Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Computers and Chemical Engineering 30 (2006) 1093–1101

Computers & Chemical Engineering

www.elsevier.com/locate/compchemeng

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

P. Gokulakrishnan [a,1], A.D. Lawrence [b,*], P.J. McLellan [a], E.W. Grandmaison [a]

[a] *Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada K7L 3N6*
[b] *IFM, Chemical Engineering, Linköping University, 581-83 Linköping, Sweden*

Received 28 May 2004; received in revised form 24 January 2006; accepted 13 February 2006
Available online 17 April 2006

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 $\vec{\xi}_1(t)$ 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.

Keywords: Modelling; Kinetics; Model reduction; Pollution; Sensitivity analysis; Principal component analysis; Functional principal component analysis

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 1×10^6 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,

---

[*] Corresponding author. Tel.: +46 13 286609; fax: +46 13 281399.
E-mail address: lawrence@ifm.liu.se (A.D. Lawrence).

[1] Present address: Combustion Science and Engineering, Inc., 8940 Old Annapolis Road, Suite L, Columbia, MD 21045, USA.

0098-1354/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compchemeng.2006.02.007

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).