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Investigation of the Effect of Correlated Uncertain Rate Parameters on a Model of Hydrogen Combustion Using a Generalized HDMR method

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Abstract

The High Dimensional Model Representation (HDMR) method has been applied in several previous studies to obtain global sensitivity indices of uncorrelated model parameters in combustion systems. However, the rate parameters of combustion models are intrinsically correlated and therefore uncertainty analysis methods are needed that can handle such parameters. A generalized HDMR method is presented here, which uses the Rosenblatt transformation on a correlated model parameter sample to obtain a sample of independent parameters. The method provides a full set of both correlated and marginal sensitivity indices. Ignition delay times predicted by an optimized hydrogen–air combustion model in stoichiometric mixtures near the three explosion limits are investigated with this new global sensitivity analysis tool. The sensitivity indices which account for all the correlated effects of the rate parameters are shown to dominate uncertainties in the model output. However these correlated indices mask the individual influence of parameters. The final marginal uncorrelated sensitivity indices for individual parameters better indicate the change of importance of homogeneous gas phase and species wall-loss reactions as the pressure is increased from above the first explosion limit to above the third limit. However, these uncorrelated indices are small and whilst they provide insights into the dominant chemical and physical processes of the model over the range of conditions studied, the correlations between parameters have a very significant effect. The implications of this result on model tuning will be discussed.

Keywords: *global sensitivity analysis, HDMR, correlated parameters, hydrogen explosion limits*

1. Introduction

Combustion models usually have many parameters, the quantification of which involves a level of uncertainty. Uncertainty analysis is widely used in combustion chemistry [1, 2] to investigate the uncertainty of simulation results knowing the uncertainty of model parameters. A critical step in determining such predictive uncertainty is the determination of the extent of uncertainty in model input parameters. One possibility for the assessment of input uncertainties is the investigation of the parameters one-by-one by tracing the source of the parameter value. A measurement that aims to determine a kinetic or thermodynamic parameter is usually called a direct one. The evaluation of the systematic and statistical errors of these direct measurements allows an estimation of the uncertainty of each parameter [3]. In most uncertainty analysis studies carried out so far in combustion chemistry (see *e.g.* [4-9]), the model parameters were considered to be uncorrelated, since no information was available on their joint distributions.

Indirect measurements can be interpreted only by multi-parameter models. In combustion, such indirect measurements include determinations of laminar burning velocities, species concentration profiles or ignition delay times. Rate parameters of combustion mechanisms are intrinsically correlated, since the mechanisms are developed not only based on direct measurements, but also to reproduce the results of indirect measurements. Traditional methods for mechanism development inevitably involve some tuning of parameters within their suggested uncertainty limits, in order to reproduce indirect measurements over selected sets of conditions. This approach however, does not provide information on the correlation of rate parameters. An alternative approach is the systematic optimization of reaction mechanisms (see *e.g.* [10-13]), where the highly sensitive model parameters are fitted to experimental data. Such methods can provide information on parameter correlations.

Sheen and Wang calculated the covariance matrix of the fitted parameters for ethylene and *n*-heptane combustion mechanisms [14-16], which carries information on the joint uncertainty of the parameters. The optimized rate parameters were Arrhenius *A* parameters and 3rd body collision efficiency factors. Turányi *et al.* [17-20] extended the methodology to the determination of all Arrhenius parameters *A*, *n*, *E* of important reaction steps together with the fitting of the important 3rd body collision efficiency factors. They also calculated the covariance matrix of all determined parameters. It is expected that the joint uncertainty of model input parameters will be available for more and more combustion systems as optimization methods become more widespread. Therefore, development of global uncertainty and sensitivity analysis techniques is needed that can utilize the newly available, more realistic correlated uncertainty of the parameters.

In this article a new global sensitivity analysis methodology is presented that is able to handle the correlated uncertainty information obtained by mechanism optimization methods. This new method is applied to the investigation of the explosion limits of a hydrogen–air combustion system.

2. Methods

2.1 HDMR Global Uncertainty Analysis

The aim of sensitivity analysis is to assess how the values of the model parameters influence the modelling results. Local sensitivity analysis [21] is regularly used in combustion modelling practice. The drawback of local methods is that they provide information on the importance of a parameter when all parameters of the model take their nominal value, and therefore cannot easily capture any nonlinear effects. In global sensitivity analysis, all model parameters may take any value within their joint domain of uncertainty and the importance of parameters is investigated within this domain. Uncertainty analysis methods assess the uncertainty of model results, knowing the uncertainty of model parameters. Global sensitivity analysis includes global uncertainty analysis, since the former

provides information on both the uncertainty of model output and the contribution of the parameters to the uncertainty of the predictions. A wide range of global uncertainty and sensitivity analysis methods have been elaborated [2], which differ in computational requirements and the information provided.

The High Dimensional Model Representation (HDMR) method [22-26] has several advantageous features. This method has several variants and the description below concentrates on the random sampling method (RS-HDMR) which is used in the present work.

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

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

where constant f_0 represents the mean value of the model output across the input sample, $f_i(x_i):R \rightarrow R$ is the contribution of the i -th input parameter x_i to $f(\mathbf{x})$; $f_{ij}(x_i, x_j):R^2 \rightarrow R$ 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 [27] and can be expressed using an orthogonal polynomial basis:

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

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

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 . 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:

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

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), the partial variances can be calculated and the sensitivity indices of the parameters can be determined:

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

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

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 [27].

Here we follow the approach of Mara and Tarantola [28] to calculate sensitivity indices of models with dependent parameters. A similar approach was also published by Zhou *et al.* [29]. This method was encoded and coupled to the GUI-HDMR program of Ziehn and Tomlin [30, 31]. The methodology is applicable for any distribution of model inputs, but since the covariance matrix of the optimized combustion mechanism is 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 [28] suggested the application of the Rosenblatt transformation [32] 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 $\mathbf{x} = (x_1, x_2, \dots, x_n) \in R^n$ denote a random vector with an absolutely continuous distribution function $F(\mathbf{x}) = F(x_1, x_2, \dots, x_n): R^n \rightarrow R$. Consider the following transformation of the vector

$$\bar{x}_1 = F_1(x_1) \tag{5a}$$

$$\bar{x}_i = F_i(x_i | x_1, \dots, x_{i-1}), i=2 \dots n \tag{5b}$$

The transformed parameters $\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n$ are uniformly and independently distributed on the interval [0,1]. This transformation can be expressed explicitly when F is a normal distribution

with mean vector \mathbf{m} and covariance matrix $\mathbf{C} = \{c_{ij}\}$. Let $C^p = \{\{c_{ij}\}: i, j = 1 \dots p \leq n\}$, $|C_{ij}^p|$ 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

$$\bar{x}_1 = \Phi\left(\frac{x_1 - m_1}{\sqrt{c_{11}}}\right) \quad (6a)$$

$$\bar{x}_k = \Phi\left(x_k - m_k + \sum_{j=1}^{k-1} \left(\frac{|C_{kj}^k|}{|C_{kk}^k|}\right) (x_j - m_j)\right) / \sqrt{\frac{|C^k|}{|C_{kk}^k|}}, k = 2 \dots n \quad (6b)$$

where Φ is the standard normal distribution function, which converts a standard normal *pdf* to a standard uniform *pdf*. This means that without applying 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 according to the standard normal distribution of the transformed model inputs. Equation (6) shows that the covariance matrix of the sample must be positive definite.

2.3 Interpretation of the Sensitivity Indices of Transformed Parameters

The transformed parameters $\bar{x}_1, \bar{x}_2, \dots, \bar{x}_n$ 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^- , which is in fact identical to the sensitivity index S_1^{corr} 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 sensitivity

index $S_1^{\text{total}} = S_1^{\text{total}} = S_1^{\text{corr_total}}$. Performing the transformation for each of the indices $i= 1, 2, 3$, etc., in turn, sensitivity indices S_i^{corr} and $S_i^{\text{corr_total}}$ can be calculated for each parameter independently of the later transformations that aim to decorrelate the parameters. This total sensitivity index $S_i^{\text{corr_total}}$ 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 $S_i^{\text{corr_total}}$ 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. We denote the second selected parameter by subscript 2 and hence 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 $S_n = S_{n-(n-1)-\dots-2-1} = S_n^{\text{uncorr}}$ which shows the totally uncorrelated contribution of parameter x_n to the variance of $f(\mathbf{x})$. The marginal sensitivity, $S_n^{\text{total}} = S_{n-(n-1)-\dots-2-1}^{\text{total}} = S_n^{\text{uncorr_total}}$ is the total sensitivity index of parameter n without the influence of correlations with any other parameter [28]. While the intermediate sensitivity indices in the middle of the sequence of decorrelation depend on the order of the selection of parameters, the final uncorrelated sensitivity indices S_n^{uncorr} and $S_n^{\text{uncorr_total}}$ are independent of this order.

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

In the present work, for simplicity we restrict the discussion to the correlated $S_i^{\text{corr_total}}$ and uncorrelated total sensitivity indices. If both of these indices are close zero, then the investigated parameter $S_i^{\text{uncorr_total}}$ is of low importance. If the correlated index $S_i^{\text{corr_total}}$ is large (e.g. close to 1), this means that parameter x_i is important. However, if its uncorrelated total index $S_i^{\text{uncorr_total}}$ is small, then its influence on the output variance involves strong correlations with other parameters. Finally, if a parameter has a large uncorrelated index, then it strongly contributes to output variance, without correlated effects with the other parameters. Within the context of individual parameter tuning, really this is only feasible if this latter condition is satisfied for a given set of target outputs.

3. The investigated system

In the present work the hydrogen combustion mechanism of Varga *et al.* [33] was investigated, which was published along with the covariance and correlation matrices of the determined parameters (reproduced here in Supplemental Material). These parameters are 30 Arrhenius parameters of 11 elementary reactions and the third body collision efficiencies of Ar, H₂ and H₂O for reaction H+O₂+M=HO₂+M. These are all parameters that were determined to be important using the following procedure. Parameters having large local sensitivity coefficients at any of the experimental conditions considered were identified, the prior uncertainty limits of these parameters were determined based on direct measurements and theoretical calculations, and in a trial optimization the importance of the parameters was checked by calculating the posterior uncertainty limits. Those

parameters were accepted as important for which the posterior uncertainty limits were narrower compared to the prior uncertainty limits. The covariance matrix shows that there is always a strong correlation among Arrhenius parameters of the same elementary reactions, as expected from the structure of the Arrhenius equation [34]. In accordance with the large number of indirect experimental data used, these rate parameters could be determined with low uncertainty, and also a strong correlation among all the determined parameters was identified. This is expected, as the simulation results at the conditions of indirect experiments can depend strongly on multiple parameter values and thus changing different parameters can have similar effects on the simulated results. It is important to note that from a mathematical point of view, all correlations, arising between Arrhenius parameters of the same or different reactions, can be handled identically. We assume that the covariance matrix belongs to a multivariate normal distribution, truncated at the upper and lower limits of the rate coefficients.

The mechanism was investigated near the first, second and third explosion limits of the stoichiometric hydrogen–air system. Diffusion and loss of species to the reactor walls is important in the phenomena of explosion limits, therefore species loss reactions were added to the model. We adopted the approach of Wang and Law [35], who modelled the wall-loss of species H, O, OH, HO₂ and H₂O₂ as first order removal reactions, allowing spatially homogeneous simulations of ignition delays. The other species have low sticking coefficients and therefore the corresponding rate coefficients are nearly zero. The wall-loss rate coefficients had temperature dependence $k = A \cdot (T/K)^n$, and parameters A and n were calculated for a 7.4 cm diameter, spherical quartz reactor using the kinetic theory of gases [35]. The rate parameters are given in Table 1. As no information was provided for the uncertainty of the wall-loss reactions, and we could not find well-characterised experiments that would reveal the interaction of wall and homogeneous phase rate parameters, a temperature independent uncertainty of 20% ($3\sigma(\ln A) = 0.2$) was assumed, and these parameters

were assumed to be uncorrelated with all other rate parameters. No uncertainty was assumed for the $n = 0.5$ parameters, as these parameters are derived from the kinetic theory of gases.

Table 1. Rate parameters used for the modelling of the loss of species to the reactor walls

Reaction	A / s^{-1}	n
H → wall	2.95	0.5
O → wall	0.737	0.5
OH → wall	0.715	0.5
HO ₂ → wall	1.54	0.5
H ₂ O ₂ → wall	0.152	0.5

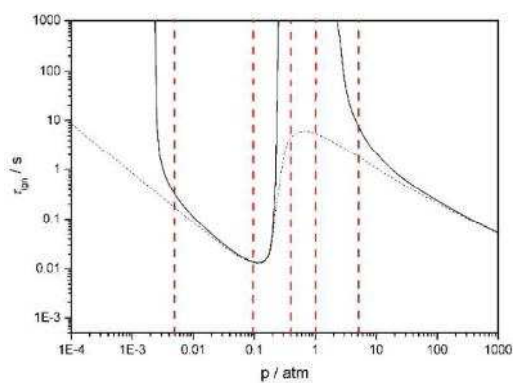


Figure 1. Simulated ignition delay times as a function of the pressure using the original mechanism of Varga *et al.* [33] (dotted line) and using the same mechanism with wall reactions added (black solid line). The red vertical dashed lines mark the five selected pressure values where the uncertainty analyses were carried out.

Homogeneous, isochoric, adiabatic simulations were carried out to calculate the ignition delays of a stoichiometric hydrogen-air mixture at initial temperatures of 800 K, at various pressures. The ignition delays were defined as the difference between the zero time of the simulations and the maximum of time derivative of the pressure. In Fig. 1, the calculated ignition delays are plotted as a function of pressure. The figure shows that without wall reactions there are no explosion limits, but by adding the wall reactions clear and sharp explosion limits appear. Five initial pressure values were selected (0.005, 0.1, 0.4, 1 and 5 atm) belonging to just below and above the three explosion limits. These five cases will be investigated in detail. Such an investigation was not carried out below the first explosion limit, as the system transitioned extremely sharply into the non-reactive regime, and its behavior could not be characterized through ignition delays.

Samples of sizes between 10,000 and 250,000 were generated in order to test the convergence of the computed sensitivity indices. Since good convergence (approximately 10^{-5} accuracy in the sensitivity indices) was achieved between sample sizes of 100,000 and 250,000, the results presented are based on a 250,000-element sample which was generated according to the joint *pdf* of the parameters. Simulations were carried out at each condition to calculate the respective ignition delays. The method described above was used to determine the correlated and uncorrelated sensitivity indices at these conditions. The model inputs were the important rate parameters of the Varga *et al.* [33] mechanism and the five Arrhenius parameters of the wall-loss reactions. The sensitivity indices were calculated with respect to the $\alpha = \ln A$, n , and $\varepsilon = E/R$ parameters, and the model output was the logarithm of the calculated ignition delay time.

4. Results and Discussion

The correlated and uncorrelated sensitivity indices were calculated at the five conditions. The correlated sensitivity indices showed very similar patterns in each investigated case for the chemical

reactions. As an example, the calculated correlated sensitivity indices at 5 atm are given in Fig. 2. The high correlations between parameters mean, that the effect of changing one parameter leads to all other correlated parameters being changed. The similarity of the correlated sensitivity indices indicates that the rate parameters act as a correlated group rather than through isolated individual effects. This also suggests that the predictive power of the model could be improved by decreasing the uncertainty of almost any of the rate parameters, if this information is fed back to the process of mechanism optimization based on large numbers of direct and indirect measurements and the final correlation structure remains similar. Conversely, it suggests that the tuning of individual parameters to new sets of data in isolation should not be carried out. The reason is that whilst the description of a new data set could be perhaps improved by changing the rate parameters which are important only for the conditions of the corresponding experiment, this might worsen the reproduction of the other experimental data. Improvement of the rate parameters of a mechanism should be based on considering the new and the previously existing data together. This might result in the change of many correlated rate parameters.

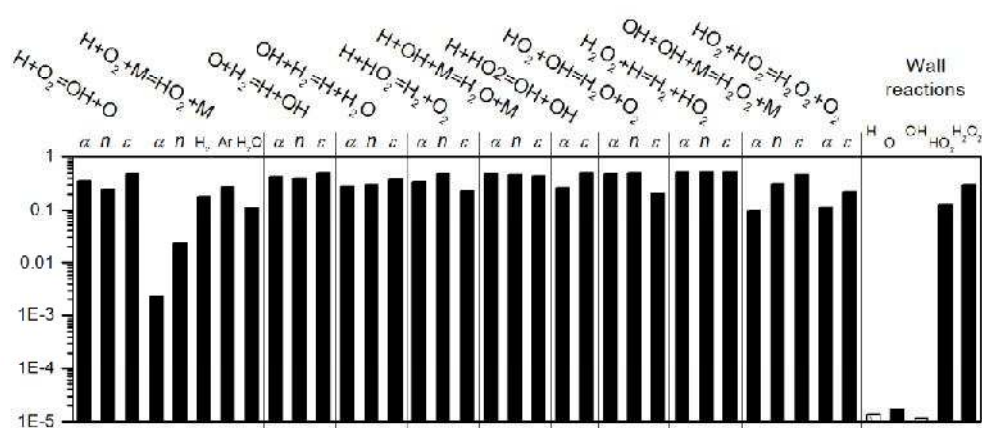


Figure 2. Correlated sensitivity indices at 5 atm, for each parameter. The black bars show the correlated first-order sensitivity indices.

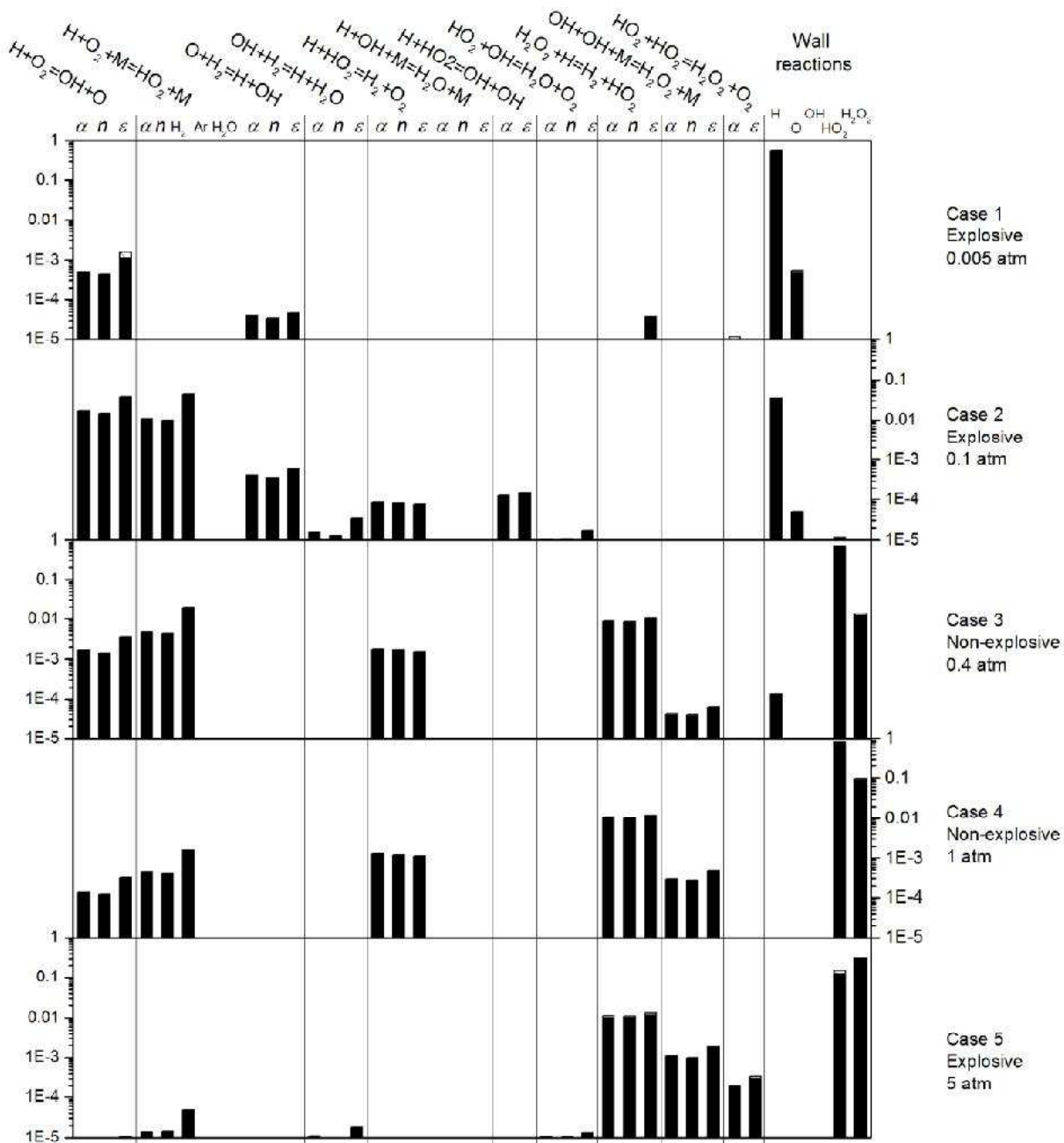


Figure 3. Uncorrelated sensitivity indices at the five investigated conditions, for each parameter. Full black bars show the uncorrelated first-order sensitivity indices, and hollow bars show the further contributions from higher-order terms. For reaction $\text{H}+\text{O}_2+\text{M}=\text{HO}_2+\text{M}$ the parameters marked with species names refer to the respective third body collision efficiencies, and for the wall-loss reactions they refer to the species the reaction depletes.

This latter point is further demonstrated in Fig. 3 which shows the uncorrelated sensitivity indices, highlighting the marginal individual influence of parameters on the model variance. The uncorrelated indices are generally small for the none wall-loss rate parameters. This is due to the fact

that the uncorrelated indices take into account only the contribution that comes from the individual uncertainty of the respective model parameter, without its effect through correlations. Therefore a much more limited variation in the parameter values is covered by the uncorrelated behavior than the by the whole distribution, leading to the relatively small contributions to the overall model output variance.

Despite the small values of the uncorrelated indices, they can be utilized to identify the rate parameters that are chemically important at the respective conditions. Above the first explosion limit (case 1, $p_0 = 0.005$ atm; short ignition delay) the wall-loss of H and O radicals, and the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ have individual effects on the simulated ignition delays. Below the second explosion limit (case 2, $p_0 = 0.1$ atm; short ignition delay) the ignition delay time is determined by the rate parameters of chain branching reactions $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ and $\text{O} + \text{H}_2 = \text{H} + \text{OH}$, and chain terminating reactions $\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$, $2\text{OH} + \text{M} = \text{H}_2\text{O}_2 + \text{M}$ and $\text{H} \rightarrow \text{wall}$. Due to the low reactivity of HO_2 compared to H and O, reactions $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ and $2\text{OH} = \text{H} + \text{HO}_2$ also act as important chain termination reactions. All these reactions are well known important elementary steps between the 1st and 2nd ignition limits.

Going above the second explosion limit (case 3, $p_0 = 0.4$ atm; long ignition delay) the sensitivity pattern changes dramatically. Reactions $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ and $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ are still very important, and a new important reaction is $\text{H}_2\text{O}_2 + \text{H} = \text{H}_2 + \text{HO}_2$. Also wall losses of HO_2 and H_2O_2 become important. The sensitivity pattern is similar just below the third explosion limit (case 4, $p_0 = 1$ atm; long ignition delay).

Above the third ignition limit (case 5, $p_0 = 5$ atm; short ignition delay) the previously important reactions $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, $\text{O} + \text{H}_2 = \text{H} + \text{OH}$ and $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ become negligible. The important reactions are $\text{H}_2\text{O}_2 + \text{O}_2 = 2\text{HO}_2$, $\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{H}$, $\text{H}_2\text{O}_2 + \text{M} = 2\text{OH} + \text{M}$. Summing up these elementary reaction steps (taking the second reaction twice) provides gross reaction $2\text{H}_2 + \text{O}_2 = 2\text{H} + 2\text{OH}$, which

produces highly reactive intermediates. The important wall reactions become the loss reactions of HO₂ and H₂O₂.

The importance of homogeneous gas phase and heterogeneous wall-loss reaction determined by the uncorrelated sensitivity indices are in accordance with the analysis of Wang and Law [35]. They emphasized the importance of wall-loss reactions near the third explosion limit, which was confirmed here. A definite advantage of our approach is that the reaction importance determined this way belongs to the whole domain of uncertainty of the rate parameters, not only their nominal values.

5. Conclusions

Several authors have developed methods to carry out global sensitivity analysis of models with correlated parameters [27-29]. These articles contained descriptions of methodologies, with demonstration on simple, few-parameter, mainly artificial models. Shannon *et al.* [36] carried out a global sensitivity analysis of a master equation model using a special approach based on ordering of the covariance matrix. This however is the first article in which a real correlated multi-parameter model is investigated by fully general global sensitivity approach which was based on coupling the use of the Rosenblatt transformation [28] with an optimized RS-HDMR method [25]. The new method was applied to investigate the importance of chemical reactions and wall-loss processes near the explosion limits of hydrogen-air combustion system on the calculated ignition delay times.

The results show that the correlated sensitivity indices dominate the output variance for all parameters except the wall-loss rates. These indices are well applicable to assess how the uncertainty of the model results can be decreased and suggest that further experimental data should be incorporated within an optimization approach since the parameters do not act in isolation on the predicted outputs. These indices however, do not carry information on the individual importance of parameters. On the contrary, the uncorrelated sensitivity indices can be used to identify which

parameters have individual effects on the model outputs. However, in the present case their small values indicate that the overwhelming majority of the model variance results from the correlated effects between parameters. The methodology described here is expected to become important in the near future, when information on the correlation of the uncertainty of rate parameters will be available for many combustion systems from mechanism optimization methods.

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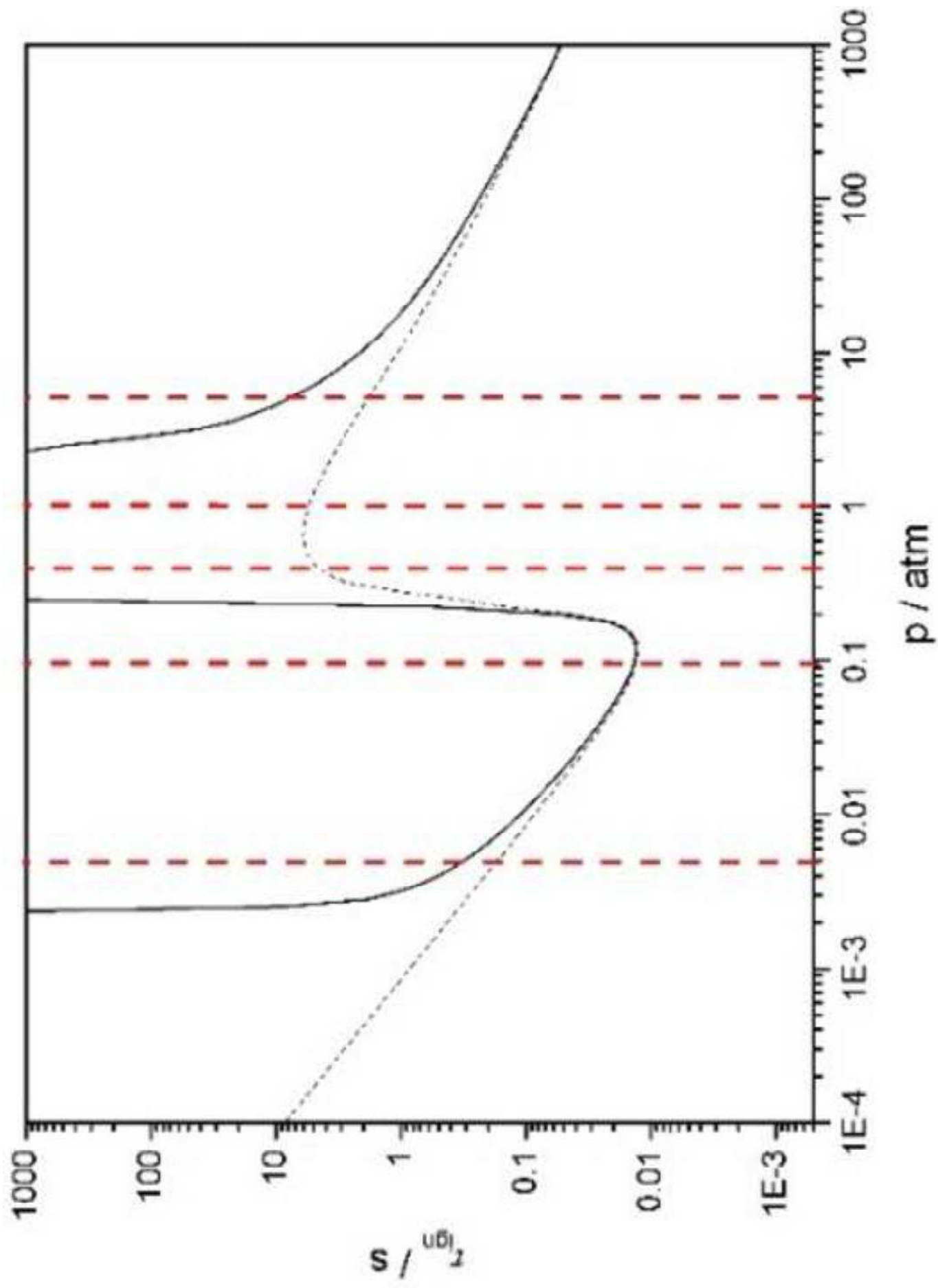
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Figure 1. Simulated ignition delay times as a function of the pressure using the original mechanism of Varga et al. [33] (dashed line) and using the same mechanism with wall reactions added (black solid line). The red vertical dashed lines mark the five selected pressure values where the uncertainty analyses were carried out.

Figure 2. Correlated sensitivity indices at 5 atm, for each parameter. The black bars show the correlated first-order sensitivity indices.

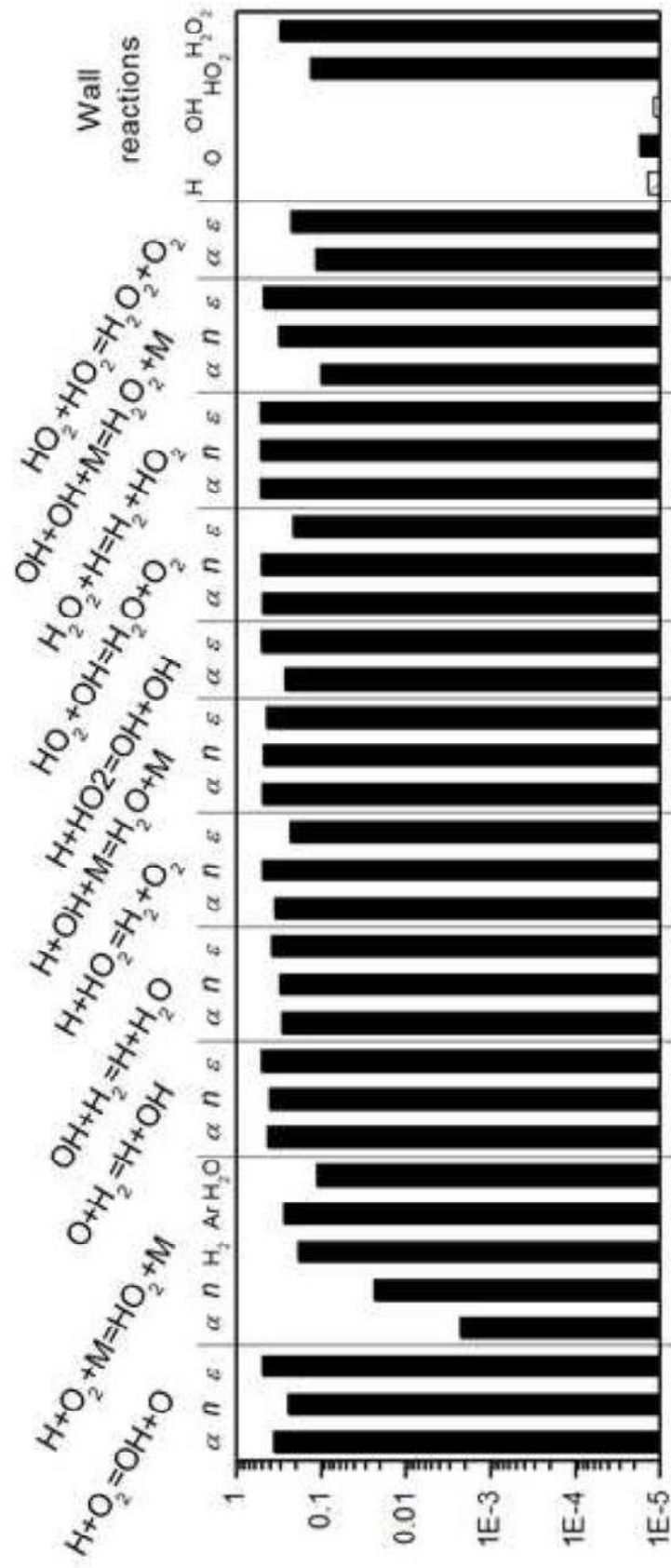
Figure 3. Uncorrelated sensitivity indices at the five investigated conditions, for each parameter. Full black bars show the uncorrelated first-order sensitivity indices, and hollow bars show the further contributions from higher-order terms. For reaction $\text{H}+\text{O}_2+\text{M}=\text{HO}_2+\text{M}$ the parameters marked with species names refer to the respective third body collision efficiencies, and for the wall-loss reactions they refer to the species the reaction depletes.

*Figure
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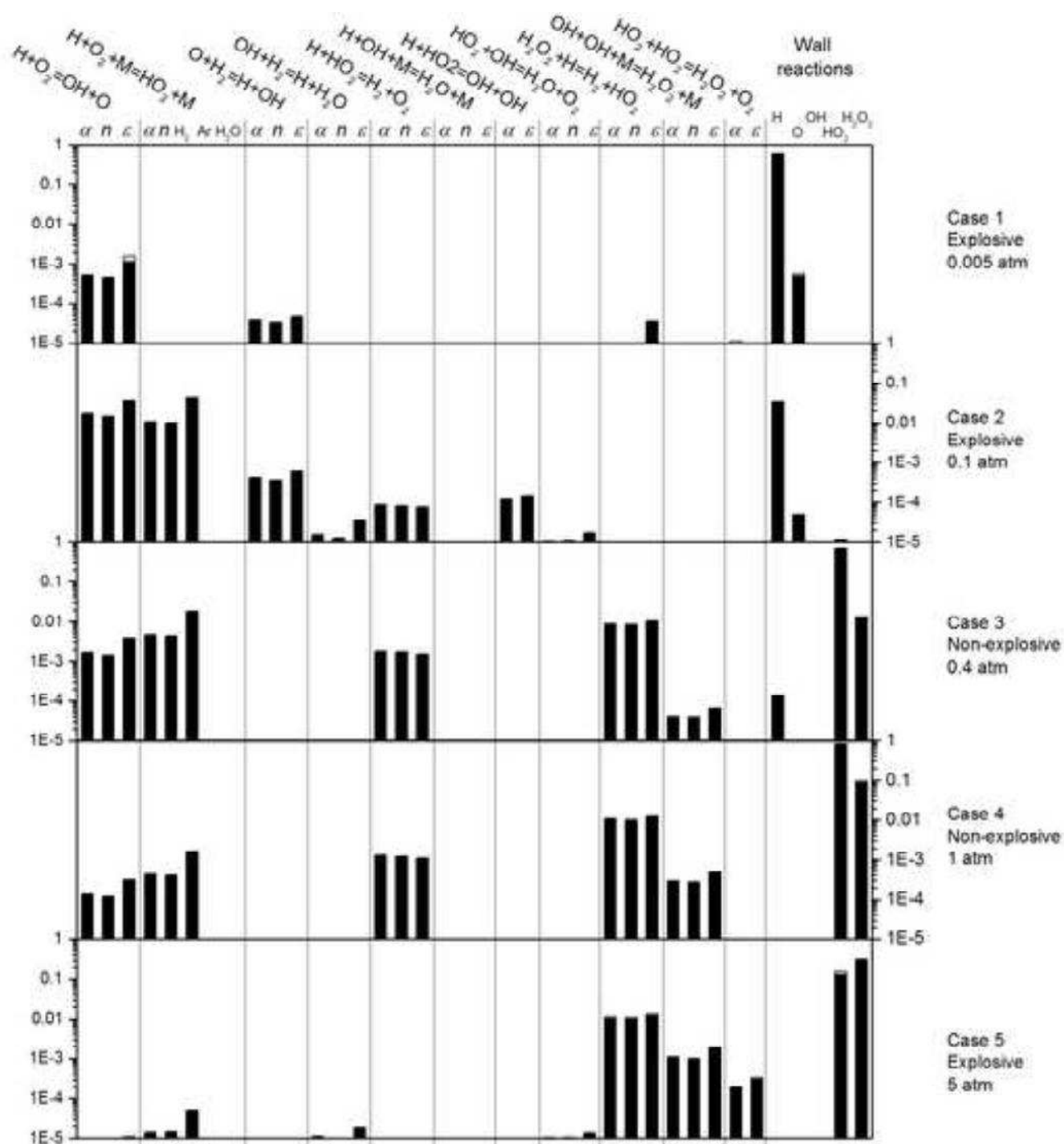


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