# Novel Method for the Determination of Process Safety Time

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Nowadays process safety is a key issue at the design and operation of a production process. Unfortunately, at the application of process hazard analysis (PHA) techniques the time aspect of operation and the dynamical behaviour of the process are neglected. This is due to the small number of easily available tools which can be applied to perform dynamical process simulation and dynamical analysis. However, in recent times dynamical models are increasingly applied to support the solution of any tasks related to process safety. Another problem that makes it difficult to take into account time, is the lack of a standardized concept and evaluation system to integrate the obtained information into the design procedure of safety integrated system (SIS). The aim of this article is to investigate the role of time in the design of process safety elements (PSEs), and to define the connection between the process and the time by using the process safety time (PST) term, as well as to give a methodology how PST can be designed based on the process simulator and applied in the development of PSEs. The developed methodology is based on dynamical analysis of the system and the possible safety actions. Based on this methodology, an algorithm has been developed to detect unsafe situations and to determine the necessary safety actions that can be used to avoid the undesired states of operation. The algorithm has been applied in the solution of an industrial problem related to reactor runaway.

*Key words:*
Process safety time, reactor runaway, mathematical modelling, packed bed tubular reactor, dynamical simulation

## 1. Introduction

Nowadays process safety is a key issue in the design and operation phases of a production process. The development of a SIS and the identification of possible hazards by any kind of PHA techniques, require well-detailed knowledge about the technology.[1] Beside classical alarm management, a SIS performs specified functions to achieve or maintain the safe state of the process when unacceptable or dangerous process conditions are detected. Safe state is a state of the process operation where the hazardous event occurs with a very low probability. The set of safe states defines the safe operating regions.

A logic solver is required to receive the sensor input signal(s), to make appropriate decisions based on the nature of the signal(s), and to change its outputs according to user-defined logic. Next, the change of the logic solver output(s) results in the final element(s) taking action on the process (e.g. closing a valve) to bring it (back) to a safe state. To avoid possible abnormal situations, one or more independent protection layers can be applied. To analyze the number of protection layers and to design each layer the layer of protection analysis (LOPA) can be applied.[2] The possible protection layers have a hierarchy where process design and the basic process control systems are at the bottom level. Hence, the design of a reliable and controllable process is crucial.

Unfortunately, in these techniques the time and dynamic behaviour of the process are neglected. This is due to the small number of easily available tools which can be applied to perform dynamical process simulation. Often the supplement of this kind of tool is just the first problem; since information about the dynamic behaviour of the process is needed to develop process simulators there is a need for information about the dynamic behaviour of the process. It should not be forgotten that acquiring necessary information always has a price. In the process industry, the information about the process is usually measured data which can be (or should be) completed with the operator's experiences. In recent years, huge amounts of data are collected every second, and archived even in the simplest technology. Hence, mathematical models can be integrated into safety analysis of a working process in low-cost by processing the archived data. The problem with model development arises when the mathematical model of a non-existent process

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must be compiled to support the design of the process. For obtaining necessary information, many experiments must be designed and performed, which significantly increases the cost of the model development.

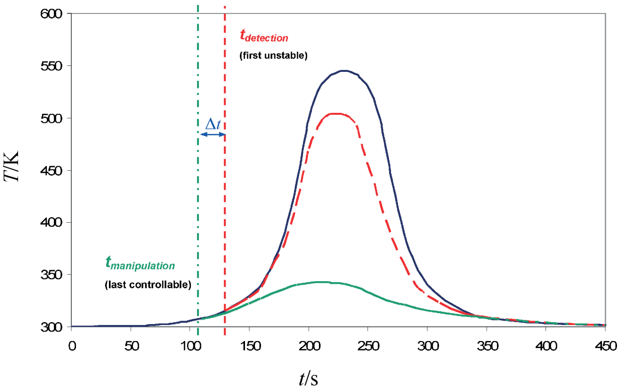
Fortunately, the importance of models in safety analysis was recognized by some research groups in the past decade and the dynamical models were increasingly applied to support the solution of any tasks related to process safety.[3–6] The usage of mathematical models allows not only to generate the deviations from normal operating conditions, but also to simulate and analyze the influence of these deviations and the trajectory of the possible safety actions.

Another problem that makes it difficult to take into account time, is the lack of a standardized concept and evaluation system to integrate the obtained information into the design procedure of SIS. The possible explanations of time in safety analysis are summarized in Table 1. Next to the meaning of time, the introduced ways of determination are also collected based on sources. Table 1 can be separated into three parts based on different time aspects in each source. Some examples for the probabilistic approach to time in SIS can be seen in the top section of Table 1. The middle section collects some examples from the viewpoint of dynamical behaviour of PSEs, while the last section introduces the time aspects from dynamical behaviour of the process. However, a method to determine PST is not given. PSEs are the possible safety actions, which can be applied to prevent the operation from the development of abnormal situations.

Table 1 – *Possible explanations for process safety time*

| Name | Meaning | Way of determination | Source |
|---|---|---|---|
| Time of occurrence | The time when fault occurs. | To predict time of occurrence, scale maps are applied based on a general relationship between length and time scales that reflect the time constants over which phenomena occur at different lengths of behavior. | [7] |
| Mean Time To Failure | Mean time for failure to occur. | In the reliability prediction simulation, Weibull distributions are applied to calculate the hazard rates. | [8] |
| Reaction time | The reaction time is conceptualized as the minimum time required to execute the requested motor response once the stimulus has been detected. | Reaction time is measured based on the application of race models. | [9] |
| Execution time | Measured execution time of the system. | Execution time is measured. | [10] |
| Expected time to repair | Average time to recognize the cause of out-of-control and repair the process | It is based on experience gained in earlier studies. | [11] |
| Response time | The time between detection of the event and response of the system. | ARAMIS approach is applied to calculate the response time. | [12] |
| Safety reaction time | The time needed to detect a problem and initiate a safety shut down to the control element. | To calculate safety reaction time an algorithm is developed based on the known process control safety connection parameters in network. | [13] |
| Time-in-Alarm | The time between timestamps of alarm and return-to-normal events. | To determine Time-in-Alarm it is recommended to perform some simulation experiments. | [14] |
| Irreducible minimum | The minimum time of response, usually approximately 100 ms. | This is a theoretical minimum. | [15] |
| PST | PST of a given process is in essence the fault-tolerant time of that process, prior to becoming a dangerous condition. | There is no information how to determine. | [16] |
| PST | PST is the time between detection of the hazard and the time to bring a process to a safety state. | The determination of PST should be based on experience. | [17] |
| PST | PST is the period of time in which the process can be operated without protection and without entering a dangerous condition. | It is determined by the process, so it should be determined by some measurements. | [18] |

The aim of this paper was to investigate the role of time in the development of PSEs and to define the connection between the process and time by using the PST term. In our case, PST means the operating time before the detection of unsafe situations to avoid the development of these unsafe situations as shown in Fig. 1. Apart from defining this connection, the further aim was to give a methodology how PST can be determined based on the process simulator and applied in the development of PSEs.




F i g . 1 – *Mean of PST*

The essentials of the proposed methodology are the simulation of the effect of safety elements over a prediction horizon. Since different safety actions have different time demand to avoid the evolution of the unsafe situation (i.e. PST), the process operators should know which safety action(s) should be taken in a given time. For this purpose, a method for model based predictive stability analysis has been worked out based on the Lyapunov's stability analysis of simulated state trajectories. The introduced algorithm can be applied to explore the stable and unstable operating regimes of a process (set of safe states) and to determine the PST of each investigated safety elements, which information can be used in predictive alarm management (PAM). The developed methodology has been applied to an industrial benchmark problem related to reactor runaway.

Runaway means a sudden and considerable change in the process variables, hence it is a serious problem in many chemical industrial technologies where exothermic reaction(s) takes place, like oxidation processes and some polymerization technologies.[19–21] In case of a highly exothermic reaction, the thermal runaway occurs when the reaction rate excesses due to a temperature increase, causing a further temperature increase and hence a further increase in the reaction rate. It has contributed to serious industrial chemical accidents, most notably the 1984 explosion of a Union Carbide plant in Bhopal, India, that produced methyl isocyanate, and the disaster in Seveso, Italy, in 1976 which raised and stiffened industrial safety regulations. Thermal runaway is also a concern in hydrocracking and oil refinery processes. Detection of runaway has two main important aspects. On one hand, the runaway forecast has a safety aspect, since it is important for avoiding the damage of constructional material or in the worst case the explosion of the reactor. On the other hand, it has a technological aspect, since the forecast of the runaway can be used to avoid development of hot spots in the catalytic bed, which speed up catalyst ageing, or for preventing the production of by-products in huge mass, like in the synthesis of 2-octanone from 2-octanol.[4,20,22] A control system that is able to modify accordingly the operating conditions of the reactor in time decreases the costs and increases operation safety. The first step in developing such a control system is the generation of a reliable runaway criterion. Runaway criteria can be based on historical process data or the process model.[23–27] The application of data-based criterion requires measured data. This means there have to be restrictions on the forecasting in the development of runaway. Another problem with data-based methods is found in measurement conditions, e.g. measurement noise can result in false forecast. Model-based criteria require parameter sensitivity and/or stability analysis, so for the application of these kinds of criteria it is necessary to have an exact process model with correct model parameters. The stability analysis is a powerful tool for determining the boundary of stable operation conditions. Such an investigation can be based on the analysis of the mathematical reactor model with Lyapunov's indirect stability analysis method.[28,29] Lyapunov functions allow the determination of stability for nonlinear systems without the need to find exact solutions.[30] The method is based on the calculation of eigenvalues of the Jacobian matrix. Therefore, the Jacobian matrix of the model must be determined, which can be made by the derivation of the model equations with respect to state variables. The next step of Lyapunov's analysis is the calculation of the eigenvalues of the Jacobian matrix. In case all the real parts of the eigenvalues are negative, then the model is stable. However, if one of the real parts of the eigenvalues is positive, the model will be unstable at the investigated operating point.

The paper is organized as follows: to demonstrate our approach to the determination of PST, the developed algorithm based on PAM is introduced in section 2. The developed algorithm has been applied to determine PST in case of an industrial used packed bed tubular reactor with a highly exothermic reaction. Finally, section 4 summarizes the most important conclusions and highlights the message of this work.

## 2. Novel method for the determination of process safety time

Advanced process control (APC) systems should be able to forecast the variation of the operating conditions that might decrease production costs and increase the safety of production.[31] Probably due to this reason, process stability is given by two thirds of the APC users as a main profit factor but only by less than 50 % of the APC suppliers. Process stability ensures that the product meets customer specifications consistently and that operations run smoothly. Alarm management can be applied to satisfy these expectations.

The function of alarm management is to determine possible process hazards, and to give a solution on how to reduce the impact of the detected hazards. Each individual alarm is designed to provide an alert when that process indication differs from normal state. During an abnormal condition, the board operator is confronted with making decisions on numerous tasks that must be performed in an appropriate sequence. The timing and order of execution of these tasks determines the outcome of the operator's effort. For example, if two process variables deviate from normal values and can potentially cause the same significant loss, the operator should quickly decide which variable to address first. In such a case, the operator must take an action to address the variable that is more volatile or can reach the point of loss in the shortest time. Therefore, the shorter the time available to respond, the higher the priority of the alarm will be, assuming equal consequences can result. In an effective alarm management system, the main goal is to minimize the number and impact of abnormal situations. A well-designed alarm system can quickly provide the appropriate information to process operators in unsafe situations, supporting them to identify the cause and restore the plant to normal operations. The main problem with basic alarm management is that these features are static. Hence, a classical alarm management system does not respond to changes in the mode of operation or in the operating conditions. In this article, predictive alarm management (PAM) is recommended to improve the reliability of APC systems since PAM is an important goal as the operator's ability to respond to an alarm in a timely fashion determines the degree of success in preventing loss.

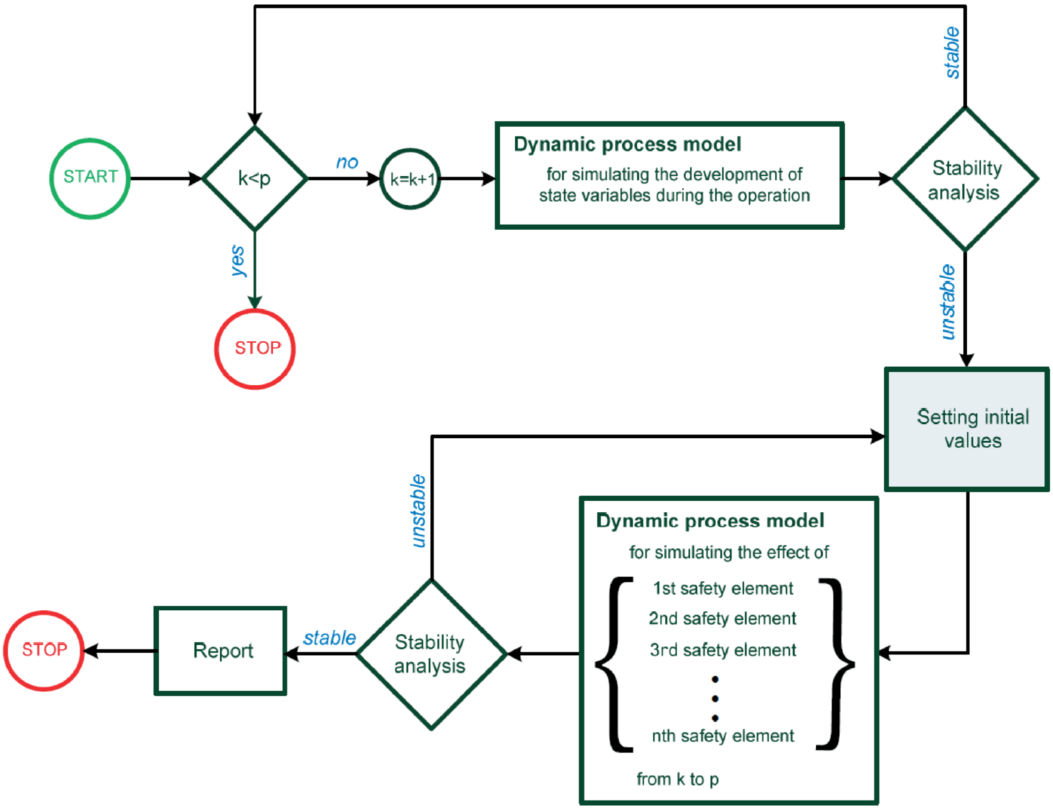
As it has been mentioned, PAM systems should be able to not only detect the alarm in an early stage, but to give advice to process operators which safety action must be applied. Apart from these requirements, PAM systems should be able to determine PST during the operation in order to inform the process operator when the highlighted safety action should be taken. Usually, process hazards cannot be avoided with the application of possible safety actions at the time of detection (e.g. in case of reactor runaway there is a last controllable operating point at each manipulation before the reactor becomes unstable, see in Fig. 1). Because safety actions can have different time demand to avoid the evolution of the unsafe situation, PST must be determined in every time step in case of all safety actions.

For the predictive analysis of the process not only is a detailed (accurate) process model required, but also a process simulator that is able to estimate trajectories of process variables in case of normal and abnormal operations. This simulator should also be able to model the dynamical behaviour of the control system, including its safety elements. This knowledge is extremely important, since these elements of the control system determine and sometimes "widen" the region of safe operation.

To allow the industrial implementation of the proposed approach, an algorithm has been developed (see Fig. 2) to determine the PST in case of all the suggested safety actions in different operating regimes. Such knowledge is extremely useful, since it can be interpreted as (multivariate) constraints defined on the process variables that can be given to operators of the process, built into the control system, or into an optimization algorithm used for the optimization of the operation.

As Fig. 2 illustrates, the first step of the proposed methodology is the application of the classical Lyapunov's stability analysis. In case the algorithm is unable to find at least one unstable state during the operation of a prediction horizon, then the simulation stops. Otherwise, it starts to find the last controllable state. The algorithm tests all the possible safety actions and determines which can be applied to avoid the development of the detected unstable state. The developed process model is applied to simulate the effect of the determined safety elements and to check which elements can be applied to avoid unstable operation.

To check the effect of safety actions in avoiding the development of abnormal situations, the algorithm makes one step back in simulation time since the aim of this analysis is to find the last controllable state. Effects of all possible safety actions are simulated by solving the process model in that simulation time. When the current state is stable, the analyzed safety element will be labelled as it




F i g . 2 – *Developed algorithm to determine PST*

can be used to avoid the development of runaway, and that state will be labelled as the last controllable state. Otherwise, the algorithm makes another step back in simulation time until it finds a stable state. To speed up the search for the last controllable state of the process, the classical secant method, used to solve univariate equations, is applied in the algorithm. The time difference between the first unstable and last controllable states is calculated in case of every safety element that seems to be applicable in avoiding the development of unstable states. This time difference is process safety time (PST). Finally, the algorithm selects the best safety element that requires the least PST.

Apart from determining PST, the introduced algorithm can be applied to explore the stable and unstable operating regimes of a process. Hence, during the operation of the process it can be used as PAM system. In this work, the developed algorithm is applied to determine the PST based on the characterization of the boundaries of stable operating regions. To achieve this aim, the developed algorithm should analyze the model of the safety system in case of several randomly generated inlet and initial conditions. The determined boundaries are hyper-surfaces in state phase, which represent the last controllable and first unstable operating points. The difference between these hyper-surfaces is the PST in each case.

After the characterization of unstable regions of operation, the results can be applied to design the inlet conditions of the reactor, and certainly the results can also be applied during the operation. If the measured state variables exceed the boundary of controllability, the first unstable state will occur soon and the operator should be warned to make some modifications in operating conditions. When the state variables cross the boundary of stability, the reactor becomes unstable at that moment and the process hazard cannot be avoided.

To sum up the proposed tool for PAM, at first all the knowledge about the analyzed system must be collected and arranged in a model. To analyze the effect of possible manipulations, a review of the safety system is required. All this information is enough to compile the proposed tool based on the earlier introduced algorithm. In the next section, the proposed approach is applied in case of an industrial benchmark problem.

## 3. Application of the developed algorithm in an industrial problem

The applicability of the previously introduced approach and algorithm is introduced in this section in characterization of safe and controllable operating regimes. The studied vertically built up reactor contains a large number of tubes with catalyst as shown in Fig. 3. A highly exothermic reaction takes place as reactants rise up in the tubes and pass through the fixed bed of catalyst particles. In this reactor, it is important to prevent the development of reactor runaway during the operation to decrease the speed of catalyst ageing. The generated heat is removed by the cooling agent circulating around the tubes in the reactor jacket. Only the properties of inlet and outlet streams are continuously measured to monitor the reactor and check the safety of operation. Steady-state temperature profiles are collected every 3–6 months to check the activity of catalytic bed. To track the development of stability boundaries, a detailed dynamic model should be developed.

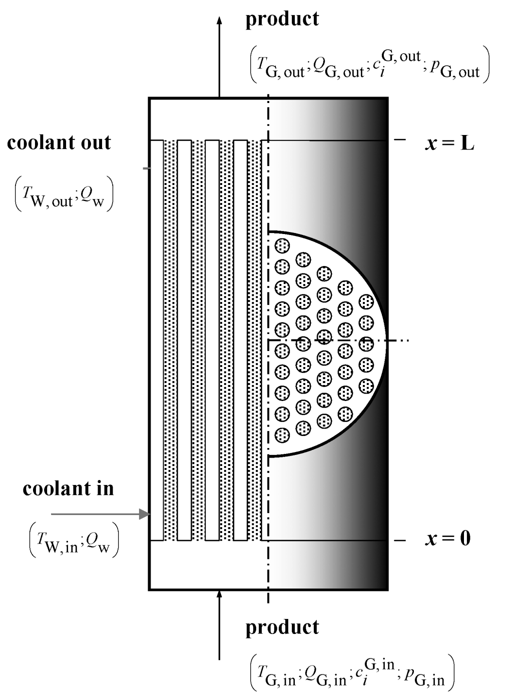



Fig. 3 – *Simplified scheme of the investigated tubular reactor*

### 3.1. Introduction to mathematical model of the investigated tubular reactor

Since a dynamical model is required to simulate the behaviour of the reactor, in addition to the geometric independent parameter, time must be also considered in the proposed model. Hence, a one-dimensional dynamic model has been developed to simulate the dynamic behaviour of the reactor. The complexity of the model allows observing how the boundaries of stability are developing in time along the catalytic bed. Since two independent variables must be considered, the developed model contains partial differential equations (PDEs) besides the ordinary and scalar expressions. All variables in PDEs correspond to the time and the position in catalytic bed along the longitudinal axis.

Reactor inside, i.e. the catalytic bed and the flowing gas are considered as a quasi-single phase and an overall reaction kinetic expression is applied to calculate the reaction rate.[32] The assumptions considered in this model are summarized as follows:

– reaction takes place in the considered quasi-single phase;

– the following reaction is considered:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}. \tag{1}$$

– to calculate the rate of reaction the Langmuir-Hinshelwood kinetic[33] is modified with a term describing the reaction equilibrium constant:

$$r_\mathrm{G} = k_0 \exp\left(-\frac{E_\mathrm{A}}{RT_\mathrm{G}}\right) \cdot \\ \cdot \frac{(p_\mathrm{A}^\mathrm{G})^{n_\mathrm{A}} (p_\mathrm{B}^\mathrm{G})^{n_\mathrm{B}} - \dfrac{p_\mathrm{C}^\mathrm{G}}{K (p_\mathrm{A}^\mathrm{G})^{1-n_\mathrm{A}} (p_\mathrm{B}^\mathrm{G})^{1-n_\mathrm{B}}}}{1 + (p_\mathrm{C}^\mathrm{G})^{n_\mathrm{C}}}, \tag{2}$$

where the following Arrhenius-type expression is applied to calculate the reaction equilibrium constant:

$$K = \exp\left(16.14 - \frac{102485}{RT_\mathrm{G}}\right). \tag{3}$$

– gas and solid temperature are considered uniform at every reactor length location;

– the radial state-variable gradients are neglected;

– axial dispersion is neglected;

– external resistance to mass and heat transport to particles is neglected;

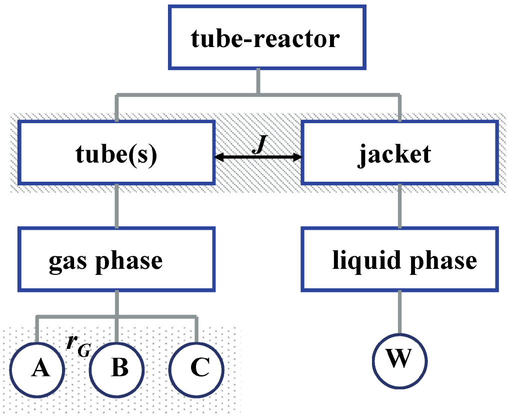
– to calculate pressure drop along the packed bed, a modified Ergun-equation is applied:

$$\frac{\mathrm{d}p_\mathrm{G}}{\mathrm{d}x} = -2 f_\mathrm{c} \frac{p_\mathrm{G} (Q_\mathrm{G})^2}{d_\mathrm{p} S^2} \frac{1-\varepsilon}{\varepsilon^3} \left(1.75 + 150 \frac{1-\varepsilon}{\mathrm{Re}}\right). \tag{4}$$

Based on these simplifications, the model structure in Fig. 4 was developed. As shown in Fig. 4, the jacket and the tubes are connected by the heat transport. Three components are in the investigated system, so three component balances and two heat balances must be built into the model. In the material balances, the convective flux and the component sources are considered:

$$V_\mathrm{G} \frac{\partial c_i^\mathrm{G}}{\partial t} + \frac{\partial (Q_\mathrm{G} c_i^\mathrm{G})}{\partial x} = \upsilon_i V_\mathrm{S} r_\mathrm{G}, \tag{5}$$

where $i = \{\mathrm{A}; \mathrm{B}; \mathrm{C}\}$.




F i g . 4 – *Hierarchical structure of the investigated tubular reactor*

In the heat balance of tubes, the convective flux, the heat produced by the reaction, and the heat transport between the jacket and tubes are considered:

$$V_G \rho_G c_p^G \frac{\partial T_G}{\partial t} + Q_G \rho_G c_p^G \frac{\partial T_G}{\partial x} = \\ = V_S r_G(-\Delta_r H) - A_{GW} J, \tag{6}$$

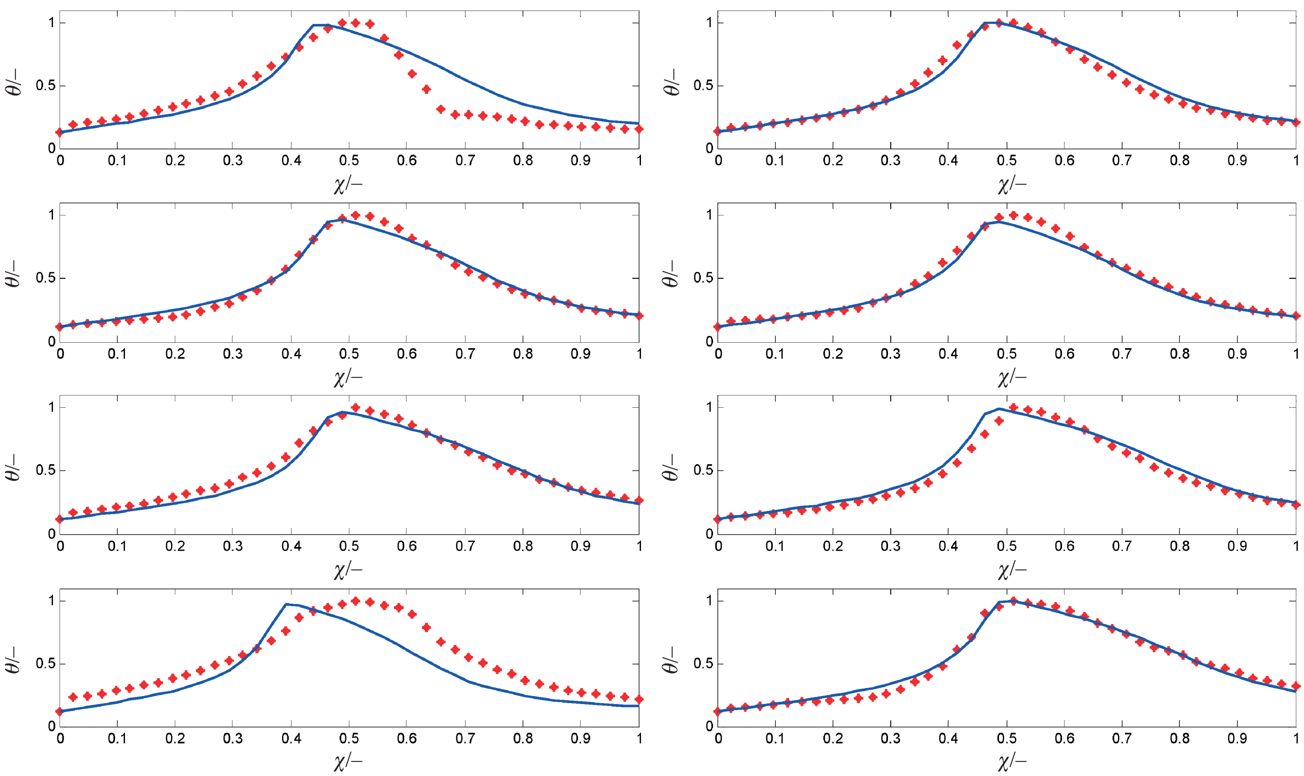
where the heat flux density is calculated by the following correlation:

$$J = \alpha_{GW}(T_G - T_W). \tag{7}$$

The reaction takes place only in tubes, so the heat produced by the reaction is not considered in the heat balance of the jacket:

$$V_W \rho_W c_p^W \frac{\partial T_W}{\partial t} + Q_W \rho_W c_p^W \frac{\partial T_W}{\partial x} = A_{GW} J. \tag{8}$$

The explanation of model variables can be found in the notation list. All the missing model parameters have been identified by comparing measured and calculated temperature profiles. The target function is the sum of squares error. A constrained minimum searching algorithm based on the trust region-reflective method was applied to find the global extrema of the defined target function.[34] Since the examined reactor is part of an industrial process, the nominal values of the reactor and the operating conditions cannot be given. However, the identified kinetic parameters are collected in the notation list. The measured and the calculated profiles (generated by solving the model with the fitted parameters) can be visually compared in Fig. 5 in the case of eight different operating conditions. All the measured temperature values have been divided by the maximal temperature of each profile and give a dimensionless temperature, which is the vertical axis in Fig. 5. However, the horizontal axis is dimensionless length. The reactor simulator has been developed in MATLAB and it can be downloaded from http://fmt.uni-pannon.hu/softcomp/. Every operating and reactor parameter characterizing the in-




F i g . 5 – *Result of the parameter identification procedure* dustrial process and reactor has been modified in this simulator.

### 3.2. Determination of PST in different operating regimes of a tubular reactor

The aim of this section is to investigate the tubular reactor with a highly exothermic reaction when manipulations must be performed to keep the reactor in a controllable region. The introduced dynamical model has been solved by using MATLAB. The evaluation of reactor temperature can be seen in Fig. 6a. The result of this simulation shows that the temperature increases very fast near the inlet position of the reactor, while the temperature maximum moves in the opposite direction of the reagent flow during start-up. In this case, the studied process can be effectively handled as a quasi-steady state system, since the residence time is 4.42 s (the feed of reagents is $Q_G$ = 0.12 m$^3$ s$^{-1}$ and the empty volume of the reactor is 0.53 m$^3$) – much less than the average time constant of the system, which is approximately 180 (as in Fig. 5 that shows the result of a dynamical simulation experiment). This confirms that the investigated reactor can be treated as a quasi steady-state system, and the unsteady perturbations can be neglected without making a significant mistake. Lyapunov's stability analysis is applied to check the stability of the model in each time step. The first unstable points in each time step are collected and plotted in Fig. 6b. In Fig. 6b, it can be seen that the boundary of stability develops as the temperature maxima, so the boundary of the unstable region is moving towards the inlet spot. As can be seen in Fig. 6b, the first unstable operating point is detected at 128 s, so the runaway of the reactor occurs during this operation and there is a need for a safety action to prevent the development of an unsafe situation.

Therefore, PSEs should be considered and ranked in different cases to enable the selection of the proper safety action. The examined operating conditions are summarized in Table 2. The first row in Table 2 represents a normal operating condition. The second row shows another normal operating condition, which is generated from the first one by varying the nominal values a little to check the reliability of the proposed approach. The third row introduces the values of operating variables in case that variable is applied as PSE. The first two from the considered PSEs represent the closing of the feeding of reagents. The third one is the reduction of the pressure in the reactor, while the last two PSEs are the reduction of the feeding temperature of the reagents and the cooling agent. Many other PSEs can be determined next to or instead of these. However, in our case the introduction to the proposed approach is the main target. The feeding of

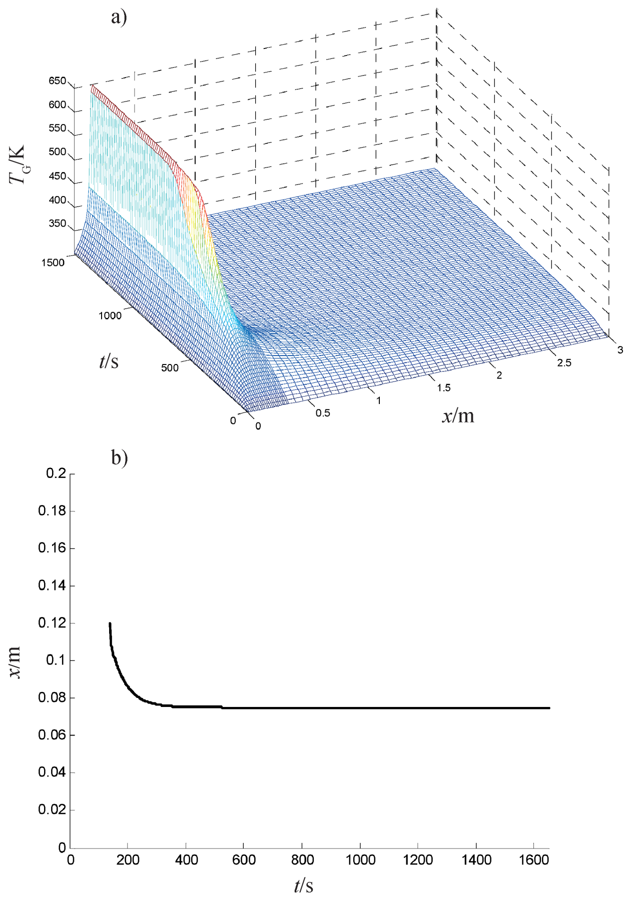



Fig. 6 – *Calculated temperature profiles in gas phase (a) and the evaluation of the stability of reactor model (b) where x represents the first unstable points along the reactor*

Table 2 – *PSEs considered to avoid the development of reactor runaway*

| | 1st PSE $c_A$/mol m$^{-3}$ | 2nd PSE $c_B$/mol m$^{-3}$ | 3rd PSE $p_G$/bar | 4th PSE $T_G$/K | 5th PSE $T_W$/K |
|---|---|---|---|---|---|
| original | 50.5 | 17.3 | 1.80 | 320 | 325 |
| modified | 48.0 | 16.5 | 1.75 | 325 | 320 |
| safety action | 0 | 0 | 1.25 | 290 | 290 |

reagents is modified from the normal conditions to generate different operating scenarios. All five possible PSEs are tested in each different scenario in case of both normal operating conditions.

The proposed approach has been applied to calculate the PSTs in each scenario for all the considered PSEs. The calculated PSTs are collected in Table 3. The time of the first unstable point is the time step when the instability is detected based on the applied analysis method. As it can be seen in Table 3, reactor runaway develops in every investigated scenario. Therefore, the considered PSEs can be tested at all the generated operating conditions.

Table 3 – *PSTs determined by the developed tool in different scenarios*

| | | | | | | |
|---|---|---|---|---|---|---|
| 1st scenario: original operating conditions | | | | | | |
| First unstable: 128 s (166 s) | | 1st PSE | 2nd PSE | 3rd PSE | 4th PSE | 5th PSE |
| Last controllable | [s] | 90 (121) | 127 (165) | 0 (165) | 0 (0) | 115 (165) |
| PST | [s] | 38 (45) | 1 (1) | ∞ (1) | ∞ (∞) | 13 (1) |
| 2nd scenario: the feeding volume of reagent B is increased by 10 % | | | | | | |
| First unstable: 121 s (156 s) | | 1st PSE | 2nd PSE | 3rd PSE | 4th PSE | 5th PSE |
| Last controllable | [s] | 89 (115) | 120 (155) | 0 (0) | 0 (0) | 96 (155) |
| PST | [s] | 32 (41) | 1 (1) | ∞ (∞) | ∞ (∞) | 25 (1) |
| 3rd scenario: the feeding volume of reagent B is increased by 100 % | | | | | | |
| First unstable: 110 s (138 s) | | 1st PSE | 2nd PSE | 3rd PSE | 4th PSE | 5th PSE |
| Last controllable | [s] | 87 (111) | 109 (137) | 0 (0) | 0 (0) | 77 (129) |
| PST | [s] | 23 (27) | 1 (1) | ∞ (∞) | ∞ (∞) | 33 (9) |
| 4th scenario: the feeding volume of reagent B is increased by 90 % | | | | | | |
| First unstable: 109 s (137 s) | | 1st PSE | 2nd PSE | 3rd PSE | 4th PSE | 5th PSE |
| Last controllable | [s] | 85 (109) | 108 (137) | 0 (0) | 0 (0) | 74 (126) |
| PST | [s] | 24 (28) | 1 (1) | ∞ (∞) | ∞ (∞) | 35 (11) |
| 5th scenario: the feeding volume of reagent A is decreased by 33.3 % | | | | | | |
| First unstable: 118 s (152 s) | | 1st PSE | 2nd PSE | 3rd PSE | 4th PSE | 5th PSE |
| Last controllable | [s] | 83 (106) | 117 (151) | 0 (0) | 0 (0) | 109 (151) |
| PST | [s] | 35 (52) | 1 (1) | ∞ (∞) | ∞ (∞) | 11 (1) |
| 6th scenario: the feeding volume of reagent A is decreased by 35 % | | | | | | |
| First unstable: 118 s (153 s) | | 1st PSE | 2nd PSE | 3rd PSE | 4th PSE | 5th PSE |
| Last controllable | [s] | 83 (106) | 117 (152) | 0 (0) | 0 (0) | 110 (152) |
| PST | [s] | 35 (47) | 1 (1) | ∞ (∞) | ∞ (∞) | 8 (1) |

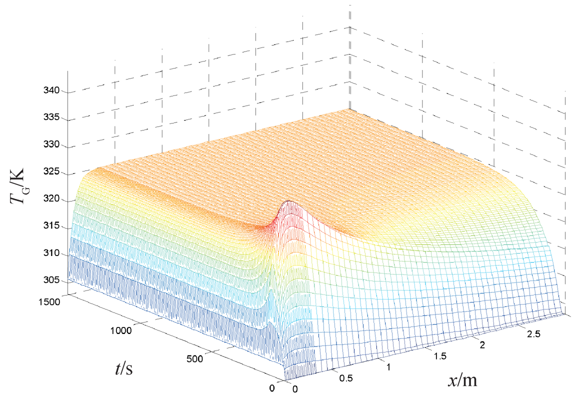
In Table 3, the bracketed values belong to the modified operating conditions in Table 2. The comparison of the time of the first unstable points in each scenario show that the modified operating condition in Table 2 is less crucial than the normal condition from the safety aspect.

The last controllable points are calculated in each scenario and in case of every PSEs. The PSTs are calculated as the difference between the first unstable and last controllable points. In Table 3, if the PST is one, that means the investigated PSE has to be applied at the time of runaway detection. The infinity sign denotes that the PSE cannot be used to avoid the development of runaway in the examined scenario.

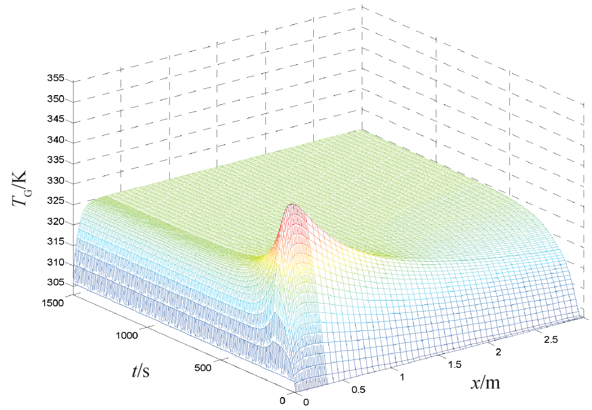
In the first scenario, two of the five possible safety elements cannot be applied to avoid the development of reactor runaway. However, the third PSE is perfect in the modified conditions for preventing the reactor from the undesired situation. The second PSE is useful at both analyzed operating conditions. More PSEs can be applied to avoid the development of runaway at the modified conditions in the first scenario, which means that the operation with respect to the modified operating conditions is less crucial from the safety aspect.

Further analysis of results shows that the third PSE works only in the first scenario. The first, second and fifth PSEs can be applied in every scenario. Although the calculated PSTs are one in case of the second PSE in every investigated situation. Therefore, the second PSE can be perfectly applied to the investigated scenario as a PSE.

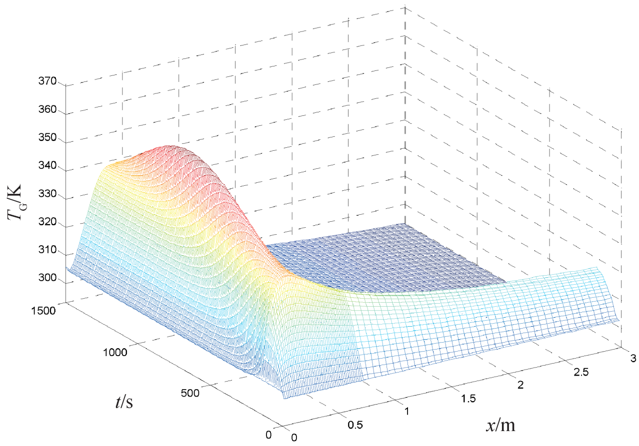
To validate the reliability of the results, the offered PSEs have been tested by tailored simulation experiments presented in Fig. 7. It is well demonstrated that the applied safety elements will be capable of avoiding runaway and will keep the reactor in safe operation regime if the safety element is applied in appropriate time.




Concentration of reagent A is decreased to 0 at 90 s




Concentration of reagent B is decreased to 0 at 127 s




The inlet temperature of cooling agent is decreased to 290 at 115 s

F i g . 7 – *Avoiding the development of reactor runaway by applying the possible safety actions in appropriate time*

## Conclusions

The development of safety instrumented Systems and the identification of possible hazards by any kind of process hazard analysis techniques require well detailed knowledge about the technology. Unfortunately, in the application of these techniques the time aspect of operation and the dynamical behaviour of the process are neglected.

The article introduces a possible aspect for the consideration of time in the development of process safety elements, and definition of the connection between the process and time by using the process safety time term. It also presents a methodology for the determination of process safety time based on process simulator and applied in the development of process safety elements. The developed methodology is based on dynamical analysis of the system and on the possible safety actions. Based on this methodology, an algorithm has been developed to detect unsafe situations and determine the necessary safety action to avoid it. The algorithm has been applied to explore the stable and unstable operating regimes of an industrial tubular reactor with a highly exothermic reaction, and to determine which safety action must be performed to prevent the development of unsafe situations. Besides these results, the algorithm has been also used to determine the process safety time for each of the considered safety elements.

In existing and operating processes, the proposed methodology can be applied to revise and tune the process alarm system. Furthermore, at the design stage of the process this tool can be used to determine the proper safety elements by selection of critical operating variables.

The main contribution is that the developed methodology can be applied to analyze complex processes in the chemical industry in which the critical conditions cannot be *a priori* defined.[35] In case of complex process systems, the last controllable time is not only the function of the operating parameters of the process unit, but also the elements of the protection layer. These together define a complex analysis task that cannot be analytically handled. The main contribution of this paper is the introduction of a numerical analysis-based methodology that can estimate PSTs related to the PSEs.

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## Notation list

$\alpha^-$ – heat transfer coefficient, $2.93e^1 + 3.43e^{-2} \cdot T_G$, W $m^{-2}$ $K^{-1}$
$A$ – contact area, $1.413e^0$, $m^2$
$S$ – cross-section area of catalytic bed, $2.826e^{-1}$, $m^2$
$Q$ – volume flow rate, $m^3$ $s^{-1}$
$c_i$ – concentration, where $i = \{A; B; C\}$, mol $m^{-3}$
$c_p$ – specific heat capacity, J $kg^{-1}$ $K^{-1}$
$\Delta_r H$ – heat of reaction, $-1.12e^5$, J $mol^{-1}$
$d_p$ – diameter of catalyst particle, $3.5e^{-3}$, m
$\varepsilon$ – solid phase/catalytic bed volume ratio, $6.3e^{-1}$, –
$E_A$ – activation energy, $2.14e^4$, J $mol^{-1}$
$f_c$ – constant in Ergun-equation, $9.869e^{-6}$, –
$J$ – heat flux density, W $m^{-2}$
$K$ – reaction equilibrium constant, –
$k_0$ – pre-exponential factor, $1.903e^1$, mol $m^{-3}$ $s^{-1}$
$\chi$ – dimensionless reactor length, –
$n$ – reaction order exponents $[n_A \; n_B \; n_C]$, [1.05 0.55 0.88], –
$\upsilon_i$ – stoichiometric number, –
$p$ – pressure, Pa
$p_i$ – partial pressure of components, Pa
$r$ – rate of reaction, mol $kg^{-1}$ $s^{-1}$
$R$ – ideal gas constant, $8.314e^0$, J $mol^{-1}$ $K^{-1}$
Re – Reynold's number, –
$\rho$ – density, kg $m^{-3}$
$T$ – temperature, K
$\theta$ – dimensionless temperature, –
$V$ – volume, $8.478e^0$, $m^3$
$x$ – reactor length, $3.0e^0$, m

## Superscripts

G – gas phase
S – solid phase
W – jacket
GW – transport between gas phase and jacket

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