Computers and Chemical Engineering 56 (2013) 37–45

Contents lists available at SciVerse ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Reduction of kinetic models using dynamic sensitivities

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ARTICLE INFO

Article history:
Received 12 November 2011
Received in revised form 30 April 2013
Accepted 9 May 2013
Available online 19 May 2013

Keywords:
Model reduction
Kinetic models
Sensitivity analysis
Pyrolysis
GRI Mech 3.0

ABSTRACT

The development of detailed chemical kinetic models is necessary for the design and optimization of complex chemical systems. However, it is also often desired to reduce the model size by excluding inconsequential chemical species and/or reactions for end-point applications, usually due to computational reasons. In this work, new model reduction methods based on dynamic sensitivities from the impulse parametric sensitivity analysis (iPSA) and the Green's function matrix (GFM) analysis have been developed. The iPSA and GFM were originally formulated to provide dynamical parameter-by-parameter and species-by-species information on how a system output behavior is achieved, respectively. The efficacies of the proposed reduction methods were compared with existing methods through applications to reduce detailed kinetic models of alkane pyrolysis and natural gas combustion (GRI Mech 3.0) and an ab initio kinetic model of industrial steam cracking of ethane.

1. Introduction

Many contemporary world problems, such as global climate change and energy issues, are in one way or another related to complex chemical processes. Examples of these processes range from atmospheric reactions to combustion and hydrocarbon processing. The understanding of these processes often necessitates the creation and use of detailed kinetic models that describe the intermediates and reactions in the system. The most important intermediates and reactions are not usually known a priori and can change depending on reaction conditions. The mechanistic knowledge that can be gained from the analysis of such models is important for the control, design or manipulation of these systems. Nevertheless, a simpler model, one that is valid under certain conditions, is often desired for computational reasons (e.g., for model-based optimization and control applications).

One of the most common formalisms used to describe chemically reacting systems is ordinary differential equations (ODEs). A variety of methods exist that can provide reduced order models from the full ODEs. The general aim of these methods is to obtain the simplest model with the fewest species and/or reactions, while still retaining the essential features of the detailed model (Petzold & Zhu, 1999). For example, reduced-order linear ODE models could be obtained using methods from linear systems theory, such as balanced truncation or generalized Grammians (Dullerud & Paganini, 2000). However, the applications of linear system methods to complex chemical processes have been limited as chemical kinetic models typically involve nonlinear rate equations.

Reductions of nonlinear ODE models are conventionally done by removing redundant or unimportant species and reactions, or by condensing a few species into one. Species reduction methods can be classified into three groups: (i) time scale analysis methods, (ii) lumping methods and (iii) compound contribution methods (Xia, Michelangeli, & Makar, 2009). Time scale analysis methods generate reduced order models by removing short lifespan species with the assumption that fast reversible reactions are in equilibrium (Turányi, Tomlin, & Pilling, 1993). However, such reduction techniques often require inputs from an experienced and knowledgeable user. Other less commonly used methods in this classification include methods using computational singular perturbation (CSP) (Lam & Goussis, 1994) and intrinsic low dimensional manifolds (ILDM) (Maas & Pope, 1992). On the other hand, lumping methods, as the name suggests, reduce model dimensionality by coalescing species, which include methods such as substrate lumping (Weekman, 1979), exact lumping (Li & Rabitz, 1989), approximate lumping (Li & Rabitz, 1990), and chemical lumping (Fournet et al., 2000). Finally, compound contribution methods rely on quantifying and ranking the contribution of species toward those of interest, the result of which is then used to remove unimportant species. Examples from this category include graph based methods such as directed relation graph without error

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http://dx.doi.org/10.1016/j.compchemeng.2013.05.003

Nomenclature

n	number of states
p	number of parameters
z	independent variable (e.g., time or spatial position)
$\mathbf{x}$	n dimensional state vector
$\mathbf{p}$	p dimensional kinetic parameter vector
$\boldsymbol{f}$	n dimensional function giving the net rate of change in the states
t	time or observation time
τ	perturbation time
$\mathbf{S}_{i,j}$	parametric sensitivity of the species x_i with respect to the parameter p_j
$\mathbf{S}^x_{i,j}$	GFM sensitivity of the species x_i with respect to the species x_j
$i\mathbf{S}_{i,j}$	iPSA sensitivity of the species x_i with respect to the parameter p_j
$\|\|\cdot\|\|_\infty$	infinite norm
g_j	iPSA-based sensitivity rank of the parameter p_j
h_i	GFM-based sensitivity rank of state i
I_j	the set of species associated with the parameter p_j

propagation (DRG) (Lu & Law, 2005) or with error propagation (DRGEP) (Pepiot-Desjardins & Pitsch, 2008) or using sensitivity analysis (Niemeyer, Sung, & Raju, 2010), and path flux analysis (PFA) (Wenting, Zheng, Xiaolong, & Yiguang, 2010).

Model reduction by removing reactions is based on the (estimated) impact of the removal on the quality of model prediction. Different methods belong to this category, and each method uses a different metric to quantify this impact. One of the most common method in this category relies on the parametric sensitivity coefficients to rank the importance of reactions (Turányi, 2008; Turányi, Bérces, & Vajda, 1989), as these coefficients reflect the ratio of changes in the system outputs with respect to perturbations in kinetic parameters or initial species concentrations (Varma, Morbidelli, & Wu, 1999). In this case, model reduction is performed by eliminating reactions whose rate constants have small sensitivity magnitudes. While this category of methods could potentially be automated, its good performance often requires knowledgeable user guidance as to which reactions to remove (Turányi, 1990a).

Other reduction methods are based on linear or non-linear programming. In this case, the model reduction is written as a constrained optimization problem, for example as an integer linear programming (ILP) (Bhattacharjee, Schwer, Barton, & Green, 2003; Mitsos, Oxberry, Barton, & Green, 2008) or nonlinear programming (NLP) (Androulakis, 2000; Edwards, Edgar, & Manousiouthakis, 2000; Petzold & Zhu, 1999). Here, the elimination of species and/or reactions is done to produce the simplest model with an acceptable model reduction error. The methods mentioned above have their own advantages and disadvantages, but a detailed comparison of these methods is out of the scope of the present study.

In this article, five new sensitivity-based model reduction methods are proposed. The crucial difference between these and existing sensitivity based methods is the use of time-dependent perturbations in the sensitivity analysis, i.e. the impulse parametric sensitivity analysis (iPSA) (Perumal & Gunawan, 2011) and the Green's function matrix (GFM) analysis (Perumal, Wu, & Gunawan, 2009; Yetter, Dryer, & Rabitz, 1985). Elsewhere, we have shown that the dynamical importance of reactions cannot be inferred from the traditional parametric sensitivity coefficients (Perumal et al., 2009), but is immediately apparent from the iPSA and GFM analysis. In particular, the iPSA and GFM can provide dynamical, parameter-by-parameter and species-by-species information on how a system output behavior is achieved, respectively. The efficacy of the proposed methods is compared to existing methods through applications to the kinetic models of alkane pyrolysis (Edelson & Allara, 1980), and natural gas combustion (GRI Mech 3.0) (Gregory et al., 1999), and an ab initio mechanistic model for industrial steam cracking of ethane (Sun & Saeys, 2011).

2. Methods

Detailed kinetic models of chemically reacting systems are often formulated as ordinary differential equations (ODEs). Such ODE models are built, for example by assuming spatially homogeneous concentrations of species (i.e., well mixed system) or steady state operation of spatially inhomogeneous systems (e.g., plug flow reactor (PFR) model). The systems dynamics can generally be written as:

$$\frac{\partial \mathbf{x}(z,\mathbf{p})}{\partial z} = \boldsymbol{f}(z,\mathbf{x}(z,\mathbf{p}),\mathbf{p}) \quad \mathbf{x}(z_0,\mathbf{p}) = \mathbf{x}_0(\mathbf{p}) \tag{1}$$

Here, the vectors $\mathbf{x}(z,\mathbf{p}) \in R^n$, $\mathbf{x}_0(\mathbf{p}) \in R^n$, and $\mathbf{p} \in R^p$ denote the system states, such as chemical species concentration and temperature, their initial or boundary conditions, and the model parameters, respectively. The independent variable $z \in R^1$ typically denotes time or spatial position. The function $\boldsymbol{f}(z,\mathbf{x}(z,\mathbf{p}),\mathbf{p}) : R^1 \times R^n \times R^p \to R^n$ describes the net rate of formation or disappearance of chemical species, or the conversion from chemical to thermal energy. The solution to the ODE model in (1) gives the trajectory of the states $\mathbf{x}(z,\mathbf{p})$ in the system.

2.1. Model reduction using parametric sensitivity analysis

Parametric sensitivity analysis (PSA) of ODE models is well established in the field of science and engineering (Turányi, 1990b; Varma et al., 1999). This analysis reveals the effect and importance of parameter values on the system states and outputs. There are two versions of the PSA: local and global. In the global PSA, one studies the change in model behavior over a range of parameter values. Here, the system sensitivities with respect to parameters are typically quantified with the help of statistical tools (Marino, Hogue, Ray, & Kirschner, 2008; Saltelli, 2008). The local PSA can be viewed as a special case of the global PSA, in which the parameter range is reduced to an infinitesimal region around the nominal values (Ingalls, 2008; Saltelli, Tarantola, Campolongo, & Ratto, 2004). In comparison to the global PSA, the formulation of local parametric sensitivities is simpler, which can be done by directly differentiating the ODE model in (1) as follows:

$$\begin{aligned} &\frac{\partial}{\partial z}\frac{\partial \mathbf{x}(z,\mathbf{p})}{\partial \mathbf{p}} = \frac{\partial \boldsymbol{f}(z,\mathbf{x}(z,\mathbf{p}),\mathbf{p})}{\partial \mathbf{x}}\frac{\partial \mathbf{x}(z,\mathbf{p})}{\partial \mathbf{p}} + \frac{\partial \boldsymbol{f}(z,\mathbf{x}(z,\mathbf{p}),\mathbf{p})}{\partial \mathbf{p}} \\ &\frac{\partial \mathbf{x}(z_0,\mathbf{p})}{\partial \mathbf{p}} = \frac{\partial \mathbf{x}_0(\mathbf{p})}{\partial \mathbf{p}} \end{aligned} \tag{2}$$

where $\partial \boldsymbol{f}/\partial \mathbf{x}$ is known as the Jacobian matrix. The parametric sensitivities in (2) are solved simultaneously with the ODE model in (1) using the direct differential method or separately using the Green's function method (Varma et al., 1999). The coefficients are usually compared using their normalized values:

$$\mathbf{S}_{i,j}(z,\mathbf{p}) = \frac{\partial \mathbf{x}_i(z,\mathbf{p})}{\partial \mathbf{p}_j}\frac{\mathbf{p}_j}{\mathbf{x}_i(z)} = \frac{\partial \log \mathbf{x}_i(z,\mathbf{p})}{\partial \log \mathbf{p}_j} \tag{3}$$

The sensitivity coefficient in (3) can be thought as the percent change in the state trajectory $\mathbf{x}_i$ at z with respect to a percent perturbation on the system parameter $\mathbf{p}_j$. The sensitivity coefficients in the local PSA are usually calculated for perturbations introduced at z_0 (see Fig. 1(a) and (b)), but more general perturbations at different z's can also be done (Turányi, 1990b). In the following, the independent variable z is taken to be the time variable t with