Periodica Polytechnica
Chemical Engineering

59(2), pp. 145-150, 2015
DOI:10.3311/PPch.2182

RESEARCH ARTICLE

Online Monitoring of Catalyst Deactivation Based on Data Reconciliation and Flowsheeting Simulator

Barbara Farsang[1*], Sándor Németh[1], János Abonyi[1]

Received 29 June 2013; accepted 31 January 2014

Abstract

Most of chemical technologies are based on heterogeneous catalytic reactions (~80%). Model based tools used for design, control and monitoring of these processes require accurate kinetic parameters of these catalytic reactions. Laboratory measurements and on-line analysers can be used to monitor decreasing catalyst activity. However these measurements are affected by errors influencing the estimation of kinetic parameters. To increase the robustness and accuracy of the estimation we developed a method based on the integrated application of data reconciliation and flowsheeting simulation. The proposed technique is applied for an industrial hydrogenation system. The estimated reaction kinetic parameters can be utilized advanced process control of the process.

Keywords

catalyst decay, data reconciliation. flowsheeting simulator, kinetic parameter estimation

1 Introduction

Life time of catalyst is an important aspect in design of chemical technologies because the cost of catalsyt is 0.22 % of the cost of petrochemical products. Rapid loss of activity causes loss of economic benefit and loss of time for production due to the interruption of process operation. At the design, operation and control it should be considered that the life time of catalyst may be shorted due to the following factors [1]:

- poisoning: contaminants in the reactor feed,
- fouling: thermal degradation (sintering, evaporation, volatilization), leaching by the reaction mixture,
- coking (formation of deposits): coverage of the surface by coke or carbon from undesired reactions of hydrocarbon reactants, intermediates, and products,
- mechanical damage.

Heterogenious catalytic system needs special attention. Table 1 shows how often the catalyst should be regenerated in case of different reactor type. The life time of catalyst also depends on the reaction, e.g. catalysts of polymerization reactions deactivate more rapidly than catalysts of methanol synthesis that can work for years without regeneration (Fig. 1).

Loss of catalyst activity can be characterised with time-dependent empirical equations. Usually this method is very time-consuming since numerous measurements should be performed to get reliable relation between catalyst activity, concentrations and operating conditions [2, 4]. Thanks to the development of analytical chemistry and catalyst characterization methods there are several tools to evaluate catalyst deactivation routes [8]. These methods need kinetics of catalytic reactions and of deactivation, pore-diffusion processes and reactor model. Rate of deactivation (da/dt) is followed up the mass flow of key components. Differential balances are set up describing the change of mass of reactants in the convective flow within a small volume element in the reactor and the change of mass of reactant in the pellet by catalytic reaction and pore diffusion. Simultaneous integration of the respective mass balances and including heat balances leads to concentration profiles along

[1] Department of Process Engineering, University of Pannonia,
P.O. Box 158, Veszprém, H-8201 Hungary
[*]Corresponding author, e-mail: farsangb@fmt.uni-pannon.hu

Table 1 Loss of activity in case of several reactor [1]

Time-scale of deactivation	Typical reactor type
Years	Fixed-bed reactor usually no regeneration
Months	Fixed-bed reactor regeneration while reactor is off-line
Weeks	Fixed-bed reactors in swing mode moving-bed reactor
Minutes-days	Fluidized-bed reactor slurry reactor continuous regeneration
Seconds	Entrained-flow reactor (riser) with continuous regeneration

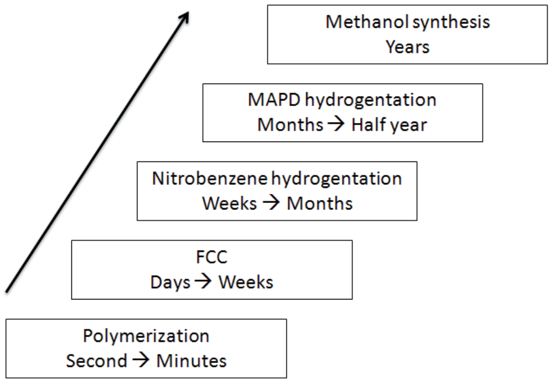

Fig. 1 Loss of activity in case of several catalytic reactions [1]

the reactor and to outlet concentrations [1]. These rigorous models can be used for dynamic simulation [11]. Although this approach gives accurate results the industrially application is constrained due to the high cost of the required measurement equipments. For some processes specific methods are available to monitor catalyst deactivation, e.g. micro-activity test (MAT) ASTM-D 3907-80 is a well known technique for a quick and simple screening of FCC catalysts [12].

Since it is hard to monitor and predict how activity decays over time, catalyst deactivation is the main bottleneck of the application of model based tools used for design, process control and monitoring. Laboratory measurements can be used to continuously re-estimate kinetic parameters [3]. However, laboratory samples are usually taken once or twice a day. When it is needed frequent information can be gained from online analysers. However, the reliability of these measurements is not as good as laboratory tests. Laboratory values and data reconciliation techniques can be used to validate and correct online measurements. A detailed model of the process and the reaction system should be applied for the identification of these kinetic parameters. For complex processes model based estimation of kinetic parameters require flowsheeting simulators thanks to the availability of thermodynamic and built in process unit models. Flowsheeting simulators utilizing validated measures can infer changes of catalyst activity.

So the question arises how we can monitor the state of technology based on some uncertain measurements and how we can develop an accurate model of technology based on these uncertain measurements using flowsheeting simulator so that catalyst deactivation is also taken into account. To increase the robustness and accuracy of the estimation of catalyst activity we developed a method based on the integrated application of data reconciliation and flowsheeting simulation. The proposed approach is described in Section 2. The presented technique is applied for an industrial hydrogenation system, where the estimated reaction kinetic parameters can be utilized advanced process control of the process. The description of technology and the results are summarised in Section 3. Finally, Section 4 draws some conclusions.

2 Iterative data reconciliation, simulation and parameter identification

Process simulators are based on first-principles (also referred as white box) models. These models consist of balance equations representing detailed physical-chemical information about the system. Unfortunately, the development of first-principle models of complex industrial process is very difficult. In particular, it is difficult to build precise first-principle models that can explain the dynamics of catalyst deactivation. When we do not have detailed *a prior* knowledge about the process, data based model can be developed because data carry information about the process. In this case historical process data is used to build statistical models to determine the relationship between inputs and outputs. However, measurements are

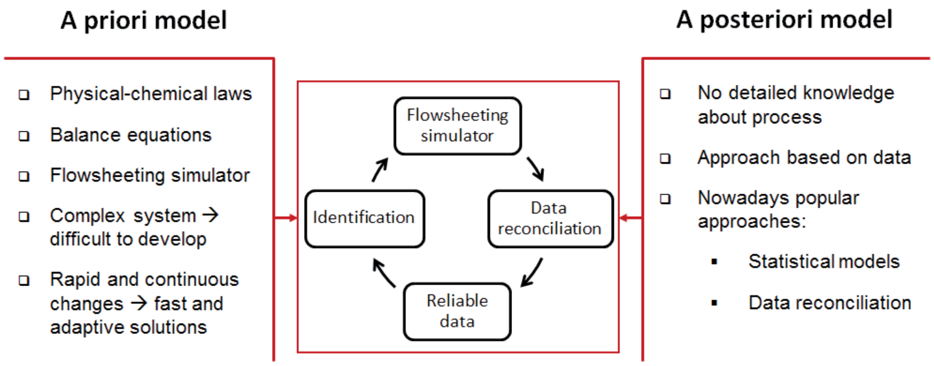

Fig. 2 Comparison of a priori and data based models

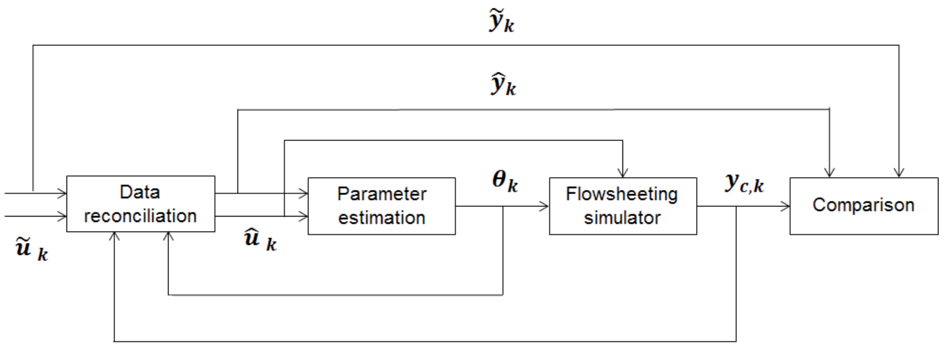

Fig. 3 Structure of procedure for treating measurement error and developing simulator

always affected by errors affecting the quality of these models. A new direction is the combination simulators and data driven statistical models [7]. Historical process data can contain this information but measurements are not consistent and they are affected by error. Using data reconciliation technique we can treat this random error. This technique allows us to check the acceptability of measurements. When accurate data is available, flowsheeting simulator gives more reliable results, that make possible further development of models.

This means, data reconciliation allows us to check the reliability of these measurements [6], and reconsolidated data can be used to build accurate models. Data reconciliation calculates minimal correction of measured variables to make them verify a set of model constraints. It minimizes the difference between the measured and reconciled values taking into account the variance of the variables and ensures that reconciled parameters satisfy balance equations as equality and inequality constraints [9, 10].

$$\textit{minimizing} \quad \phi\left(\hat{\mathbf{x}},\hat{\mathbf{z}}\right)=\left(\tilde{\mathbf{x}}-\hat{\mathbf{x}}\right)^T \mathbf{V}^{-1}\left(\tilde{\mathbf{x}}-\hat{\mathbf{x}}\right) \tag{1}$$

$$\textit{subject to} \quad \mathbf{f}\left(\hat{\mathbf{x}},\hat{\mathbf{z}}\right)=0 \quad \textit{and} \quad \mathbf{g}\left(\hat{\mathbf{x}},\hat{\mathbf{z}}\right)\geq 0 \tag{2}$$

where

- $\tilde{\mathbf{x}}$ is a vector of raw measurements for M process variables,
- $\hat{\mathbf{x}}$ is a vector of estimates (reconciled values) for M process variables,
- $\hat{\mathbf{z}}$ is a vector of estimates for unmeasured process variables ($\mathbf{z}$),
- $\mathbf{V}$ is covariance matrix of the measurements,
- $\mathbf{f}$ is a vector describing functional form of model equality constraints,
- $\mathbf{g}$ is a vector describing functional form of model inequality constraints.

The key idea of our approach is that simulator development and data reconciliation should be performed simultaneously. Firstly, raw data is reconciled. The unknown parameters of the simulator are identified based on this for reconciled data. The reconciled data and estimated parameters are used as an input of the process simulator. This improved model can be used again for reconciliation of the raw data. This procedure could be repeated while there is a significant difference between reconciled and calculated process values (Fig. 2).

To formulate the problem let us consider an $\mathbf{x}$ vector containing the vector of inputs $\mathbf{u}$ and outputs $\mathbf{y}$.

Collected historical process data ($\tilde{\mathbf{x}}_k = \{\tilde{\mathbf{u}}_k, \tilde{\mathbf{y}}_k\}$) can be compared to simulation results ($\hat{\mathbf{y}}_k$) (Fig. 3). If there is significant difference between reconciled and calculated outputs, then the unknown parameters of the simulator (Θ_k) are re-identified based on the reconciled input and outputs. Based on reconciled data and re-identified parameters new simulation is elaborated and the reconciled and calculated outputs are compared again. Reconciliation and parameter estimation procedure continues until the difference between reconciled and calculated outputs is insignificant. Since catalyst deactivation is included in Θ_k parameter, this iterative method is resulted continuously decreasing parameter in time.

In practice mostly laboratory measurements are used to estimate the kinetic parameters that can be regarded as constant between the sampling period. When the life time of catalyst is in the range of years catalyst deactivation is negligible within this period, this assumption is appropriate. When more frequent information is needed, the estimation should be based on online analysers. However, the reliability of these measurements is not as good as laboratory tests. Data reconciliation can increase the accuracy of these measurements. If simulation results that measured and reconciled values are almost identical then it can be stated that the model and the data are consistent, so they can be used for optimization. These steps can be applied in an iterative way as illustrated in Fig. 4.

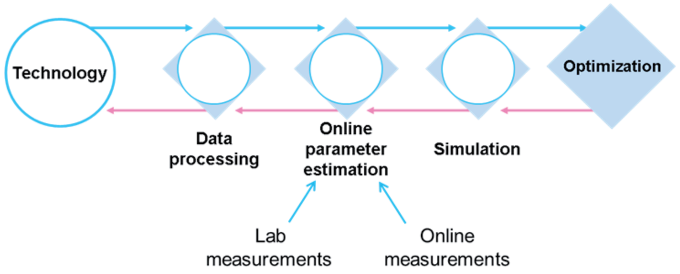

Fig. 4 Developed iterative method

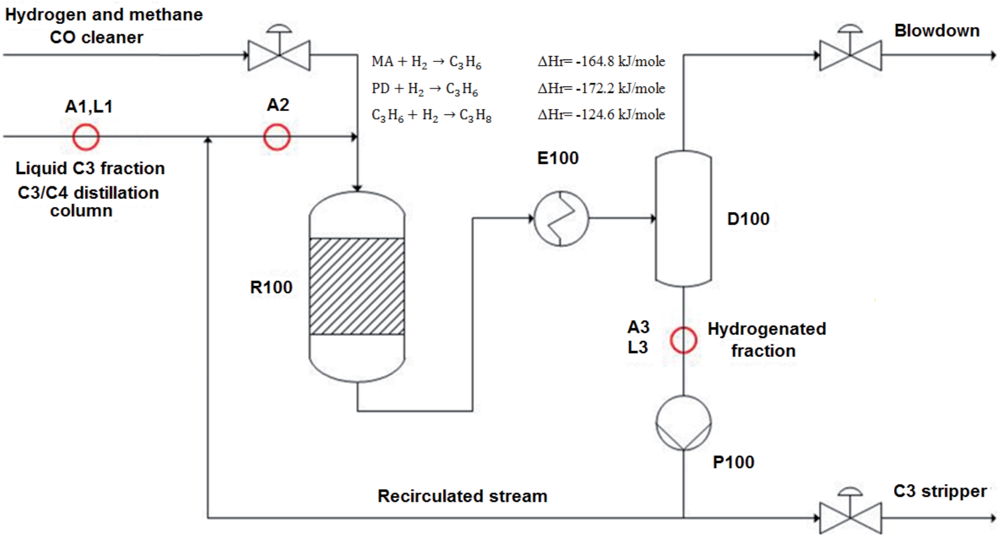

Fig. 5 Process flowsheet diagram of C3 hydrogenation system

3 Results and discussion

The proposed concept has been applied for an industrial C3 selective hydrogenation technology. Tisza Chemical Group (TVK) is Hungary's largest petrochemical company. In olefin plants polymer raw materials are produced by steam cracking of naphtha or gasoline. At high temperature numerous free radical reactions occur. Cracked gas includes different hydrocarbons. First, the light components are separated, and then the C3 fraction is separated from the C4+ fraction. C3 fraction consists of propane, propylene, methyl-acetylene (MA) and propadiene (PD). The last two components are undesirable because they poison the catalysts for polymerization reactions. Another problem is that these components are difficult to separate from the product by distillation, so these hydrocarbons should be hydrogenated. The hydrogenated stream goes to the propane-propylene separation column, then the pure propylene goes to the polypropylene polymer plant.

Figure 5 shows the flowsheet diagram of C3 hydrogenation system. The function of the technology is the transformation of methyl-acetylene and propadiene by catalytic reaction to propylene, as propylene should not be transformed to propane. Liquid olefin feed and gaseous hydrogen pass through the catalyst bed in the same direction: from top to bottom. Outlet flow of the reactor is cooled by water then hydrogen and liquid phase are separated. Recirculated flow has got two important functions: cools the reactor and dilutes the inlet C3 stream because MAPD content of input flow is high. The hydrogenation reaction is characterized by the MA content: it must be less than one mole percent.

To estimate the catalyst deactivation rate the composition of inlet and outlet stream of reactor should be known. Compositions of these streams are measured by online analysers in three locations and there are two sampling points where sample is taken for laboratory measurements. Online analysers measure propane and MA concentration. There are two laboratory measurements in every day, where the methane, ethane, propane, propylene, methyl-acetylene, propadiene, C4 and C6 contents are also measured.

The model and the flowsheeting simulator of C3 hydrogenated system are developed in Aspen Plus software to determine optimal operating parameters. Except for the one reaction kinetic parameter, all necessary information is a priori known.

In the literature the activation energy of the main hydrogenation reactions is known for all reactions (Propadiene: 4400 kJ/kmole, methyl-acetylene: 8960 kJ/kmole, propylene: 18170 kJ/kmole [5]) but pre-exponential factor should be identified based on measured data taking into account the deactivation of catalyst. The main steps of method are introduced in case of methyl-acetylene. The rate equation is described by the following equation:

$$r_{MA} = k_{MA} \cdot \left(\frac{-E_A}{RT} \right) \cdot c_{MA} \cdot c_{H_2} \tag{3}$$

where k_{MA} is the pre-exponential factor, c is a concentration in mole fraction unit, E_A is the activation energy in kJ/kmole unit, R is gas constant in kJ/kmole and T is temperature in K.

Since the high excess of hydrogen, its concentration is assumed to be constant. Thus, pre-exponential factor includes the dependence of hydrogen. So the simplified rate equation becomes as:

$$r_{MA} = k'_{MA} \cdot \left(\frac{-E_A}{RT} \right) \cdot c_{MA} \tag{4}$$

The average pre-exponential factor is estimated from laboratory data with the proposed simulator. Processed data covers two-weeks interval. Since the reaction is extremely fast, the time constant of the process is less than one minute. As the sampling time is five minutes, steady state simulation is used for the analysis. This is a great benefit because we must examine the concentration distribution along the length of reactor. We developed an Visual Basic for Excel (VBE) macro based framework to enter all historical process data to the simulator.

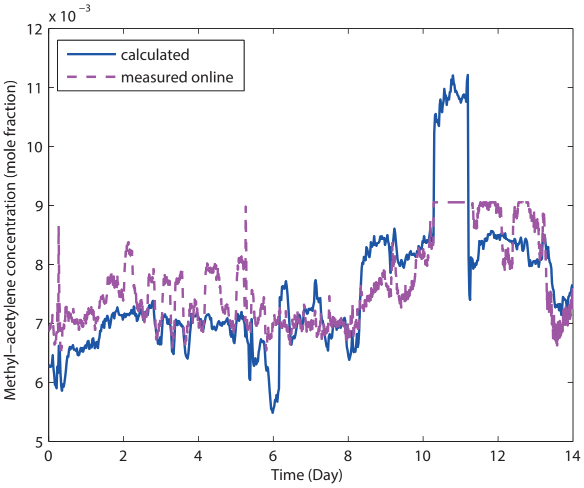

Fig. 6 Simulation results using average pre-exponential factor

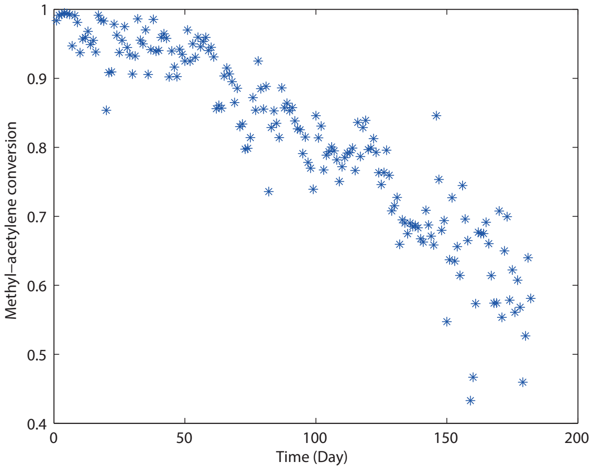

Fig. 7 Methyl-acetylene conversion decreases over time

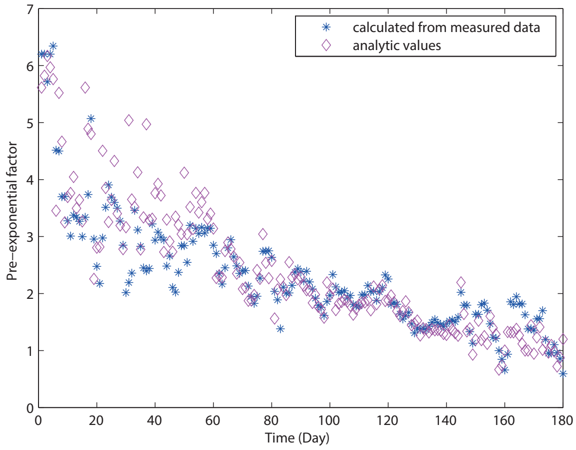

Fig. 8 Estimation of pre-exponential factor in analytical way and using flowsheeting simulator

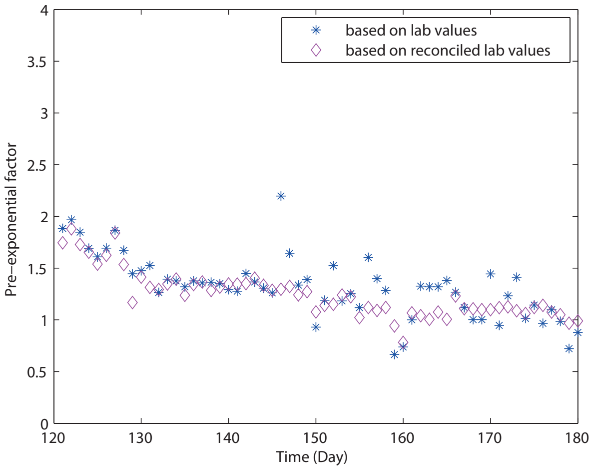

Fig. 9 Effect of data reconciliation

When all outlet concentration values are collected, they are plotted at that time. Significant differences were observed between the measured and calculated values (Fig. 6).

Therefore, a half-year interval data was also analysed. It has been found that conversion decreases (Fig. 7), so outlet MA concentration increases despite of nearly the same load. So the catalyst decay is not negligible even in a short interval. That is, the pre-exponential factor is time-dependent.

In case of every measured data pairs we estimate the pre-exponential factor with a simulator and in analytical way. Since the model is very simple it can be solved easily.

We found that the two approaches give same results. However, the standard deviation of the data set is large. This effect can be handled by data reconciliation. Based component balance equation the measured concentration values were reconciled that made possible more accurate parameter estimation. The result is shown in Fig. 9 where a small section of operation is zoomed to make the difference visible. In this figure we can see that estimated values have much lower standard deviation.

The time-dependent kinetic parameters were estimated by fitting a hyperbolic function ($y = a/(x-b)+c$) on the pre-treated measurements. We used simplex method to determine the optimal parameter values (a,b,c). This function has been built into the flowsheeting simulator. Figure 10 shows that the simulation results with reconciliation are much closer to the measured data then simulation result without reconciliation.

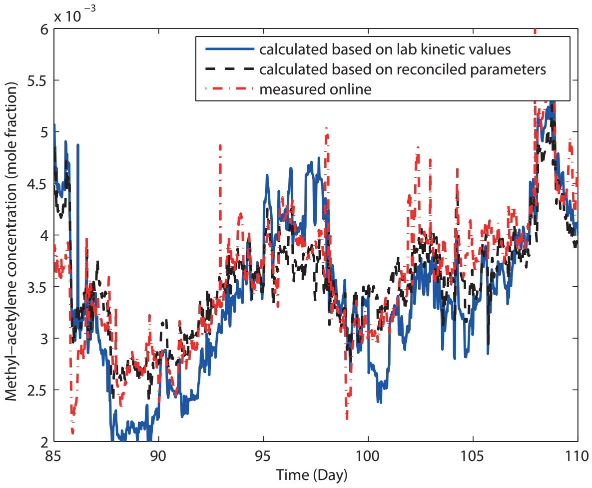

Fig. 10 Comparison of simulation results using estimated parameters based on measured and reconciled values

4 Conclusion

Model based process control and optimization of catalytic chemical processes suffer from catalyst deactivation as they need accurate estimates of reaction kinetic parameters. Data reconciliation of laboratory measurements, process variables and signals of online analysers can improve the performance of estimation. However, to get reliable data, reliable model should be used for data reconciliation and parameter identification. We developed an iterative approach to support this model development. Extracted kinetic parameter is approximated as time-varying function. This deactivation model has been incorporated to a flowsheeting simulator. The developed model describes well the operation of real system as the resulted simulator gives good prediction performance through the whole life-cycle. The results demonstrate the effectiveness of the proposed approaches. The developed simulator and monitoring algorithm can be utilized in an Advanced Process Control (APC) algorithm as APC can always use actual kinetic parameters thus taking into account the catalyst deactivation.

Acknowledgements

This reserach was realized in the frames of TÁMOP 4.2.4. A/2-11-1-2012-0001 ‘National Excellence Program Elaborating and operating an inland student and researcher personal support system convergence program’ and the TÁMOP 4.2.2/A-11/1/KONV-2012-0071 project. These projects were subsidized by the European Union and co-financed by the European Social.

A part of this work was presented at the Conference of Chemical Engineering, Veszprém, 2013.

References

[1] Baerns, M., Boskovic, G. "Catalyst deactivation." In: *Basic principles in applied catalysis*. Springer-Verlag. Berlin. pp. 477-503. 2004. DOI: 10.1007/978-3-662-05981-4_14

[2] Birtill, J. J. "But will it last until the shutdown? Deciphering catalyst decay!." *Catalysis Today*. 81 (4). pp. 531-545. 2003. DOI: 10.1016/S0920-5861(03)00152-4

[3] Farsang, B., Gomori, Z., Horvath, G., Nagy, G., Nemeth, S., Abonyi, J. "Simultaneous validation of online analyzers and process simulators by process data reconciliation." *Chemical Engineering Transactions*. 32. pp. 1303-1308. 2013. DOI: 10.3303/CET1332218

[4] Forzatti, P., Lietti, L. "Catalyst deactivation." *Catalysis Today*. 52 (2). pp. 165-181. 1999. DOI: 10.1016/S0920-5861(99)00074-7

[5] Gobbo, R., Soares, R., Lansarin, M., Secchi, A., Ferreira, M. "Modeling simulation, and optimization of a front-end system for acetylene hydrogenation reactors." *Brazilian Journal of Chemical Engineering*. 21 (4). pp. 545-556. 2004. DOI: 10.1590/S0104-66322004000400004

[6] Kadlec, P., Gabrys, B., Strandt, S. "Data-driven soft sensors in the process industry." *Computers and Chemical Engineering*. 33 (4). pp. 795-814. 2009. DOI: 10.1016/j.compchemeng.2008.12.012

[7] Kanoa, M., Nakagawa, Y. "Data-based process monitoring, process control and quality improvement: recent developments and applications in steel industry." *Computers and Chemical Engineering*. 32 (1-2). pp. 12-24. 2008.

[8] Larsson, A. C. "*Study of catalyst deactivation in three different industrial processes*." Thesis for the degree of Doctor of Technology. Växjö University. Acta Wexionensia. 106. 2007.

[9] Prata, D. M., Schwaab, M., Lima, E. L., Pinto, J. C. "Nonlinear dynamic data reconciliation and parameter estimation through particle swarm optimization: application for an industrial polypropylene reactor." *Chemical Engineering Science*, 64 (18), pp. 3953-3967. 2009. DOI: 10.1016/j.ces.2009.05.028

[10] Prata, D. M., Schwaab, M., Lima, E. L., Pinto, J. C. "Simultaneous robust data reconciliation and gross error detection through particle swarm optimization for an industrial polypropylene reactor." *Chemical Engineering Science*. 65 (17). pp. 4943-4954. 2010. DOI: 10.1016/j.ces.2010.05.017

[11] Rahimpour, M. R., Bayat, M., Rahmani, F. "Dynamic simulation of a cascade fluidized-bed membrane reactor in the presence of longterm catalyst deactivation for methanol synthesis." *Chemical Engineering Science*. 65 (14). pp. 4239-4249. 2010. DOI: 10.1016/j.ces.2010.04.018

[12] Wallenstein, D., Harding, R. H., Witzler, J., Zhao, X. "Rational assessment of FCC catalyst performance by utilization of micro-activity testing." *Applied Catalysis A: General*. 167 (1). pp. 141-155. 1998.