζ (or ω) is the damping (frequency) adjustable parameter of the output error response. The estimator converges if the celerity parameter is chosen so that the following inequality is met:

$$\omega > 2\zeta(\partial_\eta\phi_2)/(\partial_\eta h)$$

In detailed form, the estimator is given by

$$\dot{\hat{\eta}} = \hat{k}\hat{\eta} + g_\eta[\hat{\eta}, d(t), \zeta, \omega, p_e]\{y - h[\hat{\eta}, d(t), p_e]\} \quad (13a)$$

$$\dot{\hat{k}} = g_k[\hat{\eta}, d(t), \zeta, \omega, p_e]\{y - h[\hat{\eta}, d(t), p_e]\} \quad (13b)$$

$$\hat{c} = \beta(\hat{\eta}, A_0, T_v, p_\eta) \quad (13c)$$

where

$$g_\eta(\eta, d, \zeta, \omega, p_e) = 2\zeta\omega/[\partial_\eta h\ (\eta, d, \zeta, \omega, p_e)]$$
$$g_k(\eta, d, \zeta, \omega, p_e) \approx \omega^2/[\eta\partial_\eta h\ (\eta, d, \zeta, \omega, p_e)]$$

$$\zeta = 0.71, \qquad \omega = 10\,k^*, \qquad k^* \approx \partial \ln\eta/\partial t$$

k* is a representative value of the viscosity dynamics, and the value of ω means that the observer is tuned about ten times faster than the C-viscosity dynamics. In our case (k^* =0.00324 min^{-1}) this tuning yielded an adequate compromise between reconstruction rate and tolerance to measurement and modeling errors.

6. EXPERIMENTAL IMPLEMENTATION

The proposed software sensor Eq. (13) was tested in the pilot plant system presented in Figure 1. In Figure 2 are shown the on-line estimated and off- line C-viscosity values. As it can be seen, the evolution of C-viscosity is reasonably followed and there is a good agreement between the on-line and off-line values. In Figure 3, the evolution of the estimated and measured heat exchange rate are presented. Finally, in Figure 4 are presented the on-line estimated and off-line (titration) measurements of acid number. As it can be seen in the figures, the software sensor provides reasonable estimates in the light of the modeling assumptions and uncertainties. It must be pointed out that the free-volume Eq. (3) and heat transfer (Eq. 2c) correlations should be occasionally calibrated, especially when a new formulation or raw material is to be polymerized.

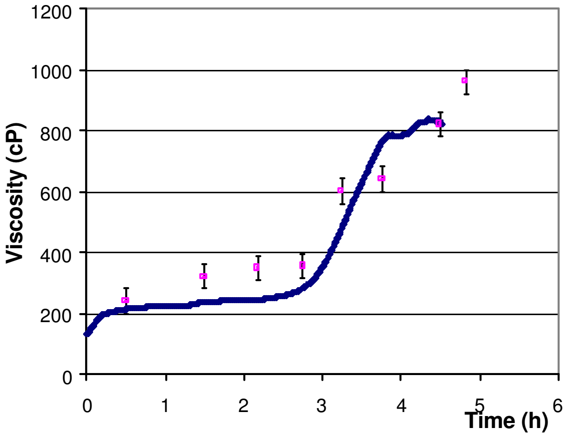

Figure 2. On-line (—) and off-line (¦) C-viscosity.

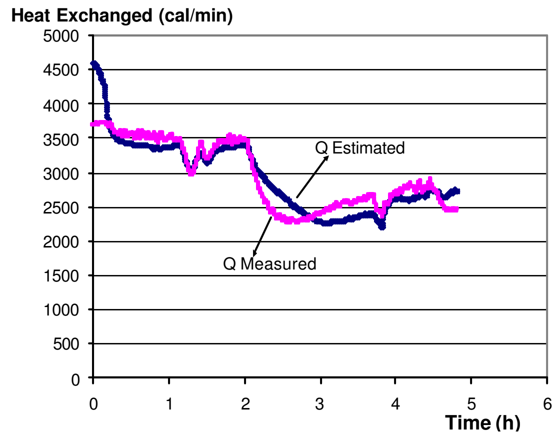

Figure 3. Estimated (—) and measured (¦) heat exchange rate.

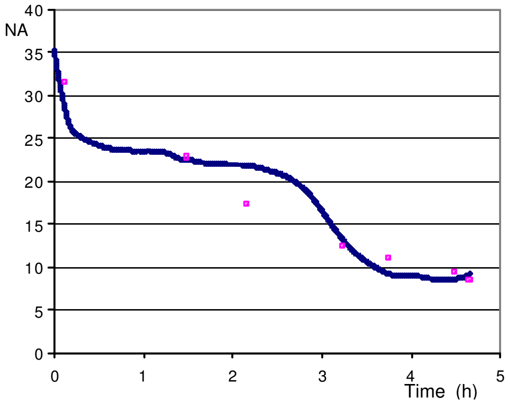

Figure 4. On-line (—) and off-line (¦) acid number.

7. CONCLUSIONS

In this work, a calorimetric software sensor to on-line estimate the cold viscosity and acid number of alkyd resins has been developed and implemented in a pilot plant. The experimental testing of the resulting software sensor shows the feasibility of drawing an on-line estimate of the cold viscosity and acid conversion based on the heat exchanged measurement. The characterization of the underlying nonlinear robust observability property enabled a unified approach to the hardware and software design aspects of the problem.

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