



UNIVERSITY OF LEEDS

This is a repository copy of *Investigation of the effect of correlated uncertain rate parameters via the calculation of global and local sensitivity indices*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/124300/>

Version: Accepted Version

Article:

Valkó, E, Varga, T, Tomlin, AS orcid.org/0000-0001-6621-9492 et al. (2 more authors) (2018) Investigation of the effect of correlated uncertain rate parameters via the calculation of global and local sensitivity indices. *Journal of Mathematical Chemistry*, 56 (3). pp. 864-889. ISSN 0259-9791

<https://doi.org/10.1007/s10910-017-0836-7>

© 2017, Springer International Publishing AG, part of Springer Nature. This is a post-peer-review, pre-copyedit version of an article published in *Journal of Mathematical Chemistry*. The final authenticated version is available online at: <https://doi.org/10.1007/s10910-017-0836-7>. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Investigation of the effect of correlated uncertain rate parameters via the calculation of global and local sensitivity indices

É. Valkó¹, T. Varga¹, A.S. Tomlin², Á. Busai¹, T. Turányi^{*,1}

¹ Institute of Chemistry, ELTE Eötvös Loránd University, Pázmány Péter stny. 1/A, Budapest, 1117, Hungary

² School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

* email: turanyi@chem.elte.hu, telephone number: +36 1 372 2500 x1109

Abstract

Applications of global uncertainty methods for models with correlated parameters are essential to investigate chemical kinetics models. A global sensitivity analysis method is presented that is able to handle correlated parameter sets. It is based on the coupling of the Rosenblatt transformation with an optimized Random Sampling High Dimensional Model Representation (HDMR) method. The accuracy of the computational method was tested on a series of examples where the analytical solution was available. The capabilities of the method were also investigated by exploring the effect of the uncertainty of rate parameters of a syngas–air combustion mechanism on the calculated ignition delay times. Most of the parameters have large correlated sensitivity indices and the correlation between the parameters has a high influence on the results. It was demonstrated that the values of the calculated total correlated and final marginal sensitivity indices are independent of the order of the decorrelation steps. The final marginal sensitivity indices are meaningful for the investigation of the chemical significance of the reaction steps. The parameters belonging to five elementary reactions only, have significant final marginal sensitivity indices. Local sensitivity indices for correlated parameters were defined which are the linear equivalents of the global ones. The results of the global sensitivity analysis were compared with the corresponding results of local sensitivity analysis for the case of the syngas–air combustion system. The same set of reactions was indicated to be important by both approaches.

Keywords: sensitivity analysis, HDMR, correlated parameters, syngas combustion

MSC code: 49Q12

ORCID ID:

É. Valkó: 0000-0003-2606-2536

T. Varga: 0000-0002-6500-9546

A. S. Tomlin: 0000-0001-6621-9492

Á. Busai: 0000-0001-6597-4867

T. Turányi: 0000-0002-1461-165X

Acknowledgement

The authors thank the support of the Hungarian National Research, Development and Innovation Office – NKFIH grants K84054 and K116117, and COST Action CM1404 “SmartCats”. The work of TV was supported by the ÚNKP-16-3 New National Excellence Program of the Ministry of Human Capacities.

1. Introduction

Chemical models based on detailed reaction mechanisms usually have many parameters, the quantification of which involves a level of uncertainty. The parameters of these models are intrinsically correlated, but most commonly used uncertainty and sensitivity methods are able to handle only uncorrelated parameters. An important step of modelling is to investigate the relationship between the uncertainty of model parameters and the uncertainty of model results. Frequently, the methods used for the determination of the uncertainty of model results are based on one-by-one modifications of the parameters. These methods fail if the parameters are correlated since the calculation of the influence of a given parameter using fixed values of the other parameters is not sufficient.

The reason why uncertainty methods that can handle uncorrelated parameters only are widely used is that usually the uncertainty of the model input parameters are assessed individually and separately, and therefore information about the correlated uncertainty of these parameters is not usually available. However, Sheen and Wang [1-3] and Turányi et al. [4-9] recently elaborated chemical kinetic model optimization strategies which are able to calculate not only the optimized values of the parameters, but also the covariance matrix of the fitted parameters. This matrix carries information about the joint uncertainty of the parameters. Investigation of the effect of correlated uncertainties of model parameters on the uncertainty of the model results is clearly a necessary next step.

In this work, global correlated, marginal sensitivity and final marginal indices were calculated to investigate the uncertainty of a target model output caused by uncertainties in the system parameters. The calculation of these sensitivity indices is based on the Rosenblatt transformation and the Random Sampling High Dimensional Model Representation Method (RS-HDMR). The basic outline of this algorithm has been published in our previous article [10] but the previous paper focused on the application of the method to investigate the effect of wall reactions on hydrogen ignition limits. In this work, the details of the methodology are described, and the accuracy of the calculated sensitivity indices is tested using several analytical examples. Local sensitivity indices for correlated parameters are defined as the linear equivalents of the global ones. Also, a chemical kinetic example related to the ignition delay times of a syngas–air mixture is investigated, and the results are compared to expectations based on reaction kinetics reasoning. The consequence of the correlated uncertainty of 55 rate parameters was investigated. This is the most complex chemical system to date where such study has been carried out. In this practically important system, the order of the convergence of the sensitivity indices and the features of the marginal sensitivity indices were investigated. The results of the global sensitivity analysis were compared to those of a more widely used local sensitivity analysis method.

2. Methods

2.1 HDMR Global Sensitivity Analysis

The aim of sensitivity analysis is the determination of the relationship between the uncertainty of the model input parameters and that of the target model result. Local sensitivity analysis is frequently used to investigate chemical kinetic models. Local methods are based on the calculation of the partial derivatives of the model result with respect to the parameters at a fixed point in the parameter space, which is identical to the nominal parameter set. Local methods are cheap and easily realizable, but the information that these methods provide is relevant only at a given point in the parameter space, and does not belong to the full uncertainty domain of the model parameters. Global sensitivity analysis provides information about the importance of the model parameters in the full uncertainty domain of the parameters and is therefore more relevant where large uncertainties exist in the input parameters, or where the model is highly nonlinear. There are many possibilities to define a ranking of the importance of parameters using global methods [11]. However, these methods are computationally expensive and knowledge about the distribution of the parameters is required. Most global uncertainty analysis methods can handle only uncorrelated parameters. New global sensitivity analysis methods which can also handle models with correlated parameters were developed in recent years [12-14]. In the next section a new sensitivity analysis method will be presented, which calculates global sensitivity indices [15] based on the Random-Sampling High Dimensional Model Representation Method [12,16,17] and the decorrelation method of Rosenblatt [18].

First, we denote the parameters of a model by $\mathbf{x}=(x_1, x_2, \dots, x_n)$ and the simulation result by $f(\mathbf{x})$ ($f: \mathbb{R}^n \rightarrow \mathbb{R}$). The result of the model can be expressed as a hierarchical expansion of the parameters:

$$f(\mathbf{x}) = f_0 + \sum_{i=1}^n f_i(x_i) + \sum_{1 \leq i < j \leq n} f_{ij}(x_i, x_j) + \dots + f_{12\dots n}(x_1, x_2, \dots, x_n) \quad (1)$$

where the constant f_0 represents the mean value of the model output across the input sample, $f_i(x_i): \mathbb{R} \rightarrow \mathbb{R}$ is the contribution of the i -th input parameter x_i to $f(\mathbf{x})$; $f_{ij}(x_i, x_j): \mathbb{R}^2 \rightarrow \mathbb{R}$ is the cooperative contribution of the i -th and j -th inputs parameters to $f(\mathbf{x})$, etc. The zeroth-order, first-order, second-order, etc. component functions are denoted by f_0, f_i, f_{ij} etc., respectively. In the present work, these expansions were truncated at second-order terms. If parameters x_1, x_2, \dots, x_n are independent, then the component functions can be determined uniquely and optimally [12] and can be expressed using an orthogonal polynomial basis:

$$f_i(x_i) = \sum_{r_i=1}^{O_i} \alpha_i^{r_i} \varphi_i^{r_i}(x_i) \quad (2a)$$

$$f_{ij}(x_i, x_j) = \sum_{r_i=1}^{O_{ij}} \sum_{q_j=1}^{O_j} \beta_{ij}^{r_i q_j} \varphi_i^{r_i}(x_i) \varphi_j^{q_j}(x_j) \quad (2b)$$

where O_i and O_{ij} denote the order and α_i, β_{ij} denote the coefficients of basis functions φ_i and φ_j . These coefficients are determined by fitting the RS-HDMR function to a sample of runs from the full model. It is important to notice that the determination of the orthogonal basis functions depends on the distribution of the input parameters. If optimal basis functions are chosen and the optimal coefficients are calculated (e.g. using a least-squares method), then sensitivity indices can be determined as detailed below.

Let V denote the total variance of $f(\mathbf{x})$, V_i the partial variance of $f(\mathbf{x})$ due to x_i alone and V_{ij} the partial variance of $f(\mathbf{x})$ due to the interactions between x_i and x_j . Let E and V denote the expected value and the variance operators, respectively. We can define the first- and second-order sensitivity indices as $S_i = V_i/V = V(E(f(\mathbf{x})|x_i))/V(f(\mathbf{x}))$ and $S_{ij} = V_{ij}/V = V(E(f(\mathbf{x})|x_i, x_j))/V(f(\mathbf{x}))$, respectively. If an accurate fit is obtained such that Eq. (2) provides a good representation of the expansion in Eq. (1), then the sum of these indices should be close to 1.

The total order effect for parameter x_i can be expressed as:

$$S_i^{\text{total}} = S_i + \sum_{j \neq i} S_{ij} + \dots = E(V(f(\mathbf{x}) | x_1, \dots, x_{i-1}, x_{i+1}, \dots, x_n)))/V(f(\mathbf{x})) \quad (3)$$

The total sensitivity index S_i^{total} measures the contribution of x_i to the output variance, including all variances caused by its interactions of any order, with any other input parameters. If the input parameters are independent, we can determine the optimal orthogonal polynomial expansion of the component functions. Using Eq. (1) and Eq. (2), the partial variances can be calculated and the sensitivity indices of the parameters can be determined:

$$S_i = \sum_{r_i=1}^{O_i} (\alpha_i^{r_i})^2 / V \quad (4a)$$

$$S_{ij} = \sum_{r_i=1}^{O_{ij}} \sum_{q_j=1}^{O_j} \beta_{ij}^{r_i q_j} / V \quad (4b)$$

$$S_i^{\text{total}} = \left(\sum_{r_i=1}^{O_i} (\alpha_i^{r_i})^2 + \sum_{r_i=1}^{O_{ij}} \sum_{q_j=1}^{O_j} \beta_{ij}^{r_i q_j} \right) / V \quad (4c)$$

This methodology is not applicable when the parameters are dependent, because in this case the polynomial expansion of the component functions is not unique, and coefficients α_i and β_{ij} cannot be used to calculate sensitivity indices [12].

Here we follow the basic idea of Mara and Tarantola [13] to calculate the sensitivity indices of models with dependent parameters using decorrelation. A similar approach was also published by Zhou et al. [14]. A new methodology is presented here, which uses the RS-HDMR method to get both correlated and final marginal sensitivity indices after the decorrelation via the Rosenblatt transformation. Unlike in previous articles dealing with the global sensitivity analysis of correlated parameters, the methodology is demonstrated not only on simple test cases, but also for a large multi-parameter chemical kinetic model and the implications of the results are discussed. The method was encoded as an extension to the GUI-HDMR program of Ziehn and Tomlin [17,19]. The general methodology is applicable for any distribution of model inputs, but since the rate parameters of the optimized combustion mechanism are assumed to have multivariate normal distribution, only the case of a normal distribution is discussed here.

2.2 Decorrelation Using the Rosenblatt Transformation

Mara and Tarantola [13] suggested the application of the Rosenblatt transformation [18] to create an uncorrelated sample from a correlated one. First, a sample must be generated based on the joint distribution function of the parameters. The Rosenblatt transformation consists of the following steps.

Let $\mathbf{X}=(X_1, X_2, \dots, X_n) \in \mathbb{R}^n$ denote a random vector with an absolutely continuous distribution function $F(\mathbf{x})=F(x_1, x_2, \dots, x_n): \mathbb{R}^n \rightarrow \mathbb{R}$. Let $\bar{\mathbf{x}}=(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n) = \mathbf{T}\mathbf{x} = \mathbf{T}(x_1, x_2, \dots, x_n)$ where transformation \mathbf{T} is given by:

$$\bar{x}_1 = P(X_1 \leq x_1) = F_1(x_1) \quad (5a)$$

$$\bar{x}_i = P(X_i \leq x_i | X_1 = x_1, X_2 = x_2, \dots, X_{i-1} = x_{i-1}) = F_i(x_i | x_1, \dots, x_{i-1}), i = 1, 2, \dots, n \quad (5b)$$

where $F_1, F_2, \dots, F_n: \mathbb{R} \rightarrow \mathbb{R}$ are the marginal distribution functions. The $\bar{\mathbf{X}} = \mathbf{T}\mathbf{X}$ random vector is uniformly distributed, and furthermore

$$P\{\bar{X}_i \leq \bar{x}_i, i = 1, \dots, n\} = \int_{\{\bar{x}_i | \bar{X}_i \leq \bar{x}_i\}} \dots \int dx_n F_n(x_n | x_{n-1}, \dots, x_1) \dots dx_1 F_1(x_1) = \int_0^{\bar{x}_n} \dots \int_0^{\bar{x}_1} d\bar{x}_1 \dots d\bar{x}_n = \prod_{i=1}^n \bar{x}_i, \quad \text{where } 0 \leq \bar{x}_i \leq 1, i = 1 \dots n.$$

Thus, the variables $\overline{x_1}, \overline{x_2}, \dots, \overline{x_n}$ are uniformly and independently distributed on the interval $[0,1]$. This transformation can be expressed explicitly if F is a normal distribution with mean vector \mathbf{m} and covariance matrix $\mathbf{C} = \{c_{ij}\}$. Let $C^p = \{c_{ij}^p\}; i, j=1 \dots p \leq n\}$, $|C_{ij}^p|$ be the cofactor of $\{c_{ij}\}$ in C^p and $|C^p|$ be the determinant of C^p . In this case, the transformed parameters can be calculated using the following equations:

$$\overline{x_1} = \Phi \left(\frac{x_1 - m_1}{\sqrt{c_{11}}} \right) \quad (6a)$$

$$\overline{x_i} = \Phi \left(x_i - m_i + \sum_{j=1}^{i-1} \left(\frac{|C_{ij}^i|}{|C_{ii}^i|} \right) (x_j - m_j) \right) / \sqrt{\frac{|C^i|}{|C_{ii}^i|}}, i = 2 \dots n \quad (6b)$$

where Φ is the standard normal distribution function, which converts a standard normal pdf to a standard uniform pdf. This means that without applying the function Φ at the end of the transformation, the transformed parameters obtained are independent with standard normal distribution functions, as applied in the present work. We used Hermite polynomials as basis functions in the RS-HDMR method according to the standard normal distribution of the transformed model inputs.

2.3 Interpretation of the Sensitivity Indices of Transformed Parameters

The transformed parameters $\overline{x_1}, \overline{x_2}, \dots, \overline{x_n}$ are standard normally and independently distributed. The RS-HDMR method is then applied using samples of these parameters, and the corresponding simulated output distributions and sensitivity indices are calculated. Since the first parameter is only transformed and not corrected by the effect of any other parameter, the sensitivity index S_1 of the first parameter is identical to that of the transformed parameter S_1^i , which is in fact identical to the sensitivity index $S_1^{\text{correlated}}$ that reflects all possible parameter correlations. The total contribution of x_1 to the variance of the output (i.e. including first-, second-order effects etc.) is indicated by the sensitivity index $S_1^{\text{total}} = S_1^{\text{total}} = S_1^{\text{total correlated}}$. By performing the transformation for each of the indices $i= 1, 2, 3$, etc., in turn, the sensitivity indices $S_i^{\text{correlated}}$ and $S_i^{\text{total correlated}}$ can be calculated for each parameter independently of the later transformations that aim to decorrelate the parameters. This total sensitivity

index $S_i^{\text{total correlated}}$ reflects the contribution that each parameter makes to the total output variance, taking into account all its possible correlations. If a parameter dominates the output variance, then we would expect this index to be close to 1. However, a large value of $S_i^{\text{total correlated}}$ can occur for a parameter which would individually have no effect on the model output, but is strongly correlated with one or more parameters that have a large effect on the model output.

The subsequent transformations aiming to decorrelate the parameters can be performed in any chosen order. Hence, having n parameters in total, in the second step we may select any of the remaining $(n-1)$ parameters. If we denote the second selected parameter by subscript 2, then S_2 represents the contribution of x_2 to the output variance, without its correlative contribution with x_1 . Notation $S_2 = S_{2-1}$ emphasizes this meaning and represents a marginal sensitivity. In a similar way the total effect can be calculated, without the influence of parameter 1, denoted by $S_2^{\text{total}} = S_{2-1}^{\text{total}}$. These marginal sensitivities are calculated in sequence and in the last step, we obtain $S_n = S_{n-(n-1)-\dots-2-1} = S_n^{\text{final marginal}}$ which shows the totally uncorrelated contribution of parameter x_n to the variance of $f(\mathbf{x})$. The marginal sensitivity, $S_n^{\text{total}} = S_{n-(n-1)-\dots-2-1}^{\text{total}} = S_n^{\text{total final marginal}}$ is the total sensitivity index of parameter n without the influence of correlations with any other parameter [13]. While the intermediate sensitivity indices in the middle of the sequence of decorrelation depend on the order of the selection of parameters, the final marginal sensitivity indices $S_n^{\text{final marginal}}$ and $S_n^{\text{total final marginal}}$ are independent of this order.

For systems with independent parameters, the importance of a parameter can be determined by a single total sensitivity measure. For correlated systems however, the picture is not so simple since both the correlated $S_i^{\text{total correlated}}$ and final marginal $S_i^{\text{total final marginal}}$ total sensitivity indices are available, as well as marginal sensitivity indices which represent partial correlations.

However, if the method described above is carried out for a case where the parameters of the model are independent, then the calculated correlated, final marginal and marginal sensitivity indices would be identical to those that could be obtained using a conventional RS-HDMR method. This is evident, since in such a situation the transformation of the parameters would leave them unchanged as there is no correlation to remove from the sample. It should be noted that in practical applications, a randomly and independently sampled set of parameters is expected to show a small degree of correlation between the parameter values, which diminishes with the increasing sample size.

Therefore, $S_i^{\text{total correlated}}$ and $S_i^{\text{total final marginal}}$ would be obtained even for a theoretically independent set of input parameters.

If both of these indices are close to zero, then the investigated parameter x_i is of low importance. If the correlated index $S_i^{\text{total correlated}}$ is large (e.g. close to 1), this means that parameter x_i is important. However, if its total final marginal index $S_i^{\text{total final marginal}}$ is small, then its influence on the output variance originates from strong correlations with other parameters. Finally, if a parameter has a large final marginal index, then it strongly contributes to output variance, without correlated effects with the other parameters.

2.4 Local Uncertainty Analysis of Models with Correlated Parameters

Local sensitivity analysis is widely used [20] in combustion modeling to identify the most important parameters for a given set of conditions, although usually the local sensitivity coefficients are related only to the nominal parameter set of the model. Usually target model outputs are chosen for evaluation in accordance with available experimental data and may include quantities such as ignition delay times, species concentrations, burning velocities etc. The purpose of the local sensitivity analysis is therefore to explore which of the model parameters are most important for the accurate prediction of experimental targets.

Here we denote the target result of an investigated model to be Y , while the parameters and the nominal parameter set are denoted by $\mathbf{p} = (p_1, p_2, \dots, p_n)$ and $\mathbf{p}^* = (p_1^*, p_2^*, \dots, p_n^*)$, respectively. Let's assume that $Y = f(p_1, p_2, \dots, p_n)$, $f: \mathbb{R}^n \rightarrow \mathbb{R}$, f is continuously differentiable, the parameters are normally distributed, $\mathbf{p} \sim N(\mathbf{p}^*, \mathbf{C})$, where $\mathbf{C} \in \mathbb{R}^{n \times n}$ denotes the covariance matrix of the parameters. We denote $Y^* = f(\mathbf{p}^*)$ and $s_i^{\text{loc}} = (\partial \ln Y / \partial \ln p_i) \in \mathbb{R}$ as the local sensitivity coefficient at \mathbf{p}^* , and $\mathbf{s}^{\text{loc}} \in \mathbb{R}^n$ as the vector which contains these sensitivity coefficients. A linear approximation of the model result Y at \mathbf{p}^* is denoted by \tilde{Y} and it can be obtained by $\tilde{Y} = Y^* + \sum_{i=1}^n s_i^{\text{loc}} (p_i - p_i^*)$. It is important to note that for linear models the global and the local sensitivity analyses are equivalent, due to the independence of the partial derivatives of \mathbf{p}^* .

The local uncertainty of the model result is defined [20] as the variance of the approximating function \tilde{Y} :

$$\mathbf{V}(\tilde{\mathbf{Y}}) = \mathbf{V}\left(\mathbf{Y}^* + \sum_{i=1}^n s_i^{\text{loc}} (\mathbf{p}_i - \mathbf{p}_i^*)\right) = \mathbf{V}\left(\sum_{i=1}^n s_i^{\text{loc}} \mathbf{p}_i\right). \quad (7)$$

Based on the analogy of the sensitivity index used in global sensitivity analysis calculations, it is possible to define its local counterpart. The local sensitivity index S_i can be calculated as the ratio of the marginal variance of the approximating function $\tilde{\mathbf{Y}}$ according to parameter i and the total variance, $S_i = \mathbf{V}(\tilde{\mathbf{Y}} | \mathbf{p}_i) / \mathbf{V}(\tilde{\mathbf{Y}})$. For a model with uncorrelated parameters, the covariance matrix is a diagonal matrix and S_i can be calculated by the equation

$$S_i = \frac{\mathbf{V}(\tilde{\mathbf{Y}} | \mathbf{p}_i)}{\mathbf{V}(\tilde{\mathbf{Y}})} = \frac{(s_i^{\text{loc}})^2 C_{ii}}{\sum_{i=1}^n (s_i^{\text{loc}})^2 C_{ii}}. \quad (8)$$

Similarly to the global sensitivity indices defined for correlated parameters, we may calculate the correlated sensitivity index and the final marginal sensitivity index for the linearized system with correlated parameters.

The correlated sensitivity index shows the effect of the uncertainty of a parameter on the uncertainty of $\tilde{\mathbf{Y}}$ considering the correlation of the parameter with all other parameters. The linear approximation of the model result is defined by a weighted sum of normally distributed variables. Therefore

$$\mathbf{V}(\tilde{\mathbf{Y}}) = (\mathbf{s}^{\text{loc}})^T \mathbf{C} (\mathbf{s}^{\text{loc}}) = \sum_{i=1}^n (s_i^{\text{loc}})^2 C_{ii} + 2 \sum_{i=2}^n \sum_{j=1}^{i-1} s_i^{\text{loc}} s_j^{\text{loc}} C_{ij}. \quad (9)$$

Accordingly

$$S_i^{\text{correlated}} = \frac{\mathbf{V}(\tilde{\mathbf{Y}} | \mathbf{p}_i)}{\mathbf{V}(\tilde{\mathbf{Y}})} = \frac{\left((s_i^{\text{loc}})^2 C_{ii} + \sum_{j \neq i} s_i^{\text{loc}} s_j^{\text{loc}} C_{ij} \right)^2}{\sum_{i=1}^n (s_i^{\text{loc}})^2 C_{ii} + 2 \sum_{i=2}^n \sum_{j=1}^{i-1} s_i^{\text{loc}} s_j^{\text{loc}} C_{ij}}. \quad (10)$$

Note, that if the off-diagonal elements of matrix \mathbf{C} are zero (i.e. the parameters are not correlated), then Eq. (10) is identical to Eq. (8).

For the calculation of the final marginal sensitivity index, the decorrelation of parameters is needed according to Section 2.2. We define an element of matrix \mathbf{D} as $D_{ij} = C_{ij} \cdot s_i^{\text{loc}} \cdot s_j^{\text{loc}}$, $i, j = 1 \dots n$. This is the covariance matrix of normally distributed parameters, $\hat{\mathbf{p}} \sim \mathbf{N}(\mathbf{p}^*, \mathbf{D})$, where $\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \dots, \hat{p}_n)$. The final marginal sensitivity indices can be calculated as $S_i^{\text{final marginal}} = \mathbf{V}(\tilde{\mathbf{Y}} | \bar{\mathbf{p}}_i) / \mathbf{V}(\tilde{\mathbf{Y}})$, where $\bar{\mathbf{p}}_i$

denotes the normally distributed parameter which belongs to parameter i , obtained by the elimination of the effects of all other parameters. As Eq. 6 shows, the Rosenblatt transformation can be carried out in an analytical way for normally distributed parameters. We denote $\mathbf{D}^p = \{\{D_{ij}\}; i, j = 1 \dots p \leq n\}$, where $|\mathbf{D}^p|$ is its determinant and $|\mathbf{D}_{ij}^p|$ is the cofactor of $\{D_{ij}\}$ in \mathbf{D}^p . To calculate the i -th final marginal sensitivity index, matrix \mathbf{D} has to be reordered in such a way that the i -th parameter and the corresponding covariance values are put in the last (n -th) row of the matrix. In every step of the decorrelation, the conditional distributions and sum of normal distributions have to be decorrelated. As a result of the last step, the decorrelated i -th parameter has a normal distribution with variance $|\mathbf{D}|/|\mathbf{D}_{nn}^n|$, as shown in Eq. (6b). The corresponding determinant values are independent of the order of the other $n-1$ parameters in matrix \mathbf{D} , since any reordering in the matrix is equivalent to the permutation of the rows and columns, and the number of permutations is always even. Therefore, the calculated determinant values are invariant of the reordering. The final marginal sensitivity indices are then calculated by $S_i^{\text{final marginal}} = |\mathbf{D}|/(|\mathbf{D}_{nn}^n| \cdot v(\tilde{Y}))$.

3. Results and discussion

The accuracy and efficiency of the method is demonstrated first on four linear test cases created for this study, and a nonlinear model of Jacques et al. [21]. For these five test cases analytical solutions are available, which allows the testing of the numerical algorithm and the checking of its convergence. The analytical solutions of our four test cases were calculated according to the procedure described in the Appendix. The analytical solution of the Jacques model was published in article [21] and is reproduced and expanded in this paper. Finally, our method was used to calculate the sensitivity indices for predicted ignition delay times in a syngas–air combustion system with respect to 55 Arrhenius parameters and third body collision efficiencies related to the rate coefficients of the chemical mechanism.

3.1 Analytical test cases

3.1.1 The global sensitivity indices

The first test case was a linear model with output function $f(x)=x_1+2x_2+3x_3$. The three parameters x_1, x_2, x_3 have standard normal distributions and are uncorrelated. Their covariance matrix, denoted by C_0 , is therefore the 3×3 identity matrix. It can be shown analytically that the sensitivity indices are $S_i^{\text{total final marginal}} = S_i^{\text{total correlated}} = i^2/14$, where $i = 1, 2, 3$. The model is linear and there is no correlation between the parameters. Therefore the correlated and final marginal sensitivity indices are equal. As Table 1 shows, our code was able to reproduce the analytical results to within an accuracy of 10^{-3} , using 10000 samples for all the four tests.

In test cases 2 to 4 a similar linear model $f(x) = x_1 + x_2 + x_3$ was investigated. The three parameters are also standard normally distributed, but are correlated and their joint distribution is characterized by covariance matrix C . Three cases are investigated, using covariance matrices C_1, C_2 and C_3 defined below.

$$C_1 = \begin{pmatrix} 1 & 0.4 & 0.3 \\ 0.4 & 1 & 0.5 \\ 0.3 & 0.5 & 1 \end{pmatrix}; \quad C_2 = \begin{pmatrix} 1 & -0.2 & 0.3 \\ -0.2 & 1 & -0.4 \\ 0.3 & -0.4 & 1 \end{pmatrix}; \quad C_3 = \begin{pmatrix} 1 & -0.49 & -0.49 \\ -0.49 & 1 & -0.49 \\ -0.49 & -0.49 & 1 \end{pmatrix}$$

Since the model is linear, the correlated and the respective total correlated indices are equal, and the same is true for the final marginal indices. Therefore, we only present the marginal sensitivity indices $S_i^{\text{correlated}}$ and the final marginal part $S_i^{\text{final marginal}}$ for the three different sets of correlation structures. The results for the four test cases are reported in Table 1.

	C_0				C_1			
	ANALYTICAL		NUMERICAL		ANALYTICAL		NUMERICAL	
	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$
x_1	0.071	0.071	0.073	0.070	0.535	0.153	0.544	0.155
x_2	0.286	0.286	0.282	0.288	0.666	0.126	0.661	0.124
x_3	0.643	0.643	0.642	0.647	0.600	0.137	0.602	0.137
	C_2				C_3			
	ANALYTICAL		NUMERICAL		ANALYTICAL		NUMERICAL	
	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$	$S_i^{\text{correlated}}$	$S_i^{\text{final marginal}}$
x_1	0.504	0.376	0.505	0.382	0.007	0.974	0.007	0.975
x_2	0.067	0.347	0.063	0.350	0.007	0.974	0.006	0.973
x_3	0.338	0.329	0.333	0.330	0.007	0.974	0.006	0.973

Table 1 The calculated analytical and numerical sensitivity indices for the first four test cases

In the second example (related to covariance matrix C_1), all parameters are important, and the correlation between the parameters has a significant effect as illustrated by the high values of $S_i^{\text{correlated}}$. The final marginal sensitivity indices are each higher than 0.1, which suggests that in this case, each parameter has a significant individual marginal effect. In the third case (covariance matrix C_2) parameter x_2 has a higher total final marginal sensitivity index than total-correlated index, which is caused by the effect of negative correlations (see Appendix). The final marginal sensitivities were also significant. In the last example (covariance matrix C_3), the same behaviour is expected for all parameters based on the symmetry of the model and the identical covariance structure. There is a significant gap between the correlated and final marginal sensitivity indices. In this example this is caused by the anti-correlation between the parameters which damps their effect on the model result. However, the final marginal sensitivity indices show that the parameters have a high individual effect. In this final case all parameters are equally important, which is natural due to the identical covariance structures of the parameters.

The fifth test example is a nonlinear model with six parameters $f(\mathbf{x}) = x_1 x_2 + x_3 x_4 + x_5 x_6$, where the parameters have a standard normal distribution with correlation matrix

$$\mathbf{C}_4 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0.3 & 0 & 0 \\ 0 & 0 & 0.3 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0.8 \\ 0 & 0 & 0 & 0 & 0.8 & 1 \end{pmatrix},$$

Here, $\rho_{34} = 0.3$ and $\rho_{56} = 0.8$ denote the correlation between parameters x_3, x_4 and x_5, x_6 respectively.

This is one of the test cases used by Jacques et al. [21], who also published a method for the calculation of the analytical values of the total correlated sensitivity indices. Here we also present the analytical calculation of the marginal sensitivity indices. Both analytical calculations are based on the fact that the variance of the product of normally distributed parameters can be calculated using the identity:

$$\begin{aligned} V(XY) &= E(X^2Y^2) - E^2(XY) = E(X^2)E(Y^2) + \text{Cov}(X^2, Y^2) - (E(X)E(Y) + \text{Cov}(X, Y))^2 \\ &= V(X)V(Y) + E^2(X)V(Y) + E^2(Y)V(X) + \text{Cov}^2(X, Y) + 2E(X)E(Y)\text{Cov}(X, Y). \end{aligned}$$

Based on these equations, the variance of the model result is

$$V(f(\mathbf{x})) = V(x_1x_2 + x_3x_3 + x_5x_6) = 1 + (1 + \rho_{34}^2) + (1 + \rho_{56}^2).$$

Since x_1 and x_2 are not correlated with the other parameters, the total marginal sensitivity indices and the final marginal index are equal to the total correlated sensitivity index for these parameters. The total correlated, final marginal and marginal sensitivity indices that belong to parameters x_3 and x_4 are equal to each other and the same is valid for parameters x_5 and x_6 . This follows from the structure of the correlation matrix and the symmetry of the model. The calculation of marginal sensitivity indices for parameters x_3 and x_6 is discussed here. The total marginal and total correlated sensitivity indices of x_3 are equal, if parameters which are uncorrelated with x_3 are separated from x_3 . The final marginal sensitivity index of x_3 is defined by $S_3^{\text{final marginal}} = V(E(f(\mathbf{x}) | \bar{x}_3)) / V(f(\mathbf{x}))$, where

$\bar{x}_3 = x_3 - E(x_3 | x_1, x_2, x_4, x_5, x_6) = x_3 - E(x_3 | x_4)$ follows from the fact that x_3 is correlated with x_4 only. Since $\bar{x}_3 \sim N(0, 1 - \rho_{34}^2)$ and the variance of the model is $V(f(\mathbf{x})) = 1 + (1 + \rho_{34}^2) + (1 + \rho_{56}^2)$, the final

marginal sensitivity index of x_3 is obtained as $S_3^{\text{final marginal}} = \frac{1 - \rho_{34}^2}{1 + (1 + \rho_{34}^2) + (1 + \rho_{56}^2)}$. The final marginal

sensitivity index of x_6 can be defined in a similar way, $S_6^{\text{final marginal}} = \frac{V(E(f(\mathbf{x}) | \bar{x}_6))}{V(f(\mathbf{x}))}$, where

$\bar{x}_6 = x_6 - E(x_6 | x_1, x_2, x_3, x_4, x_5) = x_6 - E(x_6 | x_5)$. Since $\bar{x}_6 \sim N(0, 1 - \rho_{56}^2)$,

$$S_6^{\text{final marginal}} = \frac{1 - \rho_{56}^2}{1 + (1 + \rho_{34}^2) + (1 + \rho_{56}^2)}$$

In Table 2, the columns belong to parameters x_1 to x_6 . The first row contains the calculated total correlated sensitivity indices, both the analytical solution (in bracket) and the numerical values, which belong to a sample size of 15000. From row 2 onwards, the marginal sensitivity indices are shown which were obtained by separating the effect of one, two, three and four parameters from the given parameter. The order of the decoupling of the parameters is arbitrary; in these calculations, always the preceding parameter according to their order was selected. In the last row, the total final marginal sensitivity indices are presented. These values represent the effect of a parameter without any contribution from other parameters. These indices show the case when effects of the other five parameters were eliminated from the investigated parameter.

The results given in Table 2 show that x_5 and x_6 have high total correlated sensitivity indices while the respective final marginal indices are only 0.1. This is caused by both the non-linearity of the model and the strong correlation between these two parameters. The total final marginal indices show that the individual effects of all parameters are important, describing 10% of the output variance or more. The results also indicate that the sensitivity indices do not change during the decorrelation steps in which the effects of x_1 and x_2 are removed, as was expected. For this reason, the total correlated and total final marginal indices are the same for both x_1 and x_2 .

x_1	x_2	x_3	x_4	x_5	x_6
$S_1^{\text{correlated}}$ 0.278 (0.268)	$S_2^{\text{correlated}}$ 0.277 (0.268)	$S_3^{\text{correlated}}$ 0.274 (0.292)	$S_4^{\text{correlated}}$ 0.276 (0.292)	$S_5^{\text{correlated}}$ 0.454 (0.434)	$S_6^{\text{correlated}}$ 0.454 (0.434)
S_{1-6} 0.278 (0.268)	S_{2-1} 0.277 (0.268)	S_{3-2} 0.274 (0.292)	S_{4-3} 0.228 (0.244)	S_{5-4} 0.454 (0.434)	S_{6-5} 0.102 (0.097)
S_{1-6-5} 0.278 (0.268)	S_{2-1-6} 0.277 (0.268)	S_{3-2-1} 0.274 (0.292)	S_{4-3-2} 0.228 (0.244)	S_{5-4-3} 0.454 (0.434)	S_{6-5-4} 0.103 (0.097)
$S_{1-6-5-4}$ 0.278 (0.268)	$S_{2-1-6-5}$ 0.277 (0.268)	$S_{3-2-1-6}$ 0.275 (0.292)	$S_{4-3-2-1}$ 0.228 (0.244)	$S_{5-4-3-2}$ 0.429 (0.434)	$S_{6-5-4-3}$ 0.102 (0.097)
$S_{1-6-5-4-3}$ 0.278 (0.268)	$S_{2-1-6-5-4}$ 0.277 (0.268)	$S_{3-2-1-6-5}$ 0.274 (0.292)	$S_{4-3-2-1-6}$ 0.227 (0.244)	$S_{5-4-3-2-1}$ 0.454 (0.434)	$S_{6-5-4-3-2}$ 0.102 (0.097)
$S_1^{\text{final marginal}}$ 0.278 (0.268)	$S_2^{\text{final marginal}}$ 0.278 (0.268)	$S_3^{\text{final marginal}}$ 0.239 (0.244)	$S_4^{\text{final marginal}}$ 0.228 (0.244)	$S_5^{\text{final marginal}}$ 0.097 (0.097)	$S_6^{\text{final marginal}}$ 0.102 (0.097)

Table 2 The numerically calculated and the analytical (in bracket) total sensitivity indices for test case 5.

The accuracy of the calculated sensitivity indices was investigated. Sample sizes of 1000, 2000, 4000, 6000, 8000, 10000 and 15000 were used to determine the absolute difference of the calculated and analytical sensitivity indices. The absolute difference of the numerically and analytically calculated sensitivity indices at given sample size is defined by $\max_{i=1\dots6} (|S_i^{\text{numerical}} - S_i^{\text{analytical}}|)$ for both the correlated and the final marginal indices. Fig. 1 shows that both the correlated and the final marginal sensitivity indices are close to the analytical value above 10000 samples and the order of differences is 10^{-2} .

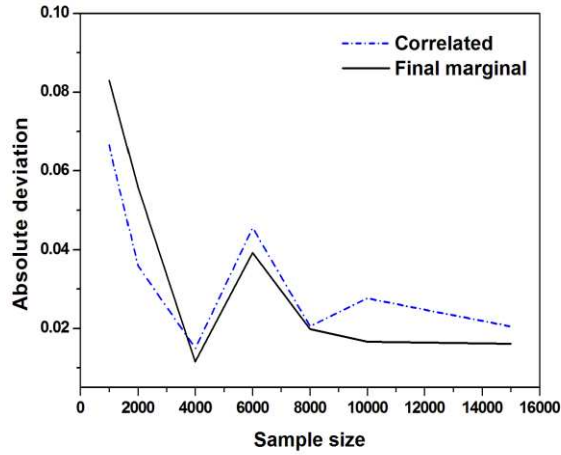


Fig. 1 The maximum of absolute differences of the sensitivity indices calculated using the indicated sample size and the analytical values for the correlated (dash-dotted line) and final marginal (solid line) sensitivity indices.

3.1.2 The local sensitivity indices

For the first four linear test cases, the calculation of the local sensitivity indices is equivalent to the calculation of the global indices, since the linear approximation of the functions is equal to the original functions. The partial derivatives of the models are constant values, since the coefficients of the linear approximations are independent of the nominal parameter sets.

For the first test case, the sensitivity coefficients are $s_1^{\text{loc}} = 1$, $s_2^{\text{loc}} = 2$, $s_3^{\text{loc}} = 3$, respectively, and for test cases 2 to 4 the local sensitivity coefficients are $s_1^{\text{loc}} = s_2^{\text{loc}} = s_3^{\text{loc}} = 1$.

For the fifth test case, $f(\mathbf{x}) = x_1x_2 + x_3x_4 + x_5x_6$, the linear approximation of the model result at $\mathbf{p}^* = (p_1^*, p_2^*, p_3^*, p_4^*, p_5^*, p_6^*)$ is denoted by \tilde{f} and the approximation function is $\tilde{f}(\mathbf{p}^*, \mathbf{x}) = p_2^* \cdot x_1 + p_1^* \cdot x_2 + p_4^* \cdot x_3 + p_3^* \cdot x_4 + p_6^* \cdot x_5 + p_5^* \cdot x_6$. Since the linear approximation function at $\mathbf{p}^* = \mathbf{0}$ is the constant zero function, the interpretation of sensitivity indices is not possible in this case. Assuming

that $\mathbf{p}^* \neq \mathbf{0}$, the variance of the approximation function \tilde{f} is $V(\tilde{f}) = \|\mathbf{p}^*\|_2^2 + 2 \cdot p_3^* \cdot p_4^* + 2 \cdot p_5^* \cdot p_6^*$, and the local correlated sensitivity indices are

$$S_1^{\text{correlated}} = \frac{(p_2^*)^2}{V(\tilde{f})}, S_2^{\text{correlated}} = \frac{(p_1^*)^2}{V(\tilde{f})}, S_3^{\text{correlated}} = \frac{(p_4^* + 0.3 \cdot p_3^* \cdot p_4^*)^2}{V(\tilde{f})},$$

$$S_4^{\text{correlated}} = \frac{(p_3^* + 0.3 \cdot p_3^* \cdot p_4^*)^2}{V(\tilde{f})}, S_5^{\text{correlated}} = \frac{(p_6^* + 0.8 \cdot p_5^* \cdot p_6^*)^2}{V(\tilde{f})}, S_6^{\text{correlated}} = \frac{(p_5^* + 0.3 \cdot p_5^* \cdot p_6^*)^2}{V(\tilde{f})},$$

respectively.

The linear approximation function \tilde{f} is accurate only in a small neighborhood of \mathbf{p}^* and therefore these sensitivity indices are relevant in this region of the domain of f . The local correlated sensitivity indices reflect the contribution of each parameter to the variance of the approximation function, taking into account all possible correlations at point \mathbf{p}^* . Global uncertainty analysis correctly shows that parameter pairs (x_1, x_2) , (x_3, x_4) , and (x_5, x_6) have equal importance. This is not revealed by the local uncertainty analysis, except for the case when the function is calculated at the nominal parameter set $\mathbf{p}^* = (p_1^*, p_1^*, p_3^*, p_3^*, p_5^*, p_5^*)$. The local final marginal sensitivity indices represent the totally uncorrelated contribution of parameter x_i to the variance of the approximation function \tilde{f} . Based on the definition above of local final marginal sensitivity indices, the corresponding final marginal indices are

$$S_1^{\text{final marginal}} = \frac{(p_2^*)^2}{V(\tilde{f})}, S_2^{\text{final marginal}} = \frac{(p_1^*)^2}{V(\tilde{f})}, S_3^{\text{final marginal}} = \frac{(1-0.3^2)(p_4^*)^2}{V(\tilde{f})}, S_4^{\text{final marginal}} = \frac{(1-0.3^2)(p_3^*)^2}{V(\tilde{f})},$$

$$S_5^{\text{final marginal}} = \frac{(1-0.8^2)(p_6^*)^2}{V(\tilde{f})}, S_6^{\text{final marginal}} = \frac{(1-0.8^2)(p_5^*)^2}{V(\tilde{f})} \text{ respectively. The local correlated and the}$$

final marginal sensitivity indices belonging to parameters x_1 and x_2 are identical (i.e. $S_1^{\text{correlated}} = S_1^{\text{final marginal}}$ and $S_2^{\text{correlated}} = S_2^{\text{final marginal}}$), which shows that these parameters are uncorrelated with the other parameters. In contrast with the result of global sensitivity analysis, $S_3^{\text{final marginal}} = S_4^{\text{final marginal}}$ and $S_5^{\text{final marginal}} = S_6^{\text{final marginal}}$ if and only if the nominal parameter set $\mathbf{p}^* = (p_1^*, p_1^*, p_3^*, p_3^*, p_5^*, p_5^*)$ is used.

In conclusion, both the local correlated and the final marginal sensitivity indices were determined for the test case of Jacques et al. [21]. The local sensitivity indices are able to reflect the fact that parameters x_1 and x_2 are uncorrelated with the other parameters. The calculated local indices are not

able to detect the same importance of parameters (x_1, x_2) , (x_3, x_4) , and (x_5, x_6) , although this property of the parameters comes directly from the structure of the model and the correlation of the parameters. The results of local sensitivity analysis are relevant in a small neighborhood of the nominal parameter set and the approximation function of the model result provides information about the parameters in this region. Local sensitivity analysis can be useful if the most probable values of the parameters are close to the nominal ones and the variances of the parameters are low. Generally, information about the relation of the parameters should be obtained using global sensitivity analysis.

3.2 Ignition delay times for the combustion of a syngas–air mixture

Detailed kinetic reaction mechanisms are widely used in many fields of science and technology. These mechanisms may contain several hundred species and several thousand reaction steps. The mechanisms contain several thousands of parameters, including rate parameters (e.g. Arrhenius parameters, third body collision efficiency parameters, parameters of pressure dependence), thermodynamic data (e.g. parameters of the temperature dependence of the enthalpies of formation), transport parameters etc. The various methods of sensitivity analysis are frequently applied for the investigation of the relationship between the values of these parameters and target simulation results obtained using such models for the purposes of model evaluation and improvement [20], [22] .

The generalized HDMR method presented in this paper is well applicable for quantifying the correlated and individual (uncorrelated) uncertainty contributions of the rate parameters to the uncertainty of the simulation results in a chemical kinetics model. This is now demonstrated for a model based on a syngas (H_2/CO) combustion mechanism containing 15 species and 18 reactions. Calculations of correlated and final marginal indices have been carried out for model simulations of ignition delay times of a stoichiometric syngas–air mixture. The conditions of the simulations correspond to the measurements of Kalitan et al. [23], who assigned the ignition delay time in a shock tube experiment to the maximum slope of the observed OH^* emission. The initial conditions of the experiment that were reproduced in our simulations were $T_0 = 1197 \text{ K}$, $p_0 = 1.1 \text{ atm}$, initial fuel composition: $\text{H}_2/\text{CO} = 10/90$, stoichiometric mixture with air. The ignition delay times were calculated in adiabatic constant volume simulations.

The syngas combustion model of Varga et al. [24] was used for the simulation of the ignition delays. During the development of this model 55 parameters were optimized, consisting of the Arrhenius parameters $\alpha = \ln A$, n , and $\varepsilon = E/R$ of 18 elementary reaction steps (including 11 low-pressure limit parameters) and 5 third body collision efficiency parameters. These parameters were fitted to an extensive collection of 7195 experimental data points in 554 datasets. All parameters were fitted that could be determined with acceptable accuracy based on these experimental data. These parameters are defined in Table 3. The covariance matrix is available from the Supplementary of article [24] and the correlation matrix is given in the Supplementary of this article. This matrix shows that there is very strong correlation between the parameters.

Simulation of the ignition was carried out for each of the samples using the SENKIN program [25] of the CHEMKIN-II program package, using strict integrator tolerance settings ($\text{ATOL} = 1.0 \times 10^{-20}$, $\text{RTOL} = 1.0 \times 10^{-09}$) to minimize the numerical uncertainty of the simulations. Correlated and final marginal sensitivity indices were calculated. The sampling, the control of simulations and the

sensitivity index calculations were carried out using our in-house developed MATLAB code called Optima [7].

The convergence of the calculated sensitivity indices was checked using increasing sample sizes. 10000, 25000, 50000, 100000, 250000 and finally 350000 normally distributed random parameter samples were generated based on the covariance matrix. The maximum of absolute differences of sensitivity indices at a given sample size and the sample size of 350000 were calculated. These values are given in Fig. 2, showing that both the correlated and the final marginal sensitivity indices are close to the converged values above 100000 samples.

	Reaction	Parameter		Reaction	Parameter		Reaction	Parameter
1	$\text{CO}+\text{OH}=\text{CO}_2+\text{H}$	ln A	20	$\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$	E/R	39	$\text{CO}+\text{HO}_2=\text{CO}_2+\text{OH}$	ln A
2	$\text{CO}+\text{OH}=\text{CO}_2+\text{H}$	n	21	$\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$	ln A	40	$\text{CO}+\text{HO}_2=\text{CO}_2+\text{OH}$	n
3	$\text{CO}+\text{OH}=\text{CO}_2+\text{H}$	E/R	22	$\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$	n	41	$\text{CO}+\text{HO}_2=\text{CO}_2+\text{OH}$	E/R
4	$\text{H}+\text{O}_2=\text{O}+\text{OH}$	ln A	23	$\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$	E/R	42	$2\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$	ln A
5	$\text{H}+\text{O}_2=\text{O}+\text{OH}$	n	24	$\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$	m_He	43	$2\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$	E/R
6	$\text{H}+\text{O}_2=\text{O}+\text{OH}$	E/R	25	$\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$	ln A	44	$\text{HCO}(+\text{M})=\text{H}+\text{CO}(+\text{M})$	LP_ln A
7	$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	LP_ln A	26	$\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$	n	45	$\text{HCO}(+\text{M})=\text{H}+\text{CO}(+\text{M})$	LP_n
8	$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	LP_n	27	$\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$	E/R	46	$\text{HCO}(+\text{M})=\text{H}+\text{CO}(+\text{M})$	LP_E/R
9	$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	m_H2	28	$\text{OH}+\text{H}_2=\text{H}+\text{H}_2\text{O}$	ln A	47	$\text{HCO}(+\text{M})=\text{H}+\text{CO}(+\text{M})$	m_Ar
10	$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	m_H2O	29	$\text{OH}+\text{H}_2=\text{H}+\text{H}_2\text{O}$	n	48	$\text{HCO}(+\text{M})=\text{H}+\text{CO}(+\text{M})$	m_He
11	$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	m_Ar	30	$\text{OH}+\text{H}_2=\text{H}+\text{H}_2\text{O}$	E/R	49	$\text{HCO}+\text{H}=\text{CO}+\text{H}_2$	ln A
12	$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	m_CO2	31	$\text{H}_2\text{O}_2+\text{H}=\text{H}_2+\text{HO}_2$	ln A	50	$2\text{OH}=\text{O}+\text{H}_2\text{O}$	ln A
13	$\text{O}+\text{H}_2=\text{H}+\text{OH}$	ln A	32	$\text{H}_2\text{O}_2+\text{H}=\text{H}_2+\text{HO}_2$	n	51	$2\text{OH}=\text{O}+\text{H}_2\text{O}$	n
14	$\text{O}+\text{H}_2=\text{H}+\text{OH}$	n	33	$\text{H}_2\text{O}_2+\text{H}=\text{H}_2+\text{HO}_2$	E/R	52	$2\text{OH}=\text{O}+\text{H}_2\text{O}$	E/R
15	$\text{O}+\text{H}_2=\text{H}+\text{OH}$	E/R	34	$2\text{OH}(+\text{M})=\text{H}_2\text{O}_2(+\text{M})$	LP_ln A	53	$2\text{H}+\text{M}=\text{H}_2+\text{M}$	ln A
16	$\text{HO}_2+\text{H}=2\text{OH}$	ln A	35	$2\text{OH}(+\text{M})=\text{H}_2\text{O}_2(+\text{M})$	LP_n	54	$2\text{H}+\text{M}=\text{H}_2+\text{M}$	n
17	$\text{HO}_2+\text{H}=2\text{OH}$	E/R	36	$2\text{OH}(+\text{M})=\text{H}_2\text{O}_2(+\text{M})$	LP_E/R	55	$2\text{H}+\text{M}=\text{H}_2+\text{M}$	E/R
18	$\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$	ln A	37	$\text{CO}+\text{O}_2=\text{CO}_2+\text{O}$	ln A			
19	$\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$	n	38	$\text{CO}+\text{O}_2=\text{CO}_2+\text{O}$	E/R			

Table 3 The investigated 55 rate parameters of the syngas combustion model. Parameters ln A, n, and E/R are transformed Arrhenius parameters, LP refers to low-pressure parameters and the m values are third body collision efficiency parameters.

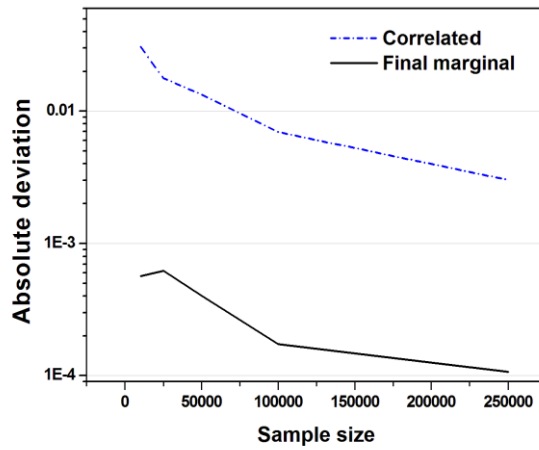


Fig. 2 The maximum of absolute differences of the sensitivity indices calculated using the indicated sample size and the sample size of 350000 for the correlated (dash-dotted line) and final marginal (solid line) sensitivity indices.

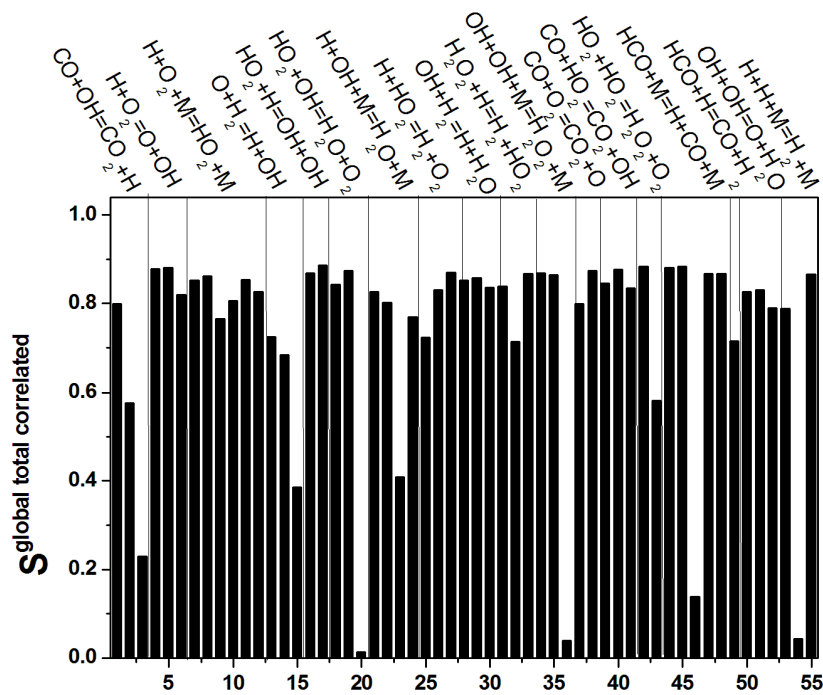


Fig. 3 The global total correlated sensitivity indices for the 55 investigated parameters of the syngas combustion model. The numbering of the parameters is given in Table 3.

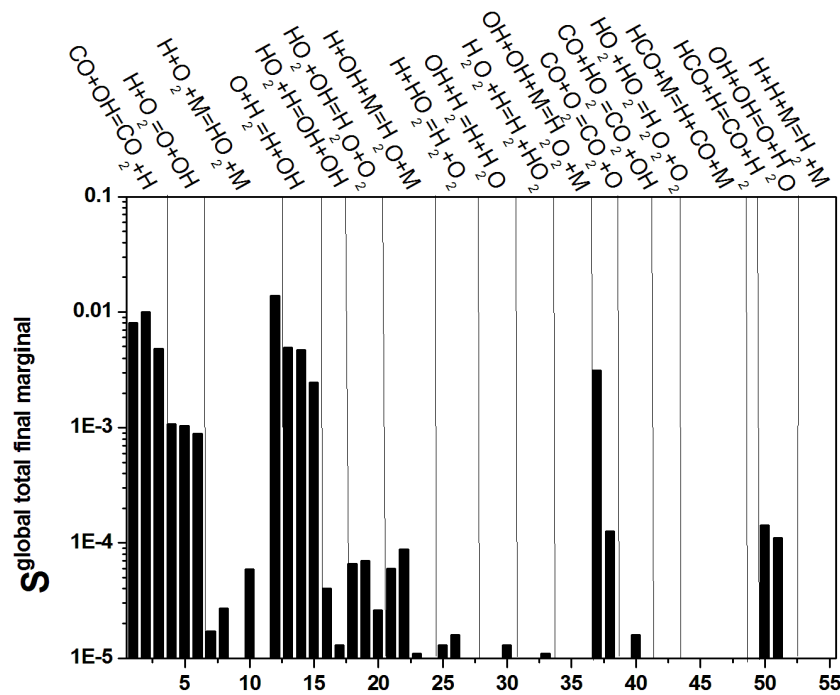


Fig. 4 The global total final marginal sensitivity indices for the 55 investigated parameters of the syngas combustion model. Logarithmic scale is used for better visibility of the smaller indices. The numbering of the parameters is given in Table 3.

3.2.1 Derivation of the final marginal sensitivity index

The calculated total correlated and total final marginal sensitivity indices are shown in Figs. 3 and 4, respectively. It can be clearly seen that a significant part of the uncertainty of the simulations is influenced by the correlations between the parameters, since the correlated indices are high for most of them. The correlations between the Arrhenius parameters of each reaction are high, as seen from the elements of the correlation matrix of the syngas combustion system, available in the Supplementary Material. The final marginal indices have typically small values, but show which parameters have a non-zero individual contribution to the uncertainty in the simulation results. This measure can help to identify reactions playing an important role at a given condition. The reactions with the highest final marginal indices for the conditions in this study are: $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$, $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, $\text{O} + \text{H}_2 = \text{H} + \text{OH}$, $\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$, $\text{OH} + \text{OH} = \text{O} + \text{H}_2\text{O}$ and $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$. Other reactions have very low final marginal indices for each of their Arrhenius parameters. This suggests that their influence on the predicted ignition delays for the studied conditions can only be via their correlation with other parameters. There are no reactions that have both low total correlated and low final marginal indices for all of their Arrhenius parameters. This means that all the reactions are important in some way even if their influence is through correlations.

Given the large differences between the total correlated sensitivity indices and the final marginal ones for the same reactions, it is interesting to explore the effects of the decorrelation ordering on the intermediate marginal indices. Fig. 5 shows two examples of the calculated marginal indices for parameter 1 ($\ln A$ of reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$) which differ in the order of decorrelation used. The total correlated sensitivity index of this parameter was calculated first. This represents the effect of the parameter, taking into account its correlations with all other parameters studied. This value is around 0.8 as also indicated in Fig. 3, and indicates a high influence of this parameter when its correlations with other parameters are taken into account. Then, in the first run (blue dashed line), the effects of parameters 2 and 3 (parameters n and E/R of reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$) were eliminated from the total correlated sensitivity index of parameter 1 (parameter $\ln A$ of reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$). Removal of the influence of correlations with parameters 2 and 3 provides a marginal sensitivity index for $\ln A$ which represents its contribution to the output variance, without its correlative contribution with the other two Arrhenius parameters that belong to reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$. It can be seen in the figure that once these internal correlations have been removed, there is a drop in the marginal sensitivity index, although it still remains significant even when its correlated effects with n and E/R are removed as also shown in Table 4. Internal correlations are clearly very important for this parameter and the covariance matrix shows that these internal correlations are both close to 1 and are negative. In the second run (black solid line), the effect of correlations with parameter 55 (parameter E/R of reaction $2\text{H}+\text{M}=\text{H}_2+\text{M}$) and then 54 (parameter n of reaction $2\text{H}+\text{M}=\text{H}_2+\text{M}$) were removed, and so on. Removal of the influence of parameters 53 to 55 means that the influence of correlations with all rate parameters related to reaction $2\text{H}+\text{M}=\text{H}_2+\text{M}$ have been eliminated as shown in Table 4. Again, this leads to a large drop in the marginal index that results from strong negative correlations between $\ln A$ for $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$ and all Arrhenius parameters ($\ln A$, n and E/R) for $2\text{H}+\text{M}=\text{H}_2+\text{M}$. Finally, in both cases the sensitivity index of parameter 1 without the effects of any other parameters was obtained, which is the final marginal sensitivity index. As shown in Fig. 5, the final marginal index that results from complete decorrelation is independent of the order in which the parameters are decorrelated. The jumps in intermediate marginal indices can change sign as the effects of correlations are gradually removed, which can result from both positive and negative correlations within the covariance matrix.

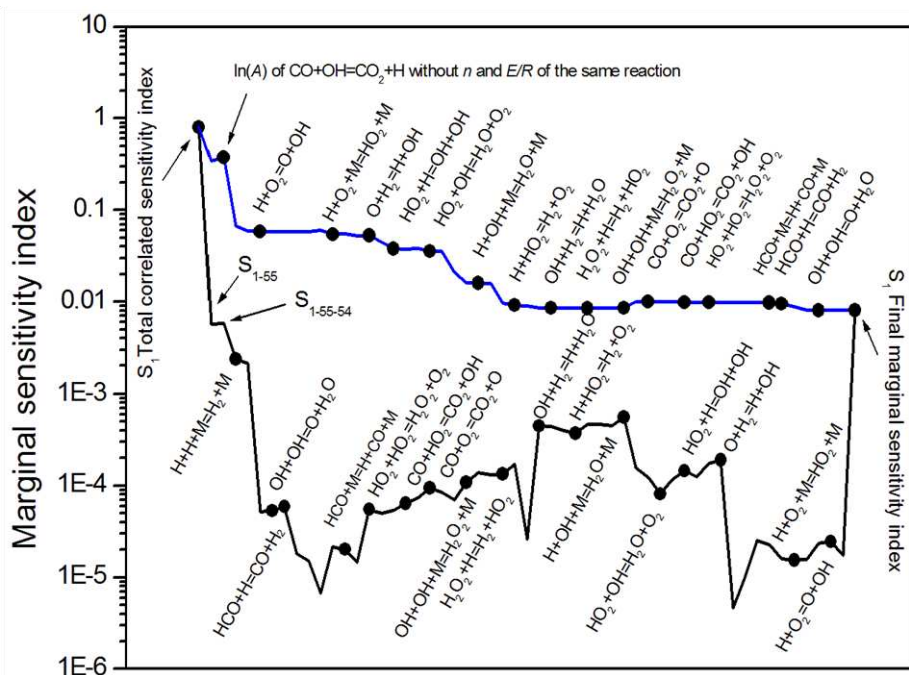


Fig. 5 Changing of the marginal sensitivity indices of parameter 1 ($\ln A$ of reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$) when the effects of the correlations between the Arrhenius parameters of each reaction step are removed one by one. In the first series, the effects of correlations with parameters 2, 3, ... , 55 were eliminated (blue dashed line) while in the second series, the effects of correlations with parameters 55, 54, ... , 2 were eliminated (black solid line). Full black circles show the points corresponding to the marginal sensitivity index where the influence of correlations with all rate parameters of the indicated reaction step have been eliminated. Both series end up at the same value of the final marginal sensitivity index, indicating that the calculated final marginal index is independent of the order of the decorrelation of the parameters.

In order to compare the global indices with local ones which are usually based on A factors only, it is useful to calculate the marginal indices for $\ln A$ of each reaction excluding its correlated effects with the other Arrhenius parameters for the same reaction. This is shown in Table 4 alongside the final marginal indices for each reaction. Once the effects of internal correlations are removed, only a few reactions have high marginal indices. These are $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$, $\text{O}+\text{H}_2=\text{H}+\text{OH}$, $\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$ and $\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$. Of these, only the first two reactions also have higher final marginal indices. $\ln A$ for $\text{H}+\text{O}_2=\text{O}+\text{OH}$ has a fairly low marginal index once correlations with the other Arrhenius parameters are removed. There are two possible reasons for this. Firstly, there is a very strong correlation between the A factor for this reaction and both of its other Arrhenius parameters. The A factor is therefore influential only through these correlations. It was also the reaction with the lowest temperature dependent uncertainty following the mechanism optimisation by Varga et al. [21] and therefore has quite a narrow range of input uncertainty.

Parameter		S ^{total correlated}	S ^{total without own Arrh. parameters}	S ^{total final marginal}
CO+OH=CO ₂ +H	ln A	0.79916	0.37602	0.00808
H+O ₂ =O+OH	ln A	0.87780	0.00168	0.00108
H+O ₂ +(M)=HO ₂ +(M)	LP_ln A	0.85323	0.00639	0.00002
O+H ₂ =H+OH	ln A	0.72525	0.10948	0.00490
HO ₂ +H=OH+OH	ln A	0.86783	0.00549	0.00004
HO ₂ +OH=H ₂ O+O ₂	ln A	0.84337	0.01172	0.00007
H+OH+M=H ₂ O+M	ln A	0.82689	0.05130	0.00007
H+HO ₂ =H ₂ +O ₂	ln A	0.72277	0.00751	0.00001
OH+H ₂ =H+H ₂ O	ln A	0.85176	0.03384	0.00001
H ₂ O ₂ +H=H ₂ +HO ₂	ln A	0.83897	0.00450	0.00000
OH+OH+(M)=H ₂ O ₂ +(M)	LP_ln A	0.86769	0.00384	0.00000
CO+O ₂ =CO ₂ +O	ln A	0.79948	0.00118	0.00313
CO+HO ₂ =CO ₂ +OH	ln A	0.84474	0.00223	0.00001
HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	ln A	0.88340	0.31538	0.00000
HCO(+M)=H+CO(+M)	LP_ln A	0.88019	0.00007	0.00000
HCO+H=CO+H ₂	ln A	0.71495	-	0.00000
OH+OH=O+H ₂ O	ln A	0.82687	0.00324	0.00014
H+H+M=H ₂ +M	ln A	0.78841	0.01837	0.00000

Table 4 Change of the total correlated global sensitivity indices of parameters ln A or (LP_ln A) due to the elimination of the corresponding Arrhenius parameters and the final marginal sensitivity indices.

3.2.2 Comparison of the results of local and global sensitivity analysis

Local sensitivity analysis is widely used [20] in combustion modelling to identify the most important parameters for a given set of conditions. Typically, local sensitivity coefficients are based on partial derivatives such as $\partial \ln \tau / \partial \ln A$, and as such, are related only to the nominal set of A factors of the model. In addition, they usually do not take into account the level of uncertainty in the input parameters or correlations between them. On the other hand, in Section 2.4 above, we demonstrated a method for calculating local sensitivity indices which can take account of both input uncertainties and parameter correlation. In this section, we compare the local sensitivity indices with the global sensitivity ones and also with the typically used local sensitivity coefficients. All local sensitivity coefficients were calculated for the ln A (or LP_ln A) parameter only using a finite difference method for simulation conditions identical to the ones used for the calculation of the global sensitivity indices.

The local total correlated and final marginal sensitivity indices are shown in Fig. 6 and the more typically used local sensitivity coefficients based on $\partial \ln \tau / \partial \ln A$ are shown in Fig. 7. Comparing the results presented in Figs. 4, 5 and 6, and in Table 4, it is clear that when the local sensitivity indices

take account of correlations they show a similar group of important reaction steps: $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$, $\text{H}+\text{O}_2=\text{O}+\text{OH}$, $\text{O}+\text{H}_2=\text{H}+\text{OH}$ and $\text{CO}+\text{O}_2=\text{CO}_2+\text{O}$ to the global indices. In common with the global indices, the calculated local total correlated sensitivity indices are high for most reactions, showing that the correlation between Arrhenius parameters $\ln A$ has a significant effect on the local sensitivity indices. Again, in common with the global indices, the local final marginal indices are small, but show a similar importance ranking for those parameters that have a non-zero individual contribution to the uncertainty in the simulation results. The results shown in Fig. 7, based on simple local partial derivatives, show a different order of importance from that calculated by the local and global methods that account for correlations and input parameter variance. The most obvious difference between the two sets of results is for $\text{H}+\text{O}_2=\text{O}+\text{OH}$ which has a high local sensitivity in Fig. 7, but showed a small marginal global sensitivity for $\ln A$ in Table 4 as well as a small final marginal local index in Fig. 6. This suggests that whilst it has a high sensitivity, the low uncertainty in the A factor for this reaction following optimization, means that this does not contribute greatly to the final model uncertainty for the conditions studied. As mentioned above, it's A factor is also strongly correlated to its other Arrhenius parameters and may therefore have a lower independent effect than for the other important reactions. Still, the three very different methods identified the same group of reactions as important.

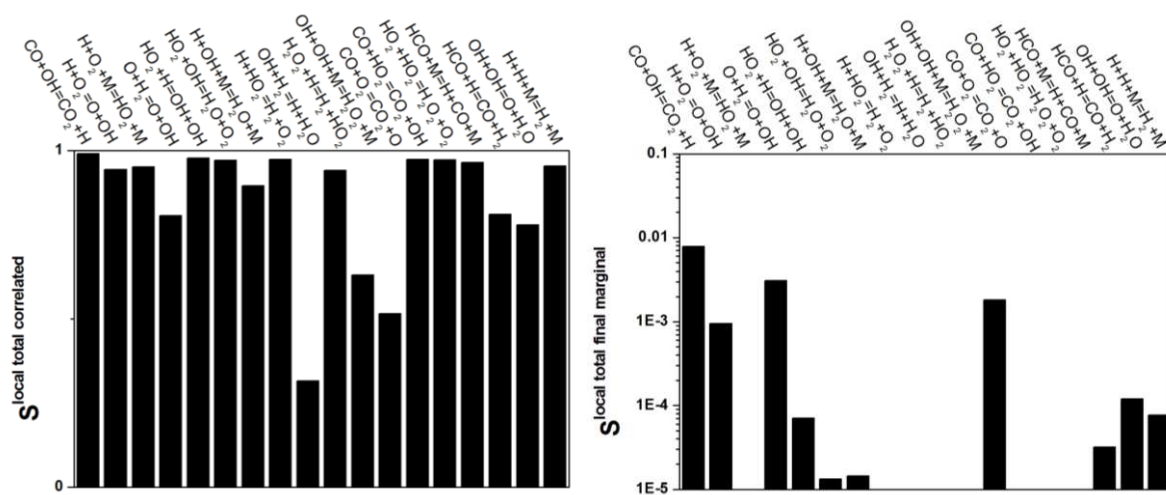


Fig. 6 The local total correlated (left) and the local total final marginal sensitivity (right) indices for the 18 investigated elementary reactions of the syngas combustion model. Logarithmic scale is used for better visibility of the smaller final marginal sensitivity indices.

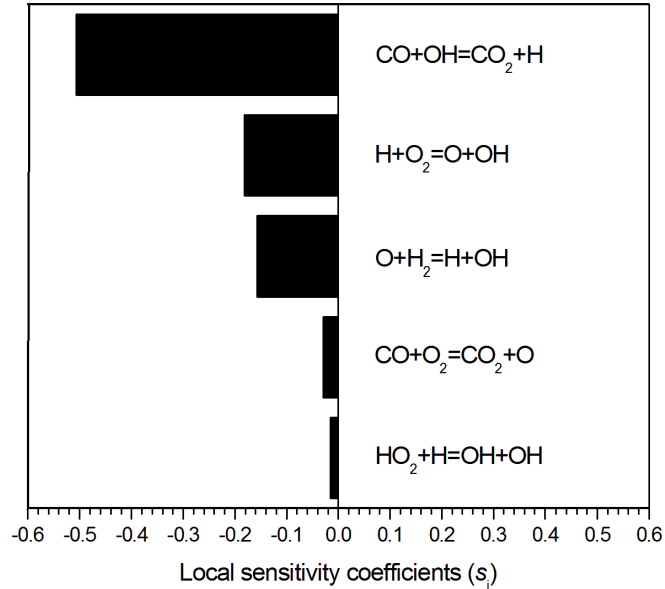


Fig. 7 The local sensitivity coefficients $\partial \ln \tau / \partial \ln A$ having the highest absolute values related to the reaction steps of the syngas combustion model.

4. Conclusions

In the present work we described a global sensitivity analysis method that is able to handle correlated parameter sets. It is based on the coupling of Rosenblatt transformation [13,18] with an optimized RS-HDMR method [17,19]. The accuracy of the computational method was tested on a series of examples where the analytical solution was available. In the Appendix, a general algorithm is provided for the analytical calculation of total correlated and final marginal sensitivity indices for a linear model with standard normally distributed parameters. The tests showed that the suggested method determines the correlated and final marginal sensitivity indices with good accuracy using a sample size of several ten thousands of parameter sets.

The capabilities of the method were then investigated for a more realistic correlated multi-parameter model by exploring the effect of the uncertainty of the rate parameters of a syngas–air combustion system on calculated ignition delay times. This model has 15 species and 48 reactions. Correlated uncertainty information in the form of a covariance matrix, obtained as a result of a parameter optimization study, was available for 55 rate parameters, which included Arrhenius parameters A , n , E of 18 elementary reactions and third body collision efficiency parameters m belonging to 3 elementary reaction steps. Normally distributed random parameter sets were generated based on the covariance matrix. The convergence of the calculated sensitivity indices was checked using increasing sample sizes of 10000, 25000, 50000, 100000, 250000 and 350000., and the accuracy of the calculated sensitivity indices was investigated.

The results of the study of the syngas combustion model show that most of the parameters have large correlated sensitivity indices, and the correlation between the parameters has a high influence on the results. The final marginal sensitivity indices are small but are meaningful for the investigation of the chemical significance of the reaction steps. It was demonstrated that the values of the calculated total correlated and final marginal sensitivity indices are independent of the order of the decorrelation steps. The parameters belonging to only five elementary reactions have non-negligible final marginal sensitivity indices. What this suggests is that for chemical kinetic mechanisms with parameters obtained based on the optimization using large data sets, the correlation between parameters cannot be neglected. This is of high importance for the future development of such mechanisms since it implies that where new observational data becomes available that provides additional constraints on the mechanism, a re-optimization process (using a systematic optimisation approach) would be required except in cases where high final marginal sensitivity indices are present for a particular parameter. The results presented here however, indicate that the final marginal sensitivities for any individual reaction within an optimized scheme are likely to be small, and therefore new data sets are unlikely to constrain individual reactions.

In chemical kinetics modelling, local sensitivity analysis is widely used. Local sensitivity indices for correlated parameters were defined, which are the linear equivalents of the global ones. The results of global sensitivity analysis were compared with the corresponding local sensitivity indices for the case of the syngas–air combustion system as well as with more typically used local sensitivity coefficients based on simple local partial derivatives. Using the equations derived here, sensitivity indices can be calculated quickly from the local sensitivity vector and the corresponding covariance matrix, without using a sophisticated global uncertainty analysis code. A high degree of similarity was seen between the global and local methods when correlations were accounted for. However, although the same set of reactions was indicated to be important by all approaches, the ordering of the importance ranking differed when simple local measures were used.

References

1. D. A. Sheen, H. Wang, *Combust. Flame* 158, 2358 (2011)
2. H. Wang, D. A. Sheen, *Prog. Energy Combust. Sci.* 47, 1 (2015)
3. D. A. Sheen, H. Wang, *Combust. Flame* 158, 645 (2011)
4. T. Turányi, T. Nagy, I. G. Zsély, M. Cserhádi, T. Varga, B. T. Szabó, I. Sedyó, P. T. Kiss, A. Zempléni, H. J. Curran, *Int. J. Chem. Kinet.* 44, 284 (2012)
5. I. G. Zsély, T. Varga, T. Nagy, M. Cserhádi, T. Turányi, S. Peukert, M. Braun-Unkhoff, C. Naumann, U. Riedel, *Energy* 43, 85 (2012)
6. T. Varga, I. G. Zsély, T. Turányi, T. Bentz, M. Olzmann, *Int. J. Chem. Kinet.* 46, 295 (2014)
7. T. Varga, T. Nagy, C. Olm, I. G. Zsély, R. Pálvölgyi, É. Valkó, G. Vincze, M. Cserhádi, H. J. Curran, T. Turányi, *Proc. Combust. Inst.* 35, 589 (2015)
8. C. Olm, T. Varga, É. Valkó, S. Hartl, C. Hasse, T. Turányi, *Int. J. Chem. Kinet.* 48, 423 (2016)
9. V. Samu, T. Varga, K. Brezinsky, T. Turányi, *Proc. Combust. Inst.* 36, 691 (2017)
10. É. Valkó, T. Varga, A. S. Tomlin, T. Turányi, *Proc. Combust. Inst.* 36, 681 (2017)
11. A. Saltelli, K. Chan, E. M. Scott, *Sensitivity Analysis*, (John Wiley&Sons Ltd., Chichester, England, 2000)
12. G. Li, H. Rabitz, *J. Math. Chem.* 50, 99 (2012)
13. T. A. Mara, S. Tarantola, *Reliab. Eng. Syst. Safe.* 107, 115 (2012)
14. C. Zhou, Z. Lu, L. Zhang, J. Hu, *Appl. Math. Model* 38, 4885 (2014)
15. I. M. Sobol', *Math. Model. Comp. Exp.* 1, 407 (1993)
16. G. Li, C. Rosenthal, H. Rabitz, *J. Phys. Chem. A* 105, 7765 (2001)
17. T. Ziehn, A. S. Tomlin, *Env. Model. Soft.* 24, 775 (2009)
18. M. Rosenblatt, *Ann. Math. Stat.* 23, 470 (1952)
19. T. Ziehn, A. S. Tomlin, <http://www.gui-hdmi.de/>
20. T. Turányi, A. S. Tomlin, *Analysis of Kinetic Reaction Mechanisms*, (Springer-Verlag Berlin Heidelberg, 2014)
21. J. Jacques, C. Lavergne, N. Devictor, *Reliab. Eng. Syst. Saf.* 91, 1126 (2006)
22. A. S. Tomlin, *Proc. Combust. Inst.* 34, 159 (2013)
23. D. M. Kalitan, J. D. Mertens, M. W. Crofton, E. L. Petersen, *J. Propul. Power* 23, 1291 (2007)
24. T. Varga, C. Olm, T. Nagy, I. G. Zsély, É. Valkó, R. Pálvölgyi, H. J. Curran, T. Turányi, *Int. J. Chem. Kinet.* 48, 407 (2016)
25. A. E. Lutz, R. J. Kee, J. A. Miller, "SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis," Report No. SAND87-8248 (1988)

Appendix: Analytical calculation of the total correlated and final marginal sensitivity indices for a linear model with normally distributed parameters

Let us consider a linear model having n parameters with model result Y . The parameters are denoted by X_i , $i=1\dots n$. The linear model is defined by equation $Y = \sum_{i=1}^n C_i \cdot X_i$, where the C_i values are the coefficients of the corresponding parameters and are constant within the model. The parameters of the model are normally distributed. Denote $\text{Cov}(X_i, X_j)$ the covariance between parameters i and j . The model result Y is defined by weighted sum of normally distributed variables, therefore the variance is defined as

$$V(Y) = \sum_{i=1}^n C_i^2 \text{Cov}(X_i, X_i) + 2 \cdot \sum_{i=2}^n \sum_{j=1}^{i-1} C_i \cdot C_j \cdot \text{Cov}(X_i, X_j).$$

The correlated sensitivity index shows the effect of the uncertainty of a parameter on the uncertainty of Y considering the correlation of the parameter with all other parameters, and it can be calculated as the ratio of the marginal variance of Y according to parameter i and the total variance

$$S_i^{\text{correlated}} = \frac{V(Y | X_i)}{V(Y)} = \frac{\left(C_i^2 \text{Cov}(X_i, X_i) + \sum_{j \neq i} C_i C_j \text{Cov}(X_i, X_j) \right)^2}{\sum_{i=1}^n C_i^2 \text{Cov}(X_i, X_i) + 2 \cdot \sum_{i=2}^n \sum_{j=1}^{i-1} C_i \cdot C_j \cdot \text{Cov}(X_i, X_j)}.$$

For the calculation of the final marginal sensitivity index, decorrelation of parameters is needed. Define an element of matrix \mathbf{D} as $\mathbf{D}_{ij} = \text{Cov}(X_i, X_j) \cdot C_i \cdot C_j$, $i, j = 1 \dots n$. This is the covariance matrix of normally distributed parameters, $\hat{\mathbf{X}} \sim N(\mathbf{0}, \mathbf{D})$, where $\hat{\mathbf{X}} = (\hat{X}_1, \hat{X}_2, \dots, \hat{X}_n)$. The final marginal sensitivity indices can be calculated as $S_i^{\text{final marginal}} = V(Y | \bar{\hat{X}}_i) / V(Y)$, where $\bar{\hat{X}}_i$ denotes normally distributed parameter i , obtained by the elimination of the effects of all other parameters. The Rosenblatt transformation can be carried out in an analytical way for normally distributed parameters. Denote $\mathbf{D}^p = \{ \{ \mathbf{D}_{ij} \}; i, j = 1 \dots p \leq n \}$; $|\mathbf{D}^p|$ is its determinant and $|\mathbf{D}_{ij}^p|$ is the cofactor of $\{ \mathbf{D}_{ij} \}$ in \mathbf{D}^p . To calculate the i -th final marginal sensitivity index, the covariance matrix \mathbf{D} has to be reordered in such a way that the i -th parameter and the corresponding covariance values are placed in the last (n -th) row of the covariance matrix. In every step of the decorrelation, the conditional distributions and the sum of normal distributions have to be decorrelated. As the result of the last step, the decorrelated i -th

parameter has a normal distribution with variance $|\mathbf{D}|/|\mathbf{D}_{nn}^n|$. The corresponding determinant values are independent of the order of the other $n-1$ parameters in the covariance matrix, since any reordering in the covariance matrix is equivalent to the permutation of the rows and columns, and the number of permutations is always even. Therefore, the calculated determinant values are invariant of the reordering. The final marginal sensitivity indices are then calculated by

$$S_i^{\text{final marginal}} = \frac{V(Y | \widehat{X}_i)}{V(Y)} = \frac{|\mathbf{D}|}{|\mathbf{D}_{nn}^n| \cdot V(Y)}.$$