Influence of parameter uncertainty on modeling of industrial ammonia reactor for safety and operability analysis

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ABSTRACT

Chemical reactors represent probably the most hazardous units of chemical industry. Safety analysis of a chemical reactor requires basic knowledge of all particular processes which can be described by mathematical models. Most of the model parameters involved in the prediction of reactor behavior are uncertain. These uncertainties can cause discrepancies mainly in the prediction by models with nonlinear behavior and they can be the source of confusion in the design of chemical reactors and consequently also in the safety and operability analysis.

The main aim of this work was to analyze the influence of uncertainties in the model parameters on the prediction of operating quantities by mathematical models with nonlinear behavior. Such analysis can be used for safety and operability analysis of an industrial catalytic ammonia reactor. The industrial fixed-bed reactor was used by a mathematical model with nine parameters. Analyses of the influence of uncertainty in a single model parameter and their combination were carried out by the Monte Carlo approach. It is shown that even a small uncertainty in one of the key parameters or in a combination of these key parameters can result in several steady states results of the operating quantities and can be the source of confusion in the design and consequently also in the safety and operability analysis.

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1. Introduction

Chemical processes require, except measurement, also optimization. This means that several analyses of a process have to be done, e.g., safety analysis, economic analysis. Mathematical modeling could be a good tool for simulations of many devices or processes in chemical industry. Modeling and its simulation can find a compromise between economically optimal and safe process operating. They are helpful in finding and preventing most of the potential critical or dangerous faults of a chemical processes. These potential hazardous faults, not identified in advance, may cause several problems not only for the process itself but also in the safety of the operational staff. Reactors representing the heart of chemical plants are often operated at extremes of pressure and temperature to achieve optimal performance but this makes them more vulnerable to equipment failures. Nowadays, examination of the reactor safety is very often based on expert experience. To analyze process hazards, the experts systematically ask questions such as 'What can go wrong if cooling fails?', 'How likely is it to happen?', 'How could it be averted or mitigated?', etc., in order to evaluate and improve the safety of the reactor operating. Answers to these and other related questions are the source of the root causes in the process of hazards identification in a chemical plant. This is, however, a complex and time consuming task. One of the most effective techniques to solve this problem is the HAZOP study.

In last years, the model-based HAZOP approach has been developed (Dimitriadis, Hackenberg, Shah, & Pantelides, 1996, Graf and Schmidt-Traub (2001), Eizenberg, Shacham, and Brauner (2006) and Srinivasan, Dimitriadis, Shah, and Venkatasubramanian (1997)). It is based on the description of a chemical plant using a mathematical model. The model-based approach with a set of mathematical equations derived from the quantitative description of a chemical plant seems to be the most straightforward procedure. Usually, the HAZOP analysis does not consider the duration and amplitude of the deviations generated during the operating. In the works of Labovský, Švandová, Markoš, and Jelemenský (2007a, 2007b, 2008) the dynamic and steady state simulation approach was proposed which is useful for the determination of the influence of failure duration and amplitude of the deviation on a reactor with very strong nonlinear behavior. These authors also stated that the investigation of such nonlinear systems is affected by the selection of an adequate mathematical model and is strongly sensitive to the uncertainties in parameters which describe physical properties, kinetics, mass and heat transfers, etc. Uncertainties in each
parameters can influence the results of any kind of nonlinear process. Mathematical models used to describe a process are mostly nonlinear. Nonlinear systems have expected results by their computation, therefore it is hard to say what influence on the results has parameter uncertainty or any combination of the parameters uncertainties. This is a very complex problem and it is hard to find answers and confidence without further analysis.

Mathematical models in all processes can include several parameters depending on the complexity of the mathematical model. They can be physical, kinetic, thermodynamic parameters, parameters of mass and heat transfer and in some cases also other ones. These parameters can be obtained from literature, empirical or semi-empirical correlations or they can be measured. Parameters of mathematical models are rarely certain or “error free”. It is hard to define how many variations they have because it is also known that some parameters are defined better than others.

Measurement, sampling, interpolation, correlation, transfer of data, insufficient knowledge, re-scaling errors, etc., result in variations and uncertainties in parameters (Hauptmanns, 1997, 2007, 2008). These variations may be prominent for some processes, analyses, modeling, etc. (Zhang & Goodchild, 2002). For example mathematical imprecision, where the uncertainties of data and/or model uncertainties can have significant influence on the results of uncertainty analyses (Heuvelink, 1998), simulation results are totally different than those obtained in practice under the same model conditions. This partial problem is a part of the needs of uncertainty analyses application of data and models (Heuvelink, 2002). For example, uncertainties are sensitive to the scales of data and model definition (Bierkens, Finke, & De Willigen, 2000). However, knowledge of literature information on the uncertainty assessment and propagation (e.g. Helton & Davis, 2003) is mostly not applied in the study of data and model uncertainty influence on e.g. mathematical modeling. For specification data and model prediction uncertainties, only several methods exist (e.g. Ayyub, 2001; Brown and Heuvelink, 2006; Goodchild, 2004; Hauptmanns, 1997, 2007, 2008): for example confidence intervals, median, average, membership functions, full probability distribution functions, relative variations, histograms. Their propagation can be calculated in many ways, e.g. by interval arithmetic (Jaulin, Kieffer, Didrit, & Walter, 2001) or parameter- and state-bounded algorithms (Schweppe, 1968), Monte–Carlo Simulation (MCS) (Gentle, 2003; Hammersley & Handscomb, 1979), generalized polynomial chaos (Xiu & Karniadakis, 2001), error-propagation equations (Taylor, 1997), direct probabilistic modeling (Jazwinski, 1970), or fuzzy logic (Zadeh, 1978). MCS methods are the most frequently used. They are simple, computation-intensive but very useful in creating methodology for universal uncertainty analyses, e.g. nonlinear modeling, where only the expected results can be computed with some confidence. MCS methods are practically useful in uncertainty analyses combining the data and model uncertainty with any number of parameters.

Methods for uncertainty assessment and propagation have been applied in soil science (Ehlschlaeger, Shortridge, Goodchild, 1997; Goovaerts, 1997; Heuvelink, Brown, & Van Loon, 2007), mining, oil and gas (Caers, 2005), geographical information science (Shi, 1998; Wu, Nunan, Crawford, Young, & Ritze, 2004), environmental engineering (Brown and Heuvelink, 2006), and safety engineering (Hauptmanns, 2007, 2008). In recent years, advances in uncertainty assessment and propagation have been paralleled by improvements in the software for sensitivity and uncertainty analyses in mathematical modeling. These software programs include generic statistical tools, such as Matlab (Delores, Kuncicky, & Moore, 2005), Mathematica (Wolfram, 2003), and more specific uncertainty packages e.g. SimLab (Saltelli, Tarantola, Campolongo, & Ratto, 2004). For research purposes, generic tools, such as Matlab, which are flexible, portable and scaleable but less intuitive and require more time than purpose-built tools, such as SimLab, are used. Currently, there are no software tools to quantify and propagate uncertainty for a wide range of data types, or to apply uncertainty analyses of nonlinear mathematical model parameters.

The main goal of this work was to define the influence of data uncertainty on the modeling of heterogeneous catalytic tubular reactors for safety analyses that exhibited strong nonlinear behavior. Our way to define the influence of data uncertainty is based on the definition of parameters variations with normal (Gauss) distribution and relative variations, and on the comparison of mathematical model results. Quantitative influence on the results is represented by histograms, locus of the outlet steady states temperature and the temperature profiles along the reactor.

2. Mathematical model

In 1989, an accident on an industrial fixed-bed ammonia synthesis reactor took place in Germany. After a sudden decrease in the reactor pressure, caused by a temporary reduction in fresh feed to the synthesis loop, the reactor operated without feedback control, became unstable and the recorded temperatures started oscillating with a period of about 6 min and a range of about 200 °C (±100 °C). The oscillation lasted for about 2 h until the pressure in the synthesis loop was restored. Such large and rapid oscillations are damaging to the catalyst. After the incident it was observed that this kind of oscillations tended to occur more frequently and for smaller disturbances (Morud & Skogeskad, 1998).

It is very important to know the boundary between normal operating conditions and potentially hazardous conditions (high temperature, high pressure) that can lead to a break down of the reactor. In many cases an industrial reactor has to work safely for a long time and it may happen that, after a small disturbance, it started oscillating. This situation can lead to hazardous sequences, like the loss of lives, property or pollution of environment. To prevent this, it is important to know the behavior of an industrial reactor in detail.

The fixed-bed ammonia synthesis reactor is described in Fig. 1, which shows a reactor consisting of three beds in series with fresh feed (w1, w2, w3) between each bed and preheating of the feed (wH) with effluents. Both, the heat exchanger and the mixers were computed using only steady state material and enthalpy balances. The heat exchanger was modeled as a standard countercurrent exchanger (Morud & Skogeskad, 1998):

\[ T_i = \Theta T_o + (1 - \Theta) T_f \]  

where \( T_i \) is the exchanger outlet temperature, \( \Theta \) is the exchanger efficiency, \( T_o \) is the reactor outlet temperature, \( T_f \) is the feed temperature.

To compute each bed of the ammonia reactor, a number of mathematical models with different complexity can be used. They can be models of plug flow reactor, models with or without axial or radial dispersion, or models with or without intraparticle diffusion. With model complexity, the number of model parameters increases. The main purpose of this work was not to demonstrate the influence of model complexity on the reactor behavior but to develop a technique to determine the influence of data uncertainty on the modeling of a heterogeneous catalytic tubular reactor for ammonia production. This is the reason for using a simple pseudo-homogeneous model with axial dispersion to compute each bed of the ammonia reactor, as a model with a few of parameters. The same technique can be used with more complex models. The
pseudo-homogeneous model with axial dispersion combines mass and energy balances:

Equations of mass balance:

\[ \frac{\partial c_i}{\partial t} + \frac{\partial wc_i}{\partial z} = v_0 \xi_i v \]  

(2)

Equations enthalpy balance:

\[ \rho C_P^i \frac{\partial T}{\partial t} + w p C_P^i \frac{\partial T}{\partial z} - \lambda_a \frac{\partial^2 T}{\partial z^2} = (-\Delta H) \xi_i v \]  

(3)

where \( \lambda_a \) in each bed is computed by the following equation (Morud & Skogeskad, 1998):

\[ \lambda_a = \frac{\Delta z u_w}{2} \]  

(4)

\[ u_w = \frac{w C_P}{m C_P} \]

where \( \Delta z \) is the grid spacing.

To solve this system of partial differential equations, the following initial and boundary conditions must be met.

Initial conditions:

\[ t = 0 \quad z_e (0, L) \]

\[ c_i = c_{i0} \quad T = T_0 \]

(5)

Boundary conditions:

\[ z = 0 \]

\[ i = 1, 2, \ldots, N_l \]

\[ c_i = c_i^L \]

\[ v^f C_i^L T^f \]

\[ z = L \]

\[ i = 1, 2, \ldots, N_l \]

\[ \frac{\partial c_i}{\partial z} = \frac{\partial T}{\partial z} = 0 \]

The reaction system of ammonia production in the gas phase is defined as follows (Froment & Bischoff, 1979):

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]  

(7)

Kinetics of this reaction is computed from the Temkin–Pyzhev equation:

\[ r_{N_2} = \frac{1}{P} \left( k_1 P_{N_2} \frac{p_{H_2}^{1.5} - p_{NH_3}}{p_{H_2}} \right) \]  

(8)

where \( p_i \) [bar] denotes the partial pressure of component \( i \),

\[ k_1 = f k_{x1} = \exp \left( \frac{E_1}{RT} \right) \]

\[ k_{-1} = f k_{-x1} = \exp \left( \frac{E_2}{RT} \right) \]

This reaction system is well known with multiple steady state and oscillation area determination (Mancusi, Merola, & Crescitelli, 2000, Morud & Skogeskad, 1998). Nonlinearities of the mathematical model are the reason for using this process in the parameters uncertainty analyses. The phenomenon of multiple steady states implies that a reactor can work at several steady states under the same operating conditions depending on initial conditions. Oscillation areas are known as specific steady states. They arise when stable steady state becomes unstable due to the influence of operating conditions changes. Fig. 2 represents the locus of the steady state, outlet temperature vs. pressure. This solution diagram has a typical ‘S’ profile and the maximum number of steady states for some values of pressure is equal to three. The desired operating point (Fig. 2 upper steady state with the pressure of 20 MPa) is located inside the region of multiplicity. Thus, branch switching may occur during the failure of the reactor pressure. Due to a close location of the point of reactor operating to the region of multiple steady states and regions of oscillation regimes, the reactor is sensitive to pressure in the context of safe operating. The decrease in pressure causes a slight growth of the outlet temperature which follows an upper stable steady state branch up to the value depicted by the filled circle (Hopf bifurcation point). After crossing the Hopf bifurcation point, the reactor entered the dynamic regime characterized by sustained oscillations.

If a further decrease in the pressure (to the value of 14 MPa, marked by an empty circle) occurs, a new steady state is reached on the lower stable steady state branch characterized by a very low outlet temperature.

From these results follows that the pressure has a significant influence on the outlet temperature, the temperature profile along the fixed-bed reactor and of course also on the conversion of ammonia. On the other hand, the region of multiple steady states determined by the position of two turn points depends on the
values of model parameters in Equations (2)–(9). The uncertainties in these parameters influence the determination of these turn points which means that the prediction of consequences on the failure change of pressure can lead to different results, for instance disappearance of the region of oscillation, different temperature profiles along the reactor or different value and position of maximal temperature in the reactor.

3. Parameter uncertainties (in the model)

Mathematical model of the fixed-bed reactor represented by Equations (1)–(9) include several parameters. They can be physical (e.g. specific heat capacity, density), kinetic (e.g. activation energies, reaction enthalpy, preexponential factors), mass or heat transfers parameters (e.g. effective axial thermal conductivity). Actual values of the model parameters for the calculated locus of the steady state, outlet temperature vs. pressure in Fig. 2 are summarized in Table 1.

These parameters can be obtained from literature, empirical or semiempirical correlations or they can be measured. Parameters of mathematical models are rarely certain or "error free". Measurement, sampling, interpolation, correlation, transfer of data, insufficient knowledge, re-scaling errors, etc., result in some variations and uncertainties in the parameters (Hauptmanns, 1997). Normally, these parameters are fixed in the prediction of chemical processes without a specified confidence bound. But, parameter uncertainties can have some (high, low, none) influence on the chemical process simulation. Unfortunately, in the present case, no information on their uncertainties is available. Therefore, the generic approach was adopted. It consists in choosing the distribution and fixing the distribution parameters. The standard distribution chosen is normal (Gauss) distribution (Hauptmanns, 1997). Its probability density function is presented in Fig. 3, where the reaction enthalpy is distributed with normal distribution.

The probability density function of normal Gauss distribution is given as:

\[ f(x | \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right) \quad x \in \mathbb{R} \]  \hfill (10)

where \( x \) is the random variable in question (e.g. heat of the reaction), \( \mu \) is the mean (value of heat enthalpy), \( \sigma \) is the corresponding standard deviation. Parameter distribution can be defined qualitatively by relative variation. A lot of relative variations have been defined by now. In this work, the relative variation of parameter \( M \) (e.g. reaction enthalpy) was defined using the following equation:

\[ R_M = \frac{\sigma_M}{M} \]  \hfill (11)

Defining the parameter distribution, the parameters are no longer considered to be fixed but their behavior is assumed to be random as a consequence of uncertainty (Hauptmanns, 1997). Of course, simulation results depend on the number of the parameter random values from the defined distribution. From the safety analyses point of view, it was decided to observe steady state maximum temperature in all reactor beds as a desired result. With an increase in the number of the random parameter values from normal distribution (number of iterations), average and standard deviation of the maximum temperature changed. But up to 1000 iterations, the average and standard deviation changes were very small. This situation is presented in Figs. 4 and 5, where all model parameters have relative variations equal to 2%. The number of random values (iterations) used in the simulation was 10 000 because of the confidence of a change of the observed results.

4. Results and discussion

Hauptmanns (1997) in his work showed that uncertainty of the reaction enthalpy has a considerable impact in the design of chemical reactors. Therefore the first analyses of the influence of uncertainty in model parameters on the results were started with reaction enthalpy. Figs. 6–9 represent the results of uncertainty analyses when relative variation of the reaction enthalpy was 4%. In Fig. 6 is depicted the histogram of the steady state outlet temperature of the ammonia reactor. It can bee seen that the simulation results are in the area of

![Fig. 3. Reaction enthalpy probability density function.](image_url)

![Fig. 4. Average maximum temperature in the ammonia reactor depending on the number of parameter values from normal distribution.](image_url)
one of the stable steady states. This area is in the surrounding of normal operating conditions and the resulting distribution of the outlet temperature is sharp. Fig. 7 represents the maximum, minimum and average temperature of the ammonia reactor and the temperature along the reactor without any variation of the model parameters. The system is nonlinear; therefore, the average temperature and the temperature without uncertainty cannot be the same. It must be noticed that there is no maximum or minimum profile in the reactor. The maximum temperature corresponds to the maximum values of the temperatures along the reactor. The minimum temperature corresponds to the minimum temperature values along the reactor, and the average result is the average of all temperatures. In Table 2, the values of the maximum and average differences between the maximum and minimum of the temperature are presented. This average was computed by the following equation:

\[
\Delta T = \frac{\int_0^L \Delta Tdz}{L}
\]  

(12)

Fig. 8 represents the locus of the steady state outlet temperature in dependence on the reaction enthalpy change in a wide range. From the results clearly follows that the variation of reaction enthalpy has strong nonlinear influence on the model. This nonlinear behavior can cause that a small change in the reaction enthalpy results in a large change in the outlet temperature. It can be seen that for media reaction enthalpy, three different steady state outlet temperatures are identified, two stable and one unstable. Media result and area of the results in the 90% confidence interval of the reaction enthalpy are also presented in Fig. 8. This normal operating point can be seen as the highest intersect of the locus of the steady state outlet temperature and the line of the median temperature. It can be seen that the relative variation of the reaction enthalpy in the 90% confidence interval is too low to create a second area of the steady state temperatures, because this interval does not include the turn point. It should be noted that the initial conditions of the operating point for all simulation were used.

Situation is changed when the relative variation of the reaction enthalpy is 5%, so the variation increased by only one percent compared to the previous situation. In Fig. 11 it is depicted that this confidential interval includes a bifurcation turn point and a second area of steady states in the surrounding of 250 °C — see Fig. 9. From these results follows that if the reaction enthalpy around the left 90% confidence interval is chosen during the safety analysis then only low values of the outlet temperature are predicted. It is clear
that these predictions lead to different interpretation of model results during the safety analysis. Fig. 10 depicts the increase in the difference of the maximum and minimum temperature compared to Fig. 7. This is due to the existence of the low steady states and it means that in this region, the temperature along the reactor can be expected if the reaction enthalpy relative variation equals 5%. It is clear that for a nonlinear system relatively small error can cause very large differences in the temperature prediction along the reactor which it caused difficulties with the prediction of exact temperature profiles during the safety analysis.

The influence of uncertainty in model parameter $E_1$ on the results was also analyzed. It was observed that if the relative variation for $E_1$ equals 1%, similar results as for the reaction enthalpy equaling 5% are obtained. The variation of activation energy $E_1$ has also very strong nonlinear influence on the model and the region of multiple steady states is identified. For instance, in Fig. 14, the 90% confidence interval of relative variation of activation energy $E_1$ equaling 1% is depicted. From Fig. 12 it is clear that only one percent variation of this parameter creates a second area of steady states. From the comparison with the reaction enthalpy variation follows that the model is more sensitive to the uncertainties in $E_1$ and $C_P$ than in the reaction enthalpy and it is less sensitive to the uncertainty in $k_1$. It is clear that for the correct prediction of the fixed-bed reactor behavior very accurate values of mainly two activation energies are needed.

This observation can be seen in Table 2, where the average of the difference between the maximum, defined by equation (12), and minimum temperatures along the reactor are summarized. From Table 2 it is clear that an increase in the relative variation of the parameter causes an increase in the values of average and maximum temperature differences in the reactor. These increases are not linear and the values change by jump when the 90% confidence interval crosses the critical region with two stable steady states. It is evident that this 90% confidence interval for the kinetic parameters $E_1$ and $E_2$ with the relative variation equaling 1% and 2%, respectively, is sufficiently large if the values of the differences in the temperature are higher than 230 °C. On the other hand, the 90% confidence interval for another kinetic parameters, the reaction enthalpy and the preexponential factor $k_1$, the relative variations equals 5% and 9%, respectively, causing these jumps if the average and maximum temperature differences reaches the values over 230 °C.

![Fig. 9. Outlet temperature histogram — reaction enthalpy relative variation equals 5%.](image)

![Fig. 10. Temperature profiles along the ammonia reactor — reaction enthalpy relative variation equals 5%.](image)

![Fig. 11. Locus of the steady state outlet temperatures in the 90% confidence interval — reaction enthalpy relative variation equals 5%.](image)

### Table 2

<table>
<thead>
<tr>
<th>Relative variations — $R$</th>
<th>$\Delta T$</th>
<th>$\Delta T_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{u_{E_1}}$ = 1%</td>
<td>32.6</td>
<td>78</td>
</tr>
<tr>
<td>$R_{u_{E_1}}$ = 4%</td>
<td>71.04</td>
<td>127.09</td>
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<tr>
<td>$R_{u_{E_1}}$ = 5%</td>
<td>233.9</td>
<td>273.72</td>
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<tr>
<td>$R_{u_{E_2}}$ = 0.1%</td>
<td>8.74</td>
<td>25.12</td>
</tr>
<tr>
<td>$R_{u_{E_2}}$ = 1%</td>
<td>255.79</td>
<td>288.15</td>
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<tr>
<td>$R_{u_{E_2}}$ = 2%</td>
<td>280.21</td>
<td>302.15</td>
</tr>
<tr>
<td>$R_{u_{E_2}}$ = 0.1%</td>
<td>7.42</td>
<td>21.80</td>
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<td>$R_{u_{E_2}}$ = 1%</td>
<td>105.25</td>
<td>163.36</td>
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<tr>
<td>$R_{u_{E_2}}$ = 2%</td>
<td>301.03</td>
<td>344.93</td>
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<tr>
<td>$R_{u_{E_2}}$ = 4%</td>
<td>12.85</td>
<td>36.74</td>
</tr>
<tr>
<td>$R_{u_{E_2}}$ = 7%</td>
<td>53.45</td>
<td>105.6</td>
</tr>
<tr>
<td>$R_{u_{E_2}}$ = 9%</td>
<td>235.46</td>
<td>271.59</td>
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</tbody>
</table>


Fig. 12. Outlet temperature histogram – activation energy $E_1$ relative variation equals 1%.

Fig. 13. Temperature profiles along the ammonia reactor – activation energy $E_1$ relative variation equals 1%.

Fig. 14. Locus of the steady states outlet temperatures in the 90% confidence interval – activation energy $E_1$ relative variation equals 1%.

Fig. 15. Outlet temperature histogram – all parameter relative variations equal 2%.

Fig. 16. Temperature profiles along the ammonia reactor – all parameter relative variations equal 2%.

Fig. 17. Outlet temperature histogram – relative variations of $E_1, E_2$ equal 2%. 
Fig. 18. Temperature profiles along the ammonia reactor – relative variations of $E_1$, $E_2$ equal 2%.

In the view of the above result, consequences for the interpretation of model predictions during the safety analysis follow. In the case of a nonlinear model (it should be noted that almost all models for chemical processes are nonlinear) small uncertainties in the key model parameter, in this case activation energy $E$, can cause different predictions of the behavior of operating quantities such as temperature, pressure, concentration,… For example, if the activation energy $E_1$ equals 89 kJ/mol and the rest of the model parameters are identical with the values in Table 1, then very low outlet temperature is reached ($T_0 = 255 \, ^\circ\text{C}$) and the temperature profile along the reactor is close to the minimum temperature in Fig. 13. On the other hand if the activation energy $E_1$ equals to median ($E_1 = 87.09 \, \text{kJ/mol}$) and the rest of the model parameters are identical with the values in Table 1, then outlet temperature of $525 \, ^\circ\text{C}$ is reached and the temperature profile along the reactor is identical with the temperature profile for the median in Fig. 13. Now, it is evident that for the nonlinear models, the prediction by error free model parameters is rather confusing and the approach of the uncertainty analysis of the model parameters represented by Figs. 6–14 should be preferred.

On the other hand, in the previous analyses, the influence of combinations of different parameters variations on the model prediction was not assumed. Therefore, in the next step the uncertainty in all parameters are analyzed. Figs. 15 and 16 represent the steady states outlet temperatures where the relative variations of all parameters equal 2% were considered. From these results follows that two different steady states were identified and the possible maximum and minimum temperature profiles along the reactor created a large region where the temperature can be expected.

Furthermore, these results were compared with the results in Figs. 17 and 18, where two most sensitive parameters ($E_1$, $E_2$) with the same variation equaling 2% were selected. As mentioned previously, uncertainties in the activation energies $E_1$ and $E_2$ have strong influence on the prediction of a fixed-bed reactor behavior. From these comparisons follows that the distribution of the outlet temperature depicted in Figs. 15 and 17 and the minimum and maximum temperature profiles along the reactor reported in Figs. 16 and 18 are almost identical.

This observation is also demonstrated in Table 3, where the average differences between the maximum and minimum temperatures along the reactor, defined by equation (12), and the maximum difference of temperatures in the reactor are summarized. From the results it is evident that the maximum and average differences of temperature did not change significantly with the increase of the number of parameters variation. This means that the contribution of the variation in both activation energies is dominant and the contribution of other parameters with the same variation can be neglected. Furthermore it can be concluded that the effect of interactions of the uncertainties in the parameters on the model prediction is not identified for this model of the fixed-bed reactor.

5. Conclusion

Uncertainty of the parameters used in the mathematical model of the reactor, which is always present, may have important impact on the prediction of the reactor behavior.

Influence of parameters uncertainty on the reactor behavior is demonstrated on the outlet reactor temperature and on the temperature profiles along the fixed-bed ammonia reactor. These uncertainties can cause discrepancies mainly in the predictions by models with nonlinear behavior and they can be the source of confusion in the design of chemical reactors and consequently also in the safety analysis. Nonlinear behavior can cause that even a small change in the reaction enthalpy results in a large change of the outlet temperature. In the case of correct prediction of a fixed-bed reactor behavior, very accurate values mainly for the two activation energies, $E_1$ and $E_2$, are needed because it was shown that even a relative variation equaling 2% in these key model parameters can cause different predictions of the behavior of the operating quantities, such as temperature inside the reactor.

It is evident that for nonlinear models the prediction by error free model parameters is rather confusing. The uncertainty analysis approach should be focused on the identification of the worst case scenarios of reactor behavior. These identified worst possible conditions should be used in process safety analysis especially if the model-based HAZOP approach is chosen.

Acknowledgement

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Table 3

<table>
<thead>
<tr>
<th>Relative variations $- R$</th>
<th>$\Delta T$ [\degree C]</th>
<th>$\Delta T_{\text{max}}$ [\degree C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0$ = 2%</td>
<td>280.21</td>
<td>302.15</td>
</tr>
<tr>
<td>$R_0 , R_1$ = 2%</td>
<td>317.19</td>
<td>345.28</td>
</tr>
<tr>
<td>$R_0 , R_1 , R_2$ = 2%</td>
<td>325.25</td>
<td>347.17</td>
</tr>
<tr>
<td>$R_0 , R_1 , R_2 , R_3$ =2%</td>
<td>330.77</td>
<td>348.65</td>
</tr>
<tr>
<td>$R_0 , R_1 , R_2 , R_3$, $R_4$ = 2%</td>
<td>331.04</td>
<td>349.13</td>
</tr>
</tbody>
</table>

$T$ temperature (\degree C)  
$c$ concentration (mol m$^{-3}$)  
$C_P$ specific heat capacity (J kg$^{-1}$ K$^{-1}$)  
$E$ activation energy (J mol$^{-1}$)  
$f$ industrial catalyst coefficient  
$\Delta H_R$ reaction enthalpy (J mol$^{-1}$)  
$k$ reaction rate constant (s$^{-1}$)  
$k_\infty$ preexponential factor (s$^{-1}$)  
$L$ reactor length (m)  
$\bar{M}$ average of parameter M  
$N_L$ number of components  
$P$ pressure (Pa)
$R$  relative variation
$T$  temperature (K)
$T_i$  exchanger outlet temperature (K)
$T_o$  reactor outlet temperature (K)
$t$  time (s)
$w$  superficial fluid velocity (m s$^{-1}$)
$w_1, w_2, w_3$  quench bed 1–3 (kg s$^{-1}$)
$wh$  inlet flow to preheater (kg s$^{-1}$)
$z$  axial axis (m)

**Greek symbols**

$r$  stochiometric coefficient
$\lambda_a$  effective axial thermal conductivity (J m$^{-1}$ s$^{-1}$ K$^{-1}$)
$\rho$  density (kg m$^{-3}$)
$\bar{\epsilon}$  reaction rate (mol m$^{-2}$ s$^{-1}$)
$\Theta$  heat exchanger efficiency

**Subscripts**

$i$  component
$0$  initial condition
max  maximal value
cat  catalyst

**Superscripts**

$f$  input

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**References**


