

## MULTIVARIATE STATISTICAL ESTIMATION OF PRODUCT QUALITY IN THE INDUSTRIAL BATCH PRODUCTION OF A RESIN

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**Abstract:** A multivariate statistical estimator of the product quality is developed for an industrial batch polymerization process producing a resin. It is shown that, for the purpose of quality estimation, the complex series of operating steps through which a batch is run can be simplified to a sequence of three estimation phases. For each phase, a PLS model for the estimation of the product quality is developed. Switching between one phase to the other one is triggered by easily detectable landmark events occurring in a batch. The performance of the resulting three-phase PLS estimator is very satisfactory.

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**Keywords:** statistical inference, soft sensing, multivariate quality control.

### 1. INTRODUCTION

Batch processing is used to manufacture high added-value goods, such as specialty chemicals and biochemicals, materials for microelectronics, and pharmaceuticals. With respect to their continuous counterparts, batch processes are easier to set up and require only limited fundamental knowledge of the underlying process mechanisms. In principle, the operation of a batch process is easy, because the processing recipe usually evolves through a series of elementary steps (e.g.: charge; heat-up/cool; mix; discharge) that can be easily carried out even without supervision, if the production facility is outfitted with a fairly large degree of automation.

One key feature of batch processes is that, by properly adjusting the operating recipe, they can achieve a consistently high and reproducible quality of the product, in spite of changes in the raw materials and in the state of the equipment or of the

utilities. However, it is often the case that batch plants are poorly instrumented and automated, and may require intervention by the operating personnel to provide online adjustments of the operating recipe to avoid the production of off-spec products. In fact, with respect to product quality control, most batch processes are run in an open-loop fashion, because information about product quality is not available online, but is obtained offline from laboratory assays of few product samples. Because of the lack of online information on product quality, it is difficult to promptly detect shifts in quality and to counteract them by adjusting the operating recipe accordingly. Therefore, a quality control strategy for a batch process often reduces to the online control of some key process variables (those whose measurements are available online) and possibly to some midcourse intervention on the operating recipe to compensate for the shifts detected in the product quality measured offline.

The performance of a batch process could be improved if accurate and frequent information on the product quality were available. Soft sensors (also

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called virtual sensors or inferential estimators) are powerful tools for this task. They are able to reconstruct online the estimate of a quality variable from the measurements of some “secondary” process variables (typically, temperatures, flow rates, pressures, ...), by using a model to relate the secondary variables to the primary ones. Developing a first-principles model to accurately describe the chemistry, mixing and heat-transfer phenomena occurring in a polymerization process requires a significant effort, and the resulting soft sensor may be computationally very demanding for online use. Data-driven soft sensors overcome these difficulties, and will be considered in this paper.

In the last two decades, multivariate statistical techniques have proved to be excellent tools for the analysis and monitoring of processes where lots of process data are available (Kourti and MacGregor, 1995). These techniques are able to compress the information contained in the available data down to a low-dimensional space that retains almost all of the original information embedded into the data. Within this space, it is possible to obtain a relationship between the (transformed) process data and the (transformed) quality data, so as to design computationally inexpensive online estimators. Several industrial applications of these techniques have been reported (Garcia-Muñoz *et al.*, 2003; Yu *et al.*, 2003; Kourti, 2005).

In this paper we exploit one of these projection methods (namely, partial-least-squares regression; Geladi and Kowalski, 1986) to design a soft sensor for the online estimation of the quality of a resin produced in an industrial batch polymerization process. The process is characterized by a fairly large number of process measurements being available online. However, these variables are noisy, auto-correlated and cross-correlated. Quality measurements are available offline, but are scarce and unevenly spaced in time. The operating procedure consists of a nominal recipe that is subject to several online adjustments made by the operators depending on the actual evolution of a batch. As a consequence, the batch duration exhibits a large variability. All of these features make each batch hardly reproducible, and the quality estimation a challenge.

## 2. THE PROCESS

The industrial process we are considering is the batch polycondensation between 1,6-hexanediol and dodecanedioic acid, which produces a polyester resin (called resin #3180) with an average molecular weight of ~3500 kg/kmol. The reaction is carried out in a stirred tank reactor with a nominal capacity of 12 m<sup>3</sup>, heated by dowtherm oil through an external coil. Several other resins are produced in the same reactor in different production campaigns.

Besides the desired product, the polycondensation reaction leads to the formation of water, which must be removed from the reaction environment to promote the forward reaction. To allow for the

removal of water, the plant is equipped with a packed distillation column (which is actually run in dry mode for the production of resin #3180), an external water-cooled condenser, and a scrubber. A vacuum pump allows to operate the plant under vacuum when needed.

The measurements of 23 process variables are routinely collected online and recorded by a process computer every 30 s. These measurements include temperatures, pressures and valve openings in different sections of the plant. The product quality is defined in terms of two indices: the resin viscosity ( $\mu$ ) and the resin acidity number ( $N_A$ ). However, quality measurements are not available online. Rather, product samples are taken manually (quite infrequently and irregularly, i.e. one sample each 1.5-2 h, depending on the operators' availability and on the actual evolution of the batch), and sent to the laboratory for analysis. The full analysis of a sample takes about 20 min. Product sampling is initiated 8-10 h after a batch is started. Typical measurement accuracies are ~10% ( $N_A$ ) and ~8% ( $\mu$ ) of the reading. Each batch is run through a sequence of operating steps, most of which are triggered manually by the operators depending on the current values of the product quality measurements. A typical sequence of operating steps is as follows.

Cleaning of the equipment and lines is done when a different resin has been produced in the preceding batch. Then, the reactants and additives are loaded. Dodecanedioic acid being a product of fermentation, its quality may change from batch to batch. Minor quality changes may be also experienced in the fresh hexanediol.

During the reactor loading, the operators set on mixing and heating, and heat-up continues until the reactants reach a temperature of 202 °C. Because the dowtherm oil serves as the hot utility for several other reactors in the same production facility and the duty of the heating furnace is fixed, the oil temperature may well change from batch to batch. This may result in different durations of the heat-up period from one batch to another one.

The temperature triggers the polycondensation reaction, hence water is generated and must be removed to improve the yield of resin. Water is generated as a vapor phase that leaves the reactor. Especially in the early stages of the batch, this vapor phase may contain significant amounts of hexanediol, which must be recovered. Therefore, the vapor phase leaving the reactor is treated in the following ways: *i*) by differential condensation, through which liquid hexanediol is recovered and recycled back to the reactor; *ii*) by total condensation in the condenser; *iii*) by washing and contact condensation in the scrubber. Switching from method *i*) to method *ii*) to method *iii*) is triggered by the measured values of  $\mu$  and  $N_A$  in the reacting mass. Therefore, any delays in the sampling and subsequent analysis of the product may severely alter the time evolution of the batch.

Vacuum is applied during the course of the reaction to improve the operation of the reactor and for safety

reasons. However, since one additional charge of fresh hexanediol and chain transfer agents is always loaded to the reactor while the reaction is proceeding, vacuum needs to be broken and then resumed when this occurs.

When the end of the batch is approaching, the reactor temperature is increased to 220-230 °C. The batch is stopped when the product reaches the desired quality targets in terms of both  $N_A$  and  $\mu$ . At that time, the product is discharged.

During the course of a batch, if  $N_A$  and  $\mu$  are failing to approach the target values in the expected amount of time, further fresh material is charged to the reactor; this requires breaking and then resuming the vacuum. Following the operators' jargon, this is known as "a correction" to a batch. Clearly, corrections are the way the operators act online to compensate for any disturbances affecting a run (changes in: quality/quantity of raw materials and additives; quality of utilities; state of the equipment). One single batch may experience from zero up to two corrections, depending on the operators' judgment. More than one third of the batches undergo to corrections.

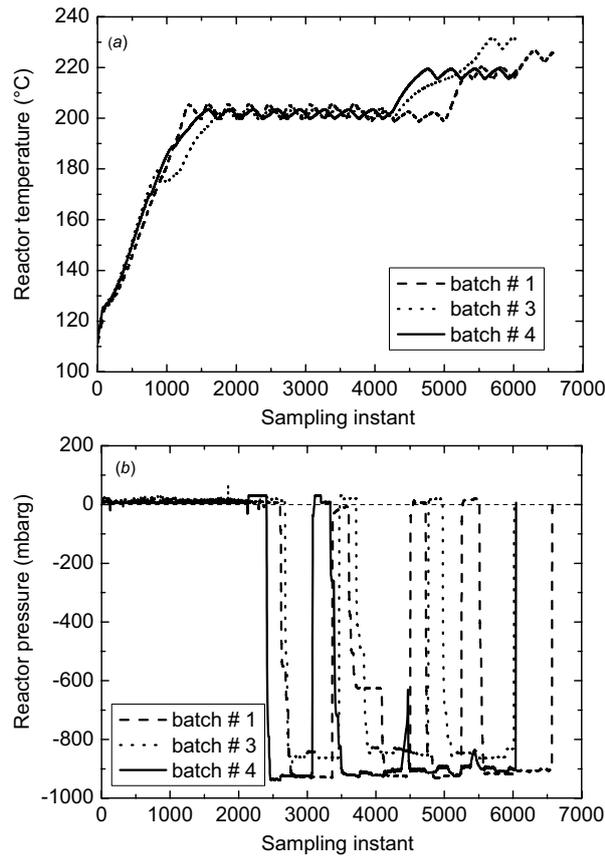


Fig. 1. Time trajectories of (a) reactor temperature and (b) reactor pressure for three different batches.

The net result of this quite complex (and mostly manually driven) operating recipe is that, although the end-point quality of the resin usually falls within a very narrow range, the "internal" variability of the batches is very large. This, for example, translates in

variable durations of the batches (the total batch time ranges between 40 and 70 h) and different shapes of the same process variable in different batches (Fig. 1).

As was noted, the switching from one operating step to the subsequent one is triggered by the measured value of the resin viscosity and/or acidity number. However, because quality measurements are available quite infrequently, the switching may be substantially delayed, with the result of poor monitoring of the product quality and increase of the duration of a batch. Therefore, as a first approach to the design of a system for the online monitoring of the whole production process, the design of a soft sensor for the estimation of  $\mu$  and  $N_A$  is considered, with the objective to make available online frequent and accurate estimations of the product quality indicators.

### 3. PROPOSED ESTIMATION APPROACH

The quality monitoring approach we have developed relies on the partial least squares (PLS) regression technique, which is shortly recalled before considering its application to the case under study.

#### 3.1 PLS regression

PLS is a regression technique that allows to deal with an overload of process data and to relate them to quality variables. In particular, it is very effective in the treatment of highly correlated and noisy data.

Let us suppose that a set of  $J$  process variables measured on  $N$  samples are collected into a  $(N \times J)$   $\mathbf{X}$  matrix. Let us also assume that  $M$  quality variables are collected into a  $(N \times M)$   $\mathbf{Y}$  matrix. All available data are properly centered and scaled before numerical treatment.

PLS reduces the dimension of the  $\mathbf{X}$  space by finding the set of latent variables (LV's) explaining the variation in the process data ( $\mathbf{X}$ ) that is most predictive of the quality data ( $\mathbf{Y}$ ).

The  $\mathbf{X}$  and  $\mathbf{Y}$  matrices are decomposed as:

$$\mathbf{X} = \mathbf{TP}^T + \mathbf{E} = \sum_{a=1}^A \mathbf{t}_a \mathbf{p}_a^T + \mathbf{E} \quad (1)$$

and

$$\mathbf{Y} = \mathbf{UQ}^T + \mathbf{F} = \sum_{a=1}^A \mathbf{u}_a \mathbf{q}_a^T + \mathbf{F} \quad , \quad (2)$$

where  $A \leq \min\{N, J\}$ ,  $\mathbf{t}_a$  and  $\mathbf{u}_a$  are the score vectors,  $\mathbf{p}_a$  and  $\mathbf{q}_a$  are the loading vectors, and  $\mathbf{E}$  and  $\mathbf{F}$  are the residual matrices. The latent vectors  $\mathbf{t}_a$  are computed sequentially from the available data for each PLS dimension ( $a = 1, 2, \dots, A$ ), such that the linear combination of the  $\mathbf{X}$  variables defined by the latent variable  $\mathbf{t}_a = \mathbf{p}_a^T \mathbf{x}$  and the linear combination of the  $\mathbf{Y}$  variables defined by the latent variable  $\mathbf{u}_a = \mathbf{q}_a^T \mathbf{y}$  maximizes the covariance between  $\mathbf{X}$  and  $\mathbf{Y}$  that is explained at each dimension, i.e. as latent

variables are added. Usually, a small number of LV's is sufficient to extract the information from  $\mathbf{X}$  and  $\mathbf{Y}$ , no matter how large the dimension of these matrices is. Cross-validation (Wold, 1978) can be used to determine the optimal number of LV's. It should be noted that, while using the first few (say, two) LV's may be sufficient for process monitoring purposes, all the dimensions determined by cross-validation are often needed when quality estimation is to be performed (MacGregor *et al.*, 1994).

When batch processes are considered, the estimation problem is complicated by the fact that the data matrices take the form of three-way arrays. PLS can be applied to such matrices by "unfolding" them to obtain two-way arrays of data (Nomikos and MacGregor, 1994).

The dataset available for the process under study includes measurements of the process variables and of the quality variables from 28 batches. This dataset was split into two parts: 24 batches constitute the reference (i.e., calibration) dataset, while the remaining 4 batches represent the validation dataset.

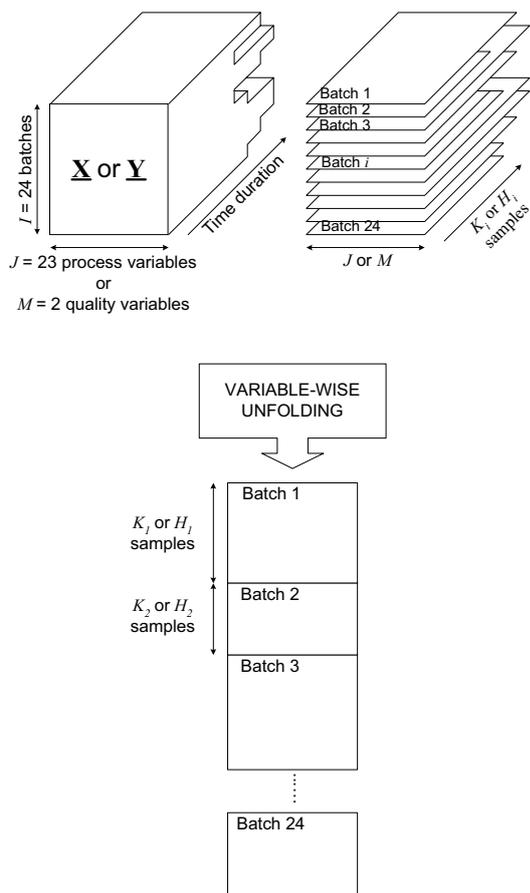


Fig. 2. Variable-wise unfolding of the process and quality data matrices.

The process data are collected in a three-way matrix  $\mathbf{X}$  (Fig. 2). Each of the  $J = 23$  columns of this matrix contains one measured process variable. Each row of  $\mathbf{X}$  corresponds to one of the  $I = 24$  reference batches. Time occupies the third dimension. Although the process variables are measured at a

regular frequency, the duration of each batch is different, and this makes the shape of  $\mathbf{X}$  "irregular". Typically, 5500-6500 measurements of each process variable are taken during a batch.

The arrangement of the  $\mathbf{Y}$  matrix is similar. However, only  $M = 2$  columns are present, which correspond to the two quality variables to be estimated ( $\mu$  and  $N_A$ ). The third dimension of  $\mathbf{Y}$  is scanned irregularly and with a much lower frequency than the one of the  $\mathbf{X}$  matrix (only 15-20 midcourse quality measurements are usually available per batch). In the  $\mathbf{Y}$  matrix, "time" refers to the time when a sample is taken, not to when the lab analysis becomes available.

One simple method to deal with this kind of unsynchronized data is to unfold the  $\mathbf{X}$  and  $\mathbf{Y}$  matrices according to the variable-wise method, as Fig. 2 illustrates (Wold *et al.*, 1998). The limitations of this unfolding method with respect to the batch-wise one are discussed by Kourti (2003). In order for the calibration matrices  $\mathbf{X}$  and  $\mathbf{Y}$  to have the same number of rows, only those process measurements that correspond to time instants where product samples are taken were included into the  $\mathbf{X}$  matrix.

### 3.2 Estimating the resin quality

As was discussed in Section 2, the operating recipe for a batch results in a complex series of operations, most of which are subject to the operators' manual intervention. Therefore, also owing to the intrinsic time-varying nature of the process, it is quite unlikely that the cross-correlation structure between the process and quality variables remains the same during the whole duration of a batch. This in turn means that a single PLS model might not be able to provide an accurate prediction of the quality variables along the whole batch.

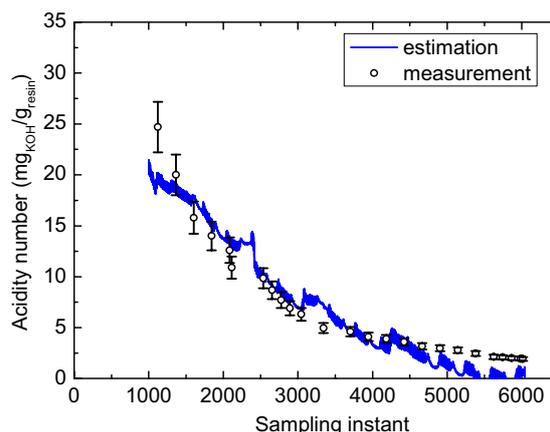


Fig. 3. Prediction of the acidity number with a single PLS model (validation batch #4). The vertical bars represent the measurement accuracy.

This is confirmed in Fig. 3, where the acidity number predicted by a single PLS model is compared to the actual values measured off line in a validation batch. It can be seen that the estimation accuracy is not satisfactory. One approach that can be considered to

overcome this problem is to derive more than one model to represent the different phases through which a batch evolves (Kourti, 2003; Ündey *et al.*, 2003). However, building a different model for each operating step would not be a viable solution, not only because the number of operating steps is large, but also because the actual number of steps in a batch is not known *a priori*, being dependent on the number of corrections the batch will be subject to. Furthermore, too few quality measurements may be available in a single operating step to build the relevant PLS model.

The approach we have taken is to analyze whether different operating steps exist in a batch that share the same correlation structure among the variables. If this is the case, the same PLS model can be used to represent these “shared” operating steps.

In the score plot of Figure 4, the first and second LV scores of a 5-LV PLS model built on the calibration dataset are plotted versus each other for the time instants where quality measurements are available. It can be seen that the score points are mainly clustered into three distinct regions of the score plane. Close inspection of the clusters revealed that all batches are characterized by a similar pattern in the “movement” of score points during a batch: a score point is located at the left of the score plane (“Phase 1” cluster) at the beginning of the operation, then moves to the center of the plane (“Phase 2” cluster) as time progresses, and finally shifts to the plane right (“Phase 3” cluster) towards the end of the batch.

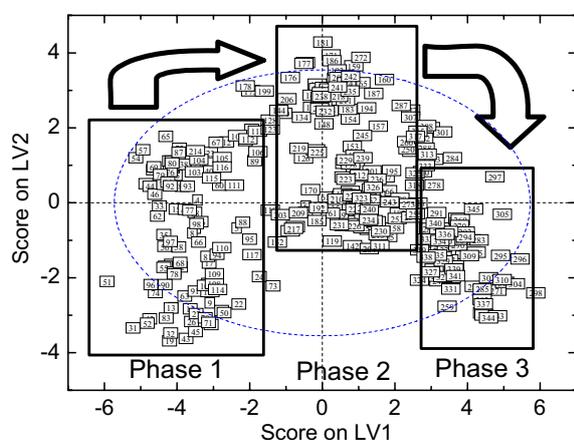


Fig. 4. Score plot on the first and second latent variables for a single PLS model predicting viscosity and number of acidity (calibration dataset).

It is expected that the correlation structure between process and quality variables is more similar for points within a cluster than for points between clusters. Otherwise stated, each cluster (i.e., each phase) may be envisioned as a series of operating steps that share the same correlation structure among the process and quality variables. Therefore, for each phase one PLS submodel can be developed to predict the quality variables from the process ones. The resulting quality estimator is therefore a three-phase PLS model.

A key issue in the development of such a multi-phase estimator is finding a proper criterion to switch from one PLS submodel to the other one. Switching from one submodel to the other one means being able to recognize online that the cross-correlation structure of the data is changing. Inspection of the process data for all reference batches revealed that switching from Phase 1 to Phase 2 occurs the first time vacuum is applied to the reactor, while Phase 3 is initiated as soon as the final rise in temperature takes place. Therefore, clearly detectable events can be recognized in a batch to trigger the model switching.

#### 4. RESULTS

A three-phase PLS model was built using the 24 reference batches. Each submodel uses five latent variables. Note that, although we forced each submodel to use the same number of LV’s, this constraint could be relaxed. In particular, it may be convenient to use more LV’s in the submodels representing Phase 1 and Phase 2 in the  $N_A$  estimator, because (as far as the acidity number estimation is concerned) the signal-to-noise ratio is more favorable at the beginning of the batch rather than at the end.

Table 1. Explained variance (EV) on the calibration dataset.

Phase	Submodel on $N_A$		Submodel on $\mu$	
	EV on X (%)	EV on Y (%)	EV on X (%)	EV on Y (%)
1	65.62	88.78	65.60	87.20
2	67.03	82.84	66.82	77.66
3	71.54	60.69	71.84	43.59

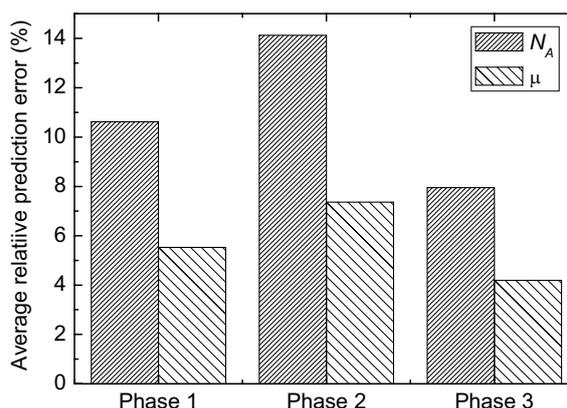


Fig. 5. Average relative prediction error on the validation datasets with the three-phase PLS model.

The submodels’ explained variance on the input and output data of the calibration dataset is listed in Table 1. To provide an overall picture of the estimator’s performance, the average relative prediction error on each quality variable is reported in Fig. 5 for each estimation phase. It can be seen that the estimation of viscosity is more accurate than the estimation of the acidity number. In any case, the average estimation

accuracy is generally well within the measurements accuracy, except for the estimation of  $N_A$  during Phase 2. This is due to the fact that most of the corrections to a batch take place during Phase 2, which is therefore subject to a much larger variability than the other phases. It is expected that adding new batches to the reference dataset can improve the representation of Phase 2.

Typical results for the estimation of the viscosity and acidity number are shown in Fig. 6. It can be seen that the estimation accuracy is greatly improved with respect to using a single PLS model (Fig. 3), particularly so by the end of the batch, when the resin quality is approaching the specification. In the batch shown in Fig. 6 each phase has a similar duration, but this is not a general behavior. In accordance to the results of Fig. 5, the estimation performance for the acidity number is slightly worse during Phase 2.

Overall speaking, however, the performance of the three-phase online estimator in predicting the evolution of the resin quality indicators was always very satisfactory.

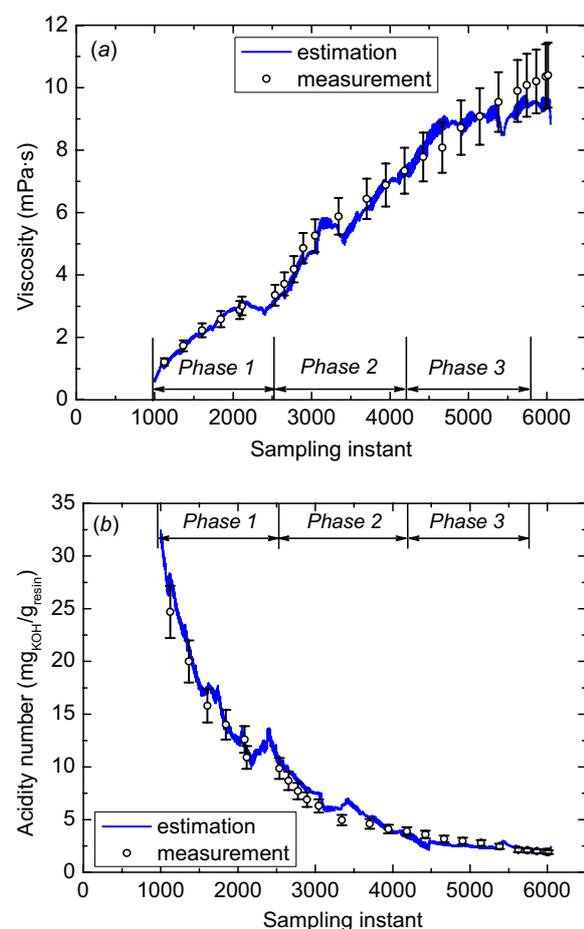


Fig. 6. Prediction of the (a) viscosity and (b) acidity number with the three-phase PLS model (validation batch #4). The vertical bars represent the measurement accuracy.

## 5. CONCLUSIONS

A multi-model PLS estimator was developed to provide online the estimation of the acidity number and viscosity of a resin produced in an industrial batch polymerization process. Although each batch is run through a complex and poorly reproducible chain of operations, it was shown that the estimation can be carried out using only three PLS submodels in sequence. Switching from one model to the other one can be triggered by easily detectable landmark events occurring in a batch. The estimator's performance is very satisfactory.

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