|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS*** ***VOL. xxx, 2025*** | A publication ofaidiclogo_grande |
| The Italian Associationof Chemical EngineeringOnline at www.cetjournal.it |
| Guest Editors: Bruno Fabiano, Valerio CozzaniCopyright © 2025, AIDIC Servizi S.r.l.**ISBN** 979-12-81206-xx-y; **ISSN** 2283-9216 |

Analysis of Chemical Process Response to the Deviation of Single and Multiple Input Parameters by Nonlinear Measures

Juraj Myšiak, Juraj Labovský, Ľudovít Jelemenský\*

Institute of Chemical and Environmental Engineering, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia

ludovit.jelemensky@stuba.sk

Modern technological progress leads to increased complexity of engineering systems, processes, and products, posing significant challenges in proper design, analysis, control, safety, and production management. On the other hand, it should be emphasized that the chemical process is basically nonlinear, which is manifested mainly in the response to malfunction changes in operating parameters. While a small change in an operating parameter can cause large, hard-to-predict, process response (unpredictable course of temperatures, pressures, levels, ...), these nonlinearities can also lead to cumulative effects in the occurrence of several fault changes which can spread in many ways and even cause system failure. Nonlinear interactions between interdependent components can lead to unexpected (unpredictable) behavior and should be taken into consideration during process hazard analyses such as HAZOP. Nonlinearity of the system's response can be manifested by high sensitivity to changes of design parameters, oscillatory behavior, or domino effect due to a different steady state reached. Knowledge of the nonlinear process response to deviations of various design parameters in different parts of the process provides significant added value in the development of unexpected scenarios of deviation-cause-consequence chains. This paper presents evaluation methods of nonlinearity indicators in chemical processes during HAZOP study based on the time response to the deviation of single or multiple parameters calculated by Aspen Plus Dynamics v14. and Matlab tools.

* 1. Introduction

Integration of mathematical modeling with the HAZOP study may potentially lead to the detection of unexpected scenario chains resulting from the nonlinearity (Baybutt, 2015). Knowledge of how the nonlinear process responds to deviations of various design parameters in different parts of the process provides significant added value in the development of unexpected scenarios of deviation-cause-consequence chains. The integration of mathematical modeling with the HAZOP study may potentially lead to the detection of some unexpected scenario chains resulting from the nonlinear nature of the process (Labovský et al., 2007, Svandova et al. 2005). Measurement of process nonlinearity in chemical processes is an important part of process response analysis to deviation effects for single or multiple input parameter faults during HAZOP analysis, and it is beneficial for a HAZOP team to be aware of any measure of nonlinearity of the system, which can indicate response predictability due to the inherent nonlinear behavior of the process.

Nonlinearity of the process response to the deviation of a single input parameter can be analyzed by nonlinearity measures (NLM) (Helbig et al., 2000). NLM can evaluate nonlinear behavior of chemical processes and show values of input parameters where nonlinear behavior appears. Also process response to multi-input parameter deviation has been analyzed by Morris (1991) sensitivity analysis.

* + 1. Nonlinear measures

Allgöwer (1995) introduced the nonlinearity measure (NLM) as the difference between the best adapted parallel linear system and the real nonlinear process for various and worst different input values of a single parameter. NLM is used to quantify the degree of nonlinearity in the input-output (I/O) behavior of nonlinear systems and allows direct comparison of the nonlinearity of different processes or different operating points of a process. The approximation of nonlinearity measure (NLM) of the dynamic nonlinear system, *N: 𝒰 × 𝒳0 → 𝒴*, with output *yN*, can be calculated through the solution of the parameter optimization problem defined as:

 (1)

where *G: 𝒰 × 𝒳0,G → 𝒴* is a linear dynamic operator belonging to the space of linear operators 𝒢. 𝒰, 𝒳0, 𝒴 are spaces of admissible inputs, initial conditions, and outputs, respectively,  is L2-norm. It should be noted that  approximates theoretical nonlinear measure, as its calculation requires the solution of an infinite dimensional nonlinear min-max-min problem and is practically infeasible. More detail information is in the work Helbig et al., (2000). For simplicity, symbol is denoted by the symbol NLM in the text. In case NLM=1, the system has strong nonlinear behavior where the parallel linear system insufficiently approximated the nonlinear system. On the other hand, if NLM=0, the system is linear due to exact approximation of nonlinear system by the parallel linear system.

NLM can quantify the nonlinear response only to deviations of a single input operating parameter. To analyze the nonlinear effect in the process response to the deviation of multiple input parameters, the method proposed by Morris (1991) is used. This method, also known as Morris elementary effect, is sometimes classified as screening sensitivity analysis method (Borgonovo and Rabitti, 2023).

The method assumes input space as *k*-dimensional unit hypercube *Hk* with the value range of [0, 1]. Sampling design uses one-at-a-time design which divides the hypercube into a *p* level grid. Sampling is done along the *l* trajectories consisting of *k+1* points used to calculate elementary effects (EEi) of the *ith* input for a given value of input parameters, *u*:

 (2)

where  is a preselected step value,  with usual values of *p* being 4, 6, 8, *p=*6 in this study, *x* is a state vector. After repeating this procedure *l* times, three sensitivity indices are calculated to denote the Morris sensitivity measures, mean of the elementary effects, *μi,* standard deviation, *σi,* and mean of the absolute value, *μi\**, proposed by Campolongo, et al., (2007).

****  (3)

**** (4)

 (5)

The first measure, mean *μi*, is an indicator of the type of process response of output *y*i,out to input change of input parameters *ui*. It should be emphasized that *yi,out* represents a process response (process pressure, temperature or mass flows,…) to the change of input parameters *uj*, and *uj* represents a deviation of any input in the sense of HAZOP methodology. The mean *μi\** directly indicates the sensitivity of output *y*i,out to control parameter *ui*. A higher value of *μi\** indicates higher contributions of control parameter on the variability of output *y*i,out. Standard deviation, *σi*, corresponds to measure of interaction or/and nonlinear effects of the parameter *ui*. High value indicates higher possibility of interactions with other input parameters or nonlinear effects of output *y*out.

* + 1. Case study

The presented quantification method of nonlinear response of the process to the deviation of a single or multiple input parameters is demonstrated on a case study of propylene glycol production by propylene oxide hydrolysis in a continuous stirred tank reactor (CSTR) and product separation by distillation (Olivier-Maget et al.,2021). This process also exhibits nonlinear behavior with experimentally proved (Furusawa et al., 1969) and mathematically identified multiplicities (Fogler, 1999). The reactions assumed in this case study are listed below:

 (6)

 (7)

 (8)

According to the process flow diagram (Fig. 1), the reactor feeds consist of an equivolumic mixture of propylene oxide with methanol and water, respectively. The inflow temperature of both streams was 24°C. The reaction was carried out in a reactor with the volume of 1.9 m3 at the pressure of 1.5 bar and design temperature of 74°C.



Figure 1. Process flow diagram of propylene glycol production unit.

Table 1 Steady state design values of the key state variables.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Stream | POX | WAT | C1-in | D1 | C2-in | D2 | W2 |
| T /°C | 24.2 | 24.0 | 71.1 | 75.4 | 104.0 | 99.4 | 190.1 |
| P /bar | 1.50 | 1.50 | 1.10 | 1.00 | 1.10 | 1.01 | 1.06 |
| Molar flow /kmol.h-1 | 105.2 | 453.6 | 525.4 | 398.0 | 127.4 | 96.9 | 30.5 |

* 1. Software methodology

The proposed software methodology consists of two separate parts. The first part is a simulation module of the analyzed chemical process, which simulates the analyzed system and its reactions to deviations in dynamic mode using Aspen Plus Dynamics v14 as simulation environment. The analyzed chemical process is created in Aspen Plus and transferred to Aspen Plus Dynamics (APD). The second part of the software methodology is the data analysis module using Matlab as analysis data environment, and communication between APD and Matlab is established via Matlab module Simulink. The data analysis module is used to identify nonlinear behavior of the system applying the nonlinearity measure (NLM) and Morris sensitivity measures.

Process deviations are chosen based on the HAZOP methodology, where they are generated by a simple logic combination of guide words (more, less, none, etc.) with selected process parameters (Kletz 1999). The case study depicted in Figure 1 consists of 230 state variables and four state variables (flow rate of mix of propylene oxide with methanol, flow rate of water, flow rate of cooling water, and input temperature of cooling water) are used to generate deviations and are set as input variables in Simulink. In this work, the step change value approach in time zero was used.

Maximum, respectively minimum, values of the deviations from the design input variables of all inflow rates are at the level of ±50%; for cooling water temperature it is at the level of ±10°C. These values define the input space, 𝒢c, in Eq. (1), which is discretized into *M* levels where each level represents one deviation with a different value. *M* deviations are set as an input parameter in Simulink and sent to APD. Here, *M* = 500 was used so that restricted space of 𝒢c sufficiently represents the space 𝒢 in Eq. (1).

After the final list of process deviations is generated, the dynamic simulation section of APD is initiated starting from initial conditions, which are equal to the values in the steady states of the process (Tab.3), the deviation from the selected input variable is applied at time zero. Time between 0 (start of simulation) and the end of simulation is discretized into a defined number of time points or time values. These time steps are used as values when simulation in APD is paused and data from APD are saved in Simulink. After each simulation of the generated deviation, the time series of the current process state is created, transferred, and saved in Simulink as input-output data. This time series contains values of important process variables which represent the system response such as temperature, pressure, flow, composition, etc., of each stream and equipment of the analyzed process.

* 1. Results and discussion

For the sake of simplicity, the term positive deviation is used for deviations with values higher than the design value and the term negative deviation for deviations with values lower than the design value. In the text, the deviations are indicated by the sign and percentage of change. When NLM values target *1,* the system has strong nonlinear behavior where the parallel linear system approximated the nonlinear system insufficiently. On the other hand, for NLM values targeting *0,* the system is linear due to exact approximation of the nonlinear system by the parallel linear system.

|  |  |
| --- | --- |
|  |  |
| Figure 2. NLM values for temperature response to the deviations of single parameters for selected parts of the propylene glycol production unit. Parameters: flow rates of mix of propylene oxide (POX) with methanol water (WAT), and cooling water (CW), and temperature of input cooling water (TCW). | Figure 3. Comparison of Morris sensitivity measures of temperature response for selected parts of the propylene glycol production unit to the deviations of four parameters - flow rates of mix of propylene oxide (POX) with methanol, water (WAT), and cooling water (CW), and temperature of input cooling water (TCW). |

Values of NLM for the response of temperature to the selected deviation are presented in Fig. 2. It is evident that NLM values indicate the nonlinear temperature response to the change of the investigated deviations in all selected parts of the process. The most nonlinear response of temperature to the deviation of feed water flow rate was observed in all selected parts of the process and the highest values of NLM were recorded in the reboiler of column C1 and in the condenser of column C2, respectively. A significant nonlinear response of temperature to the deviation of feed propylene oxide flow rate was also observed in all selected parts of the process. From the HAZOP point of view, this means that the deviation of feed flow rate of water to the reactor (high or low flow rate from design value) can cause hard-to-predict consequences in terms of temperature changes in all units of the process, especially in reboiler of column C1 and in condenser of column C2. These nonlinear responses can be seen in Figure 4., where the time response of temperature to the step changes of the deviation of feed flow rate of water to the reactor in selected parts of the process are presented. Temperature change in the reboiler of column C1 is sensitive to the size of the deviation as the largest increase in temperature is recorded at the lowest analyzed value of the deviation of -50% from the design value. For the other deviation values, the temperature change over time is not so significant. Temperature response in the column condenser of C2 is similar to the previous case, with the only difference that a significant increase in temperature is already seen at the deviation of -25% from the design value. A similar temperature course was also recorded in the reboiler of column C2, where NLM also reached a significant value as indicated by a rather nonlinear response (see Fig.4). On the other hand, temperature response in the reactor and the condenser of column C1 is more predictable than in the reboiler of columns C1 and C2, and in the condenser of column C2. In these cases, a typical nonlinear response effect to the deviation of +18% from the design value was observed, where the temperature with a large time delay unexpectedly and abruptly reaches the same value of steady state as for deviations of +25% and 50%.



Figure 4. Temperature response to deviations of input feed water flow rate for the selected parts of the process.

The above observations are in agreement with the meaning of the sensitivity measures *σi* and *μi\** reached by the Morris method (see Eq.4-5). In Figure 3, a comparison of Morris sensitivity measures *σi* and *μi\** of temperature response for selected parts of the propylene glycol production unit to the deviations of the four investigated parameters is depicted. The mean values, *μi\**, show the importance of the parameter through the distance of the points from the origin mean values. From Figure 3 it is evident that the parameters feed flow rate of water and feed flow rate of mix of propylene oxide with methanol are most important in the process. The Morris plot shows also the standard deviation values, *σi.*. The nonlinearity effect and/or interaction contribution of the parameter increases with its distance from the origin in the *σi* direction. Figure 3 also shows high values of *σi.* for the water feed flow rate in selected parts of the production unit. The highest *σi.* values were reached in the reboiler of column C1 and condenser of column C2, respectively, which*.* indicates higher possibility of interactions with other input parameters (flow rate of mix of propylene oxide with methanol, flow rate of cooling water, and temperature of input cooling water) or nonlinear effects of temperature in the selected parts of production unit.

* 1. Conclusions

Nonlinearities can render process control actions unpredictable, leading to hazardous events and operability issues that are not identified by traditional HAZOP studies. In this paper, two evaluation methods of nonlinearity indicators in chemical processes during HAZOP study are introduced based on the time response to the deviation of single or multiple parameters calculated by Aspen Plus Dynamics v14 and Matlab tools. These indicators are represented by nonlinearity measures (NLM) and sensitive measures standard deviation (*σi*),and the mean of the absolute value (*μi\**) evaluated by Morris sensitivity analysis. The presented method of nonlinear response quantification to a deviation is demonstrated on a case study of propylene glycol production. In this research, the values of NLM for the response of temperature to the deviation of four parameters (flow rate of mix of propylene oxide with methanol, flow rate of water, flow rate of cooling water, and temperature of input cooling water) were analyzed in several parts of the process. NLM values indicate the most nonlinear response of temperature to the deviation of the feed water flow rate of column C1 and condenser of column C2, respectively. These results were confirmed by the sensitivity measures *σi* and ***μi\**** obtained by the Morrismethod. This method should further be applied for other deviation-cause-consequence chains to identify unexpected scenarios based on nonlinearities.

Nomenclature

POX – propylene oxide

WAT – water

WC – cooling water

R - reactor

C1 – first distillation column

C1C – condenser of C1

C1B – boiler of C1

C2 – second distillation column

C2C – condenser of C2

C2B – boiler of C2

D1 – distillate from C1

D2 – distillate from C2

W1 – rest from C1

W2 – rest from C2

Q – heat, kW

LC – level control

PC – pressure control

Acknowledgments

This research was funded by the Slovak Scientific Agency, Grant No. VEGA 1/0511/21.

References

Allgöwer F., 1995, Definition and computation of a nonlinearity measure", 3rd IFAC Nonlin. Contr. Syst. Symp., Lake Tahoe, CA, 279-284

Baybutt P. 2015 A critique of the Hazard and Operability (HAZOP) study. Journal of Loss Prevention in the Process Industries. 33: p. 52-58

Borgonovo E., Rabitti G., 2023, Screening: from tornado diagrams to effective dimensions. Eur. J. Oper. Res. 304 (3), 1200–1211

Campolongo F., Cariboni J., Saltelli A., 2007, An Effective Screening Design for Sensitivity Analysis of Large Models. Environmental Modelling and Software 22 (10): 1509–18

Helbig, A., Marquardt, W., Allgöwer, F., 2000, Nonlinearity measures: Definition, computation and applications, Journal of Process Control, 10, 113–123

Fogler, H.S., 1999, Elements of Chemical Engineering. Prentice-Hall, Inc. London, UK, Englewood Cliffs, N.J.

Furusawa T., Nishimura H., Miyauchi T., 1969, Experimental Study of A Bistable Continuous Stirred-Tank Reactor, J. Chem. Eng. Japan, vol. 2, no. 1, pp. 95–100.

Kletz T.A., 1999, HAZOP and HAZAN: Identifying and assessing process industry hazards. Vol. Rugby, UK. IChemE. 232

Labovský J., Švandová Z., Markoš J., Jelemenský Ľ., 2007, Model-based HAZOP study of a real MTBE plant, J. Loss Prev. Process. Ind. 20, 230–237.

Morris, Max D., 1991, Factorial Sampling Plans for Preliminary Computational Experiments.” *Technometrics* 33 (2): 161–74

Olivier-Maget, N., Berdouzi F., Murillo C., Gabas N., 2021, Deviation propagation along a propylene glycol process using dynamic simulation: An innovative contribution to the risk evaluation, Journal of Loss Prevention in the process Industries 70, 104435.

Švandová Z., Jelemenský, Ľ., Markoš, J., Molnár A., 2005, Steady States Analysis and Dynamic Simulation as a Complement in the Hazop Study of Chemical Reactors. Process Safety and Environmental Protection. 83(5): p. 463-471.