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Research Article

Global Sensitivity Analysis of Large Reaction Mechanisms Using Fourier Amplitude Sensitivity Test

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Global sensitivity analysis (GSA) of large chemical reaction mechanisms remains a challenge since the model with uncertainties in the large number of input parameters provides large dimension of input parameter space and tends to be difficult to evaluate the effect of input parameters on model outputs. In this paper, a criterion for frequency selection to input parameter is proposed so that Fourier amplitude sensitivity test (FAST) method can evaluate the complex model with a low sample size. This developed FAST method can establish the relationship between the number of input parameters and sample size needed to measure sensitivity indices with high accuracy. The performance of this FAST method which can allow both the qualitative and quantitative analysis of complex systems is validated by a H_2/air combustion model and a CH_4/air combustion model. This FAST method is also compared with other GSA methods to illustrate the features of this FAST method. The results show that FAST method can evaluate the reaction systems with low sample size, and the sensitivity indices obtained from the FAST method can provide more important information which the variance-based GSA methods cannot obtain. FAST method can be a remarkably effective tool for the modelling and diagnosis of large chemical reaction.

1. Introduction

Combustion in engines with a practical fuel is very complex and is commonly described by a detailed mechanism which may involve dozens or even hundreds of reactions. However, the detailed mechanism is not well understood especially for reaction rate coefficients which may be uncertain by one or more orders of magnitude [1]. For many gas-phase elementary reactions, reaction rates have uncertainty of ± 10% to ± 30% [2, 3]. The uncertainties in the rate coefficients will significantly affect the production rate of species and ultimately affect the combustion behaviors such as temperature profile, ignition delay time, and laminar flame speed. In order to investigate the detailed mechanism with large uncertainties in the reaction rate coefficients, sensitivity analysis is employed to study how the uncertainties in the outputs can be apportioned to different sources of uncertainties in its inputs. This investigation can help researchers to determine the important reactions and reaction pathways for practical fuels and model detailed mechanism. There are two classes of sensitivity analysis techniques: local sensitivity analysis (LSA) and global sensitivity analysis (GSA) [3–5]. LSA is only applicable to the best-known model and not applicable to the model with large uncertainties in the input parameters, and it may actually produce inaccuracies in evaluating detailed mechanism [6–11]. Hence, many GSA methods have been developed to analyze complex models such as FAST [12–14], Sobol' [15], HDMR [6, 16–19], and the ordinary least squares approach [20]. These methods have been successfully applied to complex reaction models such as reaction mechanism construction [21–24] and chemical reaction mechanism analysis [6, 19, 25]. However, these GSA methods are rarely employed to evaluate large numbers of input numbers.

Sobol' method is a standard variance-based sensitivity analysis tool to evaluate the complex systems, and it can obtain accurate variance-based sensitivity indices with

a large sample size. However, it cannot be applied to the models with large numbers of input parameters [8]. Since Sobol' method does not employ the dimensionality reduction techniques like FAST and HDMR methods, it needs very large sample size to evaluate the reaction systems. Thus, the computational cost for Sobol' method will be very high. However, Sobol' method with large sample size is widely applied to validate other GSA methods through a model with small input parameters since sensitivity indices for complex reaction systems could not be analytically evaluated. In this paper, the variance-based sensitivity indices from the FAST method can be validated by comparing it with sensitivity indices from Sobol' method. Another version of the FAST method, which can identify the positive or negative effect of input parameter on products, is also validated by using other measures. When sensitivity indices obtained from the FAST method that employs the dimensionality reduction techniques is validated to be reliable, the FAST method is applied to GSA of larger numbers of input parameters.

The performance of the FAST method is validated by using it to diagnose two test cases: a H_2/air combustion model [26] and the well-known GRI3.0 (CH_4/air) combustion model [27]. A H_2/air combustion mechanism which has been defined the uncertainty factor of each reaction is commonly chosen to validate the performance of the GSA methods, such as Li et al. [8] and Davis et al. [19]. In this paper, the FAST method has been compared with other GSA methods in order to evaluate the performance of the FAST method. A GRI3.0 combustion mechanism which involves 53 species and 325 reactions is commonly applied to investigate the turbulent combustion regime [28, 29]. However, only few references of GSA methods are validated by using them to large combustion mechanisms with a small sample size and a low computational cost.

2. Methodologies

Since the reaction rate coefficients are not known with high accuracy, an uncertainty factor (UF) of a reaction rate is employed to evaluate the degree of uncertainty in the reaction rate coefficients and is defined as

$$\mathrm{UF} = \frac{k_0}{k_{\min}} = \frac{k_{\max}}{k_0}, \tag{1}$$

where k_0 is the nominal value and $k_{\min}$ and $k_{\max}$ are the upper and lower bounds of the reaction rate, respectively. A classic FAST method was developed by Cukier et al. [12–14] to evaluate chemical reaction mechanisms with large uncertainties in rate coefficients, and the effect of the reaction rate coefficients on the output parameters can be written in the following form:

$$\frac{dy_i}{dt} = f\left(k_j\right), \tag{2}$$

where k_j is the jth reaction rate and y_i is the ith product, and y_i can be the concentration of species, temperature, and ignition delay time. In this paper, perfectly stirred reactor (PSR) is selected as a reactor model to investigate the effect of uncertainties in the rate coefficients on the products. This reactor model is commonly used to predict profiles of species and ignition delay time, validate prediction ability of detailed reaction mechanisms, and evaluate the performance of the GSA methods [8, 19].

The FAST method can estimate sensitivity indices with a small sample size and low computational cost since it employs dimensionality reduction techniques. This method introduces different frequencies to represent different input parameters so that it can evaluate every input parameter with same equally spaced points [12]. When the importance of input parameters is evaluated by the FAST method, we must first choose a set of r integer frequencies, $\{\omega_1, \omega_2, \ldots, \omega_r\}$, for the input factors, where r is the number of independent reaction rate coefficients. Frequency selection is crucial for the FAST method to obtain sensitivity indices with high accuracy since frequency selection should avoid interferences up to a given order M, where M is the interference factor and commonly set as 4~6 [30]. If interferences occur on the input parameters, the sensitivity indices can be overestimated. Note that the larger the M, the more the sample size is needed. Thus, M is selected to be 4 and a criterion for frequency selection is presented as follows:

$$\begin{aligned} &\omega_j > 2(i-1) + 7, \quad j = 1, 2, \ldots, r \text{ and } i = 1, 2, \ldots, N_{\mathrm{w}}, \\ &\frac{\omega_{j=1,2,\ldots,r}}{\omega_{k=1,2,\ldots,r,k\neq j}} \neq 3, \end{aligned} \tag{3}$$

where N_{w} is an integer and it is determined by r, and the inequalities $\omega_{j=1,2,\ldots,r}/\omega_{k=1,2,\ldots,r,k\neq j} \neq 3$. $\omega_{j=1,2,3}$ can be set as 7, 9, and 11 when the model involves 3 input parameters. This formula for frequency selection can greatly avoid interferences from input parameters. When M and ω_j are given, the total sample size N for the FAST method can be determined as follows:

$$N = 2 \times M \times \max\left(\omega_j\right) + 1. \tag{4}$$

Therefore, the FAST method can establish the relationship between the number of input parameters and total sample size needed. This is a good advantage for the GSA methods to evaluate the model with large input parameters since it is difficult to determine the total sample size for the GSA methods in order to measure the sensitivity indices with high accuracy.

FAST method generates sampling points in the kth dimensional input space by the space-filling curve. In this section, a space-filling curve introduced by Saltelli and Chan [30] is adopted since it can provide a uniformly distributed sample and is presented as follows:

$$x_j(s) = \frac{1}{2} + \arcsin\left(\sin\left(\omega_j s\right)\right), \quad \forall j = 1, 2, \ldots, r, \tag{5}$$

where $x_j(s)$ is a probability density function (PDF) of the jth input parameter, s is the parametric variable varying in $(-\pi, \pi)$, which is sampled over its range using N points, and ω_j is the integer frequency determined by (3). After sample size is determined, y_i in the Fourier series can be expanded as

$$y_i(s) = \frac{A_0^{(i)}}{2} + \sum_{j=1}^{r}\left(A_{\omega_j}^{(i)}\cos\left(\omega_j s\right) + B_{\omega_j}^{(i)}\sin\left(\omega_j s\right)\right), \quad (6)$$

where Fourier amplitudes, $A_{\omega_j}^{(i)}$ and $B_{\omega_j}^{(i)}$, can be written as follows:

$$A_{\omega_j}^{(i)} = \frac{1}{2\pi}\int_{-\pi}^{\pi} y_i(s)\cos\left(\omega_j s\right)ds,$$
$$B_{\omega_j}^{(i)} = \frac{1}{2\pi}\int_{-\pi}^{\pi} y_i(s)\sin\left(\omega_j s\right)ds. \quad (7)$$

The sensitivity indices measured in the classic FAST method [12] for input factor x_j are written in the following form:

$$S_{\omega_j}^{(i)} = \sum_{p=1}^{M} B_{p\omega_j}^{(i)}. \quad (8)$$

A classic FAST method only considers the Fourier amplitude $B_{\omega_j}^{(i)}$ as sensitivity index of an input parameter x_j. Such sensitivity index can be positive or negative; the positive sign indicates increase in products with increasing x_j and the negative sign indicates decrease in products with increasing x_j since $B_{\omega_j}^{(i)}$ is proportional to dy_i/dt. Due to the symmetry properties of space-filling curve and reduction in the number of model evaluations, (7) was upgraded by Koda et al. [11] and written as follows:

$$A_{\omega_j}^{(i)} = \begin{cases} 0 & \text{if } \omega_j \text{ odd}, \\ \dfrac{1}{\pi}\displaystyle\int_0^{\pi/2} y_i(s)\cos\left(\omega_j s\right)ds & \text{if } \omega_j \text{ even}, \end{cases}$$
$$B_{\omega_j}^{(i)} = \begin{cases} 0 & \text{if } \omega_j \text{ even}, \\ \dfrac{1}{\pi}\displaystyle\int_0^{\pi/2} y_i(s)\sin\left(\omega_j s\right)ds & \text{if } \omega_j \text{ odd}. \end{cases} \quad (9)$$

The sensitivity indices measured in such a variance-based FAST method can be written in the following form:

$$S_{\omega_j}^{(i)} = \frac{\sigma_{\omega_j}^2}{\sigma_i^2}, \quad (10)$$

where $S_{\omega_j}^{(i)}$ is referred to as the first-order sensitivity index, σ_i^2 is the total variance of product y_i, and $\sigma_{\omega_j}^2$ is a part of total variance σ_i^2 and indicates the contribution of input factor x_j to the product y_i since frequency ω_j is associated with x_j. The variances σ_i^2 and $\sigma_{\omega_j}^2$ can be written respectively as follows:

$$\sigma_i^2 = 2\sum_{l=1}^{\infty}\left[\left|A_l^{(i)}\right|^2 + \left|B_l^{(i)}\right|^2\right],$$
$$\sigma_{\omega_j}^2 = 2\sum_{p=1}^{M}\left[\left|A_{p\omega_j}^{(i)}\right|^2 + \left|B_{p\omega_j}^{(i)}\right|^2\right]. \quad (11)$$

Note that $S_{\omega_j}^{(i)}$ is a normalized sensitivity index in the variance-based FAST method so that $S_{\omega_j}^{(i)}$ may be ordered with respect to y_i. Such sensitivity index is different when it is calculated by (10), and it cannot identify how an input parameter plays a positive or negative role in products.

When (3) is applied to select frequencies for input parameters, ω_j is always odd. Thus, $A_{\omega_j}^{(i)} = 0$, and a brief formula can be obtained to calculate sensitivity indices by combining the method of Cukier et al. and Koda et al. Therefore, the formula can be written as follows:

$$B_{\omega_j}^{(i)} = \frac{1}{\pi}\int_0^{\pi/2} y_i(s)\sin\left(\omega_j s\right)ds. \quad (12)$$

In the present study, sensitivity index obtained from (10) and sensitivity index obtained from (12) will be compared. In other words, sensitivity indices with or without normalization will be compared.

3. Results and Discussion

3.1. H_2/Air Reaction Mechanisms. The aim of this section is to validate the formula of frequency selection proposed in (3) and evaluate the performance of the FAST method. The H_2/O_2 combustion model developed by Konnov [26] is selected as test case to validate the performance of the FAST method since this combustion model has defined the uncertainty factor for each reaction. In addition, this model is employed to study the effect of uncertainty in the reaction rate coefficients on autoignition process, which were calculated with the Senkin code [31] for a stoichiometric H_2/air mixture at a temperature of 1000 K and pressure of 0.1 atm.

For a reaction system, products are always functions of time. Hence, the FAST and Sobol' methods are extended to obtain the profiles of sensitivity indices with time in this section. Besides that, there are a few GSA researches assessing the entire autoignition process that plays important role in the validation of a detailed mechanism. In this case, we generated logarithmically 1000 points in the range of 10^{-5} to 10^{-2} s as time points for the sensitivity indices measured by the GSA methods, and the ordinary differential equation (ODE) solver should be modified for obtaining the calculation results at fixed points in time. Figure 1 shows the probability distribution of temperature prediction due to the uncertainties in the rate coefficients. It can be seen that the uncertainties in the rate coefficients can greatly affect the autoignition process. When reactions are selected as chemical kinetics mechanisms for hydrogen combustion, the uncertainty exists in the profile of temperature prediction and other products. GSA methods provide diagnostic tools to measure the importance of reactions in order to obtain reaction kinetics mechanisms which can accurately predict combustion behaviors, and identify important reactions and reaction pathways.

Figure 2 shows the 8 most important reactions measured by two types of FAST methods. The sample size for the FAST method is only 1081 determined by (4). It is shown in Figure 2 that the important reactions measured by two FAST methods are greatly different. R22, R16, and R33 are identified by FAST1 method as greatly important reactions. However, only R16 is considered to be an important reaction

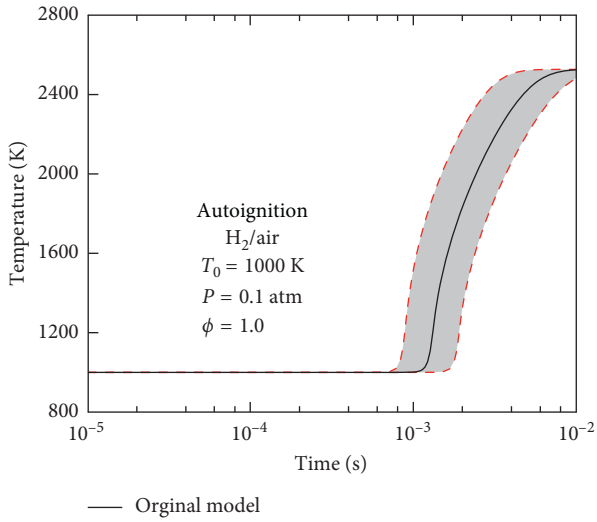

FIGURE 1: The impact of uncertainties in the rate coefficients on temperature prediction in the autoignition process. The shaded area is the probability distribution of temperature prediction, and ϕ is the equivalence ratio.

by FAST2 method and plays a positive role in output temperature. It can be seen in Figure 1 that the uncertainties in the rate coefficients hardly affect temperature prediction when the reaction time is less than 6×10^{-3} (s). However, the FAST1 method identifies important reaction in this region. Although FAST1 or variance-based methods can accurately reflect the importance of the input parameters at a particular time, it may not significantly reflect the impact of input factor on the entire reaction process. It is noted that the sensitivity indices calculated by the FAST2 method are not always within (0, 1) since these sensitivity indices are not normalized and they are proportional to y_i according to (12).

In order to validate sensitivity indices measured by FAST1 and FAST2 methods, the profiles of sensitivity indices for the FAST1 and Sobol' methods are compared. Besides that, a series of the modified combustion models are set to validate the performance of the FAST2 method. The comparison of FAST1 and Sobol' methods can validate the frequency selection presented by (3). However, the performance of the FAST2 method cannot be validated by variance-based GSA method. Therefore, an appropriately modified combustion model is constructed to illustrate the sensitivity indices obtained by the FAST2 method since it can accurately reflect the contribution of input parameter to products and identify the positive or negative effect of reactions on products. Figure 3 shows the 6 most important reactions measured by Sobol' method. Sobol' method is used to evaluate this case with 20,000 sample size for obtaining accurate sensitivity indices. It can be seen in Figure 3 that the profiles of sensitivity indices obtained by Sobol' method are in good agreement with those of the FAST1 method. Hence, the FAST1 method with new frequency selection can accurately evaluate the reaction systems. Note that computational cost is an important factor to evaluate the performance of the GSA methods, and the most time-consuming step for GSA of autoignition is solving ordinary differential equations (ODEs). For Sobol' method, the number of times for solving ODEs is based on the following formula: $C = (2 + K) \times N$, where N is a total sample size given by users, K is the number of input parameters, and C is total times of solving the ODEs. In this case, ODEs need to be repeatedly calculated by 700,000 times when Sobol' method is used to simulate the autoignition process with 20,000 sample size. The sample size for GSA of this reaction mechanism may be over 20,000 for other GSA methods in order to measure sensitivity indices with high accuracy [8, 19]. However, the FAST method can evaluate the complex reaction mechanism with only 1081 sample size and it only repeatedly calculates ODEs by 1081 times. Based on the abovementioned reasons, the importance of reactions can be quickly measured without frequently changing the sample size for other GSA methods.

In order to validate the performance of the FAST2 method, 3 modified models of H_2/air combustion are designed. For these 3 models, all the reaction rate coefficients are derived from the original model, with the exception that the rate of R22 of the original model, $k_{22}^{(0)}$, is replaced with $2.0 \times k_{22}^{(0)}$ for the first modified model, that of R16 of the original model, $k_{16}^{(0)}$, is replaced with $1.5 \times k_{16}^{(0)}$ for the second modified model, and that of R33 of the original model, $k_{33}^{(0)}$, is replaced with $2.0 \times k_{33}^{(0)}$ for the third modified model, where $k_{22}^{(0)}$, $k_{16}^{(0)}$, and $k_{33}^{(0)}$ are calculated with the original reaction rate coefficients. Figure 4 shows a comparison of output temperature profiles predicted using the original combustion model and those 3 modified combustion models. It can be found that only R16 plays an important role in output temperature, and R33 has slight impact on output temperature when reaction time is over 2×10^{-2}(s). However, output temperature is almost independent of the R22. These results are in good agreement with the analysis results from the FAST2 method. However, Sobol' method and FAST1 method regard R22 as a very important factor contributing to output temperature, which means variance-based GSA methods may not be a good tool to diagnose this system.

3.2. CH_4/Air Reaction Mechanisms. The performance of the FAST2 method has been validated by using it to GSA of the detailed mechanisms of H_2/air mixture. It can be found that the sensitivity indices without normalization may better reflect the importance of reactions in the autoignition process. Moreover, it has been validated that the FAST2 method can evaluate large reaction kinetics mechanisms with a small sample size and a low computational cost and can identify the positive or negative effect of input parameters on combustion behaviors. However, the ability to GSA of large reaction mechanisms is the most essential aspect of testing the performance of the GSA methods, and few researches involve the work for GSA of large reaction mechanisms. In this section, a CH_4/air reaction mechanism which involves 325 reactions is employed to test the performance of the FAST method. The uncertainty factor for each reaction of GRI3.0 is defined as 5.0. The mixture is considered to react at a stoichiometric CH_4/air mixture under pressure of 0.1 atm and temperature of 1000 K.

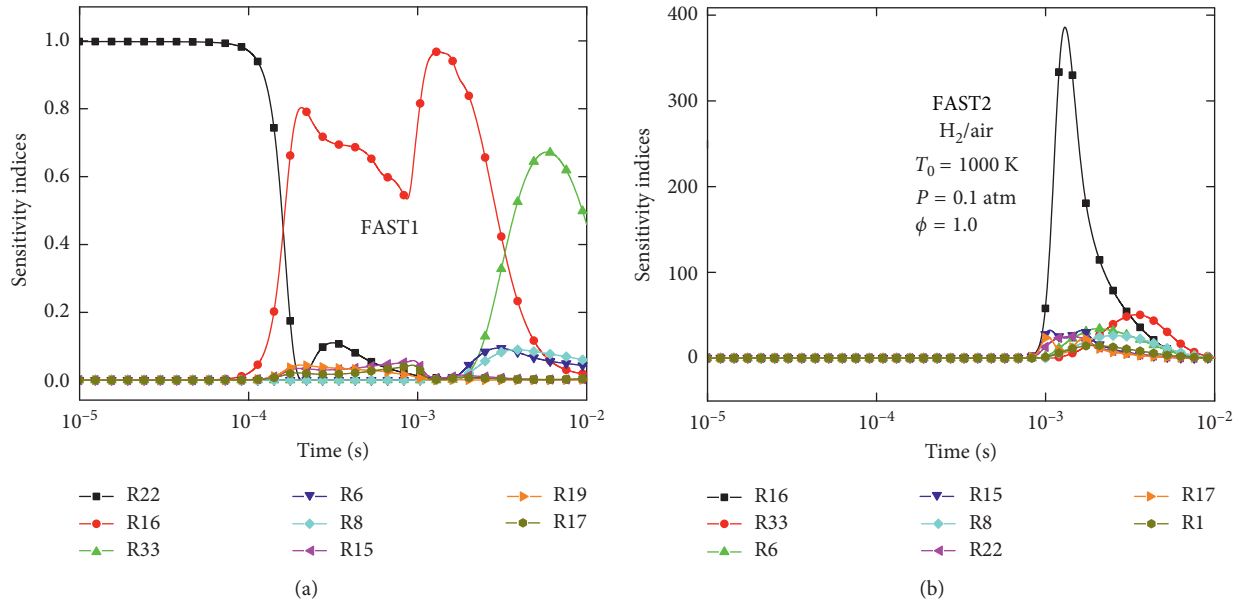

FIGURE 2: The profiles of sensitivity indices measured by two types of FAST methods. FAST1 means sensitivity indices measured by a variance-based method based on (10), and FAST2 means sensitivity indices measured by (12). R indicates the reaction, and ϕ is the equivalence ratio.

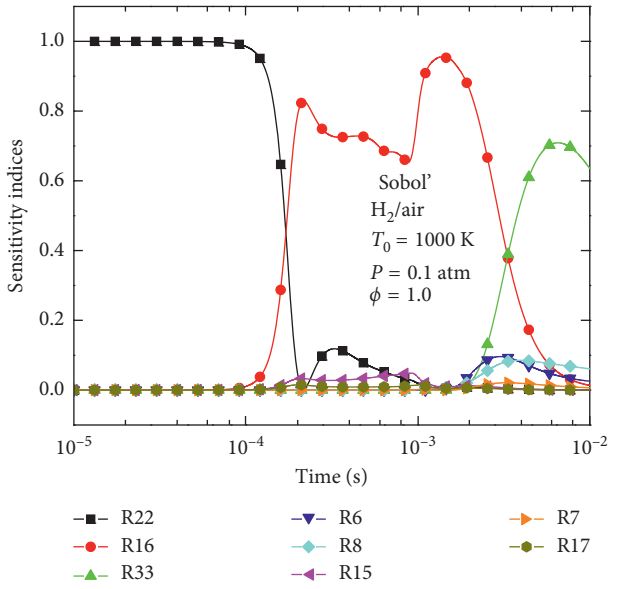

FIGURE 3: The profiles of sensitivity indices measured by Sobol's method with 20,000 sample size.

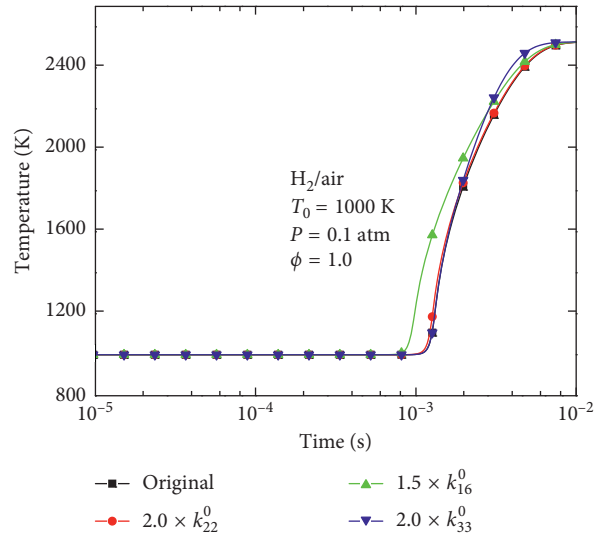

FIGURE 4: The temperature profiles predicted by an original combustion model and 3 modified models. $2.0 \times k_i^0$ indicates that the rate of the reaction (i) of this modified model is calculated with the original reaction rate k_i^0 multiplied by 2.0, and other reaction rates of the modified model are the same as those of the original model.

Figure 5 shows the 8 most important reactions identified by FAST1 and FAST2 methods. It can be found that the uncertainties in the reaction rate coefficients can greatly affect the outlet temperature or ignition delay time, and the ignition delay time may be uncertain by one order of magnitude. This uncertainty in the ignition delay time may be over experimental uncertainty estimation so that uncertainty quantification can be an important part of detailed mechanisms modelling and attract more and more researchers' interests to improve the accuracy of a chemical model [3, 23, 32]. It is further seen in Figure 5 that the positive or negative effect of a reaction on temperature and the range of its influence can be easily identified when sensitivity indices estimated by the FAST2 method are employed to evaluate the importance of reactions. This information is much useful to understand the reaction mechanisms and model reaction mechanisms. Based on the above information, it can be known how to modify the

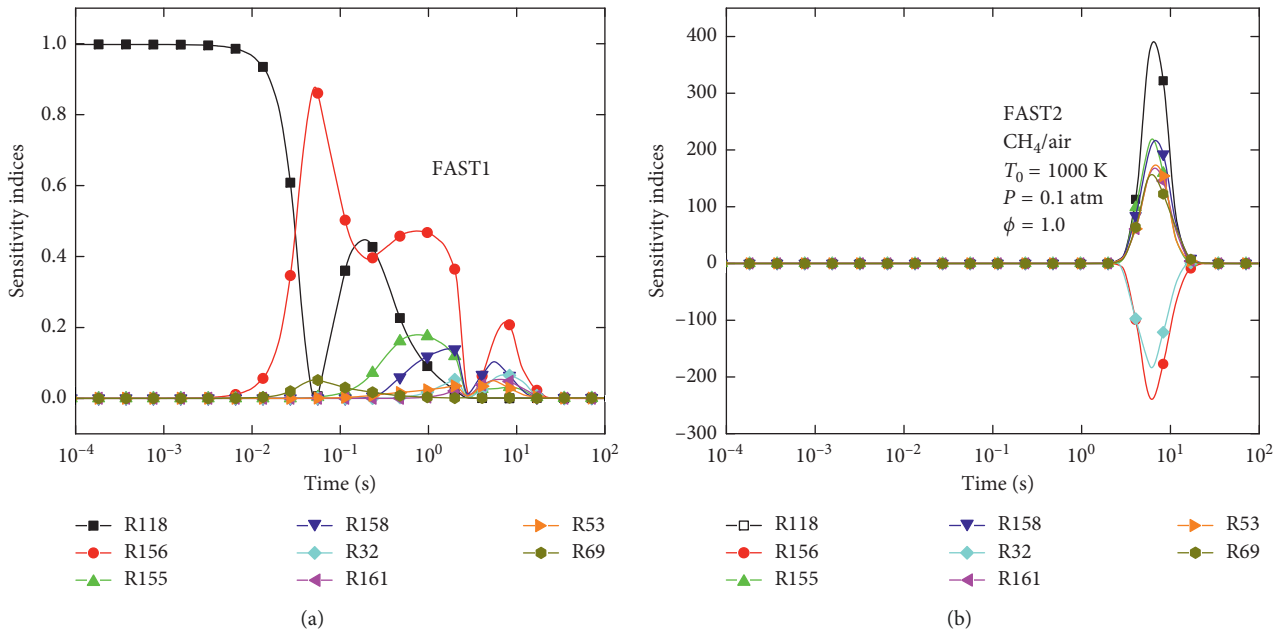

Figure 5: The profiles of sensitivity indices measured by FAST1 and FAST2 methods for CH_4/air combustion.

reaction rate coefficients in order to change the autoignition process and the range of influence of reactions can be estimated. By comparing two FAST methods, it can be found that the importance of reactions identified by two FAST methods is significantly different. R69 has little impact on the temperature estimated by the FAST1 method. In the meanwhile, R38 and R170 are certainly less important than R69 since they are not listed in the 8 most important reactions if the FAST1 method is employed to measure the importance of reactions. However, R38 and R170 are determined as the important reactions by the FAST2 method. In this section, modified combustion models are designed to validate the importance of these reactions and to determine which version of the GSA method can better reflect the impact of reactions on outlet temperature.

Figure 6 shows a comparison of output temperature profiles predicted using an original combustion model and 7 modified combustion models. It can be seen that CH_4/air combustion can be greatly enhanced by increasing the reaction rates of R38 and R170 since ignition delay time significantly reduces. These results are in good agreement with sensitivity indices measured by the FAST2 method in Figure 5. However, R38 and R170 are regarded as unimportant for output temperature by a variance-based FAST1 method. From this case and H_2 combustion model for testing the performance of the GSA methods, it can be found that the sensitivity indices obtained from the FAST1 method may not greatly reflect the importance of reactions in the autoignition process. The advantage of the FAST2 method is that it can identify the positive or negative effect of a reaction on outlet temperature. Such feature cannot be detected by the current version of variance-based GSA methods. From Figure 6, R53 and R158 have a negative impact on the outlet temperature, and R158 is more important than R53. Moreover, R156 and R170 play an important role in enhancing the autoignition process, and R156 has more impact than R170. These results correspond pretty well with the sensitivity indices measured by the FAST2 method. However, sensitivity indices measured by the FAST1 method cannot accurately describe the importance of reactions in the autoignition process.

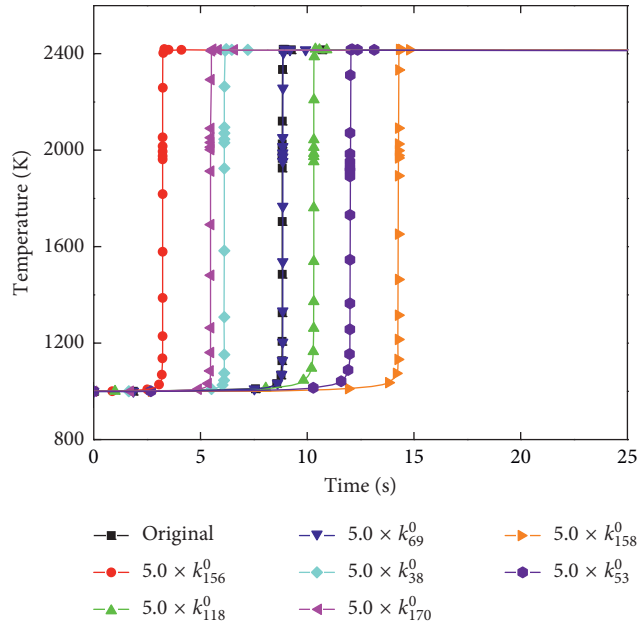

Figure 6: The temperature profiles predicted by an original combustion model and 7 modified models at a stoichiometric CH4/air mixture under pressure of 0.1 atm and temperature of 1000 K. $5.0 \times k_i^0$ indicates that the rate of the reaction (i) of this modified model is calculated with original reaction rate k_i^0 multiplied by 5.0, and other reaction rates of the modified model are the same as those of the original model.

Although variance-based GSA methods can accurately measure the sensitivity indices for most of complex models, they may not accurately reflect the impact of input parameters on products for the model which the products are varied dramatically, especially for the reaction kinetic systems. The FAST2 method can be a valuable tool to detect the importance of input parameters, and it will be an effective tool for modelling detailed mechanisms and diagnosing combustion reaction kinetic models.

4. Conclusions

In this paper, the FAST method is developed to GSA of reaction kinetic models with large input parameters and the performance of the FAST method is validated by using it to GSA of two detailed combustion mechanisms. A criterion for assigning frequencies to input parameters is presented for a model with large input parameters. Such a formula can help us to determine the minimum sample size for measuring sensitivity indices with high accuracy. Two detailed chemical reaction models are employed to validate the performance of the FAST method. It is found that the FAST method can accurately measure sensitivity indices with low sample size. Moreover, sensitivity indices obtained by two types of GSA methods with or without normalization are compared. The sensitivity indices measured by the FAST2 method can better reflect the impact of input parameters on the output parameters in the autoignition process. The FAST2 method can identify the positive or negative effect of input parameters on the products; thus, it can provide new insight into reaction mechanisms. The new FAST method can be a powerful tool for the modelling and diagnosis of chemical reaction mechanisms.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

[1] T. Turányi and A. S. Tomlin, *Analysis of Kinetic Reaction Mechanisms*, Springer Berlin Heidelberg, Berlin, Germany, 2014.

[2] T. Turányi, T. Nagy, I. G. Zsély et al., "Determination of rate parameters based on both direct and indirect measurements," *International Journal of Chemical Kinetics*, vol. 44, no. 5, pp. 284–302, 2012.

[3] H. Wang and D. A. Sheen, "Combustion kinetic model uncertainty quantification, propagation and minimization," *Progress in Energy and Combustion Science*, vol. 47, pp. 1–31, 2014.

[4] T. Turányi, "KINAL–a program package for kinetic analysis of reaction mechanisms," *Computers and Chemistry*, vol. 14, no. 3, pp. 253-254, 1990.

[5] T. Nagy and T. Turányi, "Uncertainty of Arrhenius parameters," *International Journal of Chemical Kinetics*, vol. 43, no. 7, pp. 359–378, 2011.

[6] T. Ziehn and A. S. Tomlin, "A global sensitivity study of sulfur chemistry in a premixed methane flame model using HDMR," *International Journal of Chemical Kinetics*, vol. 40, no. 11, pp. 742–753, 2008.

[7] J. Zádor, I. G. Zsély, and T. Turányi, "Local and global uncertainty analysis of complex chemical kinetic systems," *Reliability Engineering and System Safety*, vol. 91, no. 10-11, pp. 1232–1240, 2006.

[8] S. Li, B. Yang, and F. Qi, "Accelerate global sensitivity analysis using artificial neural network algorithm: case studies for combustion kinetic model," *Combustion and Flame*, vol. 168, pp. 53–64, 2016.

[9] T. Ziehn, K. J. Hughes, J. F. Griffiths et al., "A global sensitivity study of cyclohexane oxidation under low temperature fuel-rich conditions using HDMR methods," *Combustion Theory and Modelling*, vol. 13, no. 4, pp. 589–605, 2009.

[10] Y. Pei, M. J. Davis, L. M. Pickett et al., "Engine Combustion Network (ECN): global sensitivity analysis of Spray A for different combustion vessels," *Combustion and Flame*, vol. 162, no. 6, pp. 2337–2347, 2015.

[11] M. Koda, G. J. Mcrae, and J. H. Seinfeld, "Automatic sensitivity analysis of kinetic mechanisms," *International Journal of Chemical Kinetics*, vol. 11, no. 4, pp. 427–444, 1979.

[12] R. I. Cukier, C. M. Fortuin, K. E. Shuler et al., "Study of the sensitivity of coupled reaction systems to uncertainties in rate coefficients. I Theory," *Journal of Chemical Physics*, vol. 59, no. 8, pp. 3873–3878, 1973.

[13] J. H. Schaibly and K. E. Shuler, "Study of the sensitivity of coupled reaction systems to uncertainties in rate coefficients. II Applications," *Journal of Chemical Physics*, vol. 59, no. 8, pp. 3879–3888, 1973.

[14] R. I. Cukier, J. H. Schaibly, and K. E. Shuler, "Study of the sensitivity of coupled reaction systems to uncertainties in rate coefficients. III. Analysis of the approximations," *Journal of Chemical Physics*, vol. 63, no. 3, pp. 1140–1149, 1975.

[15] I. M. Sobol, "Global sensitivity indices for nonlinear mathematical models and their Monte Carlo estimates," *Mathematics and Computers in Simulation*, vol. 55, no. 1–3, pp. 271–280, 2001.

[16] G. Li, C. Rosenthal, and H. Rabitz, "High dimensional model representations," *Journal of Physical Chemistry A*, vol. 105, no. 33, pp. 7765–7777, 2001.

[17] G. Li, S. Wang, and H. Rabitz, "Practical approaches to construct RS-HDMR component functions," *Journal of Physical Chemistry A*, vol. 106, no. 37, pp. 8721–8733, 2002.

[18] G. Li, S. W. Wang, H. Rabitz et al., "Global uncertainty assessments by high dimensional model representations (HDMR)," *Chemical Engineering Science*, vol. 57, no. 21, pp. 4445–4460, 2002.

[19] M. J. Davis, R. T. Skodje, and A. S. Tomlin, "Global sensitivity analysis of chemical-kinetic reaction mechanisms: construction and deconstruction of the probability density function," *Journal of Physical Chemistry A*, vol. 115, no. 9, pp. 1556–1578, 2011.

[20] M. J. Davis, W. Liu, and R. Sivaramakrishnan, "Global sensitivity analysis with small sample sizes: ordinary least squares

approach," *Journal of Physical Chemistry A*, vol. 121, no. 3, pp. 553–570, 2017.

[21] L. Xing, S. Li, Z. Wang et al., "Global uncertainty analysis for RRKM/master equation based kinetic predictions: a case study of ethanol decomposition," *Combustion and Flame*, vol. 162, no. 9, pp. 3427–3436, 2015.

[22] A. S. Tomlin, "The role of sensitivity and uncertainty analysis in combustion modelling," *Proceedings of the Combustion Institute*, vol. 34, no. 1, pp. 159–176, 2013.

[23] S. J. Klippenstein, L. B. Harding, M. J. Davis, A. S. Tomlin, and R. T. Skodje, "Uncertainty driven theoretical kinetics studies for CH_3 OH ignition: HO_2 +CH_3 OH and O_2 +CH_3 OH," *Proceedings of the Combustion Institute*, vol. 33, no. 1, pp. 351–357, 2011.

[24] C. F. Goldsmith, A. S. Tomlin, and S. J. Klippenstein, "Uncertainty propagation in the derivation of phenomenological rate coefficients from theory: a case study of n-propyl radical oxidation," *Proceedings of the Combustion Institute*, vol. 34, no. 1, pp. 177–185, 2013.

[25] D. D. Zhou, M. J. Davis, and R. T. Skodje, "Multitarget global sensitivity analysis of n-butanol combustion," *Journal of Physical Chemistry A*, vol. 117, no. 17, pp. 3569–3584, 2013.

[26] A. A. Konnov, "Remaining uncertainties in the kinetic mechanism of hydrogen combustion," *Combustion and Flame*, vol. 152, no. 4, pp. 507–528, 2008.

[27] G. P. Smith, D. M. Golden, M. Frenklach et al., http://www.me.berkeley.edu/gri_mech/.

[28] A. R. Masri and J. D. Gounder, "Turbulent spray flames of acetone and ethanol approaching extinction," *Combustion Science and Technology*, vol. 182, no. 4–6, pp. 702–715, 2010.

[29] Y. Afarin and S. Tabejamaat, "Effect of hydrogen on H_2/CH_4 flame structure of MILD combustion using the LES method," *International Journal of Hydrogen Energy*, vol. 38, no. 8, pp. 3447–3458, 2013.

[30] A. Saltelli, S. Tarantola, and P. S. Chan, "A quantitative model-independent method for global sensitivity analysis of model output," *Technometrics*, vol. 41, no. 1, pp. 39–56, 2012.

[31] R. J. Kee, J. F. Grear, M. D. Smooke et al., "Chemkin-II, A Fortran chemical kinetics package for the analysis of gas phase chemical kinetics," Tech. Rep. SAND-89–8009, UNT Libraries Government Documents Department, Denton, TX, USA, 1989.

[32] D. A. Sheen, X. You, H. Wang et al., "Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion," *Proceedings of the Combustion Institute*, vol. 32, no. 1, pp. 535–542, 2009.