

NUMERICAL AND EXPERIMENTAL COMPARISON OF ON-LINE METHODS FOR DETECTION OF THERMAL RUNAWAY EVENTS IN BATCH AND SEMI-BATCH CHEMICAL REACTORS

Molga E.* and Lewak M.

*Author for correspondence

Department of Chemical and Process Engineering
Warsaw University of Technology
ul. Waryńskiego 1, 00-645 Warszawa
Poland
E-mail: e.molga@ichip.pw.edu.pl

ABSTRACT

In this paper the results of comparative study carried out for three *on-line* methods used to detect thermal runaway events in chemical reactors have been presented and discussed. An ability of the criterion of derivatives, the divergence criterion and the algorithm employed neural networks, all used to detect approaching thermal runaways has been compared.

INTRODUCTION

Strongly exothermic reactions carried out in batch and semi-batch reactors can at some circumstances provoke a loss of thermal control – i.e. thermal runaway event. If from some reason unexpected increase of the reactor temperature takes place, this causes an increase of the rate of heat generated due to the reaction progress, which in turn leads for further increase of the reactor temperature. So, a self acceleration effect can be observed, which can lead to very dangerous decomposition reactions in the reacting mass followed by explosions, serious damages, environment decontamination and even human losses.

Several *off-line* criteria, which help to predict safe and simultaneously economically effective operating conditions, have been elaborated to prevent thermal runaways and they are widely discussed in the literature of subject [1]. However, even during a run carried out at nominally safe operating conditions the thermal runaway can occur due to human mistake or unexpected damage of the stirring and/or cooling system. Therefore, also the *on-line* temperature control is required for early detection of approaching thermal runaway.

A few *on-line* methods are used to distinguish between safe and dangerous increases of the reactor temperature – among others the criterion of derivatives and the divergence criterion are commonly used[1]. Recently, also a new method for *on-line*

distinction between runaway and no-runaway increase of the reactor temperature is proposed [2].

NOMENCLATURE

A	[m ²]	Heat exchange surface area
c	[mol/m ³]	Molar concentration
c_p	[J/kg K]	Specific heat capacity
E	[J/mol]	Activation energy
F	[K]	Function (Eq. 8)
k	[dm ³ /mol ² s]	Kinetic rate constant
k	[-]	Iteration number
K	[-]	Number of steps forward or backward
n	[mol]	Number of moles
r	[mol/m ³ s]	Reaction rate
R_H	[-]	Heat capacity ratio (Eq.11)
t	[s]	Time
T	[K]	Temperature
V	[m ³]	Volume
Wt	[-]	Westertep Number (Eq. 7)

Special characters

ΔH_R	[J/mol]	Reaction enthalpy
$\Delta T_{ad,o}$	[K]	Adiabatic temperature rise (Eq. 10)
ε	[-]	Reactants volume ratio (Eq. 9)
ρ	[kg/m ³]	Density
$\Phi_{v,A}$	[m ³ /s]	Volumetric addition rate of reactant A
θ	[-]	Dimensionless time

Subscripts

A	Water
B	Acetic anhydrite
C	Acetic acid
c	Cooling liquid
dos	Dosed
ps	Phase space
ta	Target

The last method is based on application of neural networks, which are able to approximate a dynamic behaviour of any non-linear system.

All methods, which help to distinguish between safe and dangerous increase of the reactor temperature, can be used to elaborate an efficient and robust early warning detection system (EWDS).

Such EWDS device is indispensable to detect and evaluate dangerous situations, so to take the appropriate protective countermeasures as: pressure relief, full cooling, reaction quenching by addition of the inhibitor, cold inert liquid or dumping the reaction content into a cold catch tank.

An essential element of any EWDS is the appropriate safety criterion, which should work *on-line*, being practically independent of the monitored process and applied operating conditions.

A detailed characterisation of the safety criteria used for safe operation of batch and semi-batch chemical reactors indicates that most of safety criteria proposed in the literature cannot be used for *on-line* analysis [1]. This is because: or they are model-based, so detailed information on the reaction kinetics is required; neither they are able to work *off-line* only. Therefore in practice, only two criteria are recommended for efficient detection of thermal runaway in chemical reactors: the criterion of derivatives, called also as Hub and Jones criterion [3] and the divergence criterion [4-6]. However, it has been found that both these criteria, employed in real experimental systems suffer from inadequacy, inaccuracy or too high sensitivity to transformation of measured temperature signals so, very often they generate false alarms, etc. To improve their applicability and prevent false alarms these algorithms require a determination of additional specific experimental constants.

In this paper the method involving the neural network has been tested. The neural net transforms the temperature signal measured in the chemical reactor and detects if the system is on a trajectory approaching thermal runaway. Only simple and safe experimental thermal characterization of the reactor equipment is required in this case. This characterization can be done with heating-up and cooling-down experiments, carried out even without the exothermic reactions. The results of preliminary estimations obtained with this approach are very promising.

EXPERIMENTAL

Stirred tank reactors can be run non-continuously following two: batch or semibatch operating modes. For strongly exothermic, liquid-phase homogeneous, reaction carried out in such reactors thermal runaway events can be observed.

In this analysis, the hydrolysis of the acetic anhydrite has been chosen as the testing reaction. Due to its relatively high exothermicity, this reaction is fully representative for a set of liquid-phase homogeneous reactions, for which thermal runaway can be expected. The stoichiometric equation for the considered hydrolysis reaction read as follows:



where A – is the water, B – the acetic anhydrite and C – the acetic acid.

Because of the limited solubility of the acetic anhydrite in water, an appropriate addition of the acetic acid has been added at the reaction beginning to keep the reaction mixture always homogeneous.

A series of the experiments has been carried out in the RC1 Mettler Toledo reaction calorimeter. A detailed description of the experimental set-up is given elsewhere [7].

For semibatch operating mode, the reactant B is initially placed into the reactor vessel (with a small addition of C), while the reactant A is dosed with the chosen addition rate. A perfect mixing of the reactor content is assumed, so no temperature and concentration gradients are detected inside the reacting mixture. Also no heat and volume change effects due to mixing of the reactants A and B are noticed and unlimited mutual solubility the reactants A and B as well as the reaction product can be assumed, so the reacting mixture is always homogeneous.

In the industrial practice a jacketed reactor vessels with the cooling liquid of chosen, constant temperature T_c are usually employed. A schematic diagram of the semibatch stirred tank reactor is shown in Fig. 1.

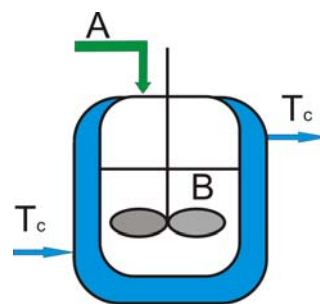


Figure 1 A schematic diagram the semibatch stirred tank reactor

For such reacting system, the appropriate mass balance equations for the compound A and B can be formulated as follows:

- for the reactant A

$$\frac{dn_A}{dt} = \Phi_{V,A} c_{A,dos} - rV \quad (2)$$

- for the reactant B

$$\frac{dn_B}{dt} = -rV \quad (3)$$

For the considered semibatch case the initial condition for the amount of reactant B reads as follows: $n_B = n_{B0}$ at $t = 0$. Notice, that after finishing of the dosing period – i.e. for $t > t_{dos}$, the addition rate of the reactant A becomes equal to zero: $\Phi_{V,A} = 0$, where t_{dos} is the dosing time.

The instantaneous volume of the reacting mixture V , as it appears in Eqs. 2 and 3, can be estimated with the following relationships; - during the dosing period (for $0 < t < t_{dos}$)

$V = V_{Bo} + \Phi_{V,A} t$, while after dosing period (for $t > t_{dos}$) this volume is constant and equal to: $V = V_{Bo} + \Phi_{V,A} t_{dos}$.

The mass balance equations (Eqs. 2 and 3) are supplemented by the energy balance equation, which for the considered case reads as follows:

$$\left(\rho V c_p\right)_{rm} \frac{dT}{dt} = \quad (4)$$

$$\left(-\Delta H_B\right) r V - \left(\rho \Phi_{V,A} c_p\right)_{dos} \left(T - T_{dos}\right) - (U A) \left(T - T_c\right)$$

where, the same as above, for $t > t_{dos}$ the addition rate becomes equal to zero: $\Phi_{V,A} = 0$.

Notice, that the actual value of the product (U A) depends on the overall heat transfer coefficient – U and the heat exchange surface area – A and it can be related to the actual volume of the reacting mixture as follows: $UA = (UA)_o \frac{V}{V_{Bo}}$.

Mass and energy balance equations (Eqs. 2-4) can be directly used also to model the batch operating mode, taking just $\Phi_{V,A} = 0$ in Eqs. 2 and 4 and placing the initial condition for the amount of reactant A as: $n_A = n_{A0}$ at $t = 0$. Volume of the reacting mixture and a value of the product (U A) in this case are constant and equal to: $V_R = V_{Bo} + V_{A0}$ and $UA = (UA)_o \frac{V_R}{V_{Bo}}$, respectively.

For known reaction kinetics the reaction rate r appearing in Eqs. 2-4 can be easily estimated and for the considered reaction scheme the second order kinetics is usually employed:

$$r = k c_A c_B \quad (5)$$

where the reaction rate constant depends on the temperature following the Arrhenius equation: $k = k_o \exp(-E/RT)$.

After transformation with the dimensionless variables and model parameters, the set of model equations (Eqs. 2-5) can be solved supplying time profiles for reactor temperature and species concentrations, respectively.

It has been found that, for any chosen reacting system, a dynamic behaviour of the semibatch reactor strongly depends on the temperature of cooling liquid – T_c and on the dosing rate – $\Phi_{V,A}$ (dosing time t_{dos}).

At some operating conditions a significant amount of unreacted compound A is accumulated. Such situation can lead to thermal runaway, so the so-called target temperature (T_{ta}) – i.e. the reference temperature of the reactor content determined for safe operating conditions, for which neither mass nor heat accumulation are observed – has been defined [8]. Within the dosing period ($0 < \theta < 1$), where θ is the dimensionless time equal to ($\theta = t/t_{dos}$) and when $T_{dos} = T_c$ (case met in industrial practice very often) this temperature reads as follows:

$$T_{ta} = T_c + \frac{1.05 \Delta T_{ad,o}}{\varepsilon [Wt (1 + \varepsilon \theta) + R_H]} \quad (6)$$

So, the target temperature T_{ta} is expressed in terms of the process and equipment parameters Wt , ε , R_H , $\Delta T_{ad,o}$, which are defined as follows:

$$Wt = \frac{(U A)_o t_{dos}}{\varepsilon (\rho c_p V)_o} = \frac{(U A)_o}{(\rho c_p)_o \Phi_{V,A}} \quad (8)$$

$$\varepsilon = \frac{\Phi_{V,A} t_{dos}}{V_{Bo}} \quad (9)$$

$$\Delta T_{ad,o} = \frac{-\Delta H_R n_{Bo}}{(\rho c_p V)_o} \quad (10)$$

$$R_H = \frac{(\rho c_p)_A}{(\rho c_p)_B} \quad (11)$$

With the definition of the target temperature (Eq. 6), the difference between the actual reactor temperature and this target temperature ($T - T_{ta}$) is a measure of a distance of the reactor temperature trajectory from the thermal runaway conditions.

During the dosing period (for $0 < \theta < 1$) the value of T_{ta} decreases gradually due to increase of the heat exchange surface area, while after completion of dosing (i.e. for $\theta > 1$) it becomes constant and T_{ta} is estimated with Eq. 6 taking $\theta = 1$.

A several runs have been carried out in the RC1 reaction calorimeter following batch and semibatch operating mode. For each the hydrolysis of the acetic anhydride has been investigated at different operating conditions - some of them led the system to thermal runaway. The representative runs, used to illustrate the results obtained in this study, are collected in Table 1. All experiments have been carried out at the isoperibolic conditions – i.e. at the constant temperature of the cooling liquid circulating in the reactor jacket – T_c .

Table 1 Hydrolysis experiments carried in the RC1 Mettler Toledo reaction calorimeter.

Run	Mode	T_c [K]	$n_{A,o}$ [moles]	$n_{B,o}$ [moles]	$n_{C,o}$ [moles]
R_1	batch	313	44.41	1.98	1.67
R_2_TR	batch	313	44.41	15.00	1.67
R_3_TR	semibatch $t_{dos} = 1918$ [s]	323	11.02	10.75	4.86
R_4	semibatch $t_{dos} = 3818$ [s]	333	7.03	7.05	2.34
R_5_TR	semibatch $t_{dos} = 3670$ [s]	323	7.98	10.75	3.60

TR remark in the name of particular run means that thermal runaway event has been observed during the reaction progress.

A typical thermal runaway behaviour obtained for the semibatch run R_3_TR is shown in Fig. 4a. Notice that for this run the reactor temperature – T overpasses the target temperature – T_{ta} .

At any time moment, a difference between the actual reactor temperature $T(t)$ and the actual target temperature $T_{ta}(t)$ is a measure of the distance between the reactor state and the safe operating conditions. This distance can be quantified defining a specific mathematical function – $F(t)$:

$$F(t) = (T(t) - T_{ia}(t)) \quad (12)$$

So, for $F(t) < 0$ the reactor is on a safe temperature trajectory, while for $F(t) > 0$ on the thermal runaway one.

SAFETY CRITERIA EMPLOYED IN THIS STUDY

Criterion of derivatives

This simple criterion is based on analysis of derivatives of the temperature measured in the reactor vessel - T_R and in the reactor jacket - T_J , respectively. According to analysis given a.o. by Hub and Jones [3], an approaching runaway can be easily detected by check the following relationships:

$$\frac{d^2T}{dt^2} > 0 \quad (13)$$

and

$$\frac{d(T - T_c)}{dt} > 0 \quad (14)$$

Values of both derivatives (given in Eqs. 13-14) simultaneously larger than zero indicate that the system is on the temperature trajectory leading to thermal runaway. No detailed information on the process and the reactor equipment is required in this case. However, a main disadvantage of this criterion is its sensitivity to the noise measured with the experimental temperature signals. This experimental noise amplified during derivation procedure can trigger off false alarms.

Due to constant values of the heat exchange surface area and the overall heat transfer coefficient assumed for derivation of this criterion, its application is limited to batch reactors.

Divergence criterion

In this criterion the analysis of the Lyapunov exponents is used to assess the thermal stability of batch and semibatch reactors [4-6]. A loss of a temperature control in the reactor is identified at the point where the divergence of the reactor system becomes positive on a segment of the reaction path.

By applying a phase-space reconstruction technique, for embedding dimension $d_E = 2$, the divergence of the considered system can be evaluated with the reactor - T and the cooling liquid - T_c temperatures [4-6]. So, the volume of the reconstructed state space can be calculated using two points at the reactor trajectory: $P_1 = [T_1, T_{c,1}]$ and $P_2 = [T_2, T_{c,2}]$ as:

$$V_{ps}(t) = \left| \det \begin{bmatrix} T_2 - T_1 & 0 \\ 0 & T_{c,2} - T_{c,1} \end{bmatrix} \right| \quad (15)$$

So, estimating the variation of the reconstructed phase space volume as:

$$\Delta V_{ps}(t) = \frac{V_{ps}(t + dh) - V_{ps}(t)}{dh} \quad (16)$$

approaching thermal runaway can be detected if $\Delta V_{ps}(t) > 0$.

To avoid false alarms an additional criterion is proposed for which the length of the time period when $\Delta V_{ps}(t) > \Delta V_{ps}^{lim}$ must exceed the certain value t^{lim} . Both values of ΔV_{ps}^{lim} and t^{lim} are estimated for each considered reactor. For the laboratory scale

RC1 reactor these values are equal to $4 \cdot 10^{-3}$ and 30 s, respectively [9].

Method employing neural networks

Neural networks are able to approximate any multivariable continuous functional dependence. So, they can be successfully applied to model a dynamic behaviour of chemical reactors [10].

Recently, an application of neural networks for *on-line* detection of thermal runaway in batch and semibatch chemical reactors has been proposed [2]. With this approach, taking into account the symbolic model of the considered reactor (Eqs. 2-4), the neural network used to detect thermal runaway should have an ability to approximate the following complex functional dependence ψ , which quantifies a distance of the actual reactor temperature trajectory from a thermal runaway state. Therefore we have:

$$F(t) = (T(t) - T_{ia}(t)) = \psi(k, E, (-\Delta H_A), (UA)_o, V_{Bo}, \Phi_{V,A}, T_c, T_{dos}, t) \quad (17)$$

where k , E , $(-\Delta H_A)$ and $(UA)_o, V_{Bo}$ are parameters (constants), which characterized the reaction and the reactor cooling abilities, respectively, while $\Phi_{V,A}, T_c, T_{dos}$ are the reactor operating variables.

If the considerations are restricted to a chosen reactor and a chosen reacting system, the functional dependence of Eq. 17 reduces to the following expression:

$$F(t) = (T(t) - T_{ia}(t)) = \psi(\Phi_{V,A}, T_c, T_{dos}, t) \quad (18)$$

In such a case, to approximate a dynamic behaviour of the considered reactor, the following set of the input signals has been proposed:

$$\begin{aligned} \mathbf{I} = & [T(k - \Delta t K_T), \dots, T(k - \Delta t), T(k), \\ & T_c(k - \Delta t K_T), \dots, T_c(k - \Delta t), T_c(k), \\ & T_{dos}(k - \Delta t K_T), \dots, T_{dos}(k - \Delta t), T_{dos}(k), \\ & \Phi_{V,A}(k - \Delta t K_T), \dots, \Phi_{V,A}(k - \Delta t), \Phi_{V,A}(k)] \end{aligned} \quad (19)$$

while the proposed set of output signals reads as follows:

$$\mathbf{O} = [F(k + \Delta t), F(k + 2\Delta t), \dots, F(k + K_F \Delta t)] \quad (20)$$

Such neural network allows us to predict in advance a distance of the actual reactor temperature trajectory from the thermal runaway conditions - i.e. it supplies values of the function F at the future time moments $(k + \Delta t, k + 2\Delta t, \dots, k + K_F \Delta t)$, if the temperatures T, T_c, T_{dos} and the dosing rate $\Phi_{V,A}$ at the previous and present time moments $(k - K_T \Delta t, \dots, k - 2\Delta t, k - \Delta t, k)$ are known.

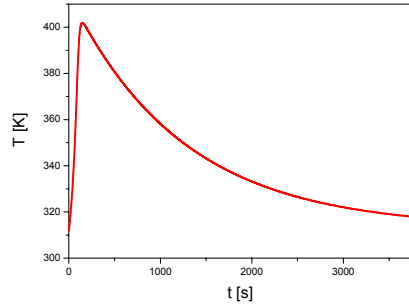
Neural network models are typically experimental ones, so in the proposed approach no additional assumptions and simplifications on the modeled system are required. Only a simple thermal characterization of the reactor equipment - i.e. the reactor itself and its cooling system - is required. This can be done safely performing a set of the reactor heating-up and cooling-down experiments, which can be carried out even without a presence of exothermic reactions. Then the appropriate neural net is trained with use of results of these characterization experiments, and employed to detect if the

reactor temperature actually measured leads to thermal runaway.

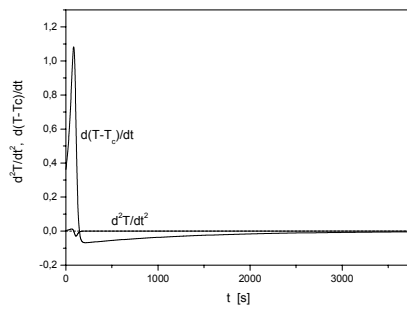
RESULTS AND DISCUSSION

Criterion of derivatives

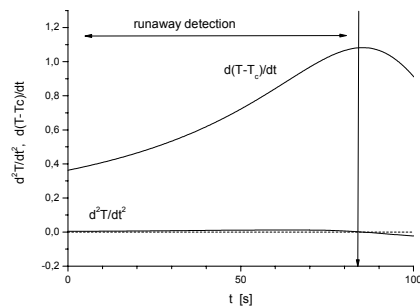
For batch operating mode, runaway indications obtained with use of the criterion of derivatives are shown in Figs. 3.



a. experimental reactor temperature profile



b. derivatives estimated on-line (Eqs. 13 and 14)



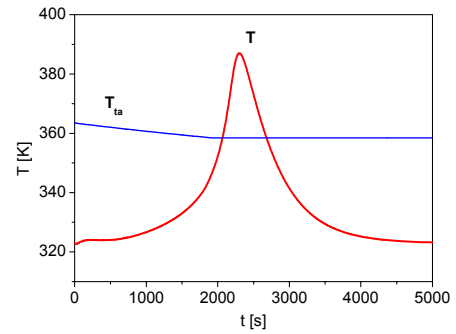
c. enlargement of the diagram given above

Figure 2 Batch run R_2_TR – runaway detected with the criterion of derivatives.

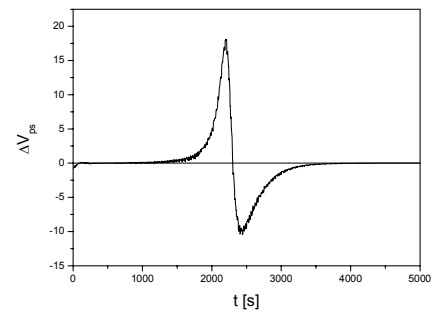
As can be observed in Fig. 3, the criterion of derivatives indicates that during carrying out the batch run R_2_TR a thermal runaway event takes place. It is detected with *on-line* derivatives criterion (Eqs. 13-14), as both derivatives are positive at the reaction beginning.

Divergence criterion

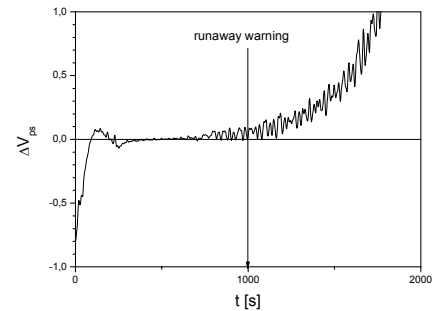
For semibatch operating mode, runaway indications obtained with use of the divergence criterion are shown in Figs. 3.



a. experimental reactor temperature profile – T and the target temperature profile - T_{ta}



b. variation of the reconstructed phase space volume



c. enlargement of the part of diagram given above

Figure 3 Semibatch run R_3_TR - runaway detected with the divergence criterion

As can be observed in Fig. 3, the divergence criterion indicates that during carrying out the semibatch run R_3_TR a thermal runaway event takes place. This observation is confirmed with experimental data plotted in Fig. 3a, which shown that for this run a loss of temperature control is noticed. Values of $\Delta V_{ps}(t)$ shown in Figs. 3b and 3c have been estimated on-line following the method given above – see Eqs. 15 and 16. Notice that the warning alarm – caused by indication of the positive value of

$\Delta V_{ps}(t)$ - is triggered off at time moment $t = 1000$ s, while the maximum of the reactor temperature - T is attained at time $t \approx 2300$ s. So, it is enough time to take safety countermeasures to stop approaching thermal runaway.

Method employing neural networks

For semibatch operating mode, runaway indications obtained with use of the neural networks criterion are shown in Figs. 4. A feedforward multilayer perceptron (MLP) have been used to model the considered problem. For the testing purposes each learning data set has been created taken data measured experimentally. A time moving window technique has been utilized to prepare the learning data [2]. For the chosen reacting system, several learning data sets have been prepared, each for the dimensionless time step $\Delta\theta = 0.01-0.05$, which corresponds to time step $\Delta t = 10-50$ [s]. Two characteristic values of the constants K_T and K_F have been taken: $K_F = 3$ and $K_T = 7$. It has been checked that a sufficiently good learning accuracy has been attained even for a few hidden neurones – i.e. for $N_H = 8-10$. The learning pattern has been prepared containing as many as $P = 1000$ patterns.

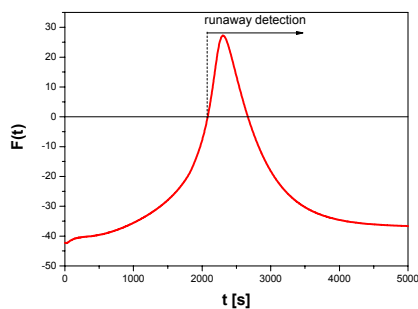


Figure 4 Semibatch run R_3_TR - runaway detected with neural network

As can be observed in Fig. 4, the neural net indicates that during carrying out the semibatch run R_3_TR a thermal runaway event takes place - this agrees with experimental observations. Notice that the warning alarm – caused by indication of the positive value of the function $F(t)$ - is triggered off at time moment $t \approx 2000$ s, while the maximum of the reactor temperature - T is attained at time much larger than 2300 s. In this case, the operator has only 300 s to take safety countermeasures to stop approaching thermal runaway, which is significantly less than with the divergence criterion.

CONCLUSION

A comparison of three *on-line* methods carried out in this study to indicate an approaching thermal runaway in chemical reactors show that the divergence criterion is the most efficient one. It informs that the reactor temperature is on the trajectory approaching thermal runaway enough early to take efficacious countermeasures. Also the method employing the neural networks for early warning detection is promising. Neural net trained with the experimental data is also able to predict

approaching runaway, although later than the divergence criterion. More investigation is required to check if the improvement of this method is possible.

Acknowledgements

This study has been supported by Polish Ministry of Science and Higher Education within a frame of the scientific grant No N209 149936 (2009-2012).

REFERENCES

- [1] Westerterp, K.R. and Molga, E., Safety and runaway prevention in batch and semibatch reactors – a review, *Chemical Engineering Research and Design*, Vol. 84(A7), 2006, pp.543-552
- [2] Molga, E., Application of neural networks for detection of thermal runaway events in chemical bath and semibatch reactors, Proceeding of ESCAPE22 (European Symposium on Computer Aided Process Engineering), 17-20 June 2012, London, UK
- [3] Hub, J. and Jones, J.D., Early on-line detection of exothermic reactions, *Plant Operation Progress*, Vol. 5, 1986, 221-229
- [4] Zaldivar, J.M., Cano, J., Alos, M.A., Sempere, J., Nomen, R., Lister, D., Maschio, G., Obertrop, T., Gilles, E.D., Bosch, J. and Strozzzi, F., A general criterion to define runaway limits in chemical reactors, *Journal of Loss Prevention in the Process Industries*, Vol. 16, 2003, pp. 187-200
- [5] Zaldivar, J.M., Bosch, J., Strozzzi, F. and Zbilut, J.P., Early warning detection of runaway initiation using non-linear approaches, *Communications in Nonlinear Science and Numerical Simulations*, Vol. 10, 2005, pp. 299-311.
- [6] Bosch, J., Kerr, D.C., Snee, T.J., Strozzzi, F. and zaldivar, J.M., Runaway detection in a pilot-plant facility, *Industrial and Engineering Chemistry Research*, Vol. 43, 2004, pp.7019-7024
- [7] Lewak, M., Process safety problems in stirred tank reactors, Ph.D. Thesis, Warsaw University of Technology, 2011 (*in Polish*)
- [8] Molga, E.J., Lewak, M. and Westerterp, K.R., Runaway prevention in liquid-phase homogenous semibatch reactors, *Chemical Engineering Science*, Vol. 62, 2007, pp.5074-5077.
- [9] Milewska, A., Modeling of batch and semibatch chemical reactors – safety aspects, Ph.D. Thesis, Warsaw University of Technology, 2007
- [10] Molga, E.J., Neural approach to support modelling of chemical reactors: problems, resolutions, criteria of application, *Chemical Engineering and Processing*, Vol.42, 2003, pp. 675-695.