Kinetic Mechanism Reduction Using Genetic Algorithms, Case Study on H_2/O_2 Reaction

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ABSTRACT: *For large and complex reacting systems, computational efficiency becomes a critical issue in process simulation, optimization and model-based control. Mechanism simplification is often a necessity to improve computational speed. We present a novel approach to simplification of reaction networks that formulates the model reduction problem as an optimization problem and solves it using genetic algorithm (GA).The aim of simplification kinetics modeling is to derive the simplest reaction system, which retains the essential features of the full system. Numerical results for H_2/O_2 combustion reaction mechanism illustrate the potential and proficiency of this approach.*

KEY WORDS: *Kinetic reduction, Optimization, Genetic algorithm, Simulation, Reaction networks.*

INTRODUCTION

Complex chemical reaction systems arise in a variety of processes, such as combustion, chemical-vapor deposition, fluid catalytic cracking and biotechnological process [1]. The incorporation of detailed chemistry in the modeling of such a process is critical for design, optimization and control. The kinetics of a detailed chemically reacting system can potentially be very complex [2]. Although the chemists may be interested in only a few species, the reaction model almost always involves a much larger number of species, some of which are radicals. These are very reactive species, which can be important intermediaries in the reaction scheme. A large number of elementary reactions are fast and some are slow. The aim of simplified kinetics modeling is to derive the simplest reaction system, which retains the essential features of the full system.

A variety of model reduction techniques have been developed to handle the problem of large and complex mechanisms. The conventional technique is to systematically apply the so-called quasi-steady state approximation to the appropriate radicals, the partial-equilibrium approximation to the fast reversible reactions and to ignore the very slow reactions. A comprehensive knowledge of chemical kinetics is usually needed, and the results obtained are expected to be valid only in some limited initial and operating condition for a limited interval of time. Usually the obtained reductions are not elementary reactions and actually represent groups of reactions lumped together. This makes the reduced model more accurate, but the physical meaning of the elementary reaction may be lost [3].

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Sensitivity analysis has often been used for the purpose of obtaining information to develop a reduced-order and simpler mechanism. Defining the rate constants of the chemical reactions as parameters under study, sensitivity analysis determines the change in the species concentration for small perturbations of the rate constants. If a reaction is slow and unimportant, it can be identified in this way. However, sensitivity analysis may also single out fast reactions, which are important and therefore, should not be deleted [4].

Lam et al., [5] have proposed the computational singular perturbation (CSP) method for automatically determining appropriate simplified kinetic models. The CSP method identifies the fast and slow modes as the system advances in time.

The reduced-order model at any given time is solvable by explicit time-stepping methods because the fast modes have been identified and approximated by algebraic constraints, leaving only the slower mode in the differential system [6].

Further, the slow manifold approach, an analysis of the eigenvalues and eigenvectors of local linearized system is used to identify the fast and slow modes, hence obtaining a reduced system [7]. Methods based on local linear analysis can be helpful in pointing out a potential problem, but it still requires a chemist to solve it. Chemical mechanisms are sufficiently nonlinear that a global approach may be warranted.

In the other approach or scheme an optimization-based method for reduction of the number of species and reactions in chemical kinetics models is described [8-10]. In this work we use genetic algorithm (GA) for kinetic model reduction.

KINETIC MODEL REDUCTION VIA OPTIMIZATION APPROACH

In this approach by posing the reaction mechanism simplification problem as an optimization problem, an objective function is formulated which should be minimized subject to a series of constraints. The structure of the optimization problem is that of a mixed-integer nonlinear programming problem (MINLP) which has both continuous and discrete variables.

To solve such optimization problems, there are several issues to be considered. It is necessary to have sets of equations, coefficients, and variables that describe the physicochemical behavior of the system.

An additional requirement in posing a reaction mechanism reduction problem as an optimization problem is a quantitative measurement of model error.

The error measurement involves comparing what is actually occurring in a real reactor to what is predicted using an equation-based kinetic model. A typical error measurement might involve the sum of squared errors between the concentration or reaction rate profiles of the "full model" and similar profile for the "reduced model".

The final requirement is an objective function to be minimized. Although several possibilities exist, the simplest is a linear equation involving some combination of the model error variables.

By posing the reaction reduction problem as an optimization problem, it is very important to find effective method to solve this problem. It would appear that solving the discrete optimization problem directly by mathematical methods could be very costly. There is almost not a mature method for nonlinear integer programming problems without convex or polynomial properties [11,12]. *Petzold* used adaptive nonlinear optimization method for solving reaction reduction problem [7]. In this method, the MINLP is firstly converted to a continuous optimization problem by adding a nonlinear constraint. Next forth, the problem is solved via a sequential quadratic programming (SQP) method. Since the classic and continuous optimization solvers can find only local optimal solutions for the nonlinear programming problems the result is not necessarily global and absolute.

Androulakis [13] and *Sirdeshpande* [10] used branch and bound (B&B) algorithm to solve this problem. The relaxed INLP at each node of B&B tree was solved using a sequential quadratic programming (SQP) method. Since the SQP method can only guarantee a local minimum, the results of the B&B strategy do not necessarily yield the smallest set of reactions.

In this work we use genetic algorithm (GA) for kinetic model reduction. The MINLP approaches worked well for small reaction system, whereas GA method was applicable to large reaction networks as well. GA has been used to solve difficult problems with objective functions that do not process "nice" properties such as continuity, differentiability, and convexity.

GENETIC ALGORITHM

GA represents a class of search and optimization procedures that are patterned after biological process of natural selection. GA solves a wide range of optimization problems, including combinatorial, discontinuous, discrete or non-differentiable, multi-modal, and even stochastic problems. GA searches the solution of a function through the use of simulated evolution, i.e. the survival of the fittest strategy. In general, the fittest individuals of any population tend to reproduce and survive to the next generation, thus improving successive generations. However, inferior individuals have the chance of surviving and also reproducing.

The use of a genetic algorithm requires the determination of six fundamental issues: chromosome representation, selection function, the genetic operators, and the creation of the initial population, termination criteria, and the evaluation function.

GAs use stochastic process to produce an initial population of models which is called parents. Then, a new population (offspring) is produced through iteration. Each iteration represents a new set of strings created according to a number of specified and predetermined performance index. The (genetic) algorithm searches for new generations with gradually improved behavior. This process is repeated a number of times until the fittest individuals evolve.

When GA is applied to optimization problems, each optimization variable is typically encoded as a string of alphabets and these strings are (usually) appended together to form a chromosome. An alphabet could consist of binary digits (0 and 1), floating point number (real GA), integers, symbols (i.e. A, B, C, D), matrices, etc. In Holland's original design, [14] the alphabet was limited to binary digits (binary GA). *Michalewiz* showed that the real-valued GA is an order of magnitude more efficient in terms of CPU time from binary GA for problems with continuous variable [15].

Fitness function provides the mechanism for evaluating each string. Having defined the initial population and the fitness function, the parameters are evaluated and assigned with a fitness value which shows how good is the selected solutions compared with others in the population. Probability of the given model being selected for the next population depends on the fitness value. The higher fitness value means higher chance of survival and generates more copies. In this way, GAs search for new generations with gradually improved behavior using three fundamental operators; *reproduction*, *crossover* and *mutation*.

Reproduction, the strings with larger fitness values, produce large number of their copies in the new generation, in this way, fitter solutions have a higher chance to survive while weaker ones perish.

There are many different ways for the production in the literature. One of the simplest procedures is the roulette wheel selection scheme. Other methods for selection are proportionate selection and tournament selection.

By crossover the strings can exchange information probabilistically with each other. For this aim, each pair is selected progressively and a random number between 0 and 1 is generated. This number is compared to a crossover probability, p_c. If the random number is greater than p_c, then the two parents pass to next generation unchanged. If not, then parents are crossed over. There are three types of crossover: single point, multi-point and uniform crossover. By mutation, the string can change their structure at randomly selected bit positions. The bits of a string are independently mutated. Mutation may generate the string, which is not produced by reproduction and crossover. So, this process is complementary to other operators. In this process, all bit positions are tested for mutation by generating a random number and comparing it with the mutation probability, p_m. If it is less than p_m the bit is changed. Otherwise it is unchanged.

Population size (N), crossover (p_c) and mutation probability (p_m) are the parameters of GA. The parameters depend on the nature of the objective function.

Reactions Model Reduction

Problem definition

Given N_s chemical species with mole fractions y_i, ($i=1,\ldots,N_s$) and N_R reaction where r_j, ($j=1,\ldots,N_R$) denotes the reaction rate of the j^{th} reaction.

The mass and energy balances for a constant-volume batch reactor are given by

$$\dot{y}_i = \sum_{j=1}^{N_R} v_{ij} r_i \quad , \quad (i = 1,\ldots, N_S) \qquad (1)$$

$$\dot{T} = -\frac{1}{\rho C_p}\sum_{j=1}^{N_R}\Delta H_j R_j \qquad (2)$$

Where v_{ij} denotes the stoichiometric coefficient of species i in the reaction j (in moles per unit time per unit volume) and ΔH_j denote the heat of reaction j. T denotes the temperature, C_p is the heat capacity and ρ is the density of reacting mixture.

The model of Eqs. (1) and (2) can be written in the following general form

$$\dot{\underline{x}} = S\times R(\underline{x}) \quad , \quad \underline{x}(0) = \underline{x}_0 \qquad (3)$$

where $\underline{x}$ is the vector of state variable

$$\underline{x} \triangleq [y_1 \ \cdots \ y_{n-1} \ T]^T \ , \ \underline{x} \subset \Re^n \ , \ n = N_S + 1$$

$$S = \begin{bmatrix} v_{11} & \cdots & v_{ij} & \cdots & v_{N_R 1} \\ \vdots & & & & \vdots \\ v_{1i} & & & & v_{N_R i} \\ \vdots & & & & \vdots \\ v_{1N_S} & \cdots & v_{iN_s} & \cdots & v_{N_R N_S} \\ \frac{\Delta H_1}{\rho C_p} & \cdots & \frac{\Delta H_i}{\rho C_p} & \cdots & \frac{\Delta H_{N_R}}{\rho C_p} \end{bmatrix}$$

S is a $(n\times N_R)$ generalized stoichiometric matrix and $R(\underline{x})$ is an N_R- dimensional reaction rate vector.

$$R(\underline{x}) = \begin{bmatrix} r_1 \\ \vdots \\ r_j \\ \vdots \\ r_{N_R} \end{bmatrix}$$

The reduced system is given by:

$$\dot{\underline{z}} = S\times D\times R(\underline{z}) \qquad (4)$$

Where $D \in \Re^{N_R \times N_R}$ is a diagonal matrix, whose diagonal elements (d_i) are either 1 or 0 (depending on whether or not reaction j is selected for the reduced mechanism). The $\underline{z}$ vector denotes the reduced state of the dynamical system. Now the problem of finding the reduced mechanism can be written as an integer constrained optimization. We minimize the error while postulating the number of reactions.

$$\min_{\underline{d}\in g^{N_R}} e = \left(\sum_{i=1}^{N_S+1} w_i \int_0^b \left(\frac{z_i - x_i}{x_i}\right)^2 dt\right)^{1/2} \qquad (5)$$

Subject to:

$$\dot{\underline{x}} = S\times R(\underline{x}) \quad , \quad \underline{x}(0) = \underline{x}_0$$

$$\dot{\underline{z}} = S\times D\times R(\underline{z})$$

$$\sum_{i=1}^{N_R} d_i = k \quad , \quad d_i = 0 \text{ or } 1$$

Where the minimum is over $d_1,\ldots,d_n$, each d_i can take the value 0 or 1, and $k \prec\prec N_R$ is number of reactions for reduced mechanism is chosen by the user. Eq. (5) has been solved by *Petzold* [7] via converting this problem to continuous constrained problem by using nonlinear constraint $g(d_1,\ldots,d_n) = 0$ that forces the d_i to take integer values:

$$g = \sum_{i=1}^{n}\left(d_i - d_i^2\right)^{\beta} = 0 \qquad (6)$$

where $\beta \geq 2$ is a parameter which controls the shape of the normalized, symmetrical Beta-function integrand.

Instead of imposing a bound on the number of reaction while minimizing the approximation error, one could postulate the inverse problem, whereby minimize the number of reaction while postulating the error:

$$\min e = \sum_{i=1}^{N_R} d_i \qquad (7)$$

Subject to:

$$e = \left(\sum_{i=1}^{N_S+1} w_i \int_0^b \left(\frac{z_i - x_i}{x_i}\right)^2 dt\right)^{1/2} \leq \delta$$

$$\dot{\underline{x}} = S\times R(\underline{x}) \quad , \quad \underline{x}(0) = \underline{x}_0$$

$$\dot{\underline{z}} = S\times D\times R(\underline{z}) \quad , \quad \underline{z}(0) = \underline{x}_0 \quad , \quad 0 \prec t \leq b$$

The above-mentioned formulations using branch & bound algorithms have been used by *Androulakis* for kinetic model reduction [13]. Since the above approaches use SQP method, it can only guarantee a local minimum, hence, the results of this strategy do not necessarily yield the smallest set of reactions. Because of the non-convexity of problems (5) and (7) we use GA to solve optimization problem. For solving the optimization

problem, it is necessary to convert constraint optimization problem to a non-constraint optimization problem by adding penalty function as such. The formulation of kinetic model reduction problem for GA is encoded as:

$$\max_{\underline{d}\in\Re^{N_R}} PI = -e + \alpha\min\left\{(k, \sum_{i=1}^{N_R} d_i), 0\right\} \qquad (8)$$

$$\dot{\underline{x}} = S\times R(\underline{x}) \quad , \quad \underline{x}(0) = \underline{x}_0$$

$$\dot{\underline{z}} = S\times D\times R(\underline{z}) \quad , \quad \underline{z}(0) = \underline{x}_0 \quad , \quad 0 \prec t \le b$$

k is the number of reaction for reduced mechanism, chosen by the user, and α denotes the penalty coefficient. It should be noted that for the traditional and engineering optimization applications it is common to formulate the case as a *minimization* problem, but due to the evolutionary philosophy of GA algorithms, the problem must be formulated as a *maximization* one. It is the reason for using the opposite sign of models error in Eq. (8).

SOLUTION METHOD

Because of the non-convexity of problem (7) for most physical systems, we have chosen genetic algorithms (GA) as the solution method. Because variables (d_i) in this problem (Eq. (8)) are binary, we use binary GA. Each d_i encoded as a bit in GA chromosomes. For example for a network with N_R reactions, we have such GA chromosome.

d_1	...	d_i	...	d_{N_R}
1	1	0	1	0

Genetic operator provides the basic search mechanism of the GA. The operators are used to create new solutions based on existing solution in the population. There are two basic types of operators: crossover and mutation. In one–point crossover, patent chromosomes have a finite probability P_c of breaking at a random point, exchanging genetic information, and thus mating to produce children for next generation. Flowing crossover, each of the chromosome bits has probability p_m of switching values. In this work for simulation of reaction network and GA, MATLAB code is used. The code consists of two main parts: the optimizer (GA code) and differential - algebra equation solver. The optimizer GA code chooses the parameters and the DAE solver computes the objective value.

CASE STUDIES

H_2/O_2 Combustion at low pressure

The full mechanism involving 20 reaction and 8 species is given in table 1. For the calculation of the equilibrium constants and all necessary thermo-physicals properties the from following equations are used. It is assumed that reacting mixture is ideal gas.

$$Ln\left(K_{eq}^{i}\right) = -\frac{\Delta G_i}{RT}$$

$$\Delta G_i = \sum_{i=1}^{N_S} v_{ij} G_i \quad , \quad j = 1,\cdots,N_R$$

$$G_i = H_i - TS_i \quad , \quad i = 1,\cdots,N_S$$

To calculate H_i, S_i, C_{pi} we have used NASA thermodynamic data [16]. The properties are given through regression formula as below:

$$\frac{C_{pi}}{R} = a_{1i} + a_{2i}T + a_{3i}T^2 + a_{4i}T^3 + a_{5i}T^4$$

$$\frac{H_i}{RT} = a_{1i} + \frac{a_{2i}}{2}T + \frac{a_{3i}}{3}T^2 + \frac{a_{4i}}{4}T^3 + \frac{a_{5i}}{4}T^4 + \frac{a_{6i}}{T}$$

$$\frac{S_i}{R} = a_{1i}Ln(T) + \frac{a_{2i}}{2}T + \frac{a_{3i}}{3}T^2 + \frac{a_{4i}}{4}T^3 + \frac{a_{5i}}{4}T^4 + a_{7i}$$

The profile to be replicated is one that corresponds to the following initial condition: H_2 mole fraction = 0.17, O_2 mole fraction=0.88, T_0 = 1000 K. The error measure was defined, as the L_2 norm of the profiles of H_2, O_2, H_2O, temperature and it is evaluated over a time period of 0.16 ms.

The results of simulation by k = 6 and α = 0.01 in Eq. (8) show that the reduced mechanism contain 6 reactions, which are {1, 2, 3, 4, 5, 7} and achieves an error of 3.3e-3. Profiles comparing the detailed and reduced mechanism are shown in Fig. 1.

The reduced mechanism for k= 9, α=0.01 in Eq. (8) contain 9 reactions, which are {1, 2, 3, 4, 5, 6, 7, 9, 16} and an error of 6.2E-4. Profiles comparing the detailed and reduced mechanism are shown in Fig. 2. It is also noted that the number of maximum generations was set to 50 and the initial population size has been selected as 80 for both runs. In addition the probability percent of crossover binary operation and mutation rate was set as 65% and 10% respectively.

Although the problem was cast in the form of Eq. (8) with a single objective in more general terms, it must be

Table1: The full mechanism H_2/O_2 Combustion at low pressure.

N0.	Reaction	$k = A*T^b*\exp(\frac{-E}{RT})$		
		A	b	E
1	$H_2+O_2=2OH$	1.70E+13	0.0	47780.0
2	$OH+H_2=H_2O+H$	1.17E+09	1.3	3626.0
3	$O+OH=O_2+H$	4.00E+14	-0.5	0.0
4	$O+H_2=H_2O+H$	5.06E+04	2.7	6290.0
5	$H+O_2+M=HO_2+M$ H_2O Enhenced by 1.86E+01 H_2 Enhenced by 2.86E+00	3.61E+17	-0.7	0.0
6	$OH+HO_2= H_2O+ O_2$	7.50E+12	0.0	0.0
7	$H+HO_2=2OH$	1.40E+14	0.0	1073.0
8	$O+HO_2=O_2+OH$	1.40E+13	0.0	1703.0
9	$2OH=O+H_2O$	6.00E+08	1.3	0.0
10	$H+H+M=H_2+M$ H_2O Enhenced by 0.00E+00 H_2 Enhenced by 0.00E+00	1.00E+18	-1.0	0.0
11	$H+H+H_2=H_2+H_2$	9.20E+16	-0.6	0.0
12	$H+H+H_2O=H_2+H_2O$	6.00E+19	-1.2	0.0
13	$H+OH+M=H_2O+M$ H_2O Enhenced by 5.00E+00	1.60E+22	-2.0	0.0
14	$H+O+M=OH+M$ H_2O Enhenced by 5.00E+00	6.20E+16	-0.6	0.0
15	$O+O+M=O_2+M$	1.89E+13	0.0	-1788.0
16	$H+HO_2= H_2+O_2$	1.25E+13	0.0	0.0
17	$HO_2+HO_2= H_2O_2+O_2$	2.00E+12	0.0	0.0
18	$H_2O_2+M=OH+OH+M$	1.30E+17	0.0	45500.0
19	$H_2O_2+H=HO_2+H_2$	1.60E+12	0.0	3800.0
20	$H_2O_2+OH=H_2O+HO_2$	1.00E+13	0.0	1800.0

NOTE: A units mole-sec-K, E units cal/mole

posed as multilevel problem in which one wishes to identify the minimum number of reactions that produce the least approximation error. One way to approach this question is to solve the original problem for different values of the k (number of reactions in reduced model). This way, we contract the set of solutions that shows the evolution of the approximation error as a function of the size of reduced network shown in Fig. 3. According of Fig. 3, we find that with up to six reactions one achieves an almost linear improvement in the error as the size of the reduced network is increased thus a set of six reactions {1, 2, 3, 4, 5 and 7} is a good description of the detailed mechanism. Any further reduction below this critical set will substantially deteriorate the quality of the reduced mechanism. This is clearly seen by the fact that the slope of the error changes drastically as we further try to reduce the size of the network. In Fig. 4 the variation of fitness functions with respect to progression of generations is shown for six-reaction. As it is clear, the optimization problem has converged after 40 generation, with a smooth and non-premature evolution.

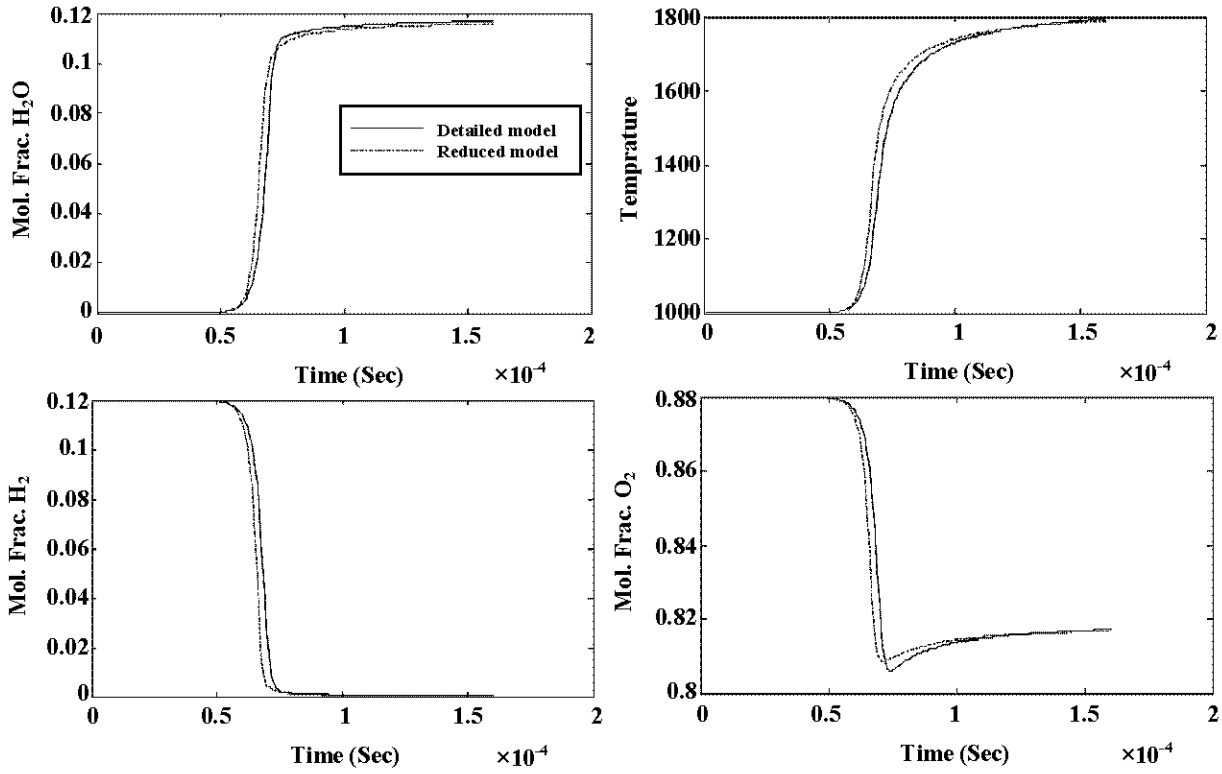

Fig. 1: Profiles comparing the detailed and reduced mechanism contain 6 reactions.

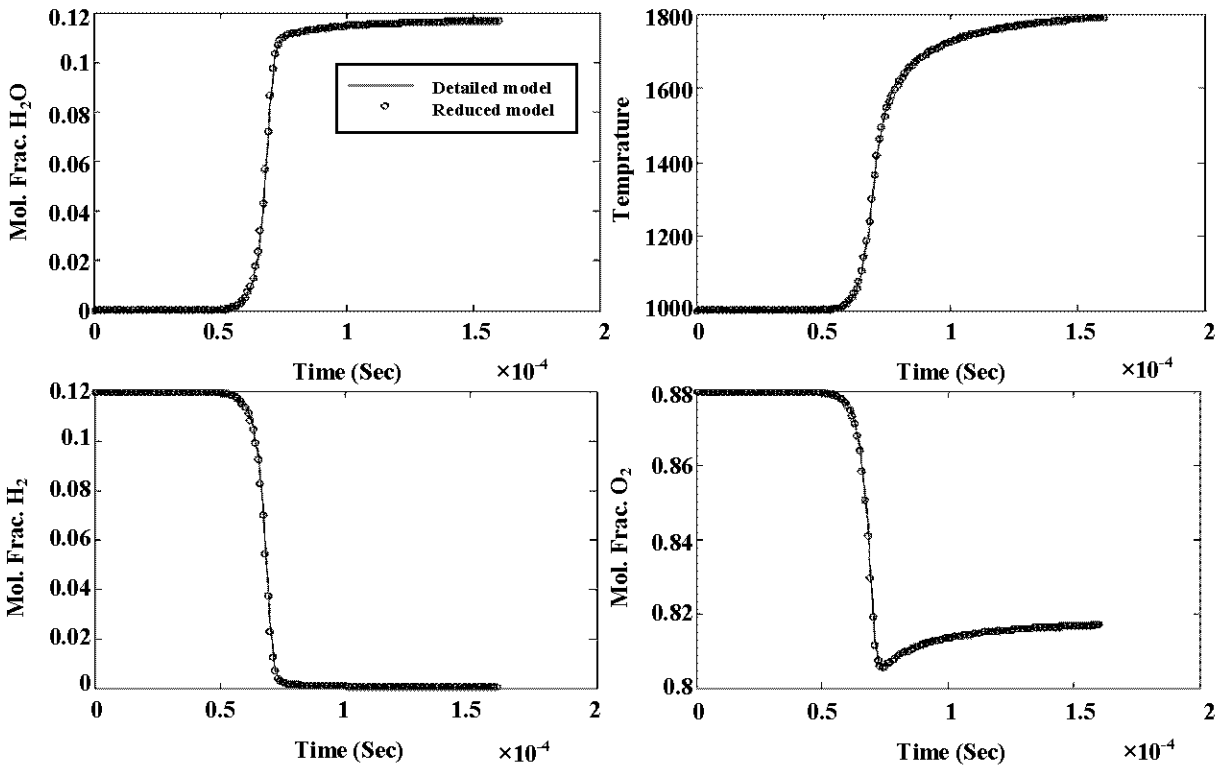

Fig. 2: Profiles comparing the detailed and reduced mechanism contain 9 reactions.

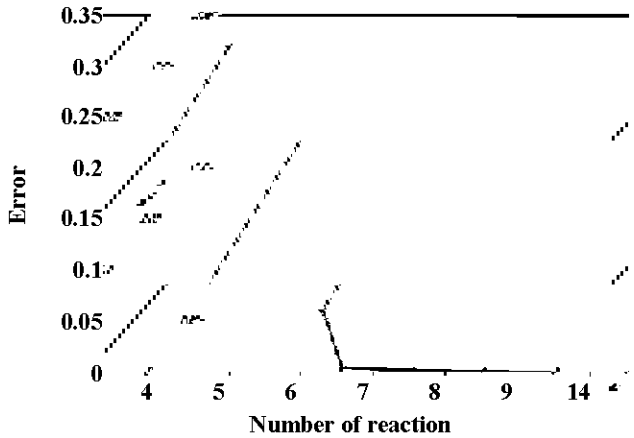

Fig. 3: The approximation error as a function of the size of reduced network.

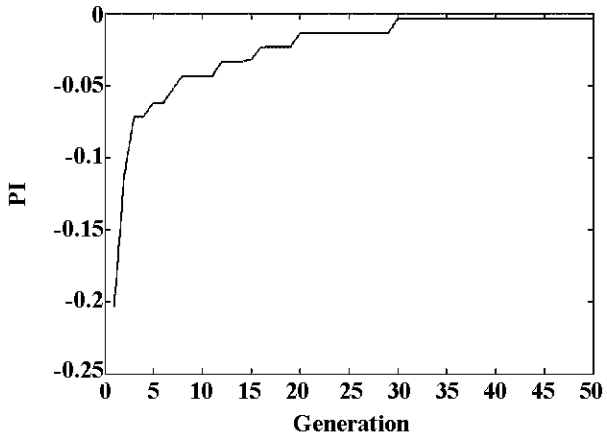

Fig. 4: The variation of objective (fitness) function versus the progressive generations for the six-reaction reduced model (k=6, α=0.01).

SUMMARY

In this work we used Genetic Algorithm (GA) for kinetic model reduction. The MINLP approaches worked well for small reaction system, whereas GA method was applicable to large reaction networks as well. We present a novel approach to simplification of reaction networks that formulates the model reduction problem as an optimization problem and solves it using genetic algorithm (GA).

The aim of simplification kinetics modeling is to derive the simplest reaction system, which retains the essential features of the full system. Numerical results for H_2/O_2 combustion reaction mechanism illustrate the potential of this approach. In the future, it is intended to exemplify and justify the more complex reaction systems.

Nomenclatures

a_{ij}	Regression coefficient
b	End of reaction time
C_p	Thermal capacity
D	Diagonal matrix
d_i	Binary number
e	Minimization error
G_j	Gibbs free energy of formation
g(.)	Nonlinear scalar function
ΔH_j	Enthalpy of Reaction
i	Index
j	Index
K^i_{eq}	Equilibrium constant
N	Population size
N_R	Number of Reactions
N_S	Number of chemical species
p_c	Crossover parameter
p_m	Mutation rate probability
PI	Performance Index, Fitness function
R	Universal gas constant
$R(\underline{x})$	Reaction rate vector
S	Matrix
S_j	Entropy of formation
T	Temperature
v_{ij}	Stoichiometric coefficient
w_i	Weight factor
$\underline{x}$	State vector
y_i	Mole fraction
$\underline{z}$	Reduced state vector
α	Parameter
β	Parameter
δ	Tolerance parameter
ρ	Density of mixture

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