Dynamic Process Monitoring of an Ammonia Synthesis Fixed-Bed Reactor

Bothinah Altaf, Gary Montague, Elaine B. Martin

Abstract—This study involves the modeling and monitoring of an ammonia synthesis fixed-bed reactor using partial least squares (PLS) and its variants. The process exhibits complex dynamic behavior due to the presence of heat recycling and feed quench. One limitation of static PLS model in this situation is that it does not take account of the process dynamics and hence dynamic PLS was used. Although it showed, superior performance to static PLS in terms of prediction, the monitoring scheme was inappropriate hence adaptive PLS was considered. A limitation of adaptive PLS is that non-conforming observations also contribute to the model, therefore, a new adaptive approach was developed, robust adaptive dynamic PLS. This approach updates a dynamic PLS model and is robust to non-representative data. The developed methodology showed a clear improvement over existing approaches in terms of the modeling of the reactor and the detection of faults.

Keywords—Ammonia synthesis fixed-bed reactor, dynamic partial least squares modeling, recursive partial least squares, robust modeling.

I. INTRODUCTION

THE continual drive to improve process safety and ensure the manufacture of high quality consistent product has led to an increased demand for the implementation of process monitoring schemes in the chemical industry. Process monitoring schemes can be developed using data generated from first principle models (i.e. a model built based on the physical and chemical relationships between variables) [1]. However, the development of a first principle model is time consuming and challenging for a complex process. Therefore, data driven methods, namely multivariate statistical projection techniques are favored. They are considered as the most effective analytical tools for the monitoring of industrial processes. The aim of this family of methodologies is to project the high dimensional process data down onto a lower dimensional sub-space that captures most of the process information. The new sub-space comprising latent variables is used for the monitoring and prediction of the behavior of the process.

Bothinah A. Altaf is with King Abdulaziz University, Jeddah, P.O.Box 80200 KSA (phone: 0096612-640-0000; fax: 0096612-695-2437; e-mail: baltaf@kau.edu.sa).

Gary M. Montague was with University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK. He is now with the school of Science and Engineering, Teesside University, Middlesbrough, Tees Valley, TS1 3BA, UK (e-mail: g.montague@tees.ac.uk).

Elaine. B. Martin was with University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK. She is now with the school of Chemical and Process Engineering (Head of school), University of Leeds, Leeds, LS2 9JT, UK (e-mail:e.martin@leeds.ac.uk).

Partial Least Squares (PLS) is one of the most widely applied multivariate statistical projection techniques due to its ability to extract information from ill-conditioned data, for example missing data and collinear data. An overview of the application of PLS for industrial process analysis, control and monitoring are available in [2]-[5].

PLS is also known as projection to latent structures as the high dimensional data is projected down onto a low dimensional sub-space by extracting latent variables that are a linear combination of the original variables. The latent variables monitoring statistics namely Hotelling's T^2 and the squared prediction error (SPE) for the input and output spaces; SPE_X and SPE_Y, respectively, can be developed. These metrics allow the detection of the changes in the process operation and hence, corrective action can be taken by the process operator. The industrial application of PLS to batch and continuous processes has been widely reported [6]-[9]. One limitation of PLS is that the basic configuration was proposed to model steady state processes and this is not the case for the most industrial process and hence extensions to PLS have been proposed.

During the last two decades, a number of extensions have been put forward to handle different types of industrial systems. For example, various dynamic PLS algorithms were developed to model dynamic process behavior [10], [11]. Different versions of recursive PLS were proposed to adapt to changes in process operating conditions [12]-[15]. Multiblock PLS algorithms were proposed to handle processes with large number of variables that could be naturally blocked or which comprised multiple unit operations [16]-[20]. More recently Total PLS was proposed to enhance the detection ability of a monitoring scheme [21].

Most modern industrial processes are time varying [22] and hence a static parameter PLS model is inappropriate. One solution proposed was recursive PLS which can be considered as a model correction, since it aims to update the reference model to account for changes in the process operating conditions while still having the ability to detect abnormal behavior. The very first recursive PLS model was proposed by Helland, et al. [23]. It updates the PLS model by incorporating the new data onto the loading matrix. One limitation of this approach is the slow computations comparing to other recursive PLS approaches.

Wold [13] developed the exponentially weighted moving average PLS (EWMA-PLS) algorithm in which more recent observations are given larger weights than the previous ones. He also proposed retaining the old PLS model to avoid the unnecessary PLS updating as in recursive PLS. Two

limitations of the Wold approach were discussed by Wang [15]. First, the original PLS model does not necessarily represent the current relationship between variables, secondly, since the EWMA-PLS algorithm is based on parameters such as the forgetting factor its sensitivity to the detection of abnormal behavior could be impacted.

Qin [12]-[14] proposed two variants of recursive PLS; a block wise PLS algorithm that is based on a moving window approach and sample wise PLS. The objective is to recursively update the PLS model so that it can reflect changes in the process operating conditions. The monitoring results will differ based on window size but this issue can potentially be addressed by using process understanding of dynamics response rates to select the window size. Another issue is that older data, which is representative of the process, is discounted in favor of a new sample that might not be representative. More specifically, in recursive PLS, three types of observation might be generated; a sample representing normal operating conditions, a statistical outlier or a sample which represents abnormal behavior. The effectiveness of a PLS model is dependent on the data used for model development. Therefore, it is important to ensure that only the data that represents normal operating condition are included in the development/updating of a PLS model [24], [25]

Wang et al. [15] introduced adaptive confidence limits for the recursive PLS statistics utilizing the sample wise recursive PLS algorithm of Qin [12] and termed it recursive PLS with adaptive confidence limits (APLS). They applied it for the modeling and monitoring of an industrial distillation process and fluid catalytic cracking unit. Issues that may arise included the fact that since the PLS model is updated whenever a new sample becomes available, statistical outliers or abnormal samples may contribute to the PLS model and secondly the confidence limits of the monitoring statistics are allowed to adapt to abnormal process behavior, which statistically should be indicated as an out of statistical control signal.

Lee, Lee et al. [25] proposed robust adaptive PLS which was based on the block wise recursive PLS algorithm and they applied it to a waste water treatment process. The main advantage of this approach is that they proposed a threshold to differentiate between outlying samples and nominal samples. If the sample was confirmed to be an outlying sample, they weighted it appropriately and included it in the model update. By weighting the outlying samples, the high leverage outliers can be changed to a normal observation and hence the robustness of the PLS model is sustained during model update [25]. They confirmed whether a sample is an outlier using the combined index (1) proposed by Qin et al. [26] which is based on the metrics of Hotelling's T^2 and the square prediction error (SPE_X).

$$\psi_t = \frac{T_t^2}{\delta_{T_t^2}^{(1-\alpha)}} + \frac{SPE_{X_t}}{\delta_{SPE_{X_t}}^{(1-\alpha)}} \qquad (1)$$

where t is the sample number, T_t^2, SPE_{X_t} are the value of the Hotelling's T^2 and the squared prediction error statistics of sample t, $\delta_{T_t^2}^{(1-\alpha)}$, $\delta_{SPE_{X_t}}^{(1-\alpha)}$ are the corresponding confidence limits for Hotelling's T^2 and Squared prediction error statistics respectively. The detailed descriptions of the formula of the monitoring statistics are given in [26], [27]. The weight function is calculated based on the weight function proposed by Pell, however, the combined index was used instead of cross validated residual used by Pell [25], [28].

Qin et al. [26] noted that Hotelling's T^2 and SPE_X behave in a complementary manner and used the combined index to simplify the fault detection task, i.e. if the combined index detects a sample as out of statistical control, it can be considered either as a statistical outlier or a fault. By weighting those samples which violate the confidence limits, the proposed scheme gives abnormal samples an opportunity to contribute to the PLS model. Therefore, a secondary test needs to be implemented to distinguish between the two types of samples. Within this paper a robust adaptive dynamic PLS algorithm is proposed that addresses the issues described and its performance demonstrated by applying it to an ammonia synthesis fixed-bed reactor.

II. PROCESS DESCRIPTION

Ammonia synthesis is performed in a fixed-bed reactor (Fig. 1), which consists of two key unit operations; three consecutive fixed-beds in which the reaction is carried out and a heat exchanger where the heat is exchanged between the inlet stream and the outlet stream and hence the heat is recycled within the process. Additionally, fresh feed is used to quench the system at various quenching points. The ammonia reactor is thus considered a complex dynamic system due to heat recycling and quenching [29]. The ammonia produced exits the reactor at the bottom of the third bed with product quality being defined in terms of concentration of ammonia. Fig. 1 shows a schematic diagram of the ammonia synthesis reactor.

Two faults which result in the reactor becoming unstable and resulting in the temperature oscillating rapidly (Fig. 2) are reviewed and since they lead to the same situation, only the first is considered in this paper. The first occurs when the overall pressure falls below 170 bar and the total fresh feed temperature is kept at a steady state. The second occurs when the total fresh feed temperature falls below 235°C and the overall pressure is maintained at a steady state. The resulting oscillations associated with the temperature damage the catalyst in the reactor [29]. The unstable behavior of the ammonia fixed-bed reactor has been widely researched in the field of control engineering [29], [30]. The simulation study used and the initial operating conditions and start up values were those published in [29].
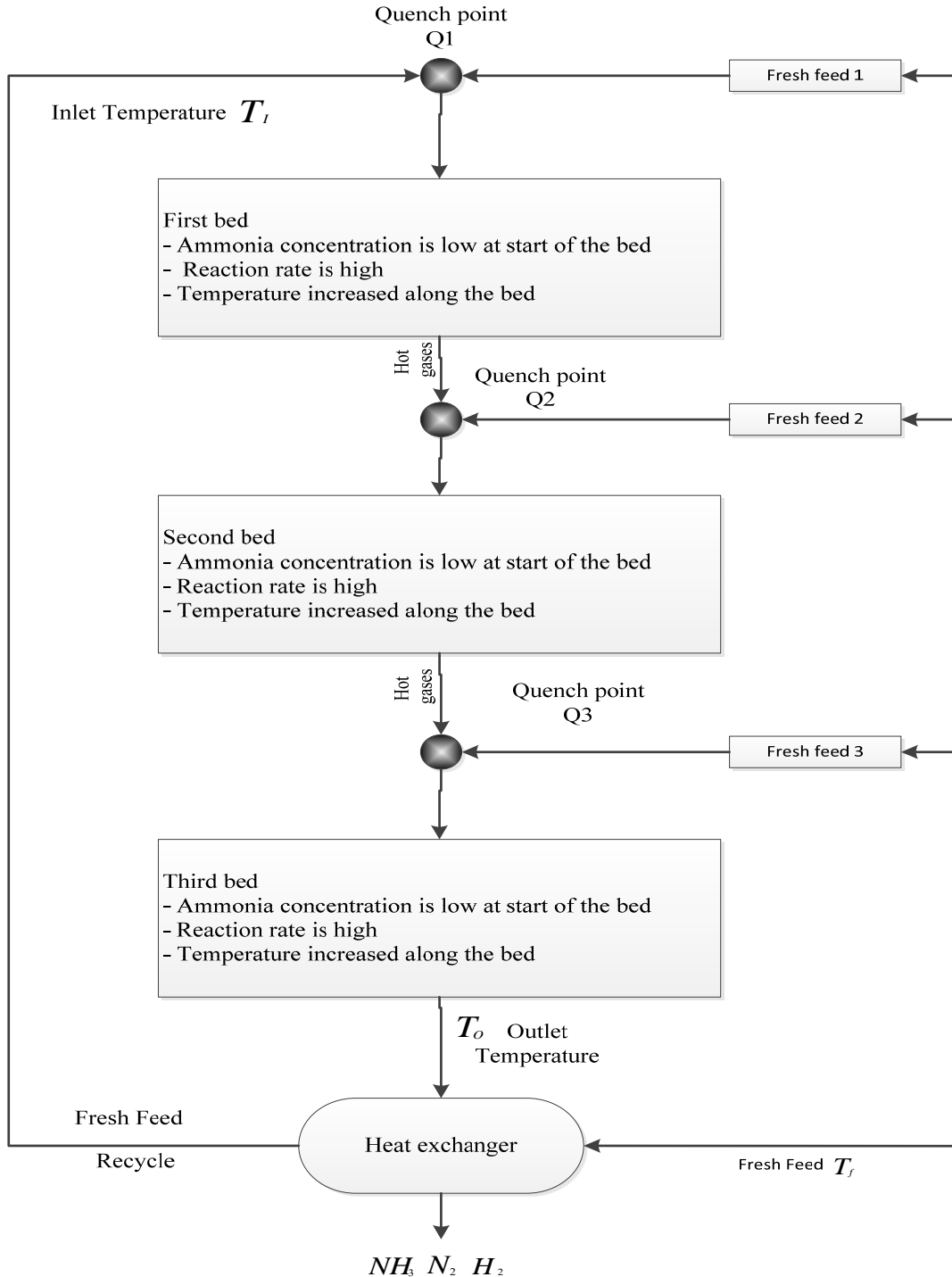
Fig. 1 Schematic representation of the ammonia fixed-bed reactor

The response and predictor variables are listed in Table I. Three data sets were generated for the analysis with the samples taken every 10 sec under open loop with the sampling time selected with knowledge of the appropriate process time constant. The first comprised 400 data points and formed the reference data-set that was used for building the calibration model. The second set contained 1000 data points and formed the validation data set. The fault occurred at the beginning of the third data set and normal operating conditions were restored after 320 points of the recorded data. The time of which the fault condition exists has been chosen to allow sufficient time for observations of the consequence.

Fig. 2 Temperature oscillation as a result of pressure falls to 150 bar in the ammonia synthesis fixed-bed reactor

TABLE I
THE RESPONSE AND PREDICTOR VARIABLES OF THE AMMONIA SYNTHESIS REACTOR

Type	name	Tag	Description
Response	C_3	y	Concentration of the ammonia
	T_i	x_1	Inlet temperature
	T_f	x_2	Temperature of total fresh feed flow
	F_e	x_3	Total fresh feed
	Q_1	x_4	First quench flow rate
Predictors	Q_2	x_5	Second quench flow rate
	Q_3	x_6	Third quench flow rate
	T_{Q1}	x_7	Temperature of the first quench
	T_{Q2}	x_8	Temperature of the second quench
	T_{Q3}	x_9	Temperature of the third quench
	P	x_{10}	Operating pressure

III. METHODS AND TECHNIQUES

A. Dynamic PLS

In most industrial applications, process behavior is dynamic and hence, a dynamic model is appropriate. A number of approaches have been proposed for dynamic PLS modeling including; modification of the PLS inner relation, augmentation of time lagged measurements and filter approaches [10], [11], [31]. A widely accepted approach is to include lagged measurements in the input matrix (i.e. incorporation of a time series) thereby considering both static and dynamic relationships. If the input matrix includes only lagged values of the input variables, it is called a Finite Impulse Response (FIR) model whilst a multivariate Auto-Regressive with eXogenous inputs (ARX) model is built if both input and output values are included in the input matrix [31], [32]. Although the use of time series is widely adopted, care is required in term of the number of lags to include since a large number of lagged values will contribute to the noise in the PLS model and the computational burden. Dynamic PLS (DPLS) modeling has been reported by a number of researchers [10], [33]. Like PLS, process monitoring can be based on Hotelling's T² and the squared prediction error (SPE) for the input and output spaces; SPE_X and SPE_Y, respectively.

B. Robust Adaptive Dynamic PLS (RADPLS)

Of the various recursive PLS approaches, the recursive PLS algorithm with adaptive confidence limits proposed by Wang et al. [15] is used as a basis of a revised methodology, the Robust Adaptive DPLS (RADPLS). The revised algorithm is based on a dynamic PLS model as opposed to a static PLS model and make use of historical reference data for the calculation of the monitoring statistics and confidence limits. For simplicity the following notation is used

$$\{X, Y\} \xrightarrow{DPLS} \{T, P, Q, U, B\} \tag{2}$$

where X and Y are the input and output matrices P and Q are the loadings T and U are the scores of the input and output matrices respectively and B is a matrix of inner regression coefficients.

When a new sample, t, becomes available, the monitoring statistics and updated limits are calculated. The combined index, ψ_t, is also calculated according to (1) with $\delta_{\psi_t}^{(1-\alpha)}$ denoting the corresponding confidence limit [27]. If the combined index of the new sample violates its limit, a secondary test needs to be conducted.

The outlying sample generated from process failure or disturbance is likely to occur consecutively whilst the statistical outlier is unlikely to do so. Therefore, similar to the Western Electrical rule [34] for the detection of out of statistical control signals in monitoring charts, three or more consecutive values of the combined index are required to lie outside the control limits when determining a process abnormality and hence, the PLS model should not be updated. Once the combined index of an incoming sample violates the limits, the parameter update should be suspended and the status of the surrounding samples checked according to the above test.

IV. RESULTS AND DISCUSSION

A. Dynamic PLS Analysis

The first data set comprising 400 samples was used to identify the reference model for the ammonia fixed-bed reactor. Static PLS showed unsatisfactory performance and failed to model the behavior of the ammonia synthesis fixed-bed reactor (results not presented) due to neglecting the dynamic characteristics of the process. Consequently, a dynamic PLS (DPLS) model was developed based on an AutoRegressive with eXogenous inputs (ARX) time series representation. The structure of the ARX representation was determined through the Akaike information criterion (AIC), which is an information measurement approach used to identify the most appropriate model amongst a class of competing models developed from recorded data [35]. Different structures, as shown in Table II, are used under different pre-processing approaches and the structure is selected based on the lowest AIC value for each pre-processing method. The selected structure of each pre-processing approach is then used for PLS modeling.
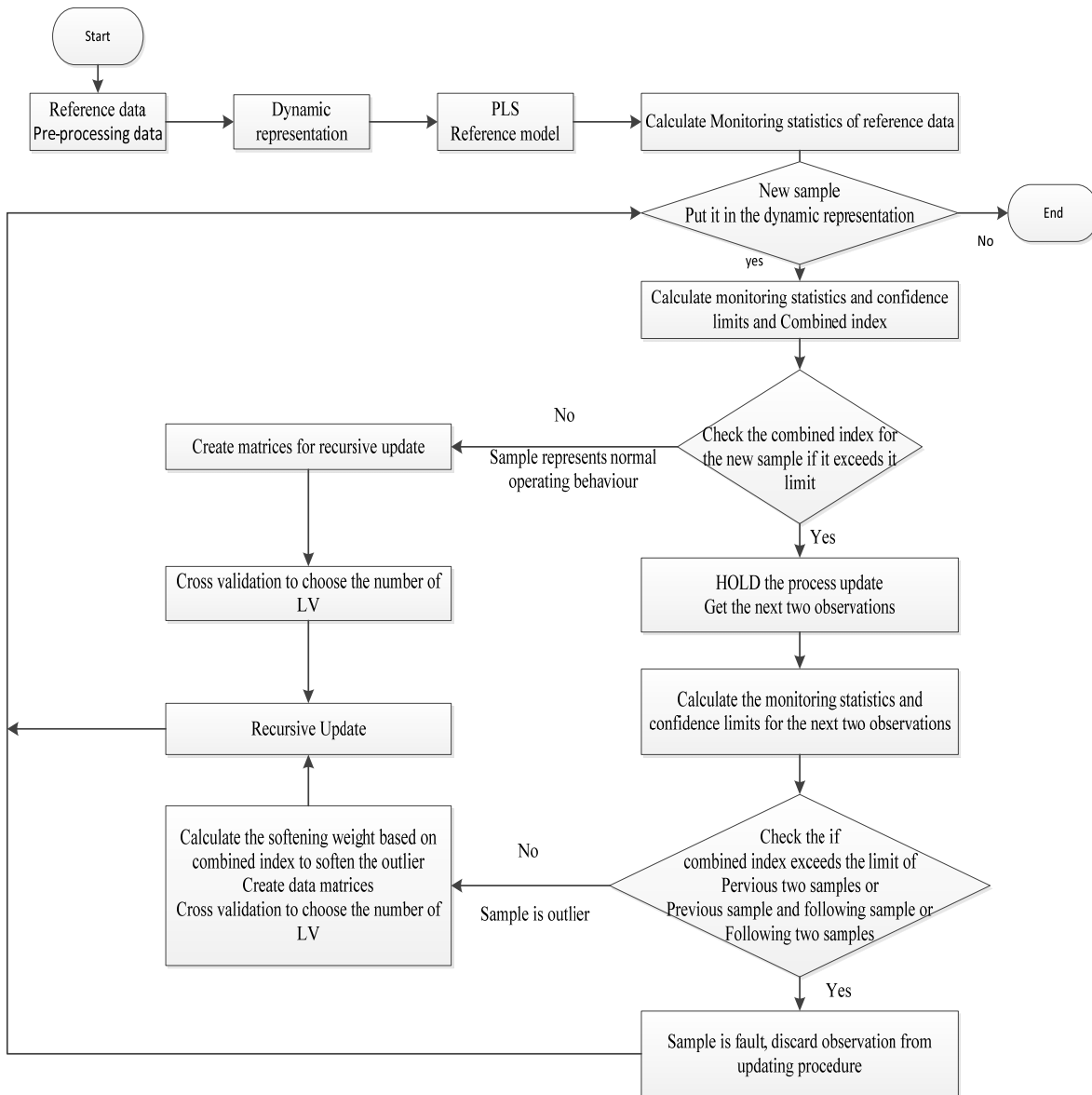
Fig. 3 Workflow of the Robust Adaptive Dynamic PLS (RADPLS) algorithm

TABLE II
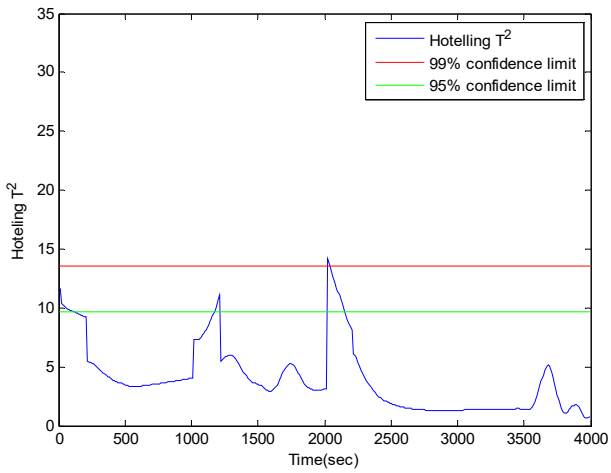THE MOST APPROPRIATE ARX STRUCTURE FOR DIFFERENT PRE-PROCESSING METHODS

Pre-processing method	ARX structure
Normalized data	$ARX(1,1,20)*$
Centred data	$ARX(1,1,3)*$
Centred input	$ARX(3,3,1)*$
No pre-processing	$ARX(10,10,1)*$

*$ARX(i,j,k)$, i represents the number of lagged output, j represents the number of lagged input and k represents the time delay between the input and output used to form the regressor matrix

A critical issue to be addressed was whether to scale the data and if so how as it is known to have an impact on model development. Of the four approaches considered (Table III), no scaling, mean centering the input only, mean centering the input and output and normalization, the latter approach was found to be the most appropriate scaling method as it considered the differences in the measurements ranges. The selection was based on the statistical metrics of Root Mean Squared Error (RMSE) and the coefficient of determination (R^2), which are used to measure the performance of the regression model.
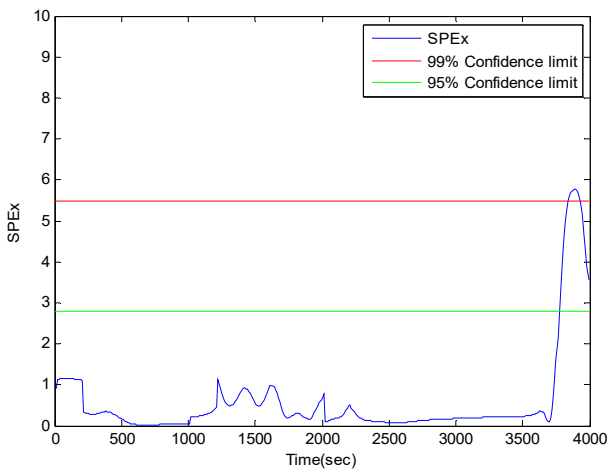
The number of latent variables to include in the model was selected using cross validation. Four latent variables corresponded to 94.63% of the total amount of variance explained in the X-block and 96.32% of the variance explained in the output. The root mean squared error for the calibration model (RMSEC) was 0.0003. The model was then validated on the validation data set (RMSEV= 0.0009) and model performance was in general acceptable.
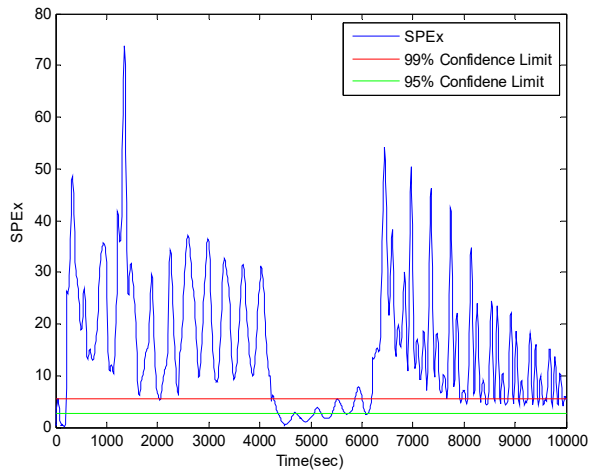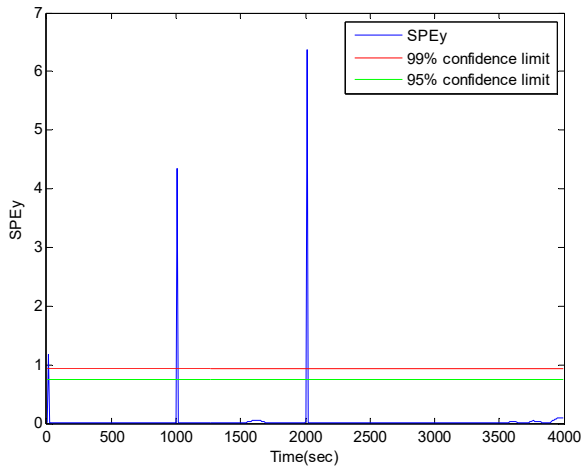
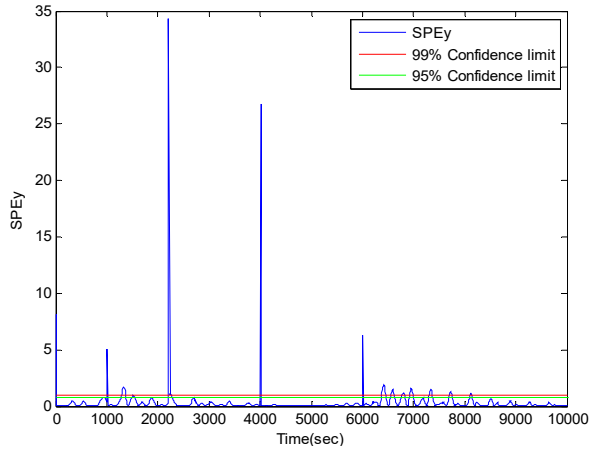Fig. 4 (a) Hotelling T^2 for the reference data set, (b) SPE_x for the reference data set, (c) SPE_y for the reference data set, (d) Hotelling T^2 for the validation data set, (e) SPE_x for the validation data set, (f) SPE_y for the validation data set

TABLE III
ROOT MEAN SQUARED ERROR AND COEFFICIENT OF DETERMINATION OF PLS
MODEL BASED ON DIFFERENT PRE-PROCESSING APPROACHES FOR
CALIBRATION AND VALIDATION DATA SETS.

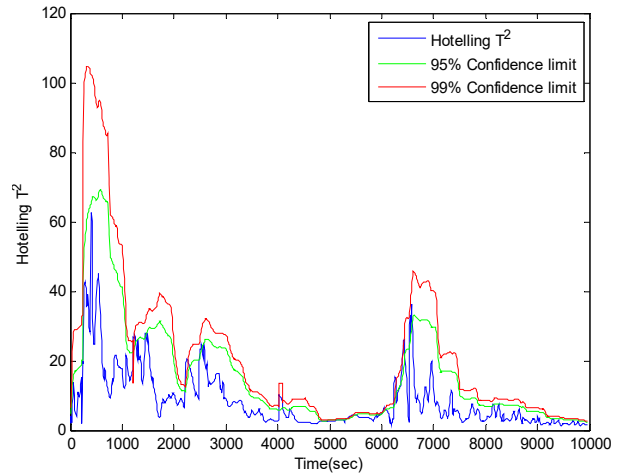| Pre-processing	RMSEC	RMSEV	R^2Cal	R^2Val
Normalization	0.0003	0.0009	0.9632	0.9346
Centring input and output	0.0006	0.00235	0.8787	0.7727
Centring input	0.0006	0.00032	0.8706	0.5143
No pre-processing	0.0004	0.0019	0.9297	0.8493

The performance of the monitoring charts for the model developed using dynamic PLS for the calibration data shows statistically acceptable monitoring charts, where the calculated false alarm rate (Table IV, Appendix) does not exceed 5% and 1% for the 95% and 99% confidence limits respectively (Figs. 4 (a)-(c)). However, the monitoring charts for the validation data representing normal operations showed some evidence that dynamic PLS is unable to monitor the behavior of the ammonia synthesis reactor as shown in Figs. 4 (d)-(f) with the monitoring charts specifically SPE_X, SPE_Y, continuously violating the confidence limits. The false alarm rates of the monitoring charts for the validation data set were much higher than the acceptable rate (Table IV, Appendix). Therefore, dynamic PLS was concluded to be inappropriate to construct a monitoring scheme for the application under normal operating conditions and hence, the results of the testing data where a fault occurred is not presented.

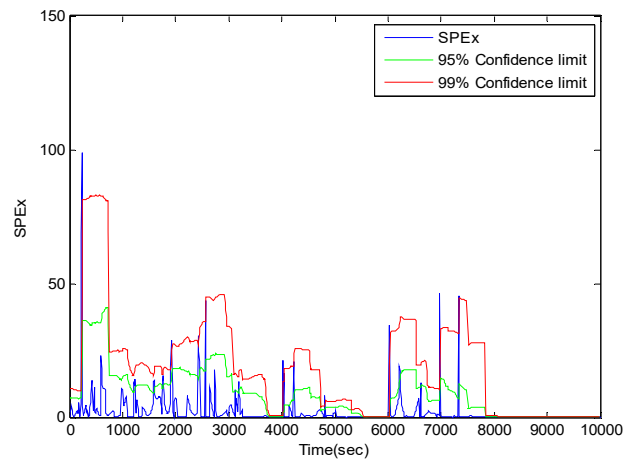### B. Robust Adaptive Dynamic PLS

The limitation of the monitoring charts observed in the implementation of dynamic PLS, where the monitoring charts produced high false alarm rates whilst the process ran within normal operating conditions, was addressed by applying RADPLS. The reference model developed in Section IV-A was used as the reference model for RADPLS. The next step was to update this model once a new sample became available. The results from the application of RADPLS for the validation data set indicate that model performance is significantly improved with RMSEV = 0.00057.

The monitoring results from the application of RADPLS for the validation data set are presented in Figs. 5 (a)-(d). It can be seen that the process is within statistical control with the statistical indices (i.e. Hotelling T^2, SPE_X and SPE_Y) remaining within the statistical confidence limits. This is expected as the data represents normal operating conditions with a few samples lying outside of the 99% and 95% confidence limits expected. The false alarm rates of the monitoring charts for the validation data, which do not exceed 5% and 1% for 95% and 99% confidence limits, verified that the approach is an efficient monitoring technique (Table V, Appendix)
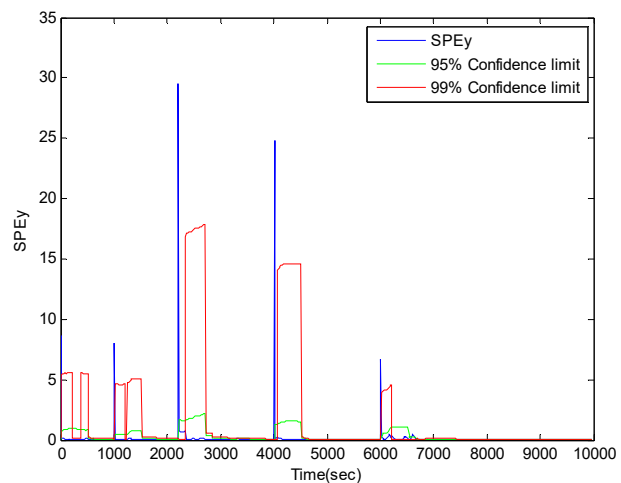
The control chart of the combined index shows that it remains within statistical control and only a few violations were observed but these were defined to be statistical outliers by the RADPLS algorithm. These results are improvements over the adaptive PLS approach [14], which did not take into account the process dynamics or the presence of statistical outliers.
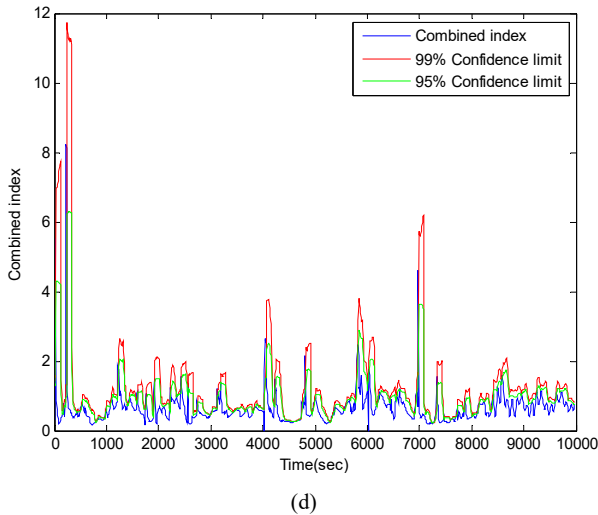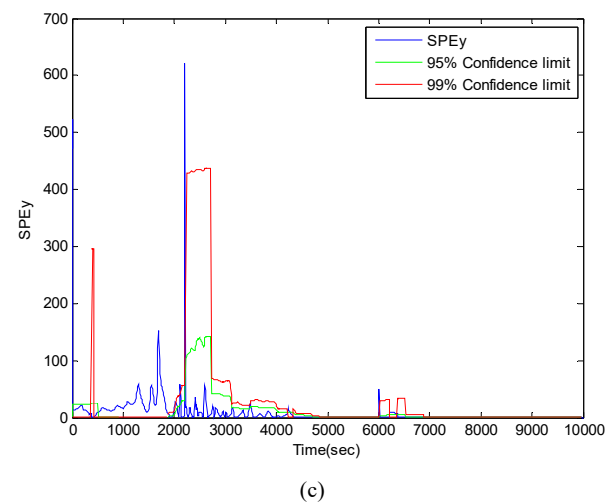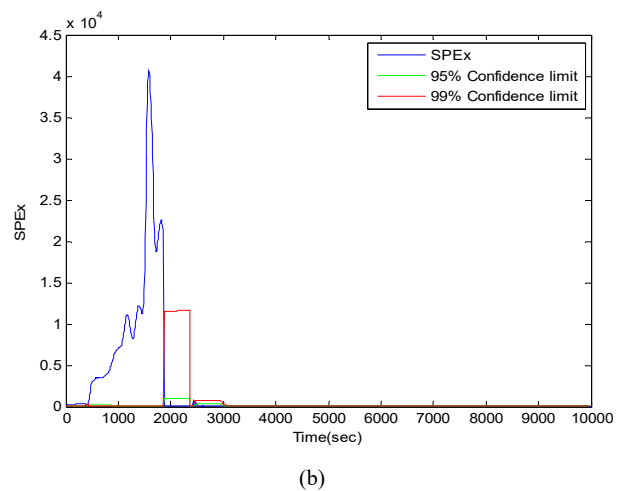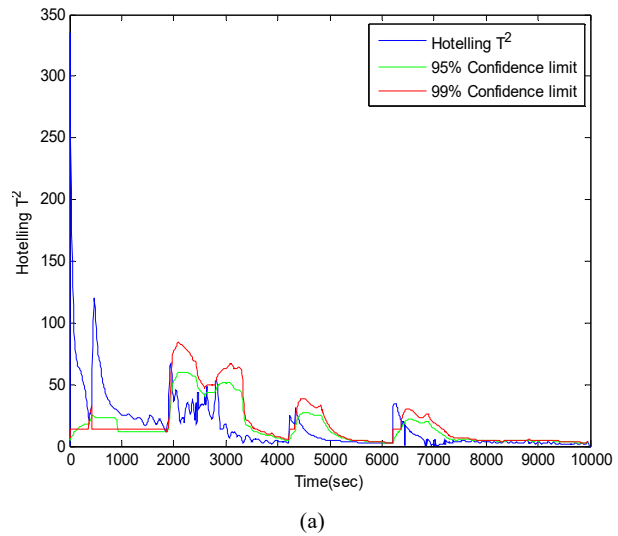
(a)

(b)

(c)

(d)

Fig. 5 (a) Hotelling T^2 for the validation data set by RADPLS, (b) SPE_X for the validation data set by RADPLS, (c) SPE_Y for the validation data set by RADPLS, (d) Combined index for the validation data

When the RADPLS algorithm was applied to the third data set (i.e. data set with fault occurring over a period of 320 samples), the statistical indices are affected by the fault as observed in Figs. 6 (a)-(c). The monitoring indices clearly indicate that the process has deviated from the previous operating conditions. The Hotelling T^2 statistic indicated the fault after two samples, whilst the SPE_X statistic identified a fault after five samples and SPE_Y indicated it after two samples. These monitoring charts show the process is out of statistical control for approximately 180 data points with a few points lying in statistical control during this period. However, it was known that 320 samples were affected by the fault as this was when normal operating conditions were restored. This occurred for the following reasons:

− The model parameters update incorrectly when the fault occurs. During process oscillation, when the signal passes through the region of normal operation, it causes the model to update. However, at this time the dynamic characteristics of the process are not representative of normal operations. This situation becomes more severe the longer the fault persists as the magnitude and frequency of the oscillation both increases as shown in Fig. 2.

− Rapid oscillations resulting from the fault (the fast dynamic behaviour of the signal) has an impact on the statistical indices because the T^2 and SPE_X are calculated as a function of the measured value of the current sample and the parameters of the previous PLS model.

− Additionally, the combined index was calculated as function of the two statistics (T^2 and SPE_X), their limits and previous PLS model. Once an observation is identified as a statistical outlier, the observation itself is weighted prior to model update. However, the adaptive limits are allowed to adapt the statistical outlier. Hence

the limits of the statistical outlier are used to calculate the combined index and its limit. This could have an impact on the functionality of the combined index as seen in Fig. 6 (d) where an outlier was identified at time t=500.
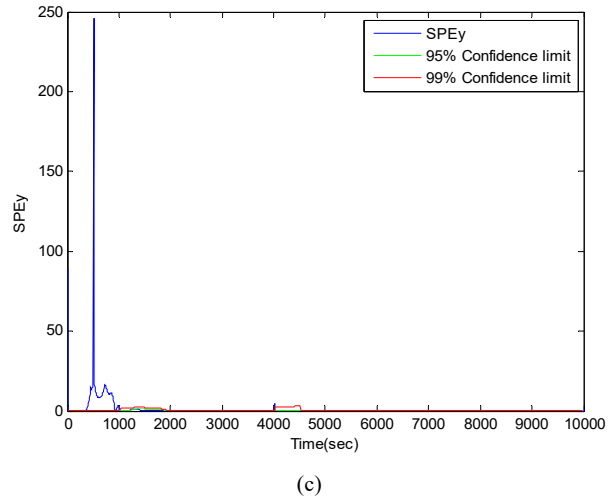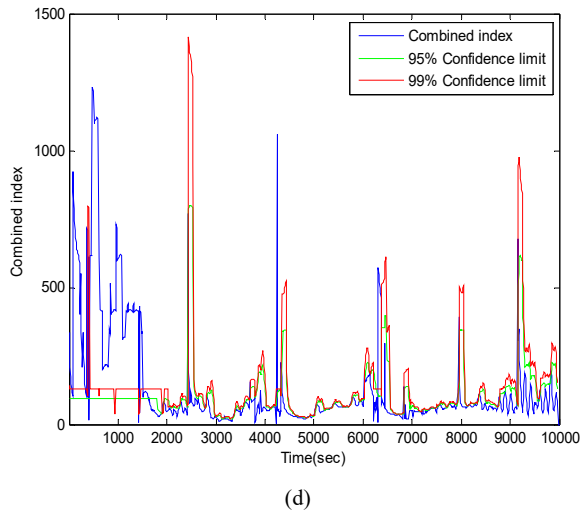

(a)

(b)

(c)

(d)

(c)

Fig. 6 (a) Hotelling T^2 for RADPLS on test data, (b) SPEx for RADPLS on test data, (c). SPEy for RADPLS on test data, (d) Combined index for RADPLS on test data
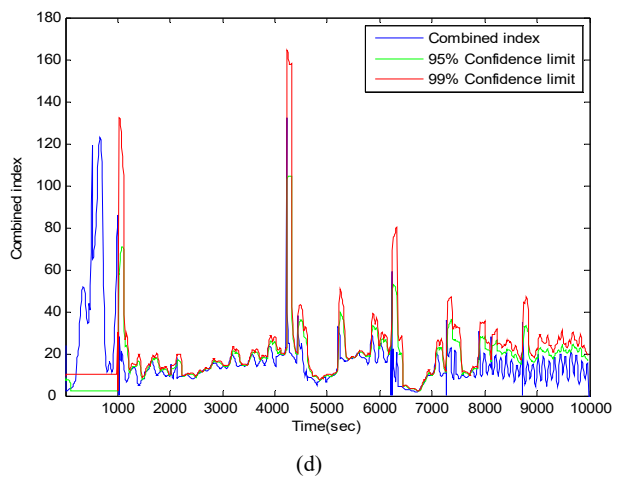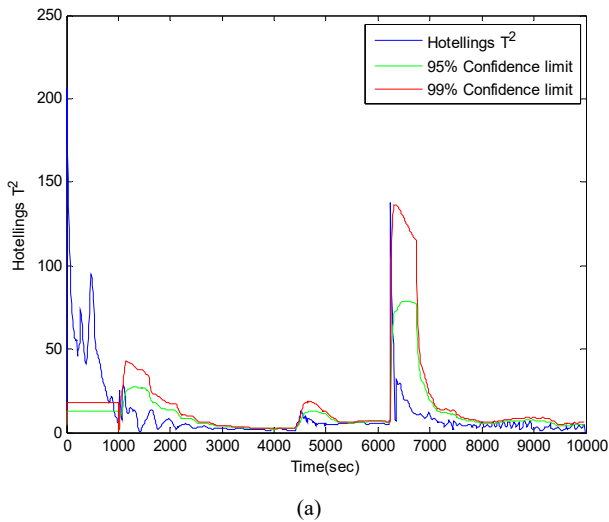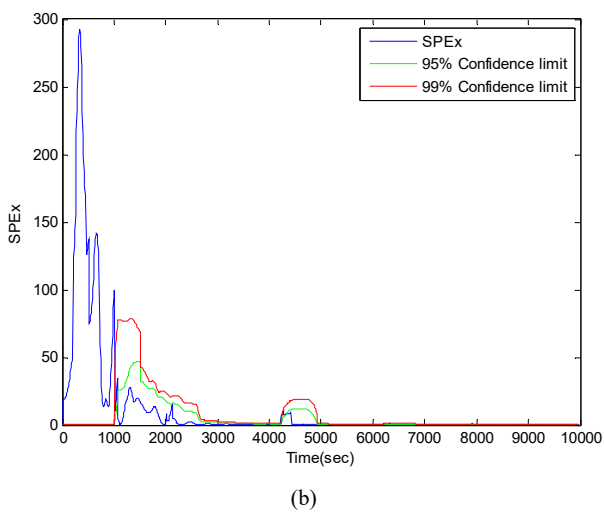

(d)

Fig. 7 (a) Hotelling T^2 for RADPLS on test data (fault100 samples, (b) SPEx for RADPLS on test data (fault100 samples), (c) SPEy for RADPLS on test data (fault 100 samples), (d) Combined index for RADPLS on test data (fault 100 samples)

(a)

From trying a different fault duration (i.e. the pressure falls to 150 bar for 100 recorded samples), it can be seen from Figs. 7 (a)–(d) that the fault was detected well.

The advantages of implementing RADPLS include the fact that the PLS model represents the nominal behavior throughout the duration of the process and hence, is sensitive to any changes in the process, including following the progression of a fault. Unlike the adaptive PLS algorithm proposed in Wang et al. [15], the model will not be affected by the fault. Furthermore, abnormal process behavior is indicated as out of statistical control and consequently the confidence limits will not adapt to the monitoring statistics

V. CONCLUSIONS

In this paper, a new approach, robust adaptive dynamic PLS, has been proposed. It was demonstrated that it can overcome the limitations of dynamic PLS and adaptive PLS through its application to an ammonia synthesis fixed-bed

(b)

reactor which exhibited complex dynamics. Static PLS showed limited performance and failed to predict the process behavior whilst dynamic PLS improved the process predictions on the validation data. However, the monitoring statistics showed that dynamic PLS produced a large number of false alarms. Application of adaptive PLS improved the model predictions capturing the changes in operating conditions. In practice these changes in the operating conditions are considered to be a process fault since the rapid and large oscillations damage the catalyst and hence these conditions should not be used in updating of the PLS model. Robust Adaptive Dynamic PLS improved the model performance and indicated when the process was out of statistical control by distinguishing between outliers and faults. This is a significant improvement for the monitoring of dynamic processes in that false alarms can be detected. This clearly seen from the comparison between false alarm rates produced from both approaches. Even though the proposed method shows some limitations in detection the full period of the fault for the aforementioned reasons, it significantly reduces the false alarm rate.

APPENDIX

TABLE IV
FALSE ALARM RATE OF MONITORING CHARTS FOR CALIBRATION AND VALIDATION DATA SETS USING DYNAMIC PLS

Chart	False alarm rate 95% confidence limits	False alarm rate 99% confidence limits
Calibration data set		
Hotelling T²	5%	1%
SPE$_X$	5%	0.75%
SPE$_Y$	2.25%	1.75%
Validation data set		
Hotelling T²	12%	8%
SPE$_X$	92%	75.1%
SPE$_Y$	24.5%	9.5%

TABLE V
FALSE ALARM RATE OF MONITORING CHARTS FOR THE VALIDATION DATA SET AND FAULT DETECTION RATE FOR THE TEST DATA SET USING ROBUST ADAPTIVE DYNAMIC PLS

Chart	False alarm rate 95% confidence limits	False alarm rate 99% confidence limits
Validation data set		
Hotelling T²	4.85%	1.11%
SPE$_X$	4.509%	0.90%
SPE$_Y$	3.1031%	0.80%
	Fault detection rate 95% confidence limits	Fault detection rate 99% confidence limits
test data set		
Hotelling T²	59.68%	56.25%
SPE$_X$	58.12%	54.68%
SPE$_Y$	62.18%	59.37%

REFERENCES

[1] C.C. Pantelides, J. G. Renfro," The online use of first-principles models in process operations: Review, current status and future needs" *Comput. Chem. Eng.* 2013, *51(0),* 136-148. DOI: 10.1016/j.compchemeng.2012.07.008

[2] P. Geladi, B. Kowalski, "Partial least square regression: A tutorial" *Anal. Chim. Acta.* 1986, *185(1),* 1-17. DOI:10.1016/0003-2670(86)80028-9

[3] A. Höskuldsson,"PLS regression methods" *J. Chemom.* 1988, *2(3),* 211–228. DOI: 10.1002/cem.1180020306

[4] S. Wold, M. Sjöström, L. Eriksson, " PLS-regression: a basic tool of chemometrics " *Chemom. Intell. Lab. Syst.* 2001, *58(2),* 109-130. DOI: 10.1016/S0169-7439(01)00155-1

[5] H. Abdi," Partial least squares regression and projection on latent structure regression (PLS Regression)" *Wiley Interdiscip. Rev.: Comput. Stat.* 2010, *2(1),* 97-106. DOI: 10.1002/wics.51

[6] M. H. Kaspar, W. H. Ray,"Chemometric methods for process monitoring and high-performance controller design" *AIChE J.* 1992, *38(10),* 1593-1608. DOI: 10.1002/aic.690381010

[7] A. Simoglou, E. B. Martin, A. J. Morris, " Multivariate statistical process control of an industrial fluidised-bed reactor "*Control Engineering Practice.* 2000, *8(8),* 893-909. DOI: 10.1016/S0967-0661(00)00015-0

[8] F. Yacoub, J. F. MacGregor," Analysis and optimization of a polyurethane reaction injection molding (RIM) process using multivariate projection methods" *Chemom. Intell. Lab. Syst.* 2003, *65(1),* 17-33. DOI: 10.1016/S0169-7439(02)00088-6

[9] O. Marjanovic, B. Lennox, D. Sandoz, K. Smith, M. Crofts," Real-time monitoring of an industrial batch process" *Comput. Chem. Eng.* 2006, *30(10-12),* 1476-1481. DOI: 10.1016/j.compchemeng.2006.05.040

[10] M.H. Kaspar, H. W. Ray," Dynamic PLS modelling for process control" *Chem. Eng. Sci.* 1993, *48(20),* 3447-3461. DOI: 10.1016/0098-1354(93)80079-3

[11] S. Lakshminarayanan, S. L. Shah, K. Nandakumar," Modeling and control of multivariable processes: Dynamic PLS approach" *AIChE J.* 1997, *43(9),* 2307-2322. DOI: 10.1002/aic.690430916

[12] S. J. Qin," Partial least squares regression for recursive system identification" presented at *32nd IEEE Conf. on Decision and Control,* Austin, USA, December 1993, DOI: 10.1109/cdc.1993.325671

[13] S. Wold," Exponentially Weighted Moving Principal Component Analysis and Projections to Latent Structuers" *Chemom. Intell. Lab. Syst.* 1994, *23(1),* 149-161. DOI:10.1016/0169-7439(93)E0075-F

[14] S. J. Qin," Recursive PLS algorithms for adaptive data modeling" *Comput. Chem. Eng.* 1998, *22(4-5),* 503-514. DOI:10.1016/S0098-1354(97)00262-7

[15] X. Wang, U. Kruger, B. Lennox," Recursive partial least squares algorithms for monitoring complex industrial processes" *Control Engineering Practice.* 2003, *11(6),* 613-632. DOI: 10.1016/S0967-0661(02)00096-5

[16] L. E. Wangen, B. R. Kowalski," A multiblock partial least squares algorithm for investigating complex chemical systems" *J. Chemom.* 1989, *3(1),* 3-20. DOI: 10.1002/cem.1180030104

[17] J.F. MacGregor, C. Jaeckle, C. Kiparissides, M. Koutoudi," Process monitoring and diagnosis by multiblock PLS methods" *AIChE J.* 1994, *40(5),* 826-838. DOI: 10.1002/aic.690400509

[18] S. Wold, N. Kettaneh, K. Tjessem," Hierarchical multiblock PLS and PC models for easier model interpretation and as an alternative to variable selection" *J. Chemom.* 1996, *10(5-6),* 463-482. DOI: 10.1002/(SICI)1099-128X(199609)10:5/6<463::AID-CEM445>3.0.CO;2-L

[19] J. A. Westerhuis, P. M. J. Coenegracht," Multivariate modelling of the pharmaceutical two-step process of wet granulation and tableting with multiblock partial least squares" *J. Chemom.* 1997, *11(5),* 379-392.

[20] X. Wang, U. Kruger, B. Lennox, P. Goulding," A novel multiblock method using latent variable partial least squares" *in Proc. Am. Control Conf.*, Arlington, VA, June 2001.

[21] D. Zhou, G. Li, S. J. Qin," Total projection to latent structures for process monitoring" *AIChE J.* 2010, *56(1),* 168-178. DOI: 10.1002/aic.11977

[22] N.B. Gallagher, B. M. Wise, S. W. Butler, D. D. White, G.G. Barna," Development and Benchmarking of Multivariate Statistical Process Control Tools for a Semiconductor Etch Process: Improving Robustness Through Model Updating" *in Proc. of ADCHEM 97,* Banff, Canada, June 1997.

[23] Helland, K., H. E. Berntsen, O. Borgen, H. Martens,"Recursive algorithm for partial least squares regression" *Chemom. Intell. Lab. Syst.* 1992, *14(1-3),* 129-137. DOI:10.1016/0169-7439(92)80098-O

[24] C. Rosen, J. A. Lennox," Multivariate and multiscale monitoring of wastewater treatment" *Water Res.* 2001, *35(14),* 3402-3410. DOI: 10.1016/S0043-1354(01)00069-0

[25] H. W. Lee, M. W. Lee, J. M. Park," Robust adaptive partial least squares modeling of a full-scale industrial wastewater treatment proces" *Ind. Eng. Chem. Res.* 2006, *46(3),* 955-964. DOI: 10.1021/ie061094+

[26] S. J. Qin, H. H. Yue, " Reconstruction based fault identification using a combined index" *Ind. Eng. Chem. Res.* 2001*, 40(20),* 4403. DOI**:** 10.1021/ie000141+

[27] S. J. Qin," Statistical process monitoring: Basics and beyond" *J. Chemom.* 2003, *17(8-9),* 480-502. DOI: 10.1002/cem.800

[28] D. J. Cummins, C. W. Andrew," Iteratively reweighted partial least squares: A performance analysis by Montecarlo simulation" *J. Chemom.* 1995, *9(6),* 489-507. DOI: 10.1002/cem.1180090607

[29] J. C. Morud, S. Skogestad," Analysis of instability in an industrial ammonia reactor" *AIChE J.* 1998, *44(4),* 888-895. DOI: 10.1002/aic.690440414

[30] E. Holter, *M.Sc. Thesis," Feedforward for Stabilization of an Ammonia Synthesis Reactor*" Department of Engineering Cybernetics, Norwegian University of Science and Technology, 2010.

[31] N. L. Ricker," The use of biased least-squares estimators for parameters in discrete-time pulse-response models" *Ind. Eng. Chem. Res.* 1988, *27(2),* 343-350.

[32] J. S. Qin, T. J. McAvoy," A data-based process modeling approach and its applications" *In Proc.of the 3rd IFAC Conf.* 1993.

[33] G. Baffi, E. B. Martin, A. J. Morris," Non-linear dynamic projection to latent structures modelling" *Chemom. Intell. Lab. Syst.* 2000, *52(1),* 5-22. DOI:10.1016/S0169-7439(00)00083-6

[34] D. C. Montgomery, *Introduction to statistical quality control.* 5th ed., John Wiley& Sons. USA 2005**.**

[35] H. Akaike," A new look at the statistical model identification" *IEEE Trans. Autom. Control.*1974, *19(6),* 716-723.