

# A functional-PCA approach for analyzing and reducing complex chemical mechanisms

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## Abstract

In industrial reactive flow systems such as furnaces and gas turbines, there are considerable variations in the temperature and concentrations of species along different spatial directions. Functional principal component analysis (fPCA) can be used to study the temporal (or spatial) evolution of reactions in a reactive flow system, and to develop simplified kinetic models to describe this behaviour. A comprehensive kinetic mechanism for CO oxidation is used to demonstrate application of fPCA to identify important reactions as a function of time. In conventional PCA, the eigenvalue–eigenvector decomposition specifically transforms the variations associated with the time (or spatial directions) and species into loadings that represent only the reactions. However, fPCA produces functional loading vectors  $\xi_i(t)$  which are functions of time or distance, whose elements are referred to as functional loadings. The functional loading vectors are the eigenfunctions of the covariance matrix associated with the sensitivity trajectories. The functional loadings are used to identify reactions playing a significant role, possibly as a function of time, and are used to develop a reduced kinetic scheme from a detailed kinetic mechanism.

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## 1. Introduction

The use of detailed chemical kinetic models of combustion and pyrolysis is becoming more widespread in the development, analysis, and control of combustion processes. However, coupling detailed kinetic models with heat, mass and momentum transfer balance equations to simulate reactive flows can produce large systems of equations that are not practical to solve with current computing technology (Hilbert, Tap, El-Rabii, & Thevenin, 2004). Much of the problem arises from the fact that, to describe the chemistry that occurs during combustion, the required number of elementary reactions in a detailed kinetic mechanism varies from several hundred to a few thousand, including a large number of intermediate species. In many cases, the main reaction pathway is largely dictated by a subset of

the entire mechanism. Hence a major objective in combustion modelling is to identify these important reactions. First-order, elementary sensitivity analysis is a popular method for doing this (Yetter, Dryer, & Rabitz, 1985). Sensitivity analysis involves perturbing the important parameters in a model (e.g., the rate constants) and seeing how the predictions change. When applied to combustion problems, or any complicated chemical scheme, challenges arise because these sensitivities will vary with reaction conditions, location in a reactor, and/or time. The scale of the problem can increase dramatically. For example, in a reaction mechanism consisting of 500 reactions and 100 species in a reactor for which values are calculated at even only 20 time steps, one ends up with  $1 \times 10^6$  sensitivity coefficients to evaluate the sensitivity of each species to each reaction at each time step. It is difficult to obtain a clear picture of what is important in this reaction mechanism looking at individual sensitivity coefficients, so multivariate analysis techniques, such as principal component analysis (PCA) are often used to extract the important information from the sensitivities (Vajda, Valko, & Turányi, 1985). PCA can be used to identify important reactions by decomposing the covariance matrix of the sensitivities,

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thereby highlighting the patterns in the sensitivity behaviour. Conventional PCA approaches produce an averaged set of principal components because they work with a large sensitivity matrix in which the sensitivity matrices at each time step are stacked vertically. In this paper, we demonstrate the use of functional principal components analysis (fPCA) (Ramsay & Silverman, 1997), which allows for decomposition of the sensitivity behaviour with time. The fPCA approach explicitly takes into account the time-varying behaviour of the sensitivities, and allows for the possibility that the dominant set of reactions can change with time.

The distinction between the work reported in this paper and the pioneering work of Turanyi lies in this treatment of the sensitivity profiles in the PCA analysis. Vajda et al. (1985) formed a large sensitivity matrix in which the sensitivities at each time step are stacked in a matrix which is subsequently decomposed. The result is an average PCA over the time horizon, and principal components that are static. This is the approach that has been used in most work that has followed on from Turanyi's original work. Researchers have also performed PCA on sensitivity matrices at given time steps—an individual PCA analysis that can be repeated at each time step along the trajectory. The resulting principal components are then examined and the significant reactions plotted at each time step. Finally, another approach that has been adopted is to integrate the sensitivity matrices over the time horizon, and apply a decomposition to this integrated sensitivity matrix. The fPCA approach that we are using treats the sensitivity trajectories as time functions and seeks to come up with a set of eigenfunctions which can be examined to identify which reactions are significant. Since we are using a discretized approach to perform the calculations, we take the sensitivity matrices at each time step and concatenate them to produce a large, “horizontal”, sensitivity matrix. This matrix is then decomposed using a PCA analysis. The loadings in the principal components reflect how sensitivities with respect to certain reactions, at possibly different time steps, produce large components. In this way, the time evolution of reactions can be taken more into account. Other researchers have also integrated or summed the sensitivity matrices at each time step, producing a time-averaged sensitivity matrix.

This paper begins with a brief review of some common model reduction techniques, focussing on sensitivity analysis and using PCA to analyse the results, pointing out the limitations with current techniques. The application of the fPCA technique is then explained in detail, and is illustrated with a well-known combustion example considered under two different operating scenarios.

## 2. Model reduction techniques

The available techniques for reducing kinetic mechanisms can be classified into two major groups: (1) consolidation methods and (2) exclusion methods. In exclusion methods, the unimportant or redundant reactions and species are eliminated, i.e., the reduced mechanism is a subset of the detailed one. In consolidation methods, on the other hand, some of the species and

reactions are expressed in terms of the others or via pseudo-species and reactions. Thus, the main difference between the two groups of methods is that, in consolidation methods, the reduced model is no longer an elementary reaction mechanism, whereas in exclusion methods it is.

Since consolidation methods alter the very nature of the elementary reaction mechanism, the reduced kinetic scheme will no longer provide molecular-level, kinetic information: the reduced kinetic mechanism may not be helpful for studying the important reactions or the reaction pathway of a certain chemical process.

## 3. Consolidation methods

Kinetic model reduction methods using time-scale analysis and lumping are two commonly used consolidation methods in combustion chemistry modelling. Time-scale analysis exploits the difference between fast and slow reactions to reduce the number of reactions and species in a detailed kinetic mechanism. Traditional reduction techniques such as the quasi-steady-state assumption (QSSA) (Chapman & Underhill, 1913) and the partial-equilibrium assumption (PEA) (Michaelis & Menten, 1913) fall under time-scale analysis. In QSSA, the net rate of production of fast-formed, intermediate species is assumed to be zero. This means that the differential equations for the fast species are replaced by algebraic equations. Similarly, in PEA, fast reactions can be assumed to be at equilibrium, and hence the net rate of the reactions is zero. Therefore, using QSSA and PEA, the number of ordinary differential equations in a system is reduced, and hence, some of the species and reactions can be expressed in terms of others. Since the application of these methods involves the experience and intuition of a modeler to determine the quasi-steady-state species and the partial-equilibrium reactions, it is often a tedious and risky operation for a large kinetic mechanism. To overcome this difficulty, Lam and Goussis (1988, 1994) proposed the computational singular perturbation (CSP) approach to identify the fast and slow modes mathematically. As well, Maas and Pope (1992a,b) used the reaction-trajectory approach known as intrinsic low-dimensional manifold (ILDM) to decouple the fast and slow reactions in a reacting system. The concept of ILDM is to identify the geometry of the reaction-trajectory in composition space, in which the reactions, with respect to the fastest time-scales, are in equilibrium. This method has been successfully used for kinetic model reduction in reactive flow systems (Bender, Blasenbrey, & Maas, 2000), since the physical time-scale, such as the diffusional time-scale, is directly coupled to the slow chemistry.

Lumping is a popular kinetic reduction method for pyrolysis, thermal degradation of polymers and the oxidation of heavy hydrocarbons (Ranzi, Dente, Goldaniga, Bozzano, & Faravelli, 2001). In the lumping method, a group of species in a detailed reaction mechanism is expressed in terms of a pseudo-species based on their chemical and physical similarities. There are many different types of lumping methods, such as exact and approximate lumping (Li & Rabitz, 1989; Li & Rabitz, 1990), linear and non-linear lumping (Li & Rabitz, 1994), and chemical and physical lumping (Frenklach, 1985).

#### 4. Exclusion methods

Although sensitivity analysis remains the popular method for identifying redundant reactions and species, integer programming based optimization methods (Petzold & Zhu, 1999; Edwards, Edgar, & Manousiouthakis, 2000; Androulakis, 2000) have been employed in recent years to develop reduced kinetic schemes. The use of non-linear optimization methods such as non-linear, integer programming preserves the non-linearity of a reaction system, as opposed to sensitivity analysis, in which linear, first-order, sensitivity coefficients are used to identify the redundant species and reactions. Also, the optimization approach can prevent the danger of eliminating the fast reactions, which have extremely low sensitivity to parameter perturbations, as demonstrated by Petzold and Zhu (1999). However, sensitivity analysis still possesses a distinct feature of providing information about the relative significance of reactions in a given kinetic mechanism (Yetter et al., 1985). This information is very useful for drawing a reaction pathway diagram or for identifying important reaction steps.

Yetter et al. (1985) demonstrated the application of the normalized sensitivity coefficients (NSC) to develop a reduced kinetic mechanism for CO oxidation. The detailed mechanism, containing 52 elementary reactions and 12 species, was reduced to 7 reactions and 8 species. The normalized sensitivity coefficient for each species with respect to each reaction was investigated individually, to rank the importance of the reactions. The reactions, which had very small values of NSC, were eliminated. However, these local, sensitivity coefficients do not carry information about the consequence of setting the value of a reaction rate to zero. A reaction does not necessarily become redundant just because it has a very small sensitivity coefficient. Thus, it is essential to investigate the joint-effects of the sensitivity coefficients when determining the redundant reactions. A multivariate statistical method such as principal component analysis (PCA), in which all the sensitivity coefficients are considered simultaneously rather than individually, is useful to study the joint-effects of the sensitivity coefficients. Vajda et al. (1985) demonstrated the application of PCA to identify redundant reactions in a detailed kinetic mechanism, and subsequently, it has been used successfully in many other applications to develop reduced kinetic models (Vajda & Turányi, 1986; Turányi, Bérces, & Vajda, 1989; Turányi, 1990; Tomlin et al., 1995; Brown, Li, & Koszykowski, 1997; Pimentel & Arbilla, 1998; Xu, Fan, & Yuan, 1999).

#### 5. Principal component analysis

Principal Component analysis uses a singular value decomposition (SVD) of the matrix of sensitivities of species concentrations with respect to kinetic coefficients to identify linear combinations of sensitivities that explain the major variation in the sensitivity matrix. A reduced set of these transformed sensitivities is identified that approximates the sensitivity behaviour. The linear combinations of sensitivities represent combinations of the original reactions; reactions that are not incorporated in

the reduced set of sensitivities are deemed to be insignificant, and are dropped from the mechanism.

When sensitivities are available as a function of time or space in a reactor, the sensitivity coefficients calculated over a period of time are stacked in a large sensitivity matrix,  $\mathbf{S}$ , to which SVD is then applied (Gokulakrishnan, 2002). By stacking the sensitivity matrices at each time step, PCA identifies a set of reactions that accounts for the significant kinetic behaviour observed by averaging the sensitivities over the time domain.

The decomposition of the sensitivity matrix can also be thought of as an eigenvector decomposition of an associated covariance matrix. If  $\mathbf{S}$  is the matrix of sensitivities, the associated covariance matrix (neglecting division by the number of time points considered) is given by  $\mathbf{C} = \mathbf{S}^T \mathbf{S}$ . The principal component loadings (i.e., the relative importance of each reaction) are given by elements of the eigenvectors of the matrix  $\mathbf{C}$ .

Scaling is an important issue, as the loadings (the elements of the eigenvectors) that define the linear transformations are strongly dependent on the relative scaling of the local sensitivities. The sensitivities are expressed in terms of logarithms of the species concentrations and kinetic parameters. This corresponds to scaling the parameter by its nominal value, and scaling the species concentration by its nominal value of the concentration at any point in time:

$$S_{i,j} = \left( \frac{k_j}{C_i} \right) \left( \frac{\partial C_i}{\partial k_j} \right) \bigg|_{T,P} = \left( \frac{\partial \ln C_i}{\partial \ln k_j} \right) \bigg|_{T,P} \quad (1)$$

For PCA of the sensitivities, the NSC are grouped to construct  $\tilde{\mathbf{S}}$  as follows:

$$\tilde{\mathbf{S}} = \begin{bmatrix} [\mathbf{S}(t_1)]_{n \times m} \\ [\mathbf{S}(t_2)]_{n \times m} \\ \vdots \\ [\mathbf{S}(t_p)]_{n \times m} \end{bmatrix}_{(n \times p) \times m} \quad (2)$$

where  $n$ ,  $m$  and  $p$  are the number of species, reactions and time steps, respectively. By performing SVD on the sensitivity matrix,  $\tilde{\mathbf{S}}$ , giving

$$\tilde{\mathbf{S}} = \mathbf{W} \mathbf{\Lambda} \mathbf{U}^T$$

where  $\mathbf{W}$  contains the normalized scores for each principal component,  $\mathbf{\Lambda}$  contains the singular values, and  $\mathbf{U}$  contains the loadings (input singular vectors, which will also be the eigenvectors of  $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$ ). The singular values are by definition the positive square roots of the eigenvalues of  $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$ . The loadings corresponding to the first principal component (the first column of  $\mathbf{U}$ ) can be evaluated:

$$\vec{\xi}_1 = \begin{bmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_j \\ \vdots \\ \xi_{26} \end{bmatrix} \quad (3)$$

Note that since the columns of this large sensitivity matrix correspond to reaction rate constants (and hence to reactions), the loadings that are produced are not a function of time. Rather, they represent average loadings over the time range considered.

A number of researchers (e.g., Vajda & Turányi, 1986) have also studied how the pattern of significant reactions can change over time by applying PCA to the sensitivity matrix at each time step. This produces a sequence of loadings that can be examined to identify significant reactions. However, because the PCA is applied independently at each time step, the loadings that are identified do not take into account linkages across time.

It should be noted that the sensitivity coefficient at a given time does reflect indirectly a cumulative effect of perturbing the reaction rate constant, since the concentration at a particular time depends on the concentration profile up to that point. However, in order to clearly see how reaction behaviour at one time influences that at another time, it is necessary to decompose the sensitivities across time, and this is the subject of the next section.

## 6. Functional PCA

The local sensitivities of the species concentrations to perturbations in the kinetic parameters are time dependent, and follow a trajectory over time or spatial position in the reactor. Consequently, it is reasonable to expect that the dominant reactions might evolve over time. In particular, one could expect that the linear combinations that explain the major variation in the sensitivities would change with time. In other words, the most appropriate SVD is one in which the eigenvectors defining the loadings are themselves functions of time, or in other words, eigenfunctions. This is the basis of functional principal component analysis (fPCA).

Functional PCA (Ramsay & Silverman, 1997), is similar to PCA in that an eigenvector decomposition of covariance is still performed, however the key difference is that the covariance is now a function of two time arguments, representing the systematic linear relationship between sensitivities at two prescribed times, following from the fact that the sensitivity profiles  $\partial C_i / \partial k_j(t)$  are functions of time. If there was a spatial component, the covariance function would be a function of position.

Functional PCA proceeds in a manner analogous to the conventional PCA case. The objective is to determine linear combinations of the original variables that maximize the explained variation, subject to constraints of having unit length, and being orthogonal to previously identified principal components. This is achieved by an eigenvector decomposition of the variance operator yielding eigenfunctions that vary with time. For a covariance function  $v(s, t)$ , the eigenfunction is defined as  $V\xi(t) = \int_0^T v(s, t)\xi(s)ds = \lambda\xi(t)$ . There are a number of computational approaches that can be used to compute the eigenfunctions. The most straightforward is to discretize time, and solve

for the eigenfunctions in terms of their values at discrete points in time. Alternatively, the eigenfunctions can be posed in terms of a suitable basis of functions (e.g., B-splines), solving in turn for the coefficients in this basis (see for example, Ramsay & Silverman, 1997).

One question that arises is how fPCA is related to the Karhunen–Loève (KL) decomposition, which has been used in many different fields for model reduction. The KL decomposition was first developed independently by Karhunen in 1946 and Loève in 1955, and provides a general framework for determining bases from self-adjoint operators (e.g., a covariance function), and expressing quantities in terms of this basis. PCA is an example of a KL decomposition, and so is functional PCA. In addition, the basic principle in KL decomposition is also known in various disciplines as Hotelling Analysis (Hotelling, 1933), proper orthogonal decomposition (Lumley, 1967), singular value decomposition (Golub & van Loan, 1989). These techniques can all be viewed as examples of KL decomposition. The distinctions arise more in the way in which these techniques are applied. For example, in some problems (e.g., fluid mechanics), there may be a spatial component, leading to eigenfunctions in the spatial dimension. In other instances, the focus is strictly on time-varying behaviour (e.g., PCA applied to batch reactor data), in which case the underlying problem is a finite-dimensional one, and eigenvectors are obtained. While functional PCA in its generic form is an example of a KL decomposition, one distinction that can be made is that fPCA techniques allow for smoothing of the time responses and/or eigenfunctions by penalizing higher-order derivatives of fitted time traces or eigenfunctions. Smoothing can also be imposed relative to some pre-conceived model of the process as well. Examples can be found in the standard functional data analysis text by Ramsay and Silverman (1997). Presentations of fPCA in the literature often start with a KL decomposition, and then go on to discuss roughness penalties.

Using the discretization approach, the eigenfunctions (loadings) are computed by forming a large NSC matrix formed by concatenating horizontally the NSC matrices at each time. The large NSC matrix is denoted  $\tilde{S}$  and has  $m$  rows and  $(n \times p)$  columns, where  $m$  is the number of species,  $n$  is the number of reactions, and  $p$  is the number of time steps. For the CO reaction example, this matrix will have 12 rows and 650 columns.

$$\tilde{S} = \begin{bmatrix} [S(t_1)]_{m \times n} & [S(t_2)]_{m \times n} & \cdots & [S(t_p)]_{m \times n} \end{bmatrix}_{m \times (np)} \quad (4)$$

An SVD is now computed for  $\tilde{S}$  (or an eigenvector decomposition can be computed for  $\tilde{S}^T \tilde{S}$ ). In this example, the loadings that are computed represent the values of the eigenfunctions at the time discretization points, that is the columns of the input rotation (eigenvector) matrix,  $U$ , consist of eigenfunctions,  $\xi_q(t)$  evaluated at the discrete time points. The eigenfunction for the first principal component can be given



as

$$\vec{\xi}_1(t) = \begin{bmatrix} \xi_1(t_1) \\ \xi_2(t_1) \\ \vdots \\ \xi_m(t_1) \\ \vdots \\ \xi_1(t_p) \\ \xi_2(t_p) \\ \vdots \\ \xi_m(t_p) \end{bmatrix} \quad (5)$$

where

$$\sum_{t=t_1}^{t_p} \sum_{j=1}^m |\xi_j(t_i)|^2 = 1 \quad (6)$$

where the discretized eigenfunction that is given by the eigenvector has unit length. The fraction of the variation in the NSCs which can be explained by a given principal component (or eigenvector) can be calculated from the eigenvalues,  $\lambda_i$ :

$$\% \text{variation} = \frac{\lambda_i}{\sum_{k=1}^{np} \lambda_k}$$

and the fractional contribution of reaction  $j$  at time step  $t$  to the variation explained by a given PC can be calculated from

$$\xi_j^2(t)$$

By plotting the eigenvector components (or the squares of the components) as stacked bars for each time step, the relative contribution of each reaction at a given time step can be assessed as well as the relative importance of the reactions at different time steps.

A reduced kinetic model structure is then determined by considering those principal components that exceed a threshold condition and then only looking at the significant loadings within each of the important principal components. Kinetic parameters not appearing as significant in the significant principal components are deleted from the kinetic mechanism. The functional approach allows changes in the kinetic scheme to be identified. In particular, if the significant chemical reactions change with time (or spatial position), the associated loadings in the eigenfunctions will change from being effectively zero to having significant values. Note that if an overall chemical mechanism is required, any reaction having a significant component in a significant principal component at some point in time is retained. This condition can be summarized mathematically as

$$\max_t |\xi(t)| > \varepsilon \quad (7)$$

where  $\varepsilon$  is a threshold value.

In this work, the application of the discretized functional PCA approach is demonstrated using a well established CO oxidation mechanism discussed by Yetter et al. (1985).

## 7. Example-reduction of CO oxidation scheme

A detailed kinetic scheme for CO oxidation, shown in Table 1, is used as an example to demonstrate the application of functional PCA. The CO oxidation model has 26 reversible, elementary reactions and 12 species (Yetter et al., 1985). Two plug-flow reactor simulations are performed using the same initial conditions (0.2% CO, 1% H<sub>2</sub>O, 2.8% O<sub>2</sub>, and 96% N<sub>2</sub>) but the user-defined temperature profiles differ slightly, as shown in Figs. 1 and 2. The residence time used is 0.8 s. As can be seen in Figs. 1 and 2, the higher initial temperature for Case II results in the oxidation of CO beginning earlier than in Case I. In Case I nothing significant happens until about 0.45 s and then complete oxidation of the CO to CO<sub>2</sub> occurs relatively rapidly such that the highest concentration–time gradient occurs at around 0.45 s. Case II shows an initial partial oxidation of the CO early, however, this slows down until the temperature is increased to about 1000 °C when further oxidation occurs, but again quenching of the reactions occurs as the temperature decreases and so complete oxidation of the CO to CO<sub>2</sub> is never accomplished. At 0.05 and 0.45 s the highest concentration–time gradient occurred in Case II.

First, the standard PCA approach is considered. The NSC values were calculated at 25 points in time for 12 species with respect to 26 reactions. The total number of elements in the NSC matrix is 7800 (25 × 12 × 26). The vertically stacked sensitivity matrix  $\tilde{S}$  for conventional PCA, has 300 rows (number of species times the number of time steps) and 26 columns.

Calculating the eigenvalues for the matrix sensitivity coefficients for the conditions depicted in Figs. 1 and 2 shows that the first principal component is the only significant one, explaining over 90% of the variation in the sensitivity coefficients. Fig. 3

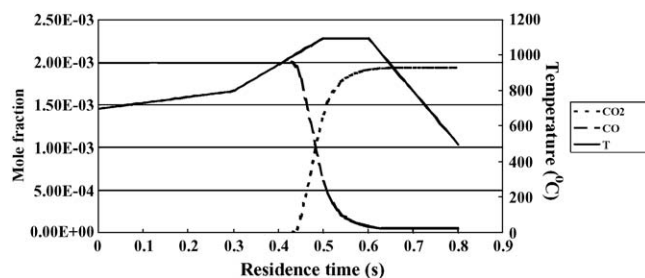


Fig. 1. Temperature and CO and CO<sub>2</sub> concentration profiles for Case I. The feed mixture comprised 0.2% CO, 1% H<sub>2</sub>O, 2.8% O<sub>2</sub>, and 96% N<sub>2</sub>.

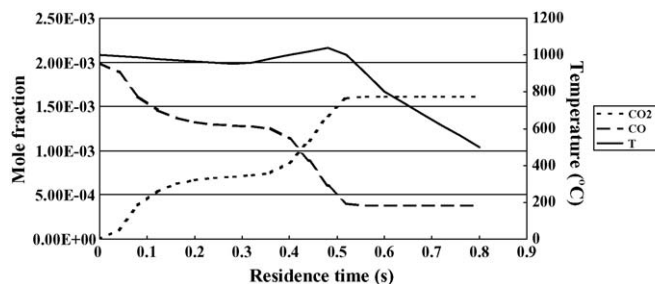


Fig. 2. Temperature and CO and CO<sub>2</sub> concentration profiles for Case II. The feed mixture comprised 0.2% CO, 1% H<sub>2</sub>O, 2.8% O<sub>2</sub>, and 96% N<sub>2</sub>.

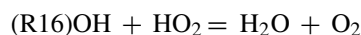
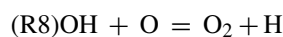
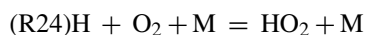
Table 1  
The CO mechanism<sup>a</sup>

No.	Reaction	A	$\beta$	$E_a$
R1.	$\text{HCO} + \text{H} = \text{CO} + \text{H}_2$	1.19E+13	0.3	0.0
R2.	$\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	1.00E+14	0.0	0.0
R3.	$\text{O} + \text{HCO} = \text{CO} + \text{OH}$	3.00E+13	0.0	0.0
R4.	$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	7.58E+12	0.0	406.0
R5.	$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$	5.80E+13	0.0	22934.0
R6.	$\text{CO} + \text{OH} = \text{H} + \text{CO}_2$	1.51E+07	1.3	−758.0
R7.	$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	2.53E+12	0.0	47688.0
R8.	$\text{OH} + \text{O} = \text{O}_2 + \text{H}$	2.02E+14	−0.4	0.0
R9.	$\text{H}_2 + \text{O} = \text{H} + \text{OH}$	5.06E+04	2.7	6290.0
R10.	$\text{OH} + \text{OH} = \text{O} + \text{H}_2\text{O}$	4.33E+03	2.7	−2485.7
R11.	$\text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}$	2.14E+08	1.5	3449.0
R12.	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	7.83E+12	0.0	1331.0
R13.	$\text{HO}_2 + \text{O} = \text{O}_2 + \text{OH}$	3.25E+13	0.0	0.0
R14.	$\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$	1.69E+14	0.0	874.0
R15.	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	4.28E+13	0.0	1411.0
R16.	$\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$	2.89E+13	0.0	−496.8
R17.	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	4.20E+14	0.0	11982.0
R18.	$\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$	1.69E+12	0.0	3755.0
R19.	$\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$	1.89E+13	0.0	−1788.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 5$ ; $\text{CO} = 2$ ; $\text{CO}_2 = 3$ ; $\text{H}_2 = 2$				
R20.	$\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$	1.00E+18	−1.0	0.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 0$ ; $\text{CO}_2 = 0$ ; $\text{H}_2 = 0$				
R21.	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	6.20E+16	−0.6	0.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 5$				
R22.	$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$	1.30E+17	0.0	45500.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 5$ ; $\text{CO} = 2$ ; $\text{CO}_2 = 3$ ; $\text{H}_2 = 2$				
R23.	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	1.60E+22	−2.0	0.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 5$				
R24.	$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	3.61E+17	−0.7	0.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 10$ ; $\text{CO} = 2.11$ ; $\text{CO}_2 = 4.2$ ; $\text{H}_2 = 2.86$ ; $\text{N}_2 = 1.3$				
R25.	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	6.17E+14	0.0	3000.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 5$ ; $\text{CO} = 2$ ; $\text{CO}_2 = 3$ ; $\text{H}_2 = 2$				
R26.	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	1.86E+17	−1.0	17000.0
Enhanced third body efficiencies: $\text{H}_2\text{O} = 5$ ; $\text{CO} = 1.87$ ; $\text{CO}_2 = 3$ ; $\text{H}_2 = 1.87$				

<sup>a</sup> Yetter et al. (1985).

shows the magnitudes of the loadings of the first principal component for the conditions specified in Figs. 1 and 2.

Fig. 3 reveals that reactions (R24), (R8), (R6), (R10) and (R16):



have the most effect on the calculated concentrations for both cases (although it must be emphasized that these are not the only reactions required to model CO oxidation), in agreement with Yetter et al. (1985). The PCA loadings are fairly similar for Cases I and II. However, reaction (R16) is important for Case I whereas it is not for Case II, and there are small differences in the loading values for some of the other reactions, but the differences do not appear to be significant. The standard procedure at this stage is then to consider these important reactions in more detail, to obtain a better understanding of how CO combustion

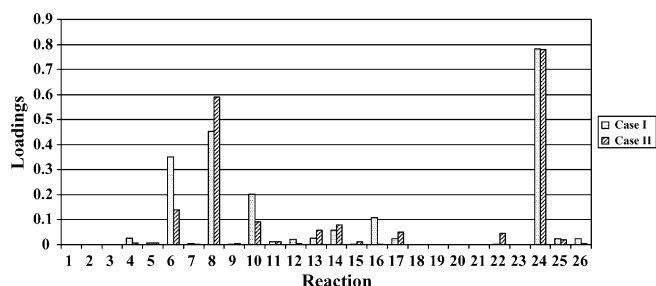


Fig. 3. Loadings from the first principal component of PCA for the simulations of Cases I and II.

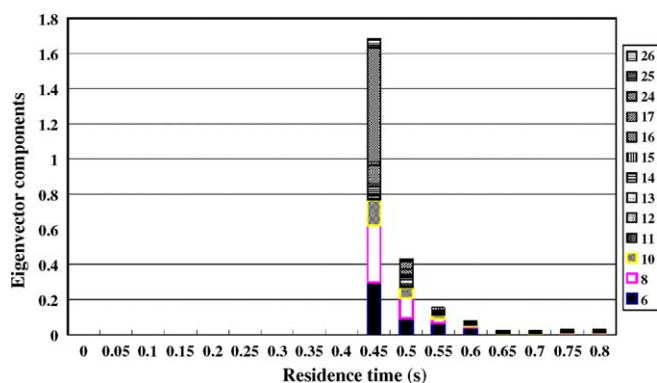


Fig. 4. Loadings from the first principal component of fPCA for the significant reactions of Case I.

is occurring. Simultaneously, the reactions with very low sensitivities are also checked to determine whether some reactions can be removed from the reaction mechanism. What must be remembered, however, is that the rankings obtained with conventional PCA are averages over the residence time or length of the reactor. It is possible and indeed quite likely that some reactions are more important at different stages during the reaction. The latter information is important for the development of a mechanism which works accurately throughout a reactor. To obtain the latter information, functional PCA is used.

The fPCA calculation is conducted by forming the horizontally concatenated sensitivity matrix shown in Eq. (4), and performing an SVD. The elements of the input rotation matrix represent the functional loadings at discrete time points, i.e., the eigenfunctions evaluated at discrete time points. Fig. 4 shows the functional loadings of the first principal component for some of the important reactions as a function of time for Case I. The functional loadings are given as a stacked-bar chart in Fig. 4, and the length of each section of a bar at each point in time represents the magnitude of the loadings at that particular time with respect to a given reaction. These loadings from functional PCA provide information about the dominant reactions at each point in time. First, it can be noticed that the CO-system is most sensitive at 0.45 s. Before this time, no reactions play any role in affecting the predicted concentration profiles (simply, because virtually no reactions are occurring during this time period). During the time period 0.4–0.5 s most of the reactions occur and hence the system is most sensitive to slight perturbations in the reaction rates of some reactions. From 0.55 s onwards, the reactions again cease for the most part, with just a relatively small amount of termination occurring, hence the decreasing significance of the loadings. Comparing the relative contributions of the various reactions at the two most important time steps, it can be seen that at 0.45 s the reactions would be ordered (R24), (R8), (R6), (R10) and (R16) while at 0.5 s, reaction (R24) becomes less important and the ordering would be (R8), (R6), (R10), (R24) and (R16); a subtle change perhaps but indicating the beginning of a shift in the nature of the reactions occurring. For Case I, the eigenvalues showed that over 90% of the variation in the NSCs can be explained by the first PC and so looking at further PCs is not necessary. In short, Fig. 4 identifies the important reactions for the oxidation of CO and how these vary with time and also

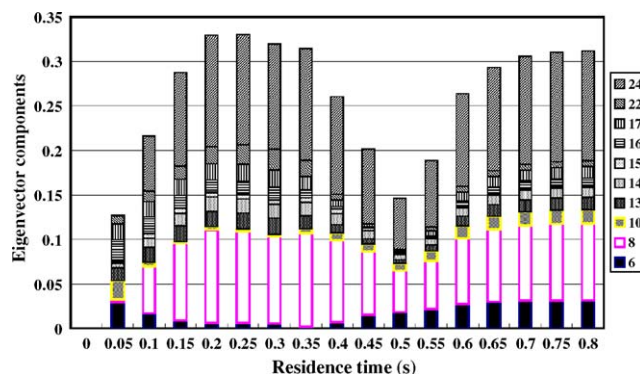


Fig. 5. Loadings from the first principal component of fPCA for the significant reactions of Case II.

where the most significant fraction of the chemistry is occurring in the time-history of the reactor.

Fig. 5 shows the functional loadings for the first principal component for Case II and shows a remarkably different pattern from what was seen in Fig. 4. First, it can be noticed that the total contribution of all the reactions at different times is fairly similar and in fact seems to be lower at the points where most of the CO is oxidized to CO<sub>2</sub> (0–0.1 s and 0.4–0.5 s). Initially this appears to be counterintuitive and inexplicable: the system is most sensitive when little reaction is occurring. However, checking the eigenvalues reveals that only 55% of the variation is explained by the first principal component, and that a further 35% is explained by the second principal component. In other words, to really understand Case II, one must look at the eigenvectors for both of the first two PCs. Fig. 6 shows the functional loadings for the second principal component for Case II and this is more what would be expected as compared to what was seen for Case I: reactions (R24), (R8), (R6), (R10) and (R16) are the most important. An interesting question is why, in an overall sense, the second principal component, which describes the oxidation of CO to CO<sub>2</sub> is not the most significant component and why the reactions during the “stagnant” periods result in a greater contribution to the overall sensitivity of the system in PC 1. One can see from Fig. 5 that reactions (R24) and (R8) are still important but some different ones become significant: (R13), (R14),

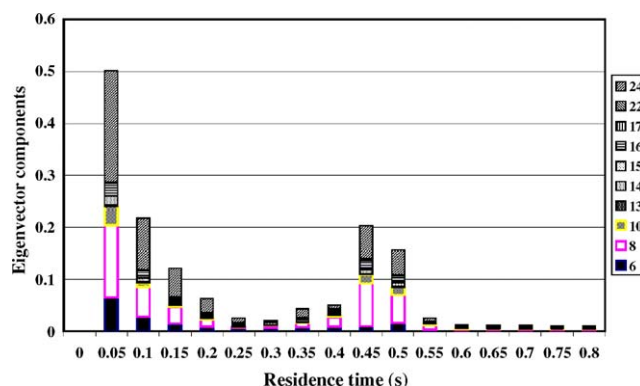


Fig. 6. Loadings from the second principal component of fPCA for the significant reactions of Case II.

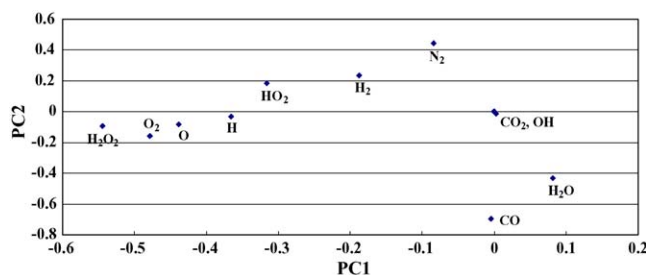


Fig. 7. The scores of the first two principal components for the simulations of Case I.

(R15), (R16), (R17) and (R22). A hint to the answer comes from the sensitivity of Case II to the exact shape of the temperature profile: a slight change produces a very different concentration profile. Increasing the temperatures a little causes the oxidation to occur very quickly and completely. Lowering the temperature slightly results in similar predictions to those shown in Fig. 1, for Case I. Because of the particular temperature profile used for Case II, the reaction kinetics are very sensitive to slight perturbations. The result is that the NSCs show significant values even when there is little reaction occurring.

Further information can sometimes be gained by looking at what is referred to in multivariate analysis as the scores, which give information about how much each species contributes to the variation seen in the NSC. Mathematically, the normalized score vectors (having unit length) are given by the columns of **W**. Figs. 7 and 8 present the scores for the first two functional principal components for Cases I and II, respectively. The species to which each point corresponds is written on the graph. The farther a point lies from the origin the greater its contribution to the variation in the NSC matrix. Additionally any species lying near each other tend to be correlated (or have similar effects in explaining the variation in the NSCs). For Case I shown in Fig. 7, remember that most of the variation was explained by the first principal component and so the distribution of species along the first principal component (the *x*-direction) is of most interest. Fig. 7 shows that the key species are  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{O}$ ,  $\text{H}$  and  $\text{HO}_2$ , i.e., the key radical species or those contributing to the radical pool. Fig. 8, for Case II breaks the species into two groups: those that are critical for the oxidation of  $\text{CO}$  (i.e., those showing significant values on the second principal component (*y*-axis)),  $\text{O}$ ,  $\text{O}_2$ ,  $\text{H}$  and  $\text{H}_2\text{O}_2$ , and those that are most influential

in determining whether the oxidation can begin or not, mainly  $\text{HO}_2$  but including  $\text{H}_2\text{O}_2$ , and  $\text{N}_2$  in a negative sense.

The above discussion shows that the order of the importance of reactions in functional PCA varies with time, and hence, this would allow one to study the predominant reactions at each point in time. However, the loadings of conventional PCA give an overall ranking of the reactions over the entire time range. Thus, functional PCA provides more detailed information about the contributing reactions to  $\text{CO}$  oxidation than conventional PCA. In Figs. 4 and 5, the order of significance of the reactions varies with time. Thus, functional PCA will facilitate the construction of a locally reduced-mechanism at each point in time, and this concept is referred to as adaptive chemistry in a rate-based construction of detailed kinetic models (Green et al., 2001). Since practical combustion systems have large variations in concentrations and temperature, the application of functional PCA is useful to identify important reactions at different spatial locations. For the modelling of a practical combustion system, the locally reduced kinetic mechanism can be constructed using functional PCA at each grid point in three-dimensional space such that the reduced-mechanism is small enough to incorporate into the numerical simulation of fluid dynamics. In the previous examples, the importance of the reactions was evaluated by taking into consideration their effect on all species' concentrations (i.e., the matrix of sensitivities included all combinations of species and reactions). In many cases it can be that one is only interested in the effect that the reactions have on specific species (e.g., only the major species). In this case, the analysis proceeds as above, with the only change being that the matrix of sensitivities only includes the terms for the species that are of interest (i.e.,  $\partial C_i / \partial k_j$  are only calculated for the combinations of the species of interest and all the reactions).

## 8. Conclusions

The application of functional principal component analysis for identifying important reactions in a combustion kinetic mechanism has been demonstrated using a well-known example evaluated under two different operating profiles. The results demonstrate that PCA applied to a large sensitivity coefficient matrix can be used to quickly identify the key reactions in a reaction mechanism, however, the importance of the reactions is averaged over the residence time or length of the reactor. Locally or briefly important reactions can be missed. Functional principal component analysis on a sensitivity coefficient matrix can be used as an alternative to study the changing importance of reactions in a mechanism throughout a reactor. Groups of reactions that contribute to different stages during a reaction sequence can be identified from loadings in different functional principal components. The scores of PCA or fPCA can be used to identify the species in a mechanism that contribute the most to the sensitivity coefficients.

## References

- Androulakis, I. P. (2000). Kinetic mechanism reduction based on an integer programming approach. *AIChE Journal*, 46, 361–371.

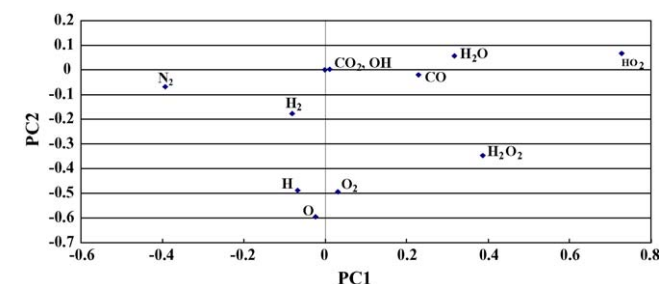


Fig. 8. The scores of the first two principal components for the simulations of Case II.



- Bender, R., Blasenbrey, T., & Maas, U. (2000). Coupling of detailed and ILDM-reduced chemistry with turbulent mixing. In *Twenty-eighth symposium (international) on combustion* (pp. 101–106).
- Brown, N., Li, G., & Koszykowski, M. L. (1997). Mechanism reduction via principal component analysis. *International Journal of Chemical Kinetics*, 29, 393–414.
- Chapman, D. L., & Underhill, L. K. (1913). The interaction of chlorine and hydrogen. *Journal of the Chemical Society-Transactions*, 103, 496–508.
- Edwards, K., Edgar, T. F., & Manousiouthakis, V. I. (2000). Reaction mechanism simplification using mixed-integer nonlinear programming. *Computers and Chemical Engineering*, 24, 67–79.
- Frenklach, M. (1985). Computer modeling of infinite reaction sequences: A chemical lumping. *Chemical Engineering Science*, 40, 1843–1849.
- Gokulakrishnan, P. (2002). *The Chemistry of Product Gas Entrainment in Low-NO<sub>x</sub>, Multi-Jet, Natural-Gas Burners*. PhD Thesis, Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada.
- Golub, G. H., & van Loan, C. F. (1989). *Matrix computations*. Baltimore: Johns Hopkins University Press.
- Green, W. H., Barton, P. I., Bhattacharjee, B., Matheu, D. M., Schwer, D. A., Song, J., Sumathi, R., Carstensen, H. H., Dean, A. M., & Grenda, J. M. (2001). Computer construction of detailed chemical kinetic models for gas-phase reactors. *Industrial and Engineering Chemistry Research*, 40, 5362–5370.
- Hilbert, R., Tap, F., El-Rabii, D., & Thevenin, D. (2004). Impact of detailed chemistry and transport models on turbulent combustion simulations. *Progress in Energy and Combustion Science*, 30, 61–117.
- Hotelling, H. (1933). Analysis of a complex of statistical variables into principle components. *Journal of Educational Psychology*, 24, 417–441.
- Lam, S. H., & Goussis, D. A. (1988). Understanding complex chemical kinetics with computational singular perturbation. In *Twenty-second symposium (international) on combustion* (pp. 931–941).
- Lam, S. H., & Goussis, D. A. (1994). The CSP method for simplifying kinetics. *International Journal of Chemical Kinetics*, 26, 461–486.
- Li, G., & Rabitz, H. (1989). A general analysis of exact lumping in chemical kinetics. *Chemical Engineering Science*, 44, 1413–1430.
- Li, G., & Rabitz, H. (1990). A general analysis of approximate lumping in chemical kinetics. *Chemical Engineering Science*, 45, 977–1002.
- Li, G., & Rabitz, H. (1994). A general analysis of exact nonlinear lumping in chemical kinetics. *Chemical Engineering Science*, 49, 343–361.
- Lumley, J. L. (1967). The structure of inhomogeneous turbulence. In A. M. Yaglom, & V. I. Tatarski (Eds.), *Atmospheric turbulence and wave propagation* (pp. 166–178). Moscow: Nauka.
- Maas, U., & Pope, S. B. (1992a). Implementation of simplified chemical kinetics based on intrinsic low-dimensional manifolds. In *Twenty-fourth symposium (international) on combustion* (pp. 103–112).
- Maas, U., & Pope, S. B. (1992b). Simplifying chemical kinetics: Intrinsic low-dimensional manifolds in composition space. *Combustion and Flame*, 88, 239–264.
- Michaelis, L., & Menten, M. L. (1913). Die Kinetik der Invertinwirkung. *Biochemistry Zeitschrift*, 49, 333–369.
- Petzold, L., & Zhu, W. (1999). Model reduction for chemical kinetics: An optimization approach. *AIChE Journal*, 45, 869–886.
- Pimentel, A. S., & Arbilla, G. (1998). Kinetic analysis of the gas-phase reactions of methyl *tert*-butyl ether with the OH radical in the presence of NO<sub>x</sub>. *Journal of the Brazilian Chemical Society*, 9, 539–550.
- Ramsay, J. O., & Silverman, B. W. (1997). *Functional data analysis*. New York: Springer-Verlag.
- Ranzi, E., Dente, M., Goldaniga, A., Bozzano, G., & Faravelli, T. (2001). Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures. *Progress in Energy and Combustion Science*, 27, 99–139.
- Tomlin, A. S., Pilling, M. J., Merkin, J. H., Brindley, J., Burgess, N., & Gough, A. (1995). Reduced mechanisms for propane pyrolysis. *Industrial and Engineering Chemistry Research*, 34, 3749–3760.
- Turányi, T. (1990). Reduction of large reaction mechanisms. *New Journal of chemistry*, 14, 795–803.
- Turányi, T., Bérces, T., & Vajda, S. (1989). Reaction rate analysis of complex kinetic systems. *International Journal of Chemical Kinetics*, 21, 83–99.
- Vajda, S., & Turányi, T. (1986). Principal component analysis for reducing the Edelson–Field–Noyes model of the Belousov–Zhabotinsky reaction. *Journal of Physical Chemistry*, 90, 1664–1670.
- Vajda, S., Valko, P., & Turányi, T. (1985). Principal component analysis of kinetics models. *International Journal of Chemical Kinetics*, 17, 55–81.
- Xu, M., Fan, Y., & Yuan, J. (1999). Simplification of the mechanism of NO<sub>x</sub> formation in a CH<sub>4</sub>/air combustion system. *International Journal Of Energy Research*, 23, 1267–1276.
- Yetter, R. A., Dryer, F. L., & Rabitz, H. (1985). Some interpretative aspects of elementary sensitivity gradients in combustion kinetics modelling. *Combustion and Flame*, 59, 107–133.